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Water splitting at ion-exchange membranes and potential differences in soil during electrodialytic soil remediation

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Abstract

The optimum current for electrodialytic soil remediation occurs when the limiting current of the anion-exchange membrane is exceeded while that for the cation-exchange membrane is not. At this current, an acidic front will pass through the soil from the anion-exchange membrane towards the cathode, and the polluting heavy metals will be mobilized in the acidic environment. At the same time no production of base will occur from the cation-exchange membrane. A basic environment causes precipitation of hydroxides in the soil next to the cation-exchange membrane, and this will give an increase in voltage drop in the system and furthermore hinder the transport of the heavy metals out of the soil. When the acidic front passes through the soil, the voltage drop will decrease, and the end of the remediation can be predicted by the decrease in voltage to a very low level between the working electrodes.

1. Introduction

Electrochemical soil remediation methods have attracted increased interest during the last decade [1]. Common to these methods is that the cleaning agent is an electric d.c. field that is applied to the polluted soil. Most of the methods aim to remove the pollutants from the soil, and different electrochemical methods are being developed for treating both soils polluted with heavy metals [2, 3] and soils polluted with organic compounds such as NAPLs or *p*-nitrophenol [4–6]. Most research has been done on the laboratory scale, but a few pilot and full-scale remediation actions have also been performed [7, 8]. This paper deals with the electrodialytic soil remediation method which was first described in [9]. The method was developed to remove heavy metals from soils, but it has also been shown to work in other hazardous porous media, such as for the removal of Cu, Cr and As from impregnated wood waste [10] and the removal of Cd from straw ash [11].

The principle of electrodialytic soil remediation (EDR) differs from other electrokinetic remediation methods (EKR) in the use of ion-exchange membranes. In EDR the soil is placed in a desalination compartment instead of the normal electrolyte solution to be desalted in conventional electrodialysis. After the remediation, the soil is clean and the heavy metals are concentrated in the electrode compartments. The heavy metals can be concentrated further from the electrolyte solutions and reuse is possible.

One advantage of the use of ion-exchange membranes is that the products from the electrode processes will not enter the soil. In the case of inert electrodes, the OH^- produced at the surface of the cathode is prevented from entering the soil by a cation-exchange membrane, see Figure 1. The ion-exchange membranes furthermore ensure that only a very limited amount of the applied current is wasted in carrying harmless ions from one electrode compartment to the other. Because there is no competition in the soil between easily mobile ions from the electrode compartments and the ions originating from the soil, concentrations of heavy metal obtained after remediation with EDR can be less than with EKR [12].

The ion exchange membranes limit the durrent density that can be used in the remediation action described in this paper. Even if ion-exchange membranes are placed as shown in Figure 1, the soil pH will change during the electrodialytic treatment. These pH changes are also discussed.

2. Water splitting at ion exchange membranes

In systems with NaCl as the only salt nearly all of the current is carried by salt cations in cation-exchange membranes, even at very high current densities. In contrast pH changes are observed at the anion exchange membranes. Thus the limiting current is lower for an anion exchange membrane than a cation exchange

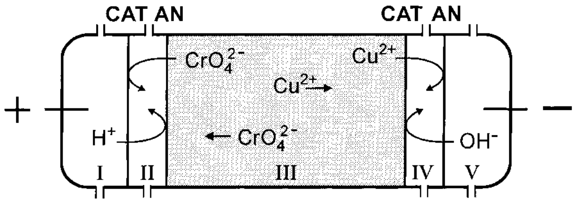

Fig. 1. Principle of electrodialytic soil remediation. (CAT: cation exchange membrane, AN: anion exchange membrane).

membrane in NaCl solutions. Most anion exchange membranes contain quaternary ammonium groups. Simons [13] found indications that water splitting in the anion exchange membrane was related to these groups and later Rubinstein et al. [14] showed clearly that water splitting is indeed determined by the nature of the charged groups.

Most cation exchange membranes contain sulfonic acid groups. As long as the solution which is depleted of ions contains only NaCl, the cation exchange membrane gives rise to no noticeable water splitting. Oda and Yawataya [15] found that introducing various cations, such as Ca^{2+}, Mg^{2+}, and NH_4^+ in the solutions next to the cation exchange membrane, gave rise to an increase in the H^+ and OH^- ion fluxes. Simons [16] showed that phenol, taurine and glyine in solution also gave increased water splitting at the cation exchange membrane.

