Comparison of electrodialytic removal of Cu from spiked kaolinite, spiked soil and industrially polluted soil

Lisbeth M. Ottosen [a,*], Katarina Lepkova [b], Martin Kubal [b]

[a] *Department of Civil Engineering, Kemitorvet, Building 204, Technical University of Denmark, 2800 Lyngby, Denmark*
[b] *Institute of Chemical Technology, Technicka 5, Praha 6, Czech Republic*

Abstract

Electrokinetic remediation methods for removal of heavy metals from polluted soils have been subjected for quite intense research during the past years since these methods are well suitable for fine-grained soils where other remediation methods fail. Electrodialytic remediation is an electrokinetic remediation method which is based on applying an electric dc field and the use of ion exchange membranes that ensures the main transport of heavy metals to be out of the pollutes soil. An experimental investigation was made with electrodialytic removal of Cu from spiked kaolinite, spiked soil and industrially polluted soil under the same operational conditions (constant current density 0.2 mA/cm^2 and duration 28 days). The results of the present paper show that caution must be taken when generalising results obtained in spiked kaolinite to remediation of industrially polluted soils, as it was shown that the removal rate was higher in kaolinite than in both spiked soil and industrial polluted soil. The duration of spiking was found to be an important factor too, when attempting to relate remediation of spiked soil or kaolinite to remediation of industrially polluted soils. Spiking for 2 days was too short. However, spiking for 30 days resulted in a pattern that was more similar to that of industrially polluted soils with similar compositions both regarding sequential extraction and electrodialytic remediation result, though the remediation still progressed slightly faster in the spiked soil. Generalisation of remediation results to a variety of soil types must on the other hand be done with caution since the remediation results of different industrially polluted soils were very different. In one soil a total of 76% Cu was removed and in another soil no Cu was removed only redistributed within the soil. The factor with the highest influence on removal success was soil pH, which must be low in order to mobilize Cu, and thus the buffering capacity against acidification was the key soil characteristics determining the Cu removal rate.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Electrodialytic remediation; Copper; Ion exchange membranes; Soil and kaolinite; Spiking

1. Introduction

Electrokinetic soil remediation methods have gained interest since these methods are well suited for fine-grained soils where other methods as, e.g. soil washing or pump and treat methods are impractical or impossible to use. The electrokinetic methods are based on application of an electric dc field to the soil, and because the electric conductivity is highest in the fine fraction of the soil where also most pollutants are adsorbed, the electric field is strongest exactly where the pollution is mainly found. Electrodialytic remediation is one of the electrokinetic methods, which differs in the use of ion exchange membranes for separation of soil and processing solutions.

To mobilize most heavy metals from soils, acidification is very effective, and for electrokinetic remediation the development of an acidic front often results in a successful remediation. In order to remove heavy metals from the whole soil volume it is necessary to prevent development of an alkaline front in the opposite direction. For example, Suer et al. [1] showed, that heavy metals precipitate into forms that fall into the residual fraction of a sequential extraction (i.e. to the hardest bound fraction) in the alkaline zone. In electrodialytic remediation development of an alkaline front is prevented with a cation exchange membrane.

Electrokinetic remediation of spiked kaolinite has been studied extensively in laboratory scale, e.g. Refs. [2,3]. Several models have been developed, too, e.g. a mathematical model for multicomponent species transport under coupled hydraulic, electric and chemical potential differences [4] and a two-dimensional model for electrokinetic remediation of Cu

* Corresponding author. Fax: +45 45 88 59 35.
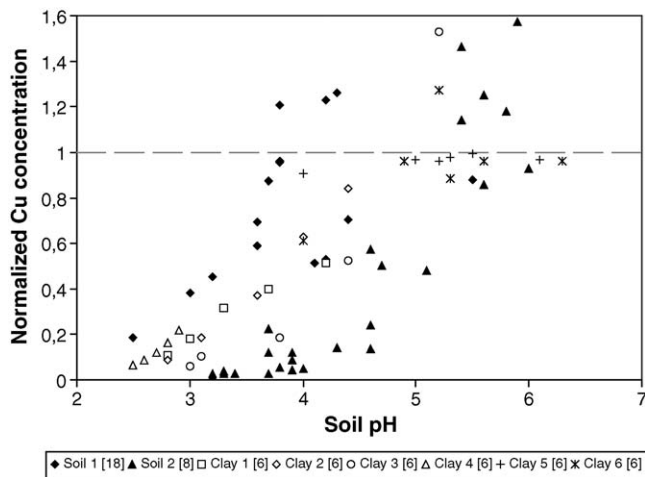*E-mail address:* lo@byg.dtu.dk (L.M. Ottosen).

