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Electrochemical Analysis of Ion-Exchange Membranes with Respect to a Possible Use in Electrodialytic Decontamination of Soil Polluted with Heavy Metals†

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ABSTRACT

Transport numbers in different metal chloride solutions were estimated using the emf method for two ion-exchange membranes: Ionics CR67 HMR412 (cation-exchange membrane) and Ionics AR204 SXRA 7639 (anion-exchange membrane). The cation-exchange membrane was found to work nearly ideally for NaCl and $CaCl_2$ solutions even at high concentrations, whereas deviation from ideality was seen for $ZnCl_2$ and $CuCl_2$ solutions. The anion-exchange membrane showed transport numbers for the anion around 0.95 for NaCl, $CaCl_2$ and $ZnCl_2$ solutions for the concentration range investigated. Electrodialytic desalting experiments taken as a simplified simulation of the electrokinetic decontamination method showed that it was possible to remove all ions in the simulated soil volume, with a sharp increase in the potential difference over the soil volume as a result, and that it was possible to control the metal content in the different solutions in the electrodialytic decontamination method.

Key Words. Ion-exchange membranes; Electrodialysis; Transport numbers; Desalting; Heavy metals; Soil decontamination

† Dedicated to Jørgen Birger Jensen (1937–1995).
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INTRODUCTION

Processes for decontamination of heavy metal polluted soils have gained increasing interest during recent years due to the need and obligation for a clean environment. Especially the use of electric current to mobilize heavy metals in soil has great potential; this process is called electrokinetic soil remediation. Several research teams are investigating this concept worldwide (1–6), and various patents based on different process designs and conditions have been issued (7–11).

At the Technical University of Denmark a new concept of electrokinetic soil remediation has been developed (12–15) with the purpose of eliminating different disadvantages by introducing ion-exchange membranes in the process in a way known from electrodialysis (16). This concept is called electrodialytic soil remediation. Even though the process was shown to be successful in laboratory experiments, two mayor questions have arisen in connection with the function of the ion-exchange membranes: 1) How much do the ion-exchange membranes deviate from ideal ion-exchange properties, and 2) Would it be possible to desalt a solution completely for ions by electrodialysis using the membranes. These questions have an important bearing on the efficiency of the method and therefore on the level of heavy metal concentration in the soil that could be reached after remediation.

The aim of the present work is to answer these two questions for a specific set of ion-exchange membranes which are currently being used in the study of electrodialytic soil remediation. In order to reach a full understanding of electrodialytic soil remediation, it is necessary to examine the role of ion-exchange membranes in the process in known systems consisting only of electrolyte solutions before adding soil to the process.

BACKGROUND

The concept generally used for electrokinetic remediation of soil can be summarized as shown in Fig. 1. As illustrated in the figure, heavy metal ions are continuously removed from the soil due to a direct current electric field. Furthermore, uncharged heavy metal species and organic compounds are removed due to electroosmotic flow (17) which occurs when current passes through a porous medium, e.g., soil, consisting of charged particles. The passive membranes can be regarded as physical separators between the soil and electrode compartment and which prevent the soil and salt solutions from mixing.

This concept has proven to work satisfactorily, and remediation of the soil has been possible, but there are still three obvious disadvantages existing in the concept used in Fig. 1:

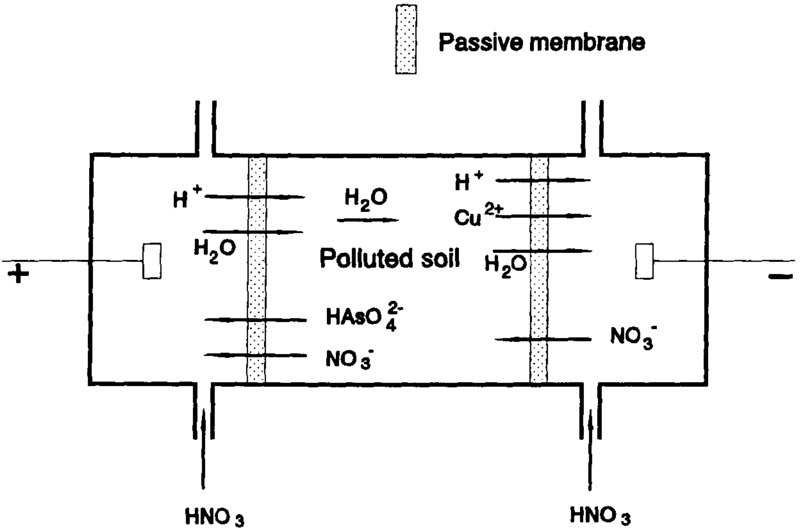


FIG. 1 The principle of the electrokinetic remediation method with passive membranes.

1. Ions will be driven into the soil simultaneously with ions being led out of the soil. This results in a waste of energy in transporting ions between the two electrode compartments. Because the mobility of ions in the soil is lower than in the electrolytes, more ions will be transported into the soil than there are heavy metal ions removed from the soil until a steady state is reached.
2. When heavy metals from the soil enter the electrolyte solutions, they might alter their charge in response to the solution properties. The result could be that heavy metals reenter the soil in the electric field.
3. If inert electrodes (e.g., platinum) are used, the electrode processes would most likely be

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

at the cathode, and

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$$

at the anode. This means that OH^- ions are produced at the cathode and passed into the soil in the electric field. In the same manner, H^+ ions are produced at the anode and passed into the soil. Where the H^+ front meets the OH^- front, a large amount of heavy metals precipitate in the soil (1).