In soil Ca and Mg are very common elements and a variety of organic compounds are also present. Thus, water splitting at the cation exchange membrane in electrodialytic soil remediation must be taken into consideration.

3. Acidification of the soil during electrodialytic treatment

There are numerous differences between the electrodialysis of a solution and a soil. An important difference is that the solution is stirred whereas the soil is not. This means that concentration profiles are more likely to develop in the soil than in the solution. In the soil the number of free ions is controlled by adsorption/desorption processes as well as precipitation/dissolution processes. The existence of electrical double layers also influences the passage of current. Furthermore the ions can be expected to move more slowly in the soil because of its porous structure.

Most soils have a higher cation exchange capacity (CEC) than anion exchange capacity. This means that the soil can be regarded as a cation exchanger and most of the current in the soil is carried by cations. In EDR a cation exchanger is thus placed next to a anion exchange membrane in front of the anode. The interface here can be expected to be rapidly depleted of ions.

Even when the ion exchange membranes in EDR are placed as shown in Figure 1, the soil is acidified during the remediation process [17]. Anion exchange membranes are not 100% ideal and thus some of the acid may originate from the anolyte but it is likely that water splitting at the anion exchange membrane is of great importance to this acidic front due to the low limiting current of the anion exchange membane.

4. Experimental details

4.1. *Analytical*

The soil concentrations of Cu were measured after pretreatment of the soil as described in Danish Standard (DS259). 1.0 g of dry soil and 20.0 mL (1:1) HNO_3 were heated at 200 kPa (120 °C) for 30 min. The liquid was separated from the solid particles through a nuclepore filter and diluted to 100 mL. Cu was measured by atomic absorption spectrophotometry. All Cu concentrations in the soil are given on dry soil basis.

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

The water content was found as the weight loss after heating a sample for 24 h at 105 °C.

4.2. *Experimental soil*

The experimental soil was sampled at a site polluted with Cu, Cr and As from 40 years of wood preservation (1936–77). This investigation only covered Cu. The soil was sampled at an area devoid of vegetation because of the high degree of pollution. The sampling depth was 5 to 15 cm.

Some characteristics of the experimental soil are given in Table 1.

4.3. *Apparatus*

Cells with three compartments were used in this investigation because it was the membranes in contact with the soil that were of interest. Two types of soil compartments were used and the rest of the equipment did not vary between the two series. In cell I, see Figure 2(a), the soil compartment was 3 cm long. In the soil, at a distance of 1.5 cm from the membranes, four measuring silver electrodes were placed in a circle. In cell II; see Figure 2(b), the soil compartment was 15 cm long and 20 silver electrodes were placed in the soil (four electrodes in five rows). The silver electrodes reached 0.8 cm into the soil and had a diameter of 1.0 mm. The reason for measuring the voltage at four points at each distance was to minimize the effect on the results of the

Table 1. Some characteristics of the experimental soil

Cu concentration	910 mg kg^{-1}
Soil pH	5.4
Organic matter (glowed at 550 °C)	3.6%
Carbonate content (Scheibler method)	$<0.2\%$
Fine fraction (<0, 063 mm)	27.2%

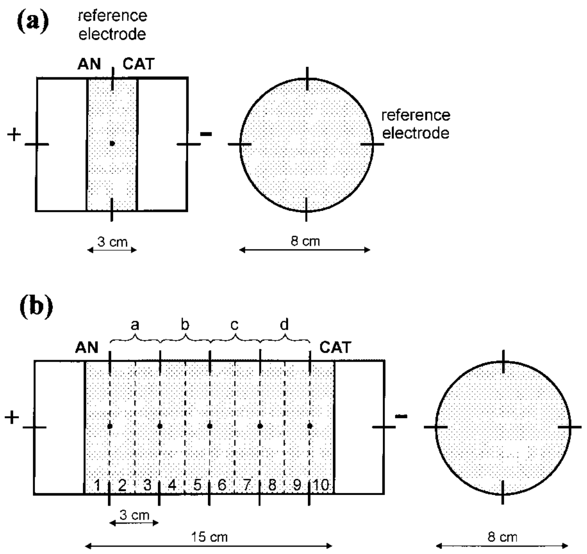

Fig. 2. The laboratory cells (a) used for series 1 and (b) used for series 2.

inhomogenity of the soil. The cells were made of Plexiglas. The internal diameter of the cell was 8 cm. The ion exchange membranes were obtained from Ionics (anion exchange membrane 204 SZRA B02249C and cation exchange membrane CR67HUY N12116B). The charged groups were sulfonated copolymers at the cation exchange membrane and quaternary ammonium at the anion exchange membrane.