Fig. 1. Relation between pH_{H_2O} and normalized Cu concentration (final concentration/initial concentration) during electrokinetic treatment. Results compiled from Refs. [7], [9] and [11].

spiked kaolin [5]. Other investigations with remediation of spiked soils have been conducted, e.g. with Cu removal from different spiked spoils [6] and Cu, Zn and Pb removal form different clay types [7]. So has experiments with soils sampled at polluted sites, e.g. from mine tailing [8] and wood preservation [9]. The common aim of the investigations is the development of electrokinetic methods for remediation of soil from actually polluted sites. However, it can be difficult to compare remediation results obtained with spiked kaolinite and spiked soil with remediation of soil from polluted sites. Spiking of soil in laboratory by equilibrating a soil with the contaminant in solution does not reproduce the contaminant geochemistry encountered for soils sampled at polluted sites [10]. Further for kaolinite a very limited variety of sorption sites for heavy metals is present and this further complicates comparison.

In Fig. 1, the results from three investigations are compiled: [7,9] and [11]. In these studies pH was measured in H_2O. The clays in investigation [7] were sampled at six different Japanese sites and spiked in laboratory (aged for 1 year) and remediated by an electrokinetic method. The soils in Refs. [9] and [11] were sampled at wood preservation sites, in Denmark and Portugal, respectively, and treated by the electrodialytic method. Even though the experimental set-up and processing parameters varied between the investigations it is still possible to compare the pH—normalized concentration patterns, since pH in both methods is the overall determining parameter for Cu mobilization. Fig. 1 shows that Cu is generally removed at highest pH in the wood preservation soil [9] and at lowest pH in wood preservation soil [11], e.g. at pH = 4 no removal was obtained in soil [11] whereas more than 80% Cu was removed from soil [9]. This indicates different retention mechanisms for Cu in the two soils. The clays fall in between the two soils in Fig. 1. There is also a distinct difference in the pH at where Cu is removed from the clays. No difference in pH where Cu removal starts originating from spiking contra industrially polluted soil was seen in Fig. 1. However, the clays had been spiked for 1 year, which is quite long compared to most other investigations. For a short spiking

time it is expected that equilibrium of adsorption has not been reached and here a less pronounced relation between pH and removal can be expected, since some Cu is mobile even before acidification starts.

In Ref. [12] a similar figure for pH—normalized Cu concentration is given for different Danish industrially polluted soils, however, in this investigation the soil pH was measured in KCl. In the figure from Ref. [12] the one soil was sampled at the same site as soil 2 in Fig. 1. However in this investigation this soil was the one where pH was the lowest before Cu was desorbed. In Ref. [12] it was found that Cu was mobilized at a higher pH in calcareous soils than in non-calcareous soils.

In the different results published with remediation of spiked soils, spiked kaolinite and industrially polluted soil several key parameters are often varying, making a direct comparison impossible based on already published results. The present investigation is an experimental comparison of electrodialytic removal of Cu from spiked kaolinite, spiked soil and three soils from actual polluted sites.

In the different papers reporting experimental work with remediation of spiked soils, the duration of the spiking is varying. This may influence the remediation result. In the present paper kaolinite and soil were spiked for both 2 and 30 days in order to investigate the influence of spiking time on the overall electrodialytic removal of Cu.

2. Electrodialytic remediation and experimental set-up

Electrodialytic soil remediation is based on a combination of applying an electric dc field to a heavy metal polluted soil and the use of ion exchange membranes to separate soil and processing solutions, e.g. Refs. [9,13]. The laboratory cells used for this investigation consist of four compartments as shown in Fig. 2: anode compartment (I), soil compartment (II), concentration compartment (III) and cathode compartment (IV). Between the soil and compartment (I) an anion exchange membrane (AN), which only allows passage of anions, is placed. Between the soil and the electrolyte solution in compartment (III) a cation exchange membrane (CAT), which allows only passage of cations, is placed. The idea of the ion exchange membranes is that no current is wasted in transporting ions from one electrode compartment through the soil into the second electrode
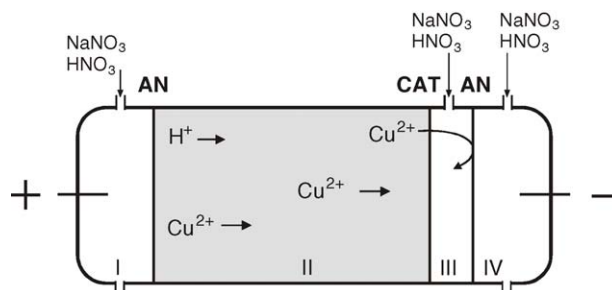

Fig. 2. The principle of electrodialytic remediation exemplified by a laboratory cell. The polluted soil is placed in compartment (II). Compartments I–III have separate circulation systems. (AN, anion exchange membrane; CAT, cation exchange membrane).

compartment. Furthermore the conditions in the soil are not as dependent on the choice of electrolyte solution as it would have been if chemically passive membranes were used. This is beneficial especially when further concentration of the removed heavy metals for reuse is planned.

