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Determination of the diffusion coefficient of ionic species in Boom Clay by electromigration.

First Evaluation

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BLG-736

Waste and Disposal Unit
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March, 1997

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1. Description of the project

After leaching out of their primary encapsulation (glass, concrete, metallic canister, backfill), Boom Clay acts as the final barrier for the radionuclides before they are released into the aquifer. The release of the radionuclides depends on the migration through the porous Boom Clay. The migration of the radionuclides is mainly controlled by diffusion. The determination of the diffusion coefficient is of key importance to study the feasibility of a geological disposal of high-level radioactive waste.

Because of the good retardation properties of the Boom Clay, migration is very slow. Classical diffusion experiments as pure diffusion, flow-through, percolation can last several years. Any method which can speed up the migration in a way that reliable migration parameters can be obtained in a shorter period is therefore of interest.

Electromigration is the movement of ions under the influence of an electrical field. It causes the ions to move at a constant velocity towards the electrode of opposite charge. This velocity is related to the ionic mobility (μ). A relationship between the mobility and the diffusion coefficient is given by the law of Einstein[1].

2. Scope of the project

The scope of the project is to use the electrokinetic method to obtain migration parameters of radionuclides in the Boom Clay in a short time.
In this respect, we first have to demonstrate the feasibility of the method.
When this is achieved, the method will be applied to determine the diffusion coefficients of radionuclides, to validate the diffusion coefficients obtained by other methods.
Further on, the method will also be used to study different aspects of migration as speciation, retardation...

3. Electrokinetic phenomena

Applying a potential gradient over a water saturated porous medium invokes three phenomena[2,3] which are of interest in our application:

$\Rightarrow$ Electromigration: movement of ionic species
$\Rightarrow$ Electrophoresis: movement of colloidal particles
$\Rightarrow$ Electro-osmosis: movement of water

3.1 Electromigration

Electromigration is the movement of an ion in an electric field towards the electrode of opposite charge. Under influence of the potential gradient, the ion will attain a constant velocity called the drift speed (v) which is given by

$$v = \mu E$$
eq. 1

v= drift speed [m/s]
μ= ionic mobility [m²/Vs]
E= electric field [V/m]

The law of Einstein relates the ionic mobility with the diffusion coefficient:

$$D = \frac{\mu KT}{Ze}$$

eq. 2

D= diffusion coefficient [m²/s]
μ= ionic mobility [m²/Vs]
K= Boltzmann constant, $1.38 \ 10^{-23}$ [J/K]
T= Temperature [K]
Z= valence [-]
e= electron charge, $1.6 \ 10^{-19}$ [C]

3.2 Electro-osmosis

Electro-osmosis can be explained by the presence of an electric double layer at the charged surface of the porous medium. The negative charged clay surface is compensated by cations in the pore water. Under the influence of an electric field, the cations in the double layers will move to the cathode. Due to viscous drag, pore water will move together with the cations resulting in a bulk flow of water towards the cathode.

The Helmholtz-Smoluchowski model describes the electro-osmosis. Despite serious drawbacks, it is still the most widely used model because of its simplicity:

$$v_{eo} = \frac{\varepsilon \xi E}{\eta}$$

eq. 3

v_{eo}= electro-osmotic velocity [m/s]
ε= dielectric permittivity of water, 7.12 10^{-10} [C^2/Nm^2]
ξ= zeta potential [V]
E= electric field [V/m]
η= viscosity, 1 10^{-3} [Ns/m^2]

3.3 State-of-the-Art

Migration of species under influence of an electric field finds many applications. Tiselius established the technique of electrophoresis for the separation of proteins and was rewarded the Nobel Prize.
Further developments lead to new advanced techniques for the separation of ions by HPCE (High Performance Capillary Electrophoresis) or CIA (Capillary Ion Analysis) where the ions are separated on their difference in mobility[4].

Electrokinetic soil processing is an emerging technology[3,5] in waste remediation, soil decontamination, soil stabilisation, sludge treatment...The combined effect of electromigration and electro-osmotic flow is very efficient for the removal of hazardous waste[6,7,8,9,10,11,12] (heavy metals, aromatics, radioactive contaminants) from soils. Soil stabilisation, dewatering and consolidation, is based on electro-osmosis.

Electrokinetics are also applied in the study of diffusion. The diffusion of chloride in concrete was studied by applying an electric gradient across a concrete core[13].
Electrodiffusion profiles were used to evaluate the Na self-diffusion and specific conductivity in $Na_2O.2SiO_2$ glass[14]. With the aid of electrodiffusion profiles it was also possible to study the charge of the Cu-impurities in a-As_2Se_3.Cu semiconductors[15].

These latter cases are not representative for the saturated porous media where we have to take into account sorption, ion-exchange, tortuosity, electro-osmotic flow...

3.4 Transport Equation

The transport equation derived in following paragraph is based on models describing decontamination of polluted soils by means of an electric field[16,17,18,19,20,21,22,23]

The flux of species through an elementary volume during an electrokinetic experiment is due to a concentration gradient and an electrical gradient:

$$J_t = J_c + J_e$$

eq. 4

J_t= total flux [mol/m^{2}s]
J_c= chemical flux [mol/m^{2}s]
J_e= electrical flux [mol/m^{2}s]

The chemical flux is given by Fick's first law:

$$J_c = -D\frac{\partial C}{\partial x}$$

eq. 5

D= diffusion coefficient [m^2/s]

The electrical flux has two components: electromigration (J_{em}) and electro-osmosis (J_{eo}).

$$J_{em} = -\mu\frac{\partial \phi}{\partial x}C = v_{em}C$$

$$J_{eo} = -k_e\frac{\partial \phi}{\partial x}C = v_{eo}C$$

eq. 6

ϕ= electric potential [V]
μ= ionic mobility [m^2/Vs] = DZe/KT
k_e= electro-osmotic mobility [m^2/Vs] = $\xi \varepsilon n/\eta$
n= porosity [-]
v_{em}= electromigration velocity [m/s]
v_{eo}= electro-osmotic velocity [m/s]

Introducing these formulas in equation 4 for the total flux:

$$J_t = -D\frac{\partial C}{\partial x} + (v_{em} + v_{eo})C$$

eq. 7

The sign of the electro-osmotic velocity depends on the direction of the flow, positive when the electro-osmotic flow is in the same direction as the species and negative in the opposite case.