In each electrode compartment, 0.5 L of 0.01 M $NaNO_3$ with pH adjusted to about 2 with HNO_3 was circulated. Peristaltic pumps from Masterflex were used, and the pumping rate was about 50 ml min^{-1}. Platinum-coated electrodes from Bergsöe AC was used as working electrodes, and a power supply (Hewlett Packard E3612A) was used to maintain a constant current.

4.4. *Electrodialytic soil remediation experiments*

Experimental parameters for the seven experiments carried out are shown in Table 2. When preparing each experiment, distilled water was added to the soil, and the initial water content given in Table 2 is the water content after this addition. The soil compartment was filled by hand and gas pockets in the soil were carefully avoided. During the experiments pH in the catholyte was manually controlled by adding 1:1 HNO_3 (by volume) when pH exceeded about 3. The voltage between each of the working electrodes and the measuring electrodes in the soil was measured several times during each experiment.

Table 2. Electrodialytic soil remediation experiments made

Exp.	Cell	Current /mA	Duration /day	Total charge/C	Soil weight/ g dry matter	Water content/ %
A	1	5	7	3024	279	15.5
B	1	15	7	9072	270	14.9
C	1	25	7	15 120	274	15.1
D	1	35	7	21 168	271	15.2
E	2	15	14	18 144	1340	14.8
F	2	15	28	36 288	1340	14.8
G	2	15	42	54 432	1350	15.1

At the end of the experiments, the soil was segmented into slices from anode to cathode and pH, water content and Cu concentration were measured. pH was measured in two soil samples from each slice, and Cu concentrations were measured three times in each slice.

The cathode was treated with alternating polarity in a 1 M HNO_3 solution and the amount of Cu precipitated on the cathode was measured in the solution. The ion exchange membranes were placed in 1 M HCl for 24 h to measure the amount of Cu adsorbed in them.

5. Results

5.1. *Limiting current of the system*

As a function of time the voltage between the working electrodes, the mean voltage between measuring electrodes and anode, and the mean voltage between measuring electrodes and the cathode are shown for experiments A to D in Figure 3. There were small variations (<1.5 V) in voltage between the measurements at each time, but there were no overall indications of the voltage being higher in the top, in the bottom or in the middle of the cell. The last voltage measurements in experiment D showed a larger difference (up to 4 V) between the electrodes.

After one week of current, the experiments of series 1 were stopped. The soil was segmented into three slices from anode to cathode. Each slice was about 1.0 cm thick and had a dry weight of about 90 g. In both experiments C and D, a very hard layer next to the cation exchange membrane was observed, and these layers were collected separately. The weight of these layers was 7.5 g dry matter in experiment C and 11.6 g dry matter in experiment D.

The profiles of mean pH and Cu concentration are shown in Figures 4 and 5, respectively. The water content in the soil slices varied between 8% and 16% and the water content tended to be lower at the anode end than the cathode end of the soil.

The Cu concentrations in the different parts of the cells at the end of the experiments are shown in Table 3, where mass balances for Cu are also shown.

5.2. *Relation between development of an acidic front in the soil and the overall voltage*

In experiments F and G, thin black lines were observed from the measuring electrodes in the direction of the cathode. At the end of experiment G it was visually seen that the electrodes in the top of the cell were thinner and shorter than the other measuring electrodes. In experiment F, dissolution of the anode was observed after 14 days of current. This anode was replaced.