The electrodes are placed in separate compartments (I) and (IV) where electrolyte solutions are circulated and the gases produced from the electrode processes are transported away from the electrode surfaces in these circulation systems. The heavy metals are concentrated in compartments (I) and (III) during the remediation; the heavy metals removed as anionic complexes will concentrate in compartment (I) and the heavy metals removed in cationic form will concentrate in compartment (III). Since mobilization of Cu in this investigation is a result of acidification, Cu is expected transported towards the cathode as Cu^{2+} and collected in compartment (III). In the laboratory cell (Fig. 1) the anion exchange membrane between the concentration compartment (III) and the cathode compartment (IV) hinders precipitation of Cu at the cathode. In full scale remediation an increase in volume of the cathode due to precipitation may cause problems. Thus it was chosen to concentrate Cu in a separate compartment in this investigation to simulate this situation.

During electrodialytic remediation the soil is acidified from the anode end towards the cathode end, see, e.g. Ref. [9] or [13]. This acidification is not directly linked to electrolysis at the anode but is probably a combination of proton leakage through the anion exchange membrane [14] and water splitting at this membrane, where the produced OH^- ions will pass into the anolyte whereas the protons will be transported into the soil due to the electric field [15].

The principle of the laboratory cell used for this study was as shown in Fig. 1. It was made of Plexiglas. The internal diameter of the cell was 4 cm and the length of the soil compartment was 5 cm. The ion exchange membranes were obtained from Ionics (anion exchange membrane 204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). The compartments I, III and IV have a separate circulation system each in which 0.25 L 0.01 M $NaNO_3$ with pH adjusted to 2 with HNO_3 were circulated. The working electrodes were made of platinum coated titanium wire ($\varnothing = 3$ mm), obtained from "Permascand". A power supply (Hewlett Packard E3612A) was used to maintain a constant current.

3. Experimental section

3.1. Experimental soils

Three Danish industrially polluted soils were sampled for this investigation. Two soils polluted from wood preservation (soils A and B) and the third soil was polluted from cable production (C). The soils from wood preservation sites were polluted with Cu, which is the heavy metal in focus of this investigation, but also Cr and As were polluting these soils. At the site where soil (A) was sampled, wood was preserved in the period from 1936 to 1976. During this period, the boucherie method was used, which implies that the impregnation solution dripped directly on the

soil surface. At the hot spot where the sample was taken the soil was without vegetation due to the pollution. At site (B) wood was preserved in the period from 1960 to 1981. The sampling area at the site was an area where the impregnation solutions were stored during the production and this sampling spot was without vegetation, as well. Both soil (A) and (B) were sampled in the depth of 2–20 cm. Soil (C) was sampled from a soil pile after excavation from a site polluted by cable production, and the exact time for the pollution is unknown. This soil was polluted with Cu and Zn.

The work furthermore includes spiked soil and spiked kaolinite. An unpolluted soil was sampled in a Danish forest area near by the wood preservation site (A). In the laboratory this unpolluted soil was spiked with Cu. Pure grade Kaolin obtained from Struers was spiked with Cu according to the same procedure. Chemical grade $Cu(NO_3)_2$ was dissolved in distilled water with an original pH of 7.7. Two batches were made with each soil/clay: 400 g dry soil/clay was mixed with 800 ml $Cu(NO_3)_2$ and the slurries were placed on a mechanical shaker and shaken for (a) 2 days and (b) 30 days. The slurries were centrifuged at 2500 rpm for 25 min and after removing the supernatant the soil/kaolinite was washed once with distilled water and centrifuged.

3.2. Soil characterization

The concentration of Cu was measured after pretreatment of the soil as described in Danish Standard 259: 1.0 g of dry soil and 20.0 mL (1:1) HNO_3 was 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. Cu-concentration was measured by AAS. The unit of soil concentration used in this paper is mg/kg dry matter.

Soil pH was measured by mixing 10.0 g dry soil and 25 mL 1.0 M KCl. After 1 h of contact time pH was measured using a Radiometer pH electrode. The carbonate content was determined by a volumetric calcimeter method as described in Refs. [16]. CEC was measured with a method comparable to the acid-NaCl method described in EPA Standard Method 9080. The organic content was determined as loss of ignition at 550 °C, and the grain size distribution was found by a combined sieve and pipette method.

The sequential extraction procedure used is the one recommended by the "Standards, Measurements and Testing programme of the European union" [17]. The procedure was enlarged with a residual fraction in this investigation. The conditions of the sequential extraction procedure are outlined in Table 1.

3.3. Remediation experiments

Seven electrodialytic remediation experiments were conducted, see Table 2.