The diffusion equation is given by the second law of Fick:

$$\frac{\partial C}{\partial t} = -\frac{\partial J_t}{\partial x}$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \left(v_{em} + v_{eo}\right)\frac{\partial C}{\partial x}$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V_c\frac{\partial C}{\partial x}$$

eq. 8

V_c = convection velocity [m/s]

The basic diffusion equation must be adapted for a porous medium, taking into account tortuosity and retardation (sorption) effects.

Since x is the real distance of the diffusion path, while the experimentally measured path is the end to end distance z. The ratio between both is the tortuosity: $\tau = x/z$ and is always higher than 1. In the diffusion equation we substitute ∂x by $\tau \partial z$.

Assuming a linear sorption isotherm: $C^* = K_d \cdot C$ (K_d: distribution coefficient, C^*: concentration adsorbed on the solid, C: concentration in the liquid).

The diffusion equation can now be written as follows:

$$\frac{\partial C}{\partial t} + \frac{\rho_d}{\eta}\frac{\partial C^*}{\partial t} = \frac{D}{\tau^2}\frac{\partial^2 C}{\partial z^2} - \frac{V_c}{\tau^2}\frac{\partial C}{\partial z}$$

$$R = 1 + \frac{\rho_d K_d}{\eta}$$

$$\frac{\partial C}{\partial t} = \frac{D}{R\tau^2}\frac{\partial^2 C}{\partial z^2} - \frac{V_c}{R\tau^2}\frac{\partial C}{\partial z}$$

eq. 9

R= retardation coefficient [-]
τ= tortuosity [-]
$D/R\tau^2$= apparent dispersion coefficient= D^a [m^2/s]
$V_c/R\tau^2$= apparent convection velocity= V_c^a [m/s]
ρ_d= grain density [g/cm^3]
K_d= distribution coefficient [ml/g]
η= diffusion accessible porosity [-]

Equation 9 has the form of the classical dispersion-convection equation:

$$\frac{\partial C}{\partial t} = D^a \frac{\partial^2 C}{\partial z^2} - V_c^a \frac{\partial C}{\partial z}$$

eq. 10

Due to convection, the pore water will not all travel at the same velocity and mixing occurs along the flowpath. This mixing is called mechanical dispersion and results in a dilution of the solute. This process can be described by Fick's law of diffusion where the diffusion coefficient is replaced by the dispersion coefficient. The general relationship between the dispersion coefficient and the diffusion coefficient can be described as follows:

$$D^a = D_m^a + aV_c^t$$

eq. 11

D^a = apparent dispersion coefficient [m²/s]
a = dispersion length [m]
D_m^a = apparent molecular diffusion coefficient [m²/s]
V_c^t = total apparent convection velocity [m/s]
$= |\, v_{em}^a \,| + |\, v_{eo}^a \,|$

For cationic species, V_c^t is equal to the V_c^a.

The apparent molecular diffusion coefficient, D_m^a, is the diffusion coefficient of the species in the porous medium and is the coefficient of interest.

Now we rewrite our dispersion-convection equation in terms of the diffusion coefficient as follows:

$$\frac{\partial C}{\partial t} = \left(D_m^a + aV_c^t\right)\frac{\partial^2 C}{\partial z^2} - \left(\frac{ZeE}{KT}D_m^a + \frac{v_{eo}}{R\tau^2}\right)\frac{\partial C}{\partial z}$$

eq. 12

There are two approaches to calculate the diffusion coefficient from an electromigration experiment:

1. Application of the Einstein relation.
    After the electromigration experiment, the concentration of the species in the clay is measured and a distribution profile is found. From the displacement of the distribution profile the convection velocity is calculated. If the contribution of the electro-osmosis is negligible, the convection velocity equals the electromigration velocity. This velocity can be converted to the apparent diffusion coefficient by the Einstein relation.

2. Fitting of the distribution profile.
    The distribution profile can be fitted against the measured profile, resulting in the dispersion coefficient and the convection velocity.
For the fitting we need an analytical solution of the diffusion equation.