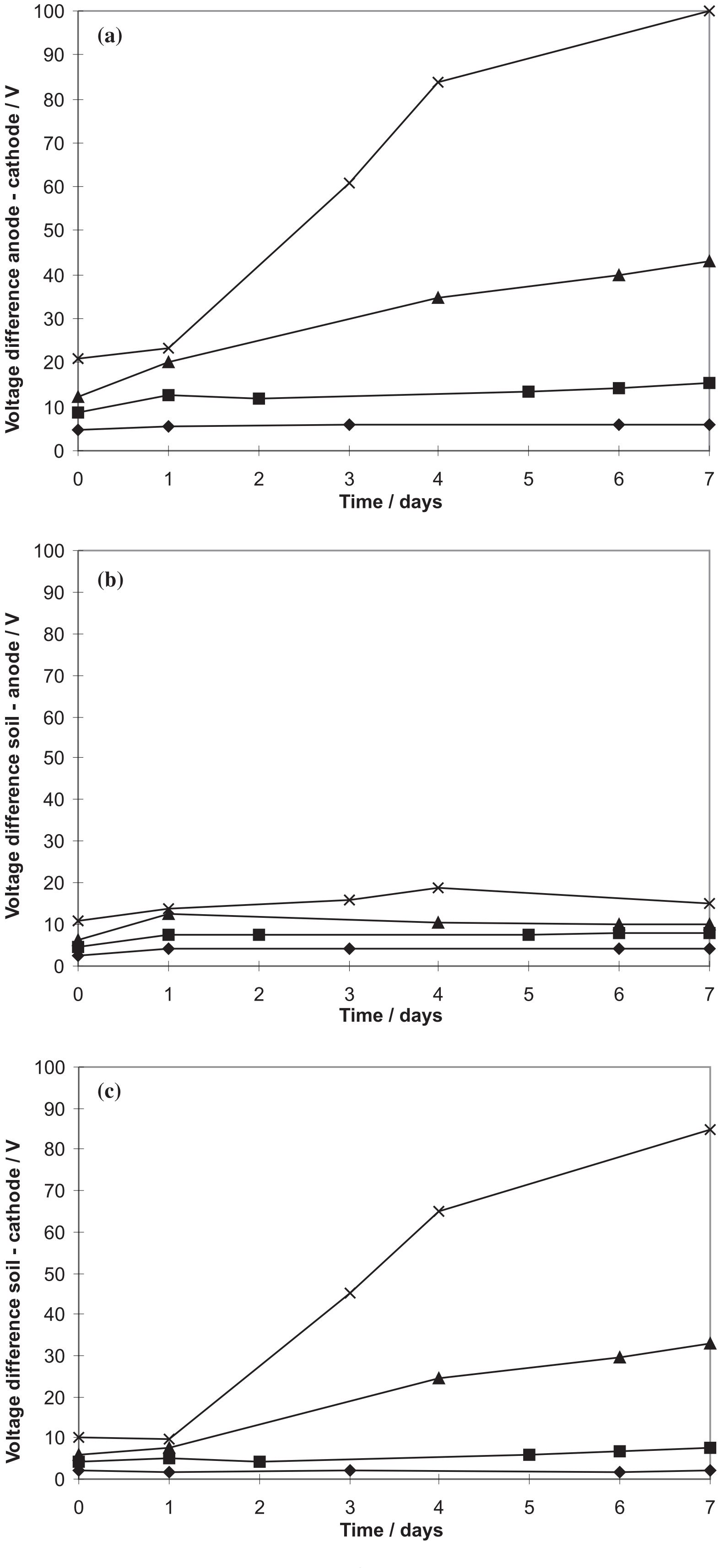

Fig. 3. (a) Voltage drop between working electrodes in experiments A (◆), B (■), C (▲) and D (×). (b) Voltage drop between anode and reference electrodes in the soil (mean values). (c) Voltage drop between cathode and reference electrodes in the soil (mean values).

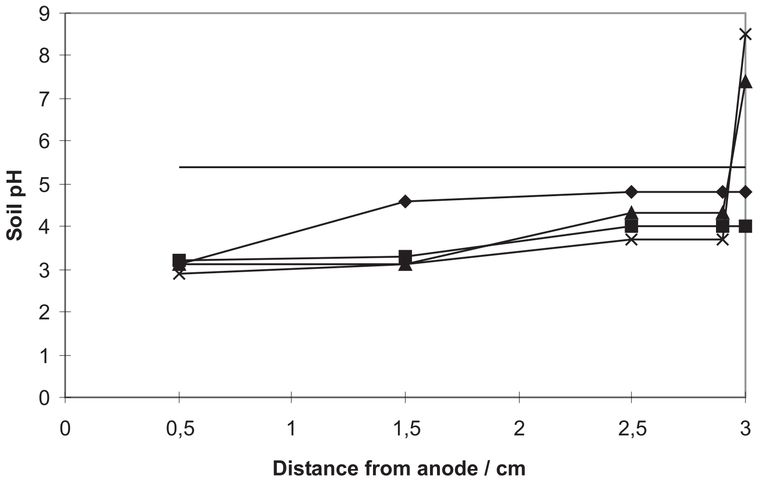

Fig. 4. pH in the soil in experiments A (◆), B (■), C (▲) and D (×).