The seven electrodialytic experiments were conducted with a constant current of 2.5 mA (corresponding to 0.2 mA/cm²). This current density was chosen from earlier experiences, where it has been found efficient and the remediation occurs without

Table 1
Outline of the sequential extraction procedure used [17]

	Chemical extractants	Operational conditions
Step 1 (exchangeable and carbonatic phase)	0.11 M acetic acid, pH = 3 (with HNO_3)	Room temperature, 16 h
Step 2(easily reducible phase)	0.1 M hydroxylamine hydrochloride, pH = 2 (with HNO_3)	Room temperature, 16 h
Step 3 (oxidisable phase)	8.8 M hydrogen peroxide	Room temperature, 1 h
	8.8 M hydrogen peroxide	85 °C
	1 M ammonium acetate pH = 2 (with HNO_3)	Room temperature, 16 h
Step 4 (residual fraction)	1:1 HNO_3	Procedure of DS259 described above

Table 2
The soils for the six electrodialytic remediation experiments

	Soil	Pollution	Cu concentration (mg/kg)	Water content (%)	Soil (g dry mass)	pH
1	Kaolin	Spiked for 2 days	260	39.3	53.6	4.8
2	Kaolin	Spiked for 30 days	300	38.2	60.6	5.1
3	Forest soil	Spiked for 2 days	320	30.5	73.3	3.8
4	Forest soil	Spiked for 30 days	320	28.2	77.3	3.7
5	Polluted soil (A)	Polluted from wood preservation	960	20.0	94.2	5.3
6	Polluted soil (B)	Polluted from wood preservation	10400	25.3	85.0	7.1
7	Polluted soil (C)	Polluted from cable production	2540	16.5	101.2	7.6

Initial Cu concentration, water content, the dry mass of soil and pH are given.

operational problems, e.g. Ref. [9]. The duration of all experiments was 28 days. The industrially polluted soils were wetted with distilled water prior to the electrodialytic experiments in order to obtain water saturated soil samples as in the case of the spiked soils.

At the end of the experiments the soil was segmented into four slices from anode towards cathode. Water content was measured and double determination of pH and total Cu concentration were made on soil from each slice. The electrodes and the membranes were treated in 5 and 1 M HNO_3, respectively, to measure the amount of Cu adsorbed to these. Finally the volume and the Cu concentration of the electrolyte solutions were measured.

4. Results and discussion

4.1. Characterization of soils

In Table 3 some characteristics for the experimental soils are listed: carbonate content, organic content, clay, silt and sand fraction, and CEC.

In soil (B) a few small pieces of wood (1–3 mm long) were observed. The pieces probably originate from the production of

impregnated wood and these small wood pieces are included in the measured percentage of organic matter in this soil.

Neither of the forest soil or wood preservation soils (A) and (B) had carbonate content higher than 0.9% but the soil polluted from cable production (C) had a high carbonate content of about 12%. The organic content varies significantly in the soils, as well, between 1.9% for soil (A) and 8.7–9.7% in the forest soil and soil (B), respectively. The organic matter and carbonates in the soils represents of adsorption sites that are not present in kaolinite. Since the organic fraction, clay and silt fractions were highest in soil (B) it is expected that this soil has the highest CEC. The amount of fine fraction in forest soil, soil (A) and soil (B) are similar, but the organic fraction is highest in the forest soil, and this is probably the reason for the higher CEC in this soil. The CEC for kaolinite was between the one for forest soil and wood preservation soil (B). The relatively high value for CEC in the kaolinite is due to the large surface area compared to the soils.

4.2. Sequential extraction

Sequential extraction is an approach based on solubility of individual solid-phase components by selective reagents.

Table 3
Characterization of the experimental soils

Soil	Carbonate content (%)	Organic content (%)	Clay (<0.002 mm) (%)	Silt (0.002–0.06 mm) (%)	Sand (0.06–2 mm) (%)	CEC (meq/g dry soil)
Kaolinite	–	–	100	0	0	9.9
Forest soil	0.9	8.6	2.4	20.3	70.8	4.2
Polluted soil (A)	0.2	1.9	3	26	67	2.2
Polluted soil (B)	0.7	9.7	4	41	55	14.0
Polluted soil (C)	12.0	3.1	2	20	71	2.9

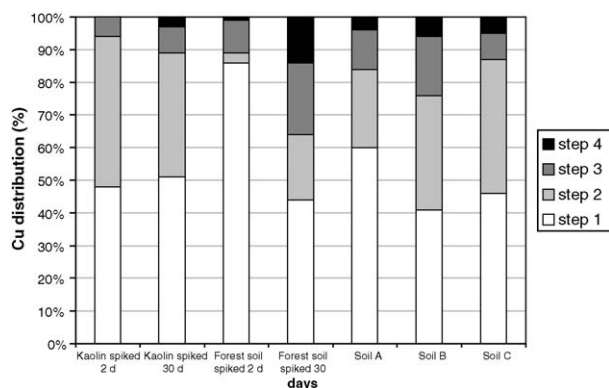Parameters for kaolinite and forest soil were measured before spiking.