At the Technical University of Denmark an optimization of electrokinetic soil remediation was developed (12–15) by introducing ion-exchange membranes in the process, resulting in electrodialytic soil remediation. Figure 2 illustrates the concept, where the ion-exchange membranes 1) prohibit the transport of ions into the soil (compartment III) from the concentrated solutions II and IV, 2) overcome the problem of charge reversal of the heavy metal species in the concentrated solutions II and IV, and 3) avoid the generation of a OH^- front in the soil. Furthermore, the electrode processes can be controlled better since no ions coming from the soil enter the electrode compartments I and V as indicated in Fig. 2. Subsequently, the heavy metals should be collected in the concentrated solutions II and IV.

An ion-exchange membrane can be regarded as an interface that preferably permits the transport of ions with either a positive or a negative charge, and prohibits the transport of ions of opposite charge. If an ion-exchange membrane separates two solutions of an electrolyte with different concentrations, the ions will tend to move from the concentrated side to the dilute side of the membrane. In addition, a potential difference, the diffusion potential, will arise between the two sides of the membrane to fulfill the electroneutrality which must exist between the two sides of the membrane (18). The counterions are preferably transported through the ion-exchange

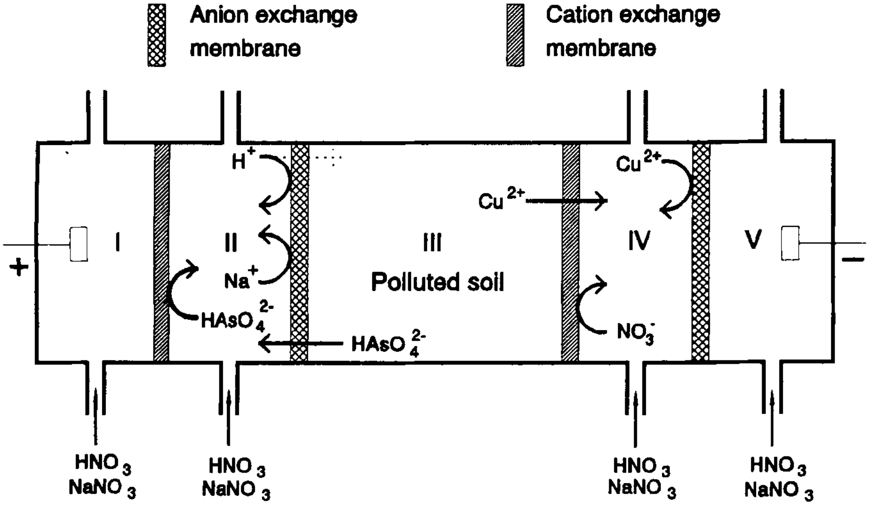


FIG. 2 The improved principle of the electrokinetic remediation method including ion-exchange membranes (electrodialytic soil decontamination).

membrane whereas the co-ions are excluded from the membrane phase because the fixed charged groups in the membrane have the same sign as the co-ions. But the transport of one counterion must be exactly counterbalanced by the transport of one co-ion (if a 1 : 1 electrolyte is considered). Therefore, an electric potential difference is created by the membrane, and it will "speed up" the transport of co-ions and "slow down" the transport of counterions. This potential can be regarded as a measure of the charge selectivity or permselectivity of the membrane.

In order to consider the application of an electric current to a soil volume using the membrane arrangement shown in Fig. 2, the limiting current of the membranes has to be studied. The limiting current for a given ion-exchange membrane is (19)

$$I_{cr} = \frac{FCD}{\delta}\left(\frac{1}{t_m - t_s}\right) \tag{1}$$

where F is Faraday's number, C is the bulk solution concentration, D is the diffusion coefficient of the counterion in the film layer adhering to the membrane, δ is the film layer thickness, while t_m and t_s are the transport numbers of the counterions transported in the membrane and solution, respectively (cf. below). In the case with soil adjacent to the membrane, the solution is the soil liquid.

Due to the cation-exchange capacity of soil, there will be more movable cations than anions. The low concentration of anions in the soil (C low), the tortuosity of the soil pores (D low), and the poor mixing in the soil (δ high) all result in a low limiting current for the anion-exchange membrane when it is adjacent to soil. When the current exceeds this critical value, the transport of anions in the soil to the anion-exchange membrane surface becomes too low, and in order to carry the current, water molecules are dissociated into H^+ and OH^- at the soil/membrane interface. The OH^- ions will pass through the anion-exchange membrane to the electrolyte solution due to the electric field, whereas the H^+ ions will move through the soil volume. The limiting current of the cation-exchange membrane will be higher than that of the anion-exchange membrane due to a higher concentration of free cations. This can also be found from Eq. (1) because the term $1/(t_m - t_s)$ will be larger for cations than for anions due to the higher transport number for cations than for anions in the soil. If the current used in the decontamination cell is lower than the limiting current for the cation-exchange membrane, but higher than the limiting current for the anion-exchange membrane, no OH^--front will be developed, whereas a certain amount of water dissociation at the anion-exchange membrane will result in a H^+-front moving through the soil volume, and this could be valuable for desorption of cationic heavy metals from the soil particles (15). In addition, the anion-exchange membrane has been observed not to prohibit completely the passage of H^+ ions through the membrane (20).