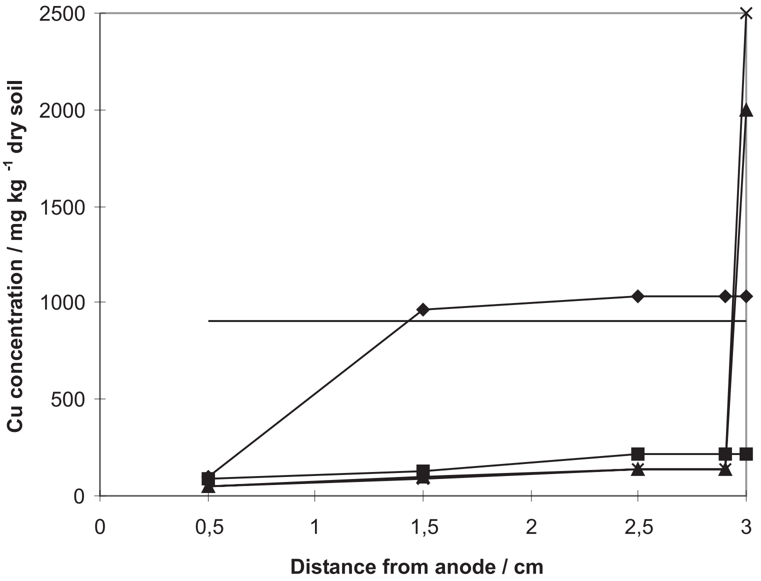

Fig. 5. Final Cu concentrations in the soil in experiments A (◆), B (■), C (▲) and D (×).

Table 3. Amount of Cu (mg) in the different parts of the cell in experiments A to G

Experiment	A	B	C	D	E	F	G
Anolyte	0.1	0.1	0.1	0	2	1	2
AN	0.2	0.1	0.1	0.1	0	49	0
Soil	199	38	160	256	1224	371	1285
CAT	7.9	20	16	22	387	32	496
Catolyte	13.4	120	65	3.4	186	269	6623
Cathode	7.5	75	9.6	1.7	47	6063	4929
Cu total (end) (mg)	228	253	251	283	1286	1283	1334
Cu total (start) (mg)	254	246	256	257	1219	1219	1229
Recovered (%)	90	103	98	110	105	105	108

The voltage difference between the working electrodes as a function of time is shown in Figure 6(a). The voltage between the anode and each measuring electrode was measured several times during the experiment. In this part of the investigation, the variation in voltage difference in the soil was in focus. Thus the results are shown for the soil between the measuring electrodes. The first voltage difference (Figure 6(b)) corresponds to slice a, see Figure 2b. This was calculated as the voltage from row 2 to anode minus row 1 to anode. Figure 6(c) corresponds to slice b, (row 3 minus row 2) and so on.

In experiments E to G, the soil was segmented into10 slices from anode to cathode, each slice being 1.5 cm long and with a dry weight of about 130 g. Profiles of pH and Cu concentration are shown in Figures 7 and 8, respectively. The water content decreased as more current was passed through the cell and the water was moved from the anode end towards the cathode end, probably due to electroosmosis. The water content in slice 1, experiment G, was 4.5% which was the lowest found.

6. Discussion

6.1. *Limiting current of the system*

From Figure 3(a) it can be seen that the voltage between the working electrodes is almost constant in the two experiments with the lowest current, experiments A and B, while the voltage is increasing in experiments C and D. From Figure 3(b) and (c) it is seen that this increase in voltage is an increase in resistance between cathode and the middle of the soil. The water content in the soil was very simular at the end of the four experiments and this means that the difference in voltage is not due to differences in soil water content.

From Figure 4 it can be seen that the soil slice closest to the anode had been acidified to a level of about 3.5 in each of the four experiments. This acidic front is expected partly to originate from water splitting at the anion exchange membrane. In experiment A, only the first slice had been acidified to a level of 3.5, and the rate of acidic front is dependent on the current density, as expected. In the three next experiments all three soil slices were acidified, but in experiments C and D pH was increased in a thin hard soil layer next to the cation exchange membrane. Even if the cation exchange membrane is not 100% ideal, the increased pH in this thin layer cannot be due to transport of hydroxyl ions through the membrane from the catholyte, because at no time in the two experiments did the pH of the catholyte exceeded 3.5. Thus the increase in pH is probably due to water splitting. The limiting current of the cation exchange membrane in this system was then between 0.3 mA cm^{-2} (experiment B) and 0.5 mA cm^{-2} (experiment C). This correlates well with [18] where the limiting current for a similar soil system was found to be between 0.40 and 0.75 mA cm^{-2}.