Fig. 3. Result from sequential extraction. Step 1 exchangeable and carbonatic phase, step 2 easily reducible phase, step 3 oxidisable phase, and step 4 residual fraction.

However it is not possible to make such procedures specially targeted on a single component [18]. Despite this shortcoming sequential extraction furnish more useful information on metal binding than available with a single extractant [19] and thus the sequential extraction procedure presented in Table 1 was used to describe differences in the experimental soils in the present investigation.

The results of the sequential extraction of Cu from the soils are shown in Fig. 3. It is seen that about 50% Cu is found in the exchangeable fraction of the kaolinite and this is in consistency with [20] where the exchangeable fraction of Cu was measured in a spiked kaolinite with the total concentration of about 140 mg Cu/kg. For both spiked kaolinite and spiked forest soil there is a tendency for Cu to be found in the higher steps of the sequential extraction after 30 days compared to 2 days which is in consistency with the result in Refs. [21] where the distribution of Cu in spiked soils was similarly investigated by sequential extraction at different spiking contact time. In kaolinite no Cu was found in the residual fraction (step 4) after 2 days but after 30 days 3% of the Cu was found in this fraction, see Fig. 2. In the spiked soil the tendency was even more pronounced from only 1% in this fraction after 2 days to 14% after 30 days. In kaolinite the other three fractions were very similar after 2 and 30 days but in the spiked soil the percentage of Cu in step 2 and 3 increased significantly between 2 and 30 days.

The sequential extraction pattern of the spiked forest soil after 30 days was more similar to the pattern from the two wood preservation soils than the pattern of the spiked kaolinite and the spiked soil after 2 days. In the spiked soil the first fraction may include both Cu in exchangeable sites and Cu that is not adsorbed since the washing process after the spiking only included wash in distilled water once. In the soils sampled at polluted sites the pollution is old and free Cu that may have been in the soil at the time of pollution has been washed out. This is a difference that must be taken into account when comparing the results from sequential extractions. Still, the percentage of Cu in the residual fraction (step 4) is highest in the spiked soil. This however, must be related to total concentrations, and since the fraction of Cu in soil (B) is about 33 times higher, the concentration related to the residual fraction is much also higher. Taking into

consideration the high total Cu concentration in soil (B), the concentration related to the residual fraction is 940 mg/kg which is approximately the same as the total Cu concentration of soil (A) and three time as much as the total Cu concentration of the spiked soils.

In Fig. 3 the pattern for the spiked soil is more similar to the industrially polluted soils after 30 days than after 2 days. This underlines the importance of choosing a long spiking time if the aim is to simulate an industrially polluted soil.

Sequential extraction procedures have been applied as tool for evaluation of electrokinetic soil remediation by different researchers. Ribeiro and Mexia [11] found that Cu generally had a higher mobility during/after electrokinetic treatment than before in a soil polluted from wood preservation. Kim and Kim [8] conducted experiments with a tailing-soil and found good removals of Cu, Cd, Pb and Zn from the first fractions of their sequential extraction procedure all over the soil volume (pH was lowered all through the soil) whereas the concentration in the residual fraction was unchanged except from a slight change in Cd, Zn and Cu concentration in the area closest to the anode (pH = 3.5). In the next slice (pH = 5) no mobilisation from the residual fraction was seen. Both of these investigations showed a mobilization from the intermediate fractions towards more mobile fractions. Suer et al. [1] conducted experiments with a soil polluted from a chloralkali factory in an electrokinetic setup allowing an acidic front from the anode end and an alkaline front from the cathode end to develop. After 182 days of current a decrease of Cu, Zn and Pb concentrations were seen in the acidic zone, and an accumulation was seen in the alkaline zone as expected. By sequential extraction it was found that significant amounts of the heavy metals in the residual fraction were found in the alkaline zone. In the acidic zone the concentration of the investigated heavy metals was decreased in the residual fraction indication mobilization of the strongest bound heavy metals. Mobilization from the residual fraction was also seen in the investigations [8] and [11].