For optimization of the electrokinetic soil decontamination method, the ion-exchange membranes should:

1. Obey nearly ideal behavior, which means that the *transport numbers* for cations should be 1 for the cation-exchange membrane and 0 for the anion-exchange membrane. The transport number can be determined by measuring the potential difference over a membrane placed between two electrolyte solutions of different concentrations. This is done by measuring the electromotive force of a concentration cell.
2. Give the possibility of cleaning the soil volume completely for mobile ions (both heavy metals and harmless ions) in the soil, and this should be registered by a sharp increase in the potential drop over the cell during the process. This can be shown by *electrodialysis measurements*, where the soil volume to be desalted is "simulated" by a salt solution.

Transport Number

The transport number (t_i) is the fraction of the total electric current through a medium that is carried by a particular ionic species (i) at a constant concentration:

$$t_i = J_{q,i}/J_q \tag{2}$$

Equation (2) can be derived to (see Ref. 21):

$$t_i = \frac{\mu_i z_i^2 C_i}{\sum_k \mu_k z_k^2 C_k} \tag{3}$$

It has been shown elsewhere (22) that measuring the potential difference with Ag/AgCl electrodes in a system consisting of two metal chloride solutions separated by an ion-exchange membrane gives the following expression for the potential difference—or electromotive force (emf):

$$\text{emf}_{(r-l)} = -\frac{\nu}{\nu_-}\frac{RT}{F}t_+ \ln\frac{a_{(r)}}{a_{(l)}} \tag{4}$$

or

$$\text{emf}_{(r-l)} = -\frac{\nu}{\nu_-}\frac{RT}{F}t_+ \ln\frac{\gamma_{\pm(r)}\cdot c_{s(r)}}{\gamma_{\pm(l)}\cdot c_{s(l)}} \tag{5}$$

where $\text{emf}_{(r-l)}$ is the potential difference between the right side and the left side of the membrane, $a_{(r)}$ and $a_{(l)}$ are the activities of the electrolyte on the right and left sides of the membrane, respectively, $c_{s(r)}$ and $c_{s(l)}$ are the concentration of the salts on the right and left sides of the membrane, respectively, $\gamma_{\pm(r)}$ and $\gamma_{\pm(l)}$ are the activity coefficients of the salt on the right and left sides of the membrane, respectively (which can be found from Ref. 23), and t_+ is the transport number of the cation through the membrane. ν and ν_- are the stoichiometric numbers of the salt:

$$A_{\nu_+}^{z_+}B_{\nu_-}^{z_-}, \qquad \nu = \nu_+ + \nu_-$$

The transport number is then given by rearranging Eq. (4):

$$t_+ = -\frac{\nu_- F \text{emf}}{\nu RT \ln \dfrac{a_{(r)}}{a_{(l)}}} \tag{6}$$

In Eq. (6) it is assumed that the transport number is independent of the concentration, which is not exactly true. If a similar differential relation is used, a transport number is obtained which is approximately independent of a fixed concentration on one side of the membrane (21):

$$t_+^* = -\frac{\nu_- F d(\text{emf})}{\nu RT d\left(\ln \dfrac{a_{(r)}}{a_{(l)}}\right)} \tag{7}$$

The transport numbers t_+ and t_+^* are apparent numbers, i.e., such a complicating phenomenon as the transport of solvent is not taken into account here.

Electrodialysis

Electrodialysis has been used for decades for desalting and in wastewater treatment (16). The remediation of soil contaminated with heavy metals can be regarded as a desalting process when ion-exchange membranes are used as separators between soil and electrolyte solutions.

If the ion-exchange membranes were working satisfactorily, the polluted soil volume could be decontaminated perfectly for the ions originally available in the soil, and no ions from the electrolyte solutions would penetrate the membranes. Therefore, the voltage drop over the electrodialytic cell should increase when a simulated soil volume is emptied of ions. Then the only way for the current to pass from the anode to the cathode would be by dissociating the water molecules in the middle compartment to H^+ and OH^- ions, which now could move in the electric field.

The only possibility for cations from the electrolytes to pass into the middle compartment would be:

1. From the cathode compartment due to interdiffusion across the cation-exchange membrane even if the electric field was directed oppositely.
2. From the anode compartment if the anion-exchange membrane is not working ideally ($t_- < 1$ for anions). In this case the gradient due to the electric field promotes the transport of cations toward the middle compartment.

Similar conditions could be outlined for anions.

The use of electrodialysis measurements as a simulation of the soil decontamination process is not completely applicable due to poor mixing in the soil volume. In electrodialysis experiments using aqueous solutions, the solutions at the membrane surfaces were well stirred. In the soil decontamination method there are concentration gradients in the soil adjacent to the membrane surface due to slow diffusion of ions in the soil volume. Furthermore, different soils have different specific cation-exchange capacities due to the negative sites on the soil particles, especially on clay and silt particles, and on the organic material in the soil. The electrodialytical measurements made here are for ion-exchange membranes in contact with different heavy metals or soil alkali metals, and an investigation of the combination of the membranes.