The mass balances for Cu in table 3 are not 100% accurate. This is mainly due to the fact that the investigation was done on a soil that had been sampled at a polluted site, and such soil samples are always very inhomogeneous. Even after mixing the soil batch carefully differences in concentration levels occur and the mass balances suffer from this. Cu was removed from the soil as cations, as expected, which can be seen from Table 3 where the main part of the Cu is in the cathode end of the cell.

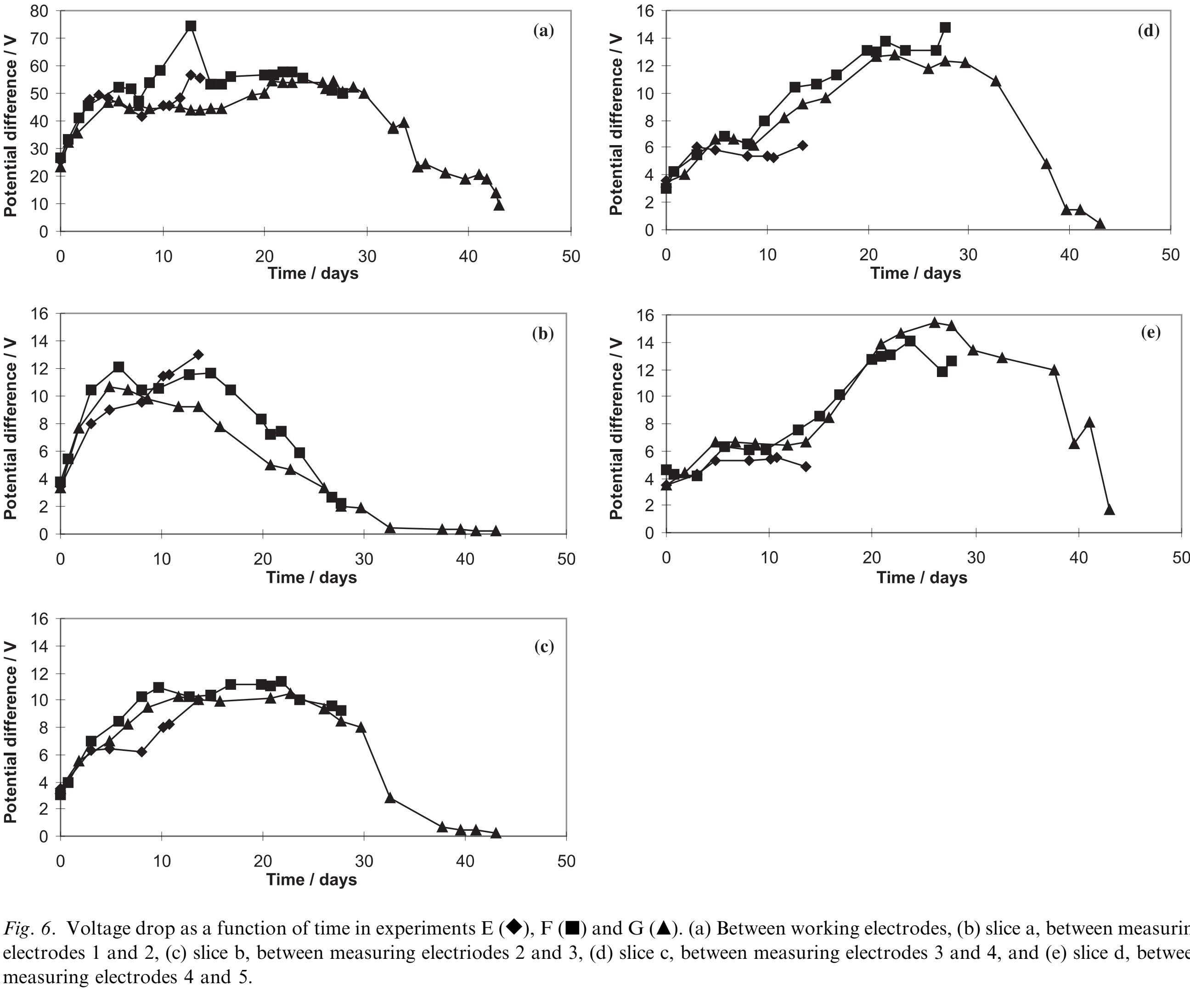

Fig. 6. Voltage drop as a function of time in experiments E (◆), F (■) and G (▲). (a) Between working electrodes, (b) slice a, between measuring electrodes 1 and 2, (c) slice b, between measuring electriodes 2 and 3, (d) slice c, between measuring electrodes 3 and 4, and (e) slice d, between measuring electrodes 4 and 5.