4.3. Remediation experiments

During the experiments the current density was kept constant at 0.2 mA/cm^2, which means that the differences in voltage measured between the working electrodes expresses the differences in total resistance of the cell. The variation in resistance during the experiments is most likely connected to the soil as it was found in Refs. [15]. The resistance in the experiments with spiked kaolinites and spiked soils (experiments 1–4) were almost constant throughout the experiments. The voltage was about 4 and 7 V in experiments 1 and 2, respectively. The only major difference between the two experiments is the spiking time and the lower resistance in the experiment with soil/clay spiked for 2 days may be due to a surplus of free ions in the kaolin spiked for 2 days only. Also for the spiked soils there was a tendency for the voltage in experiment 3 with soil spiked for 2 days to be lower than in the experiment spiked for 30 days (experiment 4), but the difference is less pronounced than in the kaolinite experiments. The mean voltage was about 18 and 20 V, respectively. In the experiments with polluted soils the voltage varied much
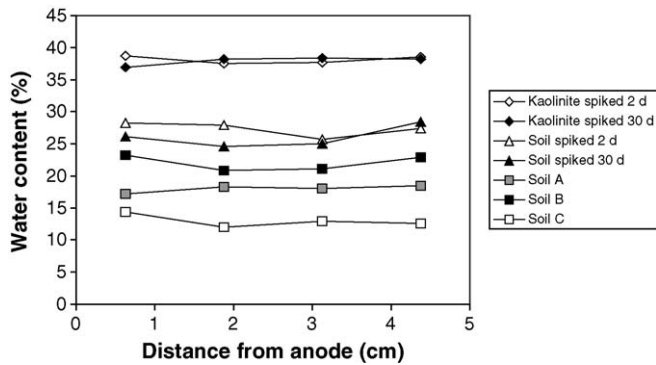
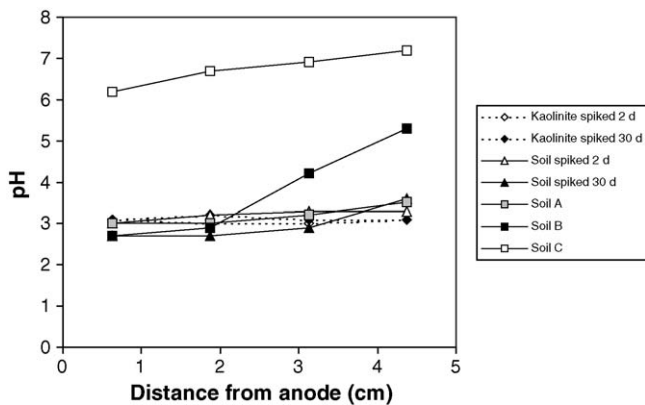Fig. 4. Water content in the kaolinites and soils after 28 days of electrodialytic treatment.

Fig. 5. Soil pH profiles in the kaolinites and soils after 28 days of electrodialytic treatment.

more than in the spiked soils. The general pattern was that the voltage started low 5–10 V and increased to a level of 30–40 V during remediation as seen in previous work [9] and [15].

Profiles in the soil with water content, pH and normalized Cu concentrations (final concentration/initial concentration) after 28 days of current are shown in Figs. 4–6, respectively.

The water content was almost the same throughout the soil in all experiment (Fig. 4). For each soil the water content was decreased a few percentages compared to the initial values (Table 2), probably due to electrosmosis. The water con-
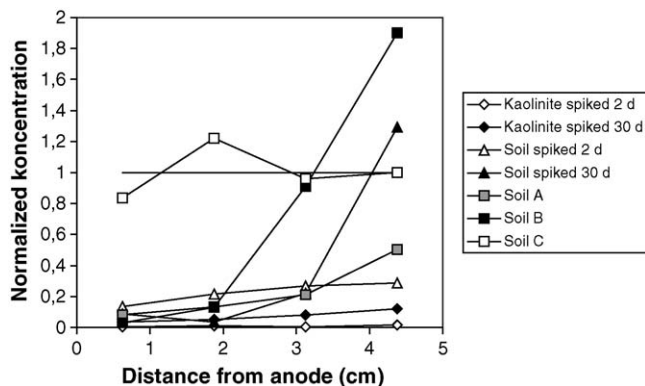

Fig. 6. Normalized Cu concentration profiles in the kaolinites and soils after 28 days of electrodialytic treatment.

tent in kaolin was highest after the experiments as it was the case initially. The general order of water content at the end of the experiments was the same as initially showing that neither of the soils was dewatered to a distinct higher extent than others.

The pH profile of soil C deviates from that of the other soils (Fig. 5) at the end of the experiments. Even after 28 days of current, pH in this soil was only decreased with one pH unit in the slice closest to the anode and this underlines that for electrokinetic remediation of calcareous soils it is beneficial to use an enhancement solution in order to increase the remediation rate, as it was shown in Refs. [22]. For the six other experiments the soil closest to the anode was acidified to approximately the same pH-level at about 2.7–3.1. For the two experiments with kaolinite, pH decreased to 3.0–3.1 throughout the soil. The pH profiles in the spiked soil differed. In the soil spiked for 2 days a final pH of 3.0–3.3 was obtained, whereas in the soil spiked for 30 days pH varied between 2.7 and 3.6. The acidic front had not reached all through soil B since pH closest to the cathode was 5.3, which is identical to the initial pH.

The developing acidic front in the soil from anode end towards cathode end is influencing the overall voltage of the cell. In the acidified part of the soil the resistance is low due to the high amount of H^+ ions. However, the resistance in the part of the soil that is yet not acidified is not constant but increasing, since the mobile ions present from the beginning are removed without being replaced to the same extent. Thus there is a clear relation to the measured pH and voltage.