EXPERIMENTAL

Materials

The membranes used were chosen from among others after preliminary experiments (22): Ionics, Inc. CR67 HMR412 (cation-exchange membrane) and Ionics, Inc. AR204 SXRA 7639 (anion-exchange membrane), which were in the ion-form corresponding to the electrolyte to be measured. The different salts used were all Merck or Riedel de Häen Analytical Grade. Electrodes used for transport number determination were Ag/AgCl electrodes (produced in the laboratory). The working electrodes used for the electrodialysis experiments were platinized titanium (BAC Bergsøe Anti Corrosion), and the measuring electrodes were calomel electrodes (Radiometer, REF401).

Procedures

Transport Numbers

The transport numbers for the two membranes were estimated for different metal chloride solutions.

The potential difference between two solutions of the same salt but with different concentrations was measured with two Ag/AgCl electrodes. The solution on one side of the membrane was kept at a constant concentration (for the cation: 0.01 M) whereas the concentration on the other side was varied from 10^{-4} to 1 M (for $CuCl_2$ only until 0.1 M). The measuring cell is shown in Fig. 3. The temperature was kept at 25.0°C during all experiments. For more experimental details, see Ref. 22.

Measurements for each salt and membrane were triplicated.

Electrodialysis Measurements

Two types of experiments were carried out:

1. Experiments were made to test the efficiency of the desalination of a solution containing heavy metals, $Cu(NO_3)_2$.
2. Experiments were made to follow the different cationic species in the electrodialysis process sketched in Fig. 2 in order to be able to control the electrode processes and the removal of cations.

In the first experiment (experiment A, see Fig. 4), 1 dm^3 0.01 M $Mg(NO_3)_2$ was placed in the anode compartment, 1 dm^3 0.01 M $Ca(NO_3)_2$ in the cathode compartment, and 1 dm^3 0.01 M $Cu(NO_3)_2$ in the middle compartment. In all three compartments the solutions were stirred by Eheim No. 1046 recirculation pumps.

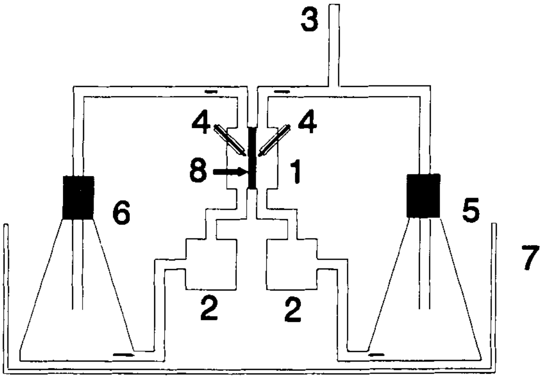


FIG. 3 The experimental setup for the emf measurements. 1: The membrane measuring cell. 2: Eheim No. 1046 recirculation pumps. 3: Thermometer. 4: Measuring electrodes: Ag/AgCl electrodes connected with a Fluke 37 Multimeter to register the potential difference. 5: Solution with varying concentration. 6: Solution with fixed concentration. 7: Thermostatic bath (25°C). 8: Membrane to be measured.

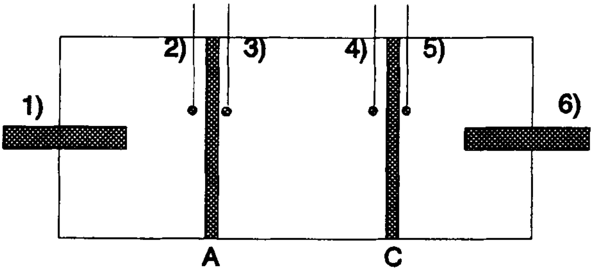


FIG. 4 The combination of working and reference electrodes and membranes. C: Cation-exchange membrane. A: Anion-exchange membrane. 1: Working anode. 2, 3, 4, 5: Reference calomel electrodes. 6: Working cathode.

The cation-exchange membrane was equilibrated with $Ca(NO_3)_2$ and the anion-exchange membrane was equilibrated with $Mg(NO_3)_2$. Concentrated HNO_3 (1 mL) was added to the cathodic electrode compartment before the beginning of the experiment in order to avoid any precipitation in the electrode compartment due to the production of OH^- from the cathode reaction.

The experiment was duplicated.

For the second type of experiment (experiment B, see Fig. 2), 1 dm^3 of a solution containing 0.005 M $Ca(NO_3)_2$ and 0.005 M $Cu(NO_3)_2$ was placed in the middle compartment (III), and each of the four other compartments (I, II, IV, and V) contained 1 dm^3 0.01 M $Mg(NO_3)_2$. In all five compartments the solutions were stirred by Eheim No. 1046 recirculation pumps.

A solution containing $Cu(NO_3)_2$ and $Ca(NO_3)_2$ was chosen in order to test the concept with both a polluting and a nonpolluting species. The presence of Cu and Ca is representative of polluted soil in Denmark—copper is a pollutant from the wood preservation industry and calcium is naturally present, e.g., as $CaCO_3$. The solutions in the four other compartments contained $Mg(NO_3)_2$, which made it possible to detect precisely the transport of divalent cations in and out of compartment III.

Experiment B was duplicated.

For both types of experiments, the variation of the concentrations in the different compartments were followed by taking 1 cm^3 solution samples at appropriate time intervals. The metal concentrations were determined by atomic absorption spectrophotometry. Corrections for the samples were made for the volumes and concentrations. The potential drops over the electrodes, over the different membranes, and over the middle compartment were registered throughout the experiments. In all experiments the current strength was a constant 10 mA (0.4 mA/cm^2 membrane surface), which was below the limiting current for the two membranes.