Considering the simple dispersion-convection equation:

$$\frac{\partial C}{\partial t} = D^a \frac{\partial^2 C}{\partial x^2} - V_c^a \frac{\partial C}{\partial x}$$

eq. 13

and the appropriate boundary conditions for this system:
- at x=∞ the concentration is zero, C(x=∞)=0,
- the initial conditions are: C(0<x<∞, t=0)=0 and C(x=0,t=0)=0

Then we obtain the following analytical solution:

$$C(x,t) = \frac{Q_0}{2S\sqrt{\pi D^a t}} \exp\left(-\frac{\left(x - V_c^a t\right)^2}{4D^a t}\right)$$

eq. 14

Q_0= the initial quantity of the species distributed in a thin layer over the cross section of the clay slab
S= cross section of the clay slab
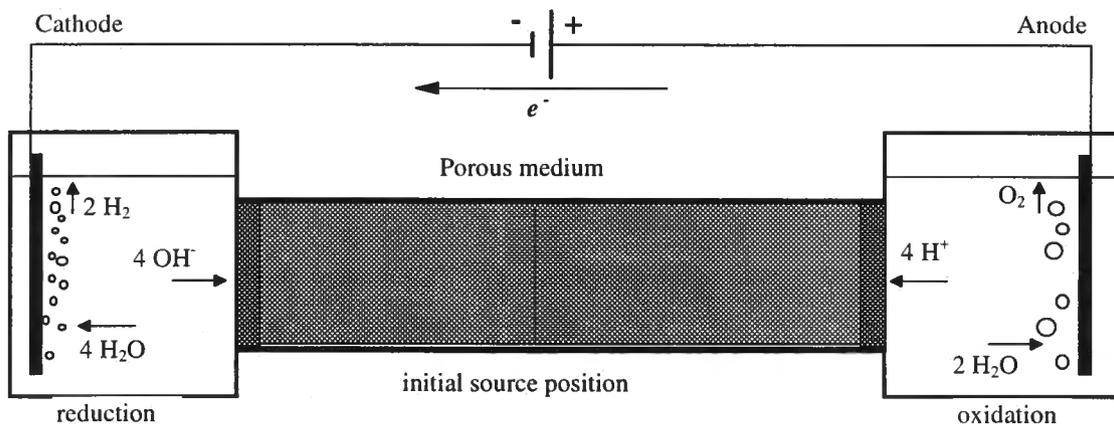
4. Experimental

4.1 Experimental set-up

Figure 1: Experimental set-up for electromigration experiments

Two Pt-electrodes connected to a power supply are immersed in the electrode compartments filled with an electrolyte solution. The electrolyte solution used is Boom Clay Water (BCW) of which the main constituent is $NaHCO_3$ (0.02M)[24]. The two compartments are connected by a cylindrical Plexiglas cell containing two clay cores of 0.05m with in-between a filterpaper

doped with a solution of the radionuclide of interest. The clay cores are confined between two porous glass filters.
At equal distances in the Plexiglas cell, small holes are drilled where needles can be inserted to measure the potential difference or a thermocouple to measure the core temperature.

4.2. Measurement of the distribution profile.

After the test, the clay core is cut in slices of about 1mm thick. These slices are brought in vials to measure the activity.
In case of a gamma emitting radionuclide, the vials are directly measured for gamma activity using a NaI(Tl)-gamma detector.
When we deal with a beta emitting radionuclide, the clay slices are put in vials containing 10ml of water and well mixed to obtain homogeneous clay pastes. These clay pastes are centrifuged for 30 minutes at 15000rpm. From the supernatant, 1ml is pipetted into a scintillation vial filled with a scintillation cocktail and measured with a liquid scintillation counter.

5. Results and Discussion

5.1. Controlling the chemical changes of the clay core during electromigration

5.1.1 pH gradient

When a potential difference is applied on the electromigration cell, electrolysis of water will occur (Figure 1) with the production of protons at the anode (oxidation) and hydroxyls at the cathode (reduction). Under influence of the electric field these ions will migrate to the opposite side thereby changing the pH of the clay. The initial pH of the Boom clay changes from 9.4 to 2 and 13 respectively at the anode and cathode. Physico-chemical perturbations of this kind seriously influence the migration and must be avoided at all times.

5.1.2 Chemical buffering

To neutralise the protons and hydroxyls we can use a chemical buffer of the same composition as the BCW. A buffer solution of 1M $NaHCO_3$ and 0.1M Na_2CO_3 is necessary to achieve a constant pH of approximately 9.4.
Electromigration experiments with Sr-85 and I-131 showed that the buffer could maintain a constant pH during the experiment (voltage: 400V, time: 2hr).
Because of the high concentration of the buffer solution, it is possible that the ionic strength of the clay will be disturbed. Changes in the ionic strength result in a change in the double layer thickness. This will affect the interaction of the ionic species with the clay layer influencing the migration.

The double layer thickness can be calculated as follows[17]:

$$\delta = \left(\frac{\varepsilon RT}{2Z^2 F\, C}\right)^{\frac{1}{2}}$$

eq. 15

δ= double layer thickness [m]
ε= dielectric permittivity of water, $7.12\ 10^{-10}$ [C^2/Nm^2]
R= gas constant, 8.314 [J/Kmol]
T= temperature [K]
F= Faraday constant, 96487 [C/mol]
C= concentration [M]
Z= valence [-]

The double layer thickness for the electrolyte solutions of 1M and 0.02M $NaHCO_3$ is respectively 0.32nm and 2.16nm.