The mobilisation of Cu in the soils is mainly due to the developing acidic front and when Cu is mobilized, mainly electromigration is responsible for the movement towards the cathode, but also electroosmosis may play a minor role. From Fig. 6 the normalized Cu concentration profiles can be seen. The two experiments with spiked kaolinite had the lowest values of normalized soil Cu concentrations at the end of the experiments. For the kaolinite that initially was spiked for 2 days, the final concentration was between 1 and 4.5 mg Cu/kg. In the experiment, where the kaolinite had been spiked for 30 days, the final concentrations were higher (between 10 and 36 mg Cu/kg). This corresponds well to the result from sequential extraction where the Cu was found harder bound after 30 days than after 2 days of spiking and thus Cu is expected adsorbed slightly stronger after 30 days. In Refs. [5] and [20] electrokinetic removal of Cu was investigated and both investigations showed a lower removal (about maximum 50% in the part of the kaolinites with the lowest Cu concentration) but a direct comparison is not possible since neither electrical parameters or duration of experiments were comparable to the experiments of the present investigation.

Also between the soils spiked for different times, the result differed. In the soil next to the anode compartment the concentration of Cu was less in the soil spiked for 30 days but closest to the cathode compartment this was switched so the concentration in this soil was higher. The two profiles are different in shape and follow the pH profiles. In the soil spiked for 2 days, the final pH was 0.3 pH units higher in the three slices closest to the anode and it is here the concentration is highest, too. In the last slice closest to the cathode pH is 0.3 pH units higher in the soil spiked

for 30 days and here Cu had even accumulated during the experiment. As for the spiked kaolinite, the overall remediation result for the spiked soils was best for the 2 days spiked samples compared to the 30 days spiked samples and again this corresponds well to the expectations from the sequential extraction.

For the three industrially polluted soils the normalized concentration profiles varied significantly. In soil C about 16% Cu was removed from the slice closest to the anode but this small amount of Cu had precipitated in the next slice, and thus no Cu was removed from this soil as a total. In soil B, which had a very high Cu content compared to the other soils, only 3% Cu was left in the first slice and this corresponds to a reduction in Cu concentration from 10,400 to 320 mg/kg. The Cu concentration was lowered in about half of the soil in this experiment. The remediation result with soil A was definitely the best of the three with industrially polluted soil. At the end of the experiment all soil in the cell meet the criteria for Cu for the soil to be used at the most sensitive use in Denmark (500 mg Cu/kg) [23].

For the three industrially polluted soils the sequential extraction could not provide an overall indication of the remediation result. This is because the sequential extraction procedure does not give information on the soil buffering capacity against acidification, which is an important factor for the success of the remediation.

Puppala et al. [24] found that remediation of a Pb spiked soil composed of kaolinite, illite, sodium montmorillonite and sand requires higher energy expenditure and longer processing period compared to remediation of spiked kaolinite and related this to a higher proton demand before mobilization of Pb. The present investigation shows that the same account for Cu removal from spiked forest soil and industrially pollutes soils compared to removal of Cu from kaolinite. The remediation of kaolinite is much faster than remediation of soils and the energy consumption is lower. Thus electrokinetic remediation results obtained with spiked kaolinite must not be converted directly to remediation of industrially polluted soil.

5. Conclusion

A variety of papers deal with electrokinetic removal of heavy metals from spiked kaolinite and spiked soils. Meanwhile caution must be taken when relating the results to remediation of industrially polluted soils. In the case of remediation of spiked kaolinite the result cannot be transferred directly to remediation of actual industrially polluted sites since the remediation of kaolinite is both faster and requires less energy. In the case of spiked soils the duration of spiking is of high importance if the aim is to simulate remediation of industrially polluted soils. It was found that 2 days of spiking was too short, but after 30 days of spiking the soil showed a pattern similar to industrially polluted soils both regarding sequential extraction and electrodialytic remediation. The soil type is further found of crucial importance to the removal rate of Cu and the soil characteristics that influence the buffering capacity the most has the highest influence on the removal rate since an acidic front must develop in order to mobilize Cu (when no enhancement solution is used). In a soil with a carbonate content of about 12%, less than 20%

Cu was removed in the soil closest to the anode, whereas more than 90% Cu was removed at the same place in the two soils with a carbonate content of less than 0.7%. Thus generalization of remediation results obtained with different spiked or industrially polluted soils should be made with care.

Acknowledgements

References

[1] P. Suer, K. Gitye, B. Allard, Speciation and transport of heavy metals and macroelements during electroremediation, Environ. Sci. Technol. 37 (2003) 177.

[2] Y.B. Acar, J.T. Hamed, A.N. Alshawabkeh, R.J. Gale, Removal of cadmium(II) from saturated kaolinite by the application of electric current, Géotechnique 44 (2) (1994) 239.