RESULTS AND DISCUSSION

Transport Numbers

The transport numbers for the two ion-exchange membranes were estimated by using Eq. (6) in different chloride solutions with both monovalent and divalent cations. Figure 5 shows the measured emf as a function of the ratio between salt activity on the two sides of the membrane for these chloride solutions for the cation-exchange membrane CR67 HMR412. The dashed lines indicate the ideal cases, where the transport numbers for the cations are 1.

In Table 1 the transport numbers are calculated from Fig. 5 according to Eq. (6). It can be seen from the figure and the table that the membrane is acting as a cation-exchange membrane close to ideality for NaCl and

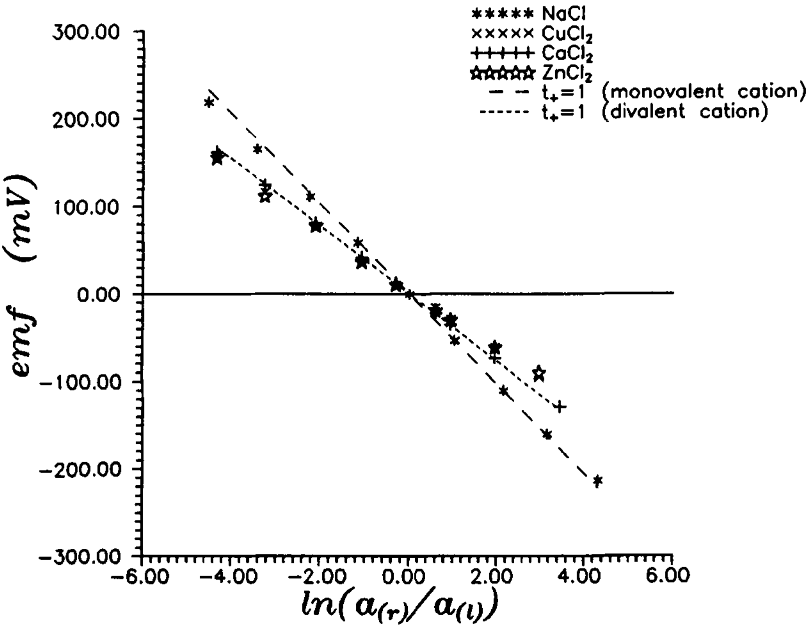


FIG. 5 emf as a function of the logarithm of the ratio between the activities on the two sides of the cation-exchange membrane for NaCl, CaCl$_2$, ZnCl$_2$, and CuCl$_2$.

TABLE 1
The Transport Numbers t_+ for NaCl, $CaCl_2$, $ZnCl_2$, and $CuCl_2$ Solutions for the Ionics CR67 HMR412 Cation-Exchange Membrane

NaCl		$CaCl_2$		$ZnCl_2$		$CuCl_2$	
ln $(a_{(r)}/a_{(l)})$	t_+	ln $(a_{(r)}/a_{(l)})$	t_+	ln $(a_{(r)}/a_{(l)})$	t_+	ln $(a_{(r)}/a_{(l)})$	t_+
−4.518	0.94 ± 0.02	−4.328	0.95 ± 0.02	−4.310	0.95 ± 0.02	−4.300	0.93 ± 0.02
−3.429	0.94 ± 0.02	−3.257	0.96 ± 0.01	−3.254	0.94 ± 0.02	−3.251	0.92 ± 0.02
−2.237	0.96 ± 0.01	−2.104	0.97 ± 0.01	−2.100	0.93 ± 0.01	−2.096	0.92 ± 0.01
−1.169	0.97 ± 0.01	−1.080	0.98 ± 0.01	−1.076	0.94 ± 0.01	−1.074	0.90 ± 0.01
0.000	0.97 ± 0.01	−0.315	0.97 ± 0.01	−0.314	0.93 ± 0.01	−0.313	0.88 ± 0.01
1.039	0.98 ± 0.01	0.601	0.98 ± 0.01	0.598	0.91 ± 0.01	0.594	0.85 ± 0.01
2.153	0.97 ± 0.01	0.946	0.98 ± 0.01	0.939	0.88 ± 0.02	0.934	0.85 ± 0.02
3.155	0.97 ± 0.02	1.961	0.96 ± 0.02	1.948	0.86 ± 0.02	1.926	0.83 ± 0.02
4.306	0.96 ± 0.02	3.417	0.96 ± 0.02	2.869	0.85 ± 0.03	2.856	0.80 ± 0.03

$CaCl_2$ solutions in all the measured activity range (concentration for NaCl: 10^{-4}–1 M; for $CaCl_2$: 10^{-4}–0.3 M). The transport numbers are approximately 0.97 for the two electrolytes in these concentration ranges. It could be expected that the transport numbers would be closer to 1 at low concentrations due to Donnan exclusion, but the transport numbers are the same throughout the concentration range.

For $ZnCl_2$ and $CuCl_2$ the picture is different. For low concentrations (less than 10^{-2} M) the transport numbers are between 0.90 and 0.95. But for increasing concentrations, the transport numbers decrease to 0.80–0.85 for 0.3 M. The reason could be that the divalent Cu^{2+} and Zn^{2+} cations are bound firmer to the ion-exchange groups in the membrane than monovalent cations.