Two tests were done to evaluate the disturbance of the ionic strength. C-14 labelled $NaHCO_3$ and Na-22 were respectively spiked into the cathode and anode compartment. The depth of penetration is studied by measuring the activity of the clay slabs. The depth of penetration is an indication for the perturbation of the ionic strength. Results are given in figure 2 and 3.
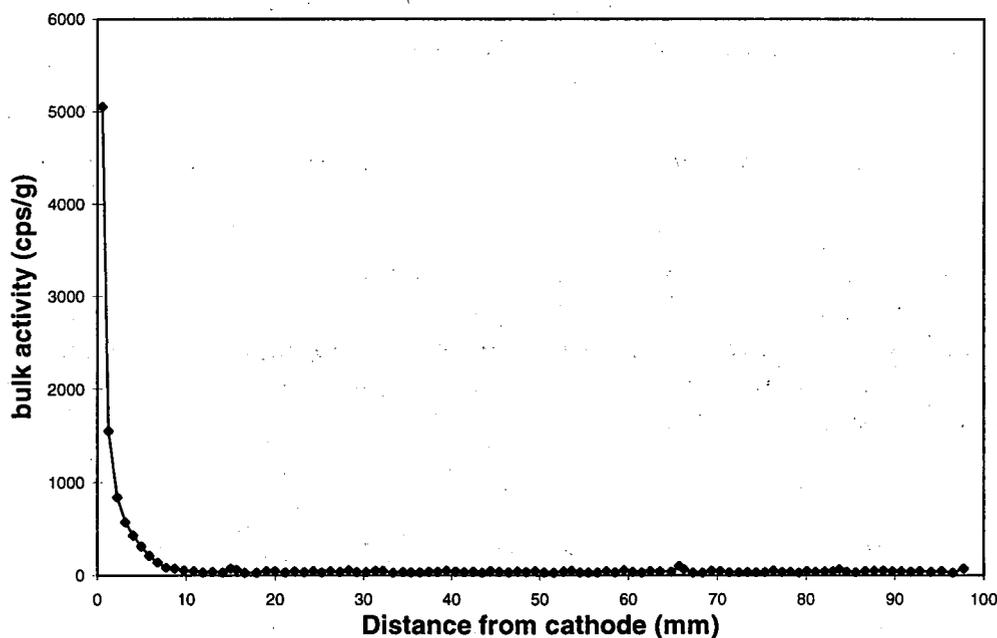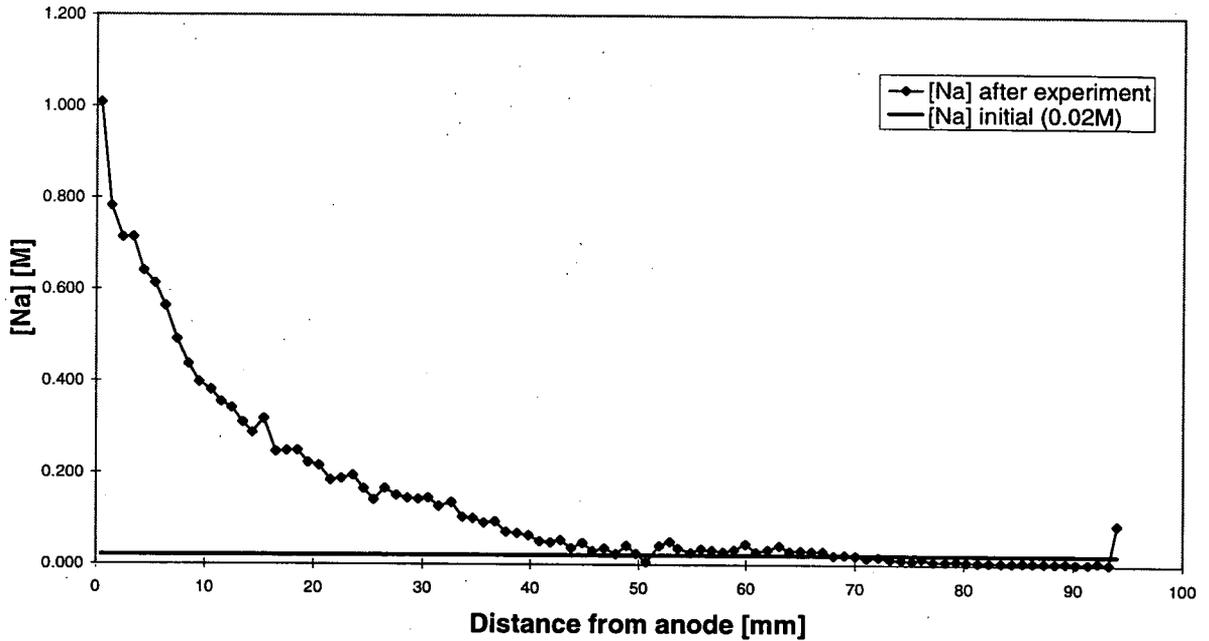

**Figure 2: Penetration of HCO_3^- into the clay core**

Figure 3: Penetration of Na⁺ in the clay core.

As can be seen from figure 3, the perturbation of the ionic strength due to the high buffer concentration is significant.
Migration experiments performed with buffer solutions of this concentration will therefore lead to migration parameters which are not relevant for the initial situation.