[3] K.R. Reddy, C. Chaparro, R.E. Saichek, Removal of mercury from clayey soils using electrokinetics, J. Environ. Sci. Health.: Part A, Toxic/Hazard. Substances Environ. Eng. A38 (2) (2003) 307.

[4] A. Alshawabkeh, Y.B. Acar, Electrokinetic remediation. (II) Theoretical model, J. Geotechnnol. Eng. 122 (3) (1996) 186.

[5] C. Vereda-Alonso, J.M. Rodríguez-Maroto, R.A. García-Delagrdo, C. Gómez-Lahoz, F. García-Herruzo, Two-dimensional model for soil electrokinetic remediation of heavy metals. Application to copper spiked kaolin, Chemosphere 54 (1994) 895.

[6] L.Y. J.-G. Sah, J. Lin, Electrokinetic study on copper contaminated soils, Environ. Sci. Health. A35 (7) (2000) 1117.

[7] S.I. Darmawa, Wada, Effect of clay mineralogy on the feasibility of electrokinetic soil decontamination technology, Appl. Clay Sci. 20 (2002) 283.

[8] S.-O. Kim, K.-W. Kim, Monitoring of electrokinetic removal of heavy metals in tailing-soils using sequential extraction analysis, J. Hazard. Mater. B85 (2001) 195.

[9] L.M. Ottosen, H.K. Hansen, S. Laursen, A. Villumsen, Electrodialytic remediation of soil polluted with copper from wood preservation industry, Environ. Sci. Technol. 31 (1997) 1711.

[10] P.S. Yarlagadda, M.R. Matsumoto, J.E. Van Benschoten, A.J. Kathuria, Characteristics of heavy metals in contaminated soils, J. Environ. Eng. 121 (4) (1995) 276.

[11] A.B. Ribeiro, J.T. Mexia, A dynamic model for the electrokinetic removal of copper from a polluted soil, J. Hazard. Mater. 56 (1997) 257.

[12] L.M. Ottosen, H.K. Hansen, A.B. Ribeiro, A. Villumsen, Removal of Cu, Pb and Zn in an applied electric field in calcareous and non-calcareous soils, J. Hazard. Mater. B85 (2001) 291.

[13] H.K. Hansen, L.M. Ottosen, B.K. Kliem, A. Villumsen, Electrodialytic remediation of soils polluted with Cu, Cr, Hg, Pb and Zn, J. Chem. Technol. Biotechnol. 70 (1997) 67.

[14] Y. Lorrain, G. Pourcelly, C. Gavach, Influence of cations on the proton leakage through anion-exchange membranes, J. Membr. Sci. 110 (1996) 181–190.

[15] L.M. Ottosen, H.K. Hansen, C.B. Hansen, Water splitting at ion-exchange membranes and potential differences in soil during electrodialytic soil remediation, J. Appl. Electrochem. 30 (11) (2000) 1199.

[16] R.H. Loeppert, D.L. Suarez, Methods of Soil Analysis. Part 3. Chemical Methods—SSSA Book Series No. 5, 1995, pp. 451–455.

[17] Z. Mester, C. Cremisini, E. Ghiara, R. Morabito, Comparison of two sequential extraction procedures for metal fractionation in sediment samples, Anal. Chim. Acta 359 (1998) 133.

[18] N.D. Kim, J.E. Fergusson, Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soils, Sci. Total. Environ. 105 (1991) 191.

[19] F.X. Han, A. Banin, W.L. Kingery, G.B. Triplett, L.X. Zhou, S.J. Zheng, W.X. Ding, New approach to studies of heavy metal redistribution in soil, Adv. Environ. Res. 8 (2003) 113.

[20] D.-M. Zhou, R. Zorn, K. Czurda, Electrokinetic remediation of copper contaminated kaolinite by conditioning anolyte and catholyte pH simultaneously, J. Environ. Sci. 15 (3) (2003) 396.

[21] M. Pietrantonio, N. Calace, B.M. Petronio, M. Pietroletti, Laboratory-polluted soils: a methodological apporach to establish equilibrium conditions for different metal chemical form in soils, J. Environ. Monit. 5 (2003) 451.

[22] L.M. Ottosen, H.K. Hansen, L. Hansen, B.K. Kliem, G. Bech-Nielsen, A. Villumsen, Contaminated Soil, 1, Thomas Telford, London, 1998, p. 471.

[23] Miljøstyrelsen. Liste over kvalitetskriterier i relation til forurenet jord (A list of quality criteria in relation to polluted soil), in Danish, 2003.

[24] S.K. Puppala, A.N. Alshawabkeh, Y.B. Acar, R.J. Gale, M. Bricka, Enhanced electrokinetic remediatio of high sorption capacity soils, J. Hazard. Mater. 55 (1997) 203.