It must be pointed out that Cu^{2+} forms complexes with both Cl^- and OH^- in aqueous solution, and especially at high concentrations [higher than 0.05 M (22)] the ratio of free Cl^- ions to the total amount of Cl becomes smaller than 1. It is the activity of the free Cl^--ions, which is included in the expression of emf, and therefore in the calculations of t_+.

The transport numbers for the anion-exchange membrane, t_-, could be estimated in the same manner following the above procedure. In this case the measured emf should be zero ($t_+ = 0$). t_- can be determined according to

$$1 = t_+ + t_- \tag{8}$$

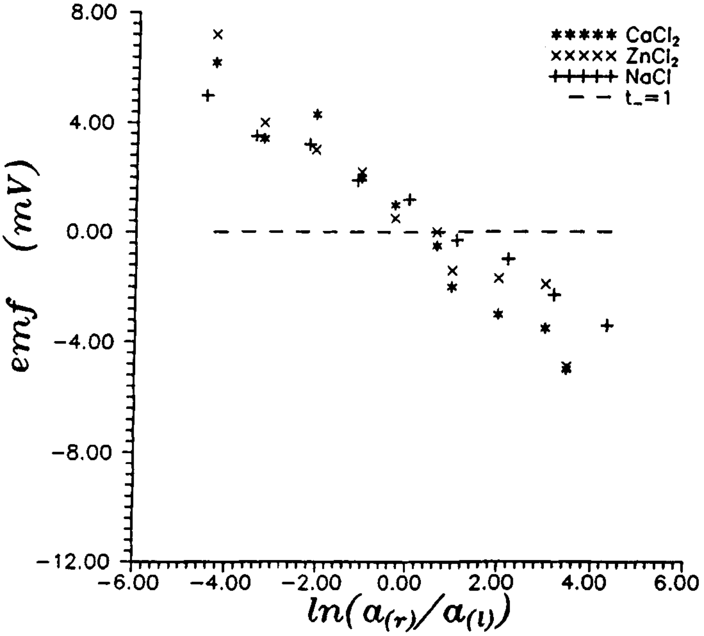


FIG. 6 emf as a function of the logarithm of the ratio between the activities on the two sides of the anion-exchange membrane for NaCl, $CaCl_2$, and $ZnCl_2$ solutions.

Figure 6 shows the measured emf as a function of the ratio between the activity of the salt on the two sides of the anion-exchange membrane for NaCl, $CaCl_2$, and $ZnCl_2$ solutions. Taking the slope of the curves as an average for the whole activity range for the t_- determination, the values of t_- for the Cl^- ion can be found as listed in Table 2. The transport numbers are 0.95 for all three analyzed electrolytes, and therefore the membrane is acting quite well as an anion-exchange membrane. The transport of anions through the membrane seems quite independent of the

TABLE 2
t_- in NaCl, $CaCl_2$, and $ZnCl_2$ Solutions for the Ionics 204 SXZL 386 Anion-Exchange Membrane

	NaCl	$CaCl_2$	$ZnCl_2$
t_-	0.95 ± 0.01	0.95 ± 0.01	0.95 ± 0.01

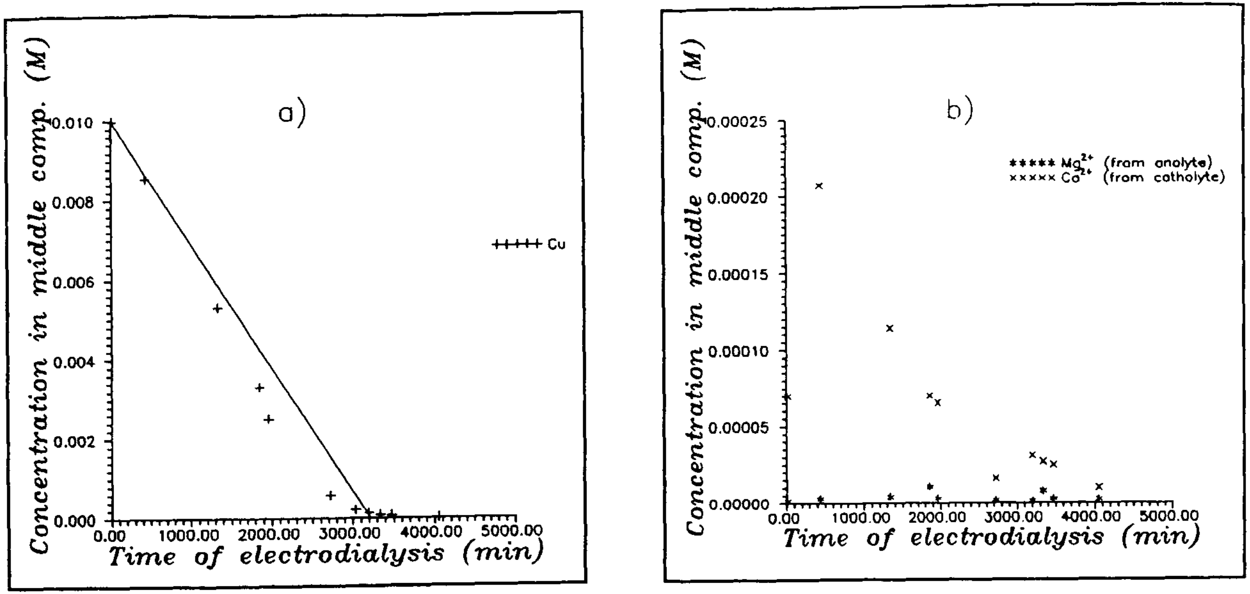
cations involved in the measurements, and this is of great interest for the potential use of this membrane in electrokinetic soil decontamination.

Electrodialysis Measurements

Figure 7 shows the development of the concentration in the middle compartment as a function of electrodialysis time for experiment A. From Fig. 7(b) it can be observed that Ca^{2+} ions at the beginning of electrodialysis are migrating from the cation-exchange membrane and the cathode compartment to the middle compartment. This is explained by the generation of the concentration gradient in the cation-exchange membrane, which allows Ca^{2+} and Cu^{2+} ions to exchange. Furthermore, some interdiffusion between Ca^{2+} and Cu^{2+} ions across the cation-exchange membrane can occur, which allows the Ca^{2+} ions to move in the direction opposite of the electric field due to the concentration gradient. Therefore, at the beginning the Cu^{2+} flux across the cation-exchange membrane toward the cathode compartment seems higher than expected based on the constant electric current used, which can be seen from the fact that the concentration of Cu^{2+} ions in the middle compartment is lower than expected (see Fig. 7a). The expected concentration level, where the ion-exchange membranes are assumed ideal, is represented by the straight line in the figure. After approximately 800 minutes the Ca concentration in the middle compartment decreases and the Ca^{2+} ions are driven back to the cathode compartment with the electric current. This is because the interdiffusion becomes less important when Cu^{2+} ions are removed to the cathodic compartment. Furthermore, a small amount of Mg^{2+} ions are driven through the anion-exchange membrane and into the middle compartment by the electric field, which indicates that the anion-exchange membrane is not completely ideal. This is seen from the presence of Mg^{2+} ions in the middle compartment as shown in Fig. 7(b).

A main problem in analyzing these data is the behavior of the H^+ ion, which is available from both electrolytic compartments. By following the pH in the middle compartment, it should be possible to get a qualitative picture of the transport of the proton, but from which electrode compartment the proton is coming is impossible to say from the experiments. Furthermore, a small amount of H^+ was originally present in the middle compartment because of the speciation and equilibrium reactions of $Cu(NO_3)_2$ in water.

Figure 8 shows the resistance over the different membranes, middle compartment, and electrode compartments. From the figure it is clearly seen that after a certain time the resistance over the electrodialysis cell and especially in the middle compartment increases as a result of the



+ | $Mg(NO_3)_2$ | anion ex. memb. | $Cu(NO_3)_2$ | cation ex. memb. | $Ca(NO_3)_2$ | -

FIG. 7 The concentration for a) Cu and b) Ca and Mg in the middle compartment as a function of electrodialysis time.

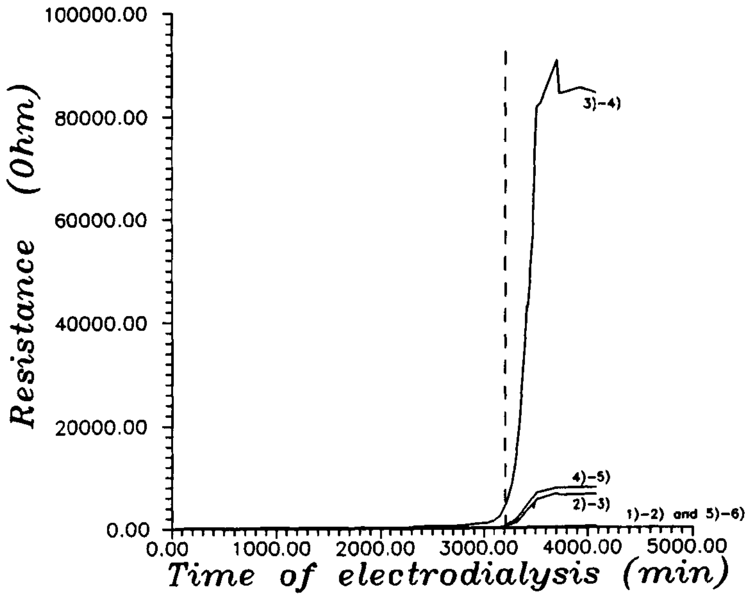


FIG. 8 The resistance between the different measuring electrodes (see Fig. 4) as a function of electrodialysis time.

desalting of the middle compartment. That the resistance over the membranes seems to increase a little is a result both of increased resistance in the membrane and the placement of the measuring electrodes, which could only be placed 1–2 mm from the membrane surfaces due to the construction of the cell, and therefore some resistance from the dilute middle compartment is included in the resistances over the membranes. In addition, the large difference in concentration between the membrane phase and the dilute solution in the middle compartment could give a concentration polarization potential difference in the layer between the membrane and the solution. The dashed line indicates the point where the middle compartment should be theoretically empty of ions if the ion exchange were working ideally. It is seen that the sharp increase in resistance appears after the dashed line, which again indicates that the membranes are not 100% charge selective as found by the emf measurements.

For experiment B using the four-membrane concept, the results could be summarized as follows. The concentrations of Cu^{2+} and Ca^{2+} in compartments III, IV, and V were followed during electrodialysis. This is shown in Fig. 9, where the concentration of Mg^{2+} in compartment III was registered as well.