5.1.2 Automatic neutralisation by circulating the electrolyte solution

An automatic neutralisation can be achieved when we circulate the electrolyte solution. This can be achieved by introducing a third electrolyte reservoir. From this reservoir we pump electrolyte solution (BCW) towards both electrode compartments at a constant drop rate. Both compartments have an overflow connected to the reservoir. In this way we can achieve a constant pH throughout the experiment without changing the ionic strength. A schematic representation is given in figure 4.
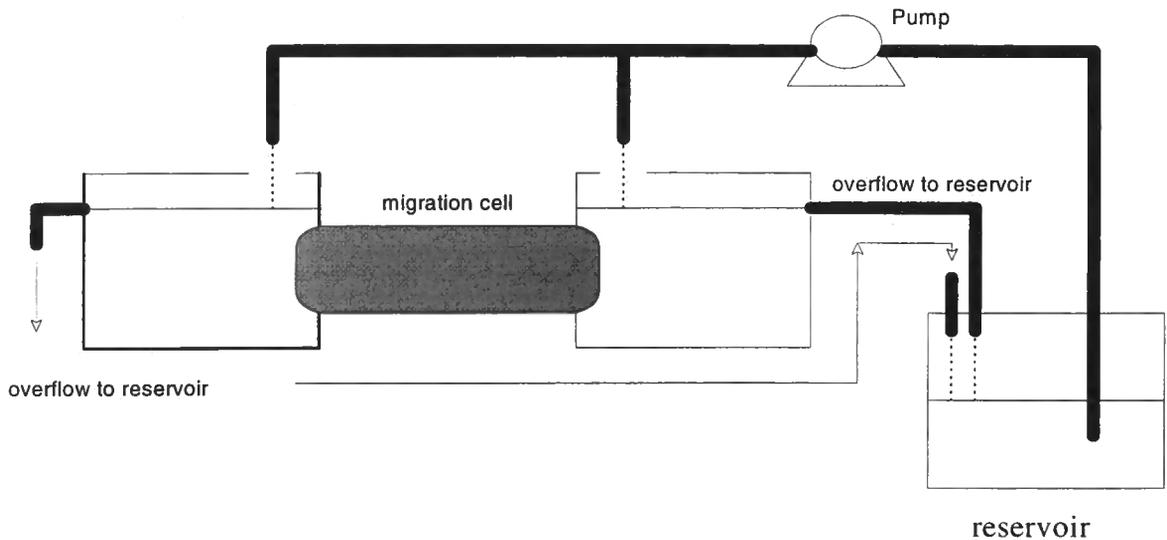
Figure 4: Experimental set-up for automatic neutralisation.

5.2 Determination of the diffusion coefficient by electromigration

5.2.1 Experiments at high voltage: 400V for 2 hrs

The first series of experiments with Sr-85, I-131 and HTO, were performed with the chemical buffering method. But as stated in previous part, this caused disturbances in the clay leading to non-reliable results.

The second series was performed using the automatic neutralisation method.
The results are given in table 1 and a typical distribution profile is given in figure 5

Table 1: Experimental results for electromigration at 400V for 2 hrs.

RN	<E> [V/m]	μ [m²/Vs]	<T> [°C]	D(E) [m²/s]	D(ref) [m²/s]	D(fit) [m²/s]
I-131	613	$9.70 \ 10^{-9}$	69	$2.84 \ 10^{-10}$	$2.40 \ 10^{-10}$	$1.30 \ 10^{-9}$
Sr-85	832	$1.01 \ 10^{-9}$	73	$1.51 \ 10^{-11}$	$1.50 \ 10^{-11}$	$3.85 \ 10^{-10}$
HTO	797	$2.27 \ 10^{-9}$	75			

D(E)= Diffusion coefficient determined by the Einstein relation
D(ref)= Diffusion coefficient used as reference[25]
D(fit)= Diffusion coefficient determined from curve fitting
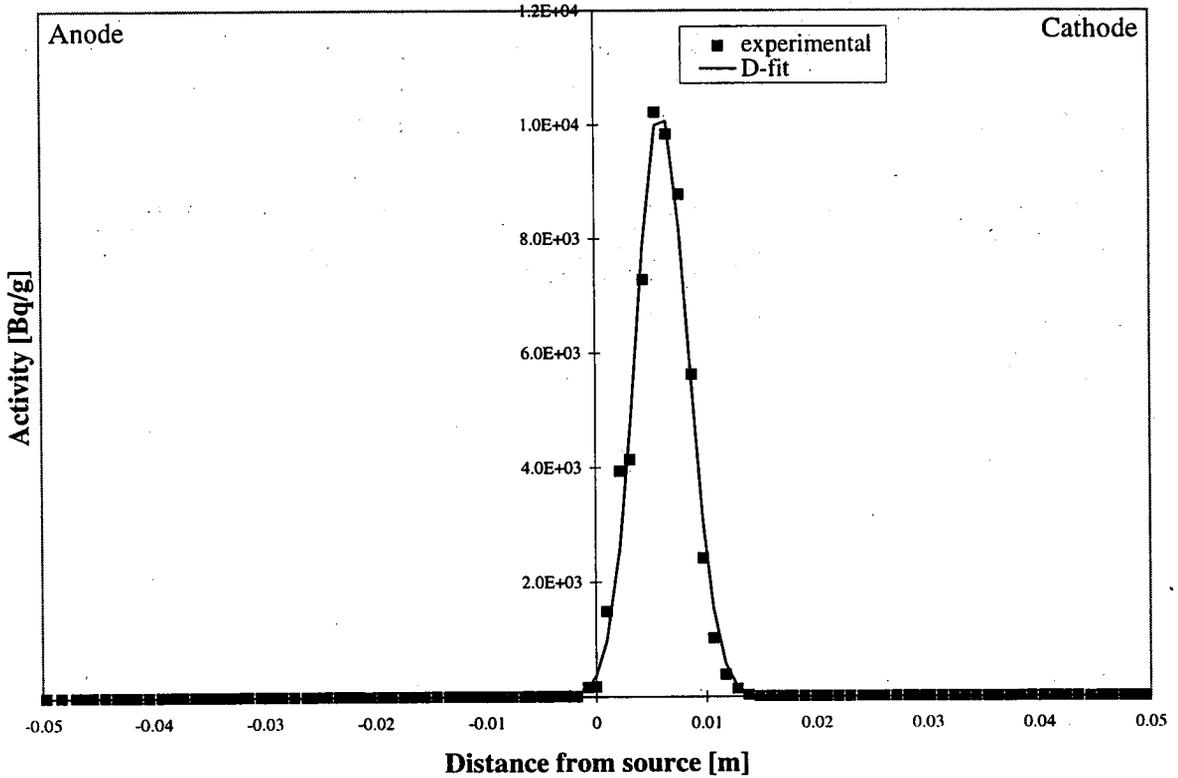
Figure 5: Activity distribution of Sr-85 after electromigration for 2 hrs at 832 V/m

Initially we considered that the contribution of the electro-osmosis on the velocity of the radionuclide is negligible and the displacement of the distribution profile is attributed only to the electromigration velocity. Dividing the velocity by the electric field, we obtain the mobility μ (Table 1) and the diffusion coefficient can be calculated by the Einstein relation. The diffusion coefficients obtained , D(E), are fairly close to the reference diffusion coefficients.

From these first results we could conclude that the contribution of the electro-osmosis is negligible. This is rather surprising because in soil processing the electro-osmosis is not negligible. It is therefore interesting to study the phenomenon of electro-osmosis. This is done by measuring the displacement of HTO under the influence of an electric field. As can be seen in table 1 the mobility is $2.27 \cdot 10^{-9}$ m^2/Vs, which has the same magnitude as the other mobilities. This means that the electro-osmosis can not be neglected and we should correct the mobilities for I and Sr for the contribution of electro-osmosis.

Recalling the theory for the convection velocity:

$$V_c^a = \frac{1}{R\tau^2}\left(v_{em} + v_{eo}\right)$$

or

$$V_c^a = v_{em}^a + \frac{v_{eo}}{R\tau^2}$$

eq. 16

For the calculation of the diffusion coefficient we need the apparent electromigration velocity, v_{em}^a.

To obtain this value we need the v_{eo} which is measured in the HTO experiment. From this experiment we obtain the velocity of HTO in a porous medium or v_{eo}/τ^2 is found. Now the relation becomes:

$$V_c = v_{em}^a + \frac{v_{HTO}}{R}$$

eq. 17

To correct the convection velocity for the electro-osmosis contribution, the retardation factor is needed. When the mobility of the HTO has the same magnitude as the total mobility, we can say that for retardation factors > 10, the electro-osmotic contribution decreases one order of magnitude and can be neglected. Thus, in case of Sr (weakly retarded[25], R~10), the assumption of neglecting the electro-osmosis can be justified.

For non-sorbed species like iodine, there is no retardation effect and we have to correct for the contribution of electro-osmosis. The corrected diffusion coefficient calculated from the Einstein relation becomes $3.56 \ 10^{-10}$ m²/s as compared to $2.84 \ 10^{-10}$ m²/s (non-corrected) and is still in good agreement with the reference value of $2.4 \ 10^{-10}$ m²/s.

Using curve fitting, the dispersion coefficient is found which differs an order of magnitude with the diffusion coefficient. To obtain the diffusion coefficient we have to consider the total apparent convection velocity.

Under influence of the electric field the transport is accelerated and the convection velocity is much higher than under hydraulic gradients. Further discussion on the determination of the diffusion coefficient form curve fitting is given in paragraph 5.2.2.

During these series of experiments we noticed a serious increase in the core temperature due to Joule heating. The temperature increased from 25 to 90°C over a period of 2 hrs. Temperature fluctuations of this kind will influence the migration.

Temperature increases can be avoided by cooling or suppression of the Joule effect by applying lower voltages.

5.2.2 Experiments at low voltage: 50V for 20 hrs

With a voltage of 50V and cooling with a fan, the temperature increase is negligible and an average temperature of 29°C over a period of 20 hrs was maintained. Under these conditions more reliable migration parameters can be obtained. The results are presented in table 2 and figures 6-8.

Table 2: Experimental results for electromigration at 50V for 20 hrs

RN	<E> [V/m]	μ_{tot} [m²/Vs]	D(E) [m²/s]	D(E)^{corr} [m²/s]	D(ref) [m²/s]	D(fit) [m²/s]
Sr-85	61	$9.70 \ 10^{-10}$	$1.30 \ 10^{-11}$	n.a.	$1.50 \ 10^{-11}$	$2.42 \ 10^{-11}$
HTO	79	$1.40 \ 10^{-9}$	n.a.	n.a.	$2.20 \ 10^{-10}$	$3.09 \ 10^{-10}$
Na-22	84	$3.50 \ 10^{-9}$	$9.11 \ 10^{-11}$	$5.47 \ 10^{-11}$	$6.55 \ 10^{-11}$	$9.55 \ 10^{-11}$

D(E)^{corr}= Diffusion coefficient calculated by the Einstein relation with the total mobility corrected by the contribution of electro-osmosis.
Na-22: The D(ref) was obtained from a pure diffusion experiment using the same EM set-up without application of a potential.
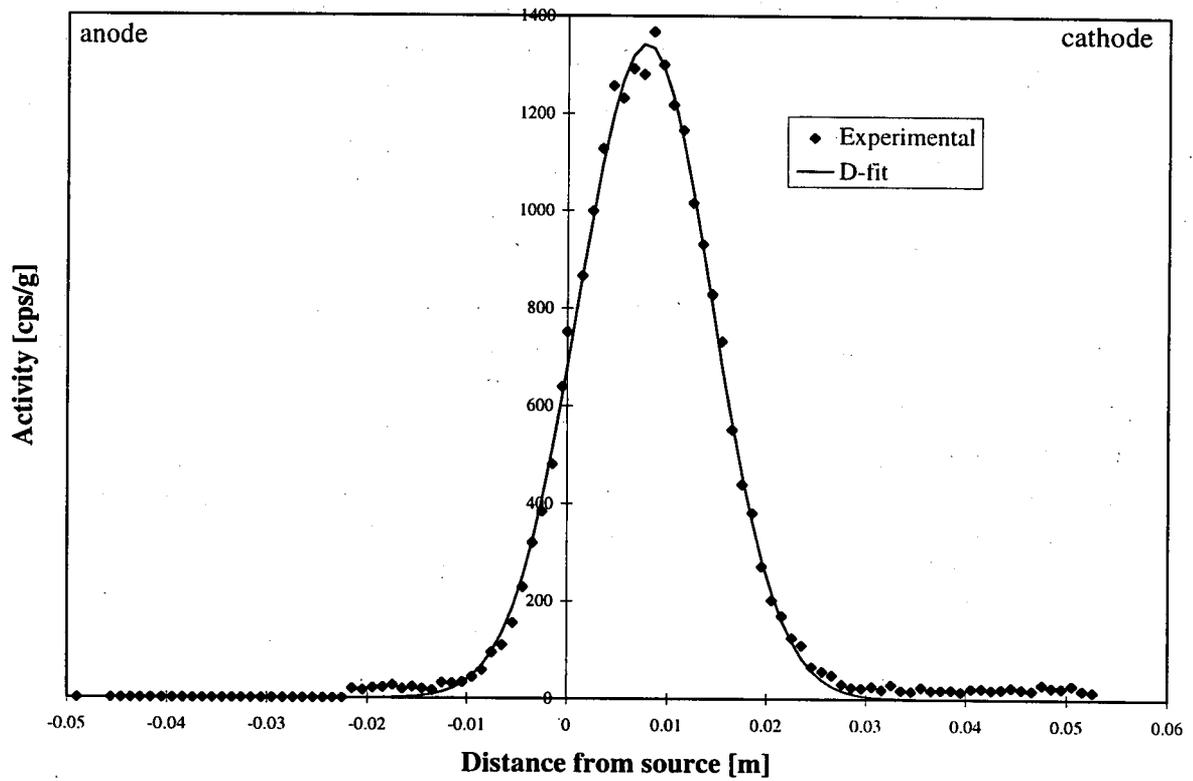n.a.= not applicable

Figure 6: Distribution profile of HTO after electromigration for 20 hrs at 79 V/m
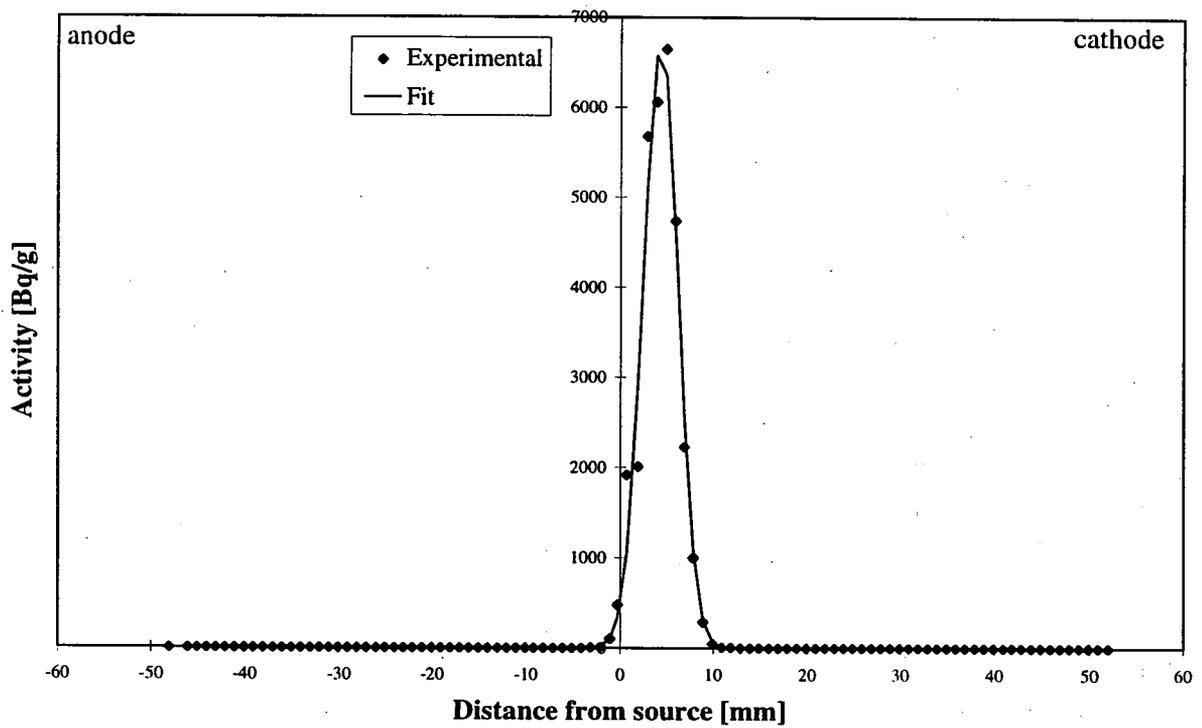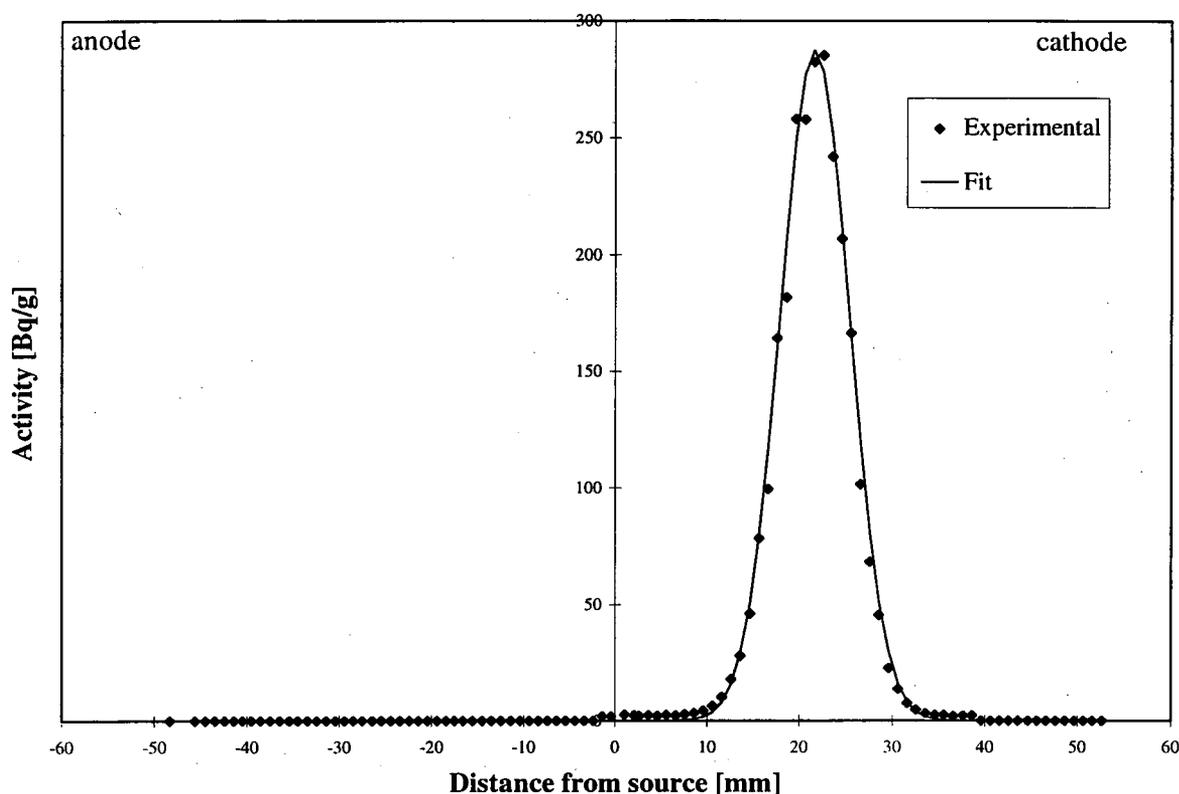

Figure 7: Distribution profile of Sr-85 after electromigration for 20 hrs at 61 V/m
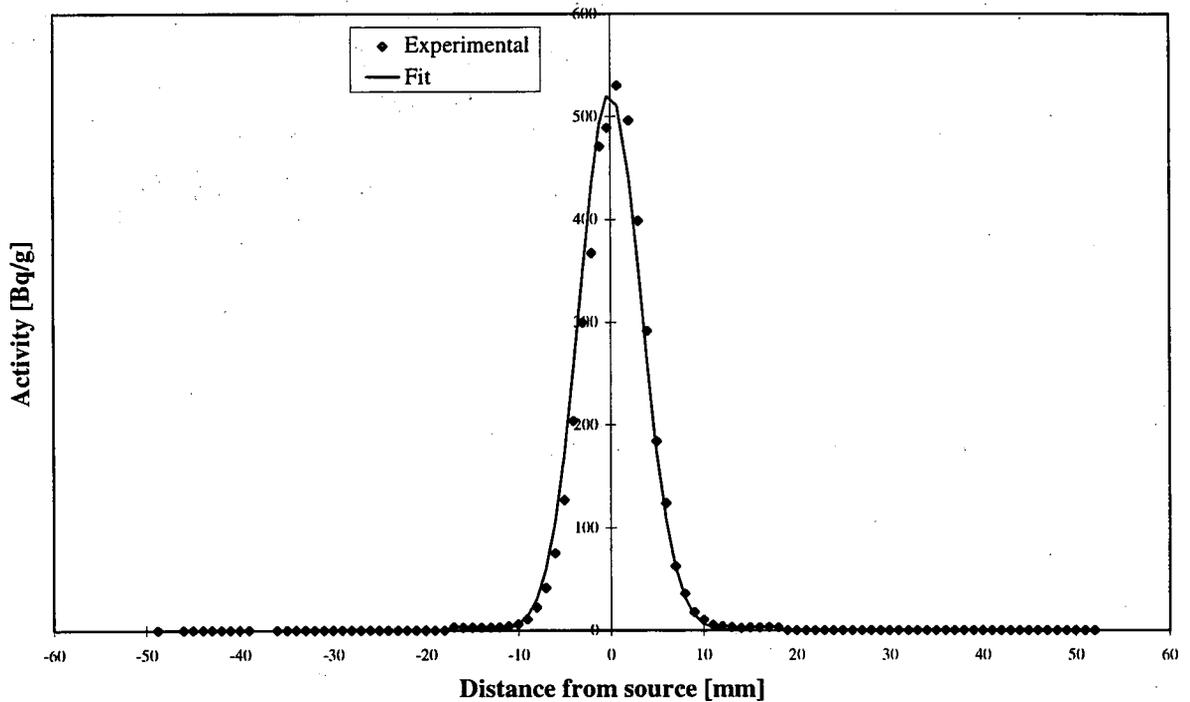
Figure 8: Distribution profile of Na-22 after electromigration for 20 hrs at 84 V/m

The mobilities are less than for the previous series of experiments, probably due to the temperature effect.

Again we obtain a good diffusion coefficient for Sr using the Einstein relation.

The clay is saturated with Na as charge balancing cation