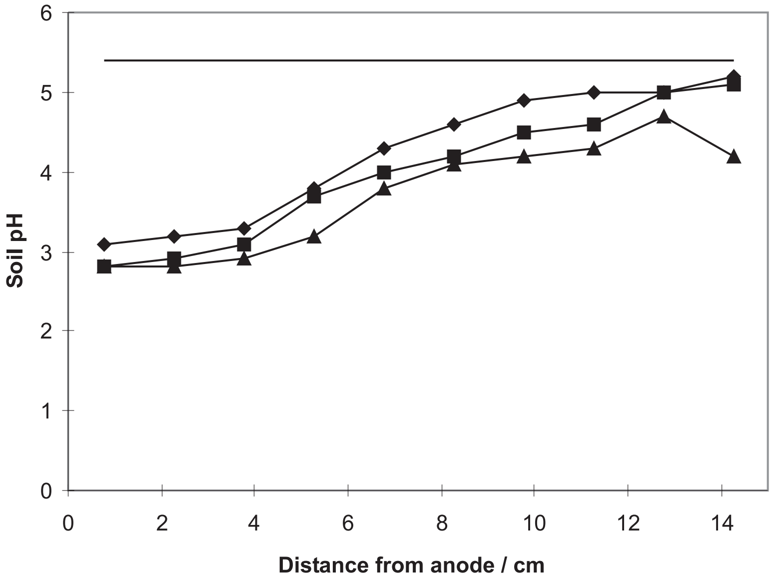

Fig. 7. Final pH profiles in the soil in experiments E (◆), F (■) and G (▲).

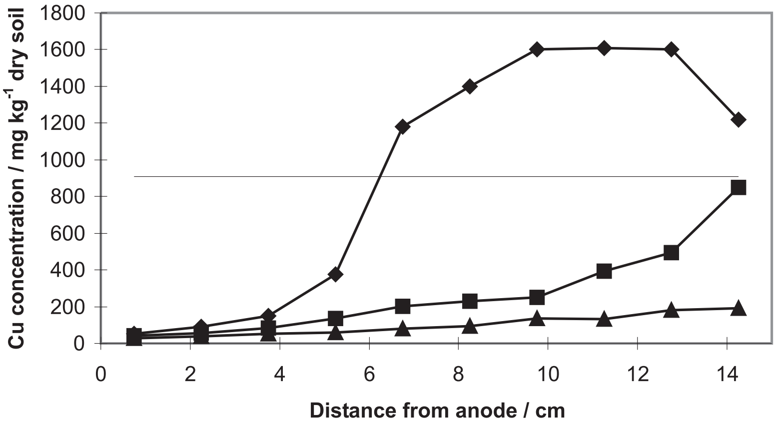

Fig. 8. Final Cu concentration in the soil in experiments E (◆), F (■), and G (▲).

It is well known that desorption of Cu from soil increases with decreasing pH (e.g., [19]). Several investigations have also shown that pH is a key parameter in electrochemical soil remediation methods (e.g., [17, 20, 21]). The Cu profiles in Figure 5 also correspond very well to the pH profiles from Figure 4. At low pH Cu was removed and at neutral to slightly basic pH conditions Cu accumulated. This means that the Cu removed from the anode end of the soil is precipitated in the soil where pH has not yet been lowered. The base produced from water splitting at the cation exchange membrane is actually hindering the Cu from entering into the catolyte, (Table 3). In the hard soil layer next to the cation exchange membrane the final Cu concentration was more than 20 times the initial concentration in experiment D.

Experiment B, where 15 mA (0.3 mA cm^{-2}) was applied to the soil, showed the best results. Here the Cu level decreased in the whole soil volume and 85% Cu was removed.

6.2. *Relation between development of an acidic front in the soil and the overall voltage*

For the second series of experiments the current density was 0.3 mA cm^{-2} because the former series of experiments showed that remediation occurs well at this current density.