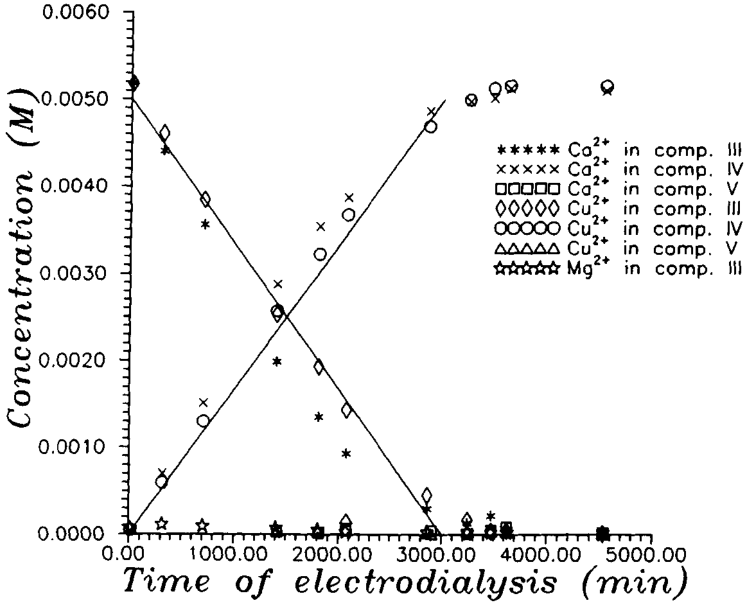


FIG. 9 The development in concentration in compartments III, IV and V as a function of electrodialysis time.

From the figure is seen that the concentration drop in compartment III closely follows the concentration rise in compartment IV for Cu^{2+} and Ca^{2+} ions. Furthermore, it can be seen that the two cationic species hardly pass the anion-exchange membrane into compartment V, which was the objective. Therefore, all cationic species coming from compartment III can be said to be in compartment IV after the experiment. Therefore, the cathode process can be regarded as being nearly independent of heavy metal cations coming out from the soil—at least for soils containing copper and calcium.

CONCLUSIONS

In NaCl and $CaCl_2$ solutions, transport numbers of average 0.97 were measured for the cation-exchange membrane CR67 HMR412, i.e., it acts nearly ideally for these electrolyte solutions. The membrane has reasonable cation-exchange properties in $CuCl_2$ ($t_+ = 0.91$) and $ZnCl_2$ ($t_+ = 0.94$) solutions with concentrations lower than 10^{-2} M. The examined anion-exchange membrane AR204 SXRA 7639 has transport numbers for the chloride anion of about 0.95 for NaCl, $CaCl_2$, and $ZnCl_2$ solutions.

This means that the main part of an electric current applied to an electrodialysis desalting cell using these membranes would be used for removing ions from the polluted middle compartment, whereas little energy would be used to transport cations across the anion-exchange membrane, and anions across the cation-exchange membrane, into the polluted volume.

The electrodialytical experiments showed that the middle compartment could be cleaned of mobile ions (in this work Cu^{2+}, Ca^{2+}, and NO_3 simulated the available ions). At the same time, placement of the ion-exchange membranes offered the possibility of controlling the flow of different ions which did not enter the electrode compartments during the experiments but stayed in the concentrated solutions. No cations of significance were seen to enter the polluted compartment through the anion-exchange membrane, but a small amount of interdiffusion of cations through the cation-exchange membrane into the middle compartment was noticed.

The concept of electrodialytic soil decontamination can be said to work when a system of $Cu(NO_3)_2$ and $Ca(NO_3)_2$ solutions is used to simulate the polluted soil volume, and it should be possible to use the results in remediation experiments with soil.

SYMBOLS

$a_{(r)}$	activity of the electrolyte on the right side of the membrane
$a_{(l)}$	activity of the electrolyte on the left side of the membrane
$c_{s(r)}$	concentration of the electrolyte on the right side of the membrane
$c_{s(l)}$	concentration of the electrolyte on the left side of the membrane
C	bulk solution concentration
C_i	concentration of ionic species i
D	diffusion coefficient of the counterion in the film layer adjacent to the membrane
emf	potential difference—or electromotive force—measured across the membrane in a concentration cell
$\mathrm{emf}_{(r-l)}$	potential difference measured between the right side and the left side of the membrane
F	Faraday constant, 96485 mol/C
I_{cr}	limiting current for the membrane
$J_{q,i}$	current carried by the ionic species i
J_q	total current
R	gas constant, 8.314 J/(K·mol)
t_m	transport number of the counterion transported in the membrane

t_s	transport number of the counterion transported in the solution
t_i	fraction of the total electric current through a medium that is carried by ionic species *i*
t_+	transport number of the cation through the membrane
t_+^*	transport number approximately independent of the activity of the solutions on the two sides of the membrane
T	temperature
z_i	electrochemical valence of ionic species *i*

Greek Letters

$\gamma_{\pm(r)}$	activity coefficient of the electrolyte on the right side of the membrane
$\gamma_{\pm(l)}$	activity coefficient of the electrolyte on the left side of the membrane
δ	film layer thickness
μ_i	mobility of ionic species *i*
ν	total number of ions formed by dissociation of an electrolyte
ν_-	number of anions formed by dissociation of an electrolyte

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