Good correlation between the pH profiles (Figure 7) and Cu profiles (Figure 8) is seen. Low pH is a catalyst for Cu removal. After 42 days of current 91% of the Cu was removed from the soil and the concentration level in slice 1 was 29 mg kg^{-1}. The voltage drop to each of the measuring electrodes was measured at each time, and there were only small differences. Again there was no clear tendency that the voltage drop should be larger in the top or in the bottom of the cell. Again it was seen that the measuring electrodes in the top of the cell were more attacked by the electric current than the others. This indicates that the current density was higher at the top. Even so, an equal current density over each cross section is used as basis for the considerations that follow.

The differences in voltage between the working electrodes, Figure 6(a), are very similar to that expected from previous experiences [17]. The curves are similar for the three experiments, except for experiment F in the period from 10 to 14 days. This was the time that dissolution of the anode was discovered, and after 14 days when this anode was replaced, the voltage returned to the same level as the other experiments. Consider now one of the soil slices for which the voltage difference as a function of time is given in Figure 6(b) to (e). In such a soil slice the current at first is carried by ions that originate from the soil. Cations from the neighbouring soil slice at the anode side pass through the actual soil slice towards the cathode and anions pass from the slice on the other side. After a period of time the acidic front will reach the soil volume from the anode side. The acidification results in an increase in desorption and dissolution processes, and thus the number of ions available to carry the current increases. The soil buffers the acidic front, but after a while the acidic front passes through the whole soil volume, so that many ions are available to carry current through the soil volume, and included in these are the H^+ ions.

The voltage curves for each of the four soil volumes follows similar patterns (Figure 6(b) to (e). First an increase, then a period with an almost constant voltage and finally a decrease to a very low level. The increases in voltage cannot be explained by pH changes or other parameters that were measured in this investigation. It is, however, clearly seen that the increase in voltage is delayed, as the distance to the anode increases and the delay may be related to the mobile ions originally in the soil.

The decrease in voltage can be correlated with the position of the acidic front. In experiment E the Cu has been removed to very low levels in slice a (Figure 8) and the acidic front has reached through the slice (Figure 7), too (i.e., after 14 days). Both pH and Cu concentration increased between slice a and b, and this indicates that the two fronts were situated exactly where the position of the measuring electrodes separated these two slices. In experiment F low Cu concentrations were found in the slices a, b and c (i.e., after 28 days) and the voltage decreased in slice c after about 30 days. After 42 days (experiment G) the two fronts hd passed slice d, too, and at about 40 days the voltage started to decrease here. Thus the decrease in voltage over each slice is related to the passage of the acidic front.

The total water content in the soil seems to be of minor importance to the voltage drop over each soil slice in the range in these experiments (i.e., 15% to 5%). Even though the water content in half of slice a is about 4.5% in the end of experiment G, the voltage drop in the same slice is only 0.2 V.

The very low voltage drop over the cell found at the end of experiment G, about 9 V, is a level that can be expected to decrease to about 5 V, a value at which it has been seen to stabilize in similar experiments. An experiment made on soil form the same site showed no increase in voltage between two and 11 months of current flow. However, in this experiment, all Cu had been removed from the soil after two months. The decrease in voltage drop over the cell may be used as an indication of the remediation being finished. This voltage drop is the opposite to that is found in electrodialysis of a solution. Here a sharp increase in voltage drop shows that the heavy metals have been removed from the desalination compartment [21].

7. Conclusion

In electrodialytic soil remediation water splitting at the anion exchange membrane can be expected. At all current densities investigated here, the lowest being $0.1\ \mathrm{mA\ cm^{-2}}$, an acidic front passed through the soil towards the cathode. This acidic front causes an increased desorption and dissolution of Cu increasing the mobility in the electric field.

Water splitting at the cation exchange membrane was observed at a current density of $0.5\ \mathrm{mA\ cm^{-2}}$ but not at a current density of $0.3\ \mathrm{mA\ cm^{-2}}$. Thus the limiting current density for the cation exchange membrane in this system is between these two values. Water splitting at the cation exchange membrane damages the remediation process. The hydroxyl ions produced precipitate with cations from the soil thus forming a hard layer next to the membrane. This causes a very high resistivity. Cu, too, was precipitated here and thus hindered its passing into the catholyte as planned. Thus it is very important to apply a current density that is less than the limiting current density at the cation exchange membrane.

When the acidic front from the anion exchange membrane passes through the soil towards the cathode, the voltage drop can show the position of the acidic front, because it decreases sharply after the passage of the front. Cu is removed from the areas with low pH, and thus the voltage drop gives an indication of how far the remediation process has progressed. It may be possible to determine when remediation has finished by the very low voltage drop between the working electrodes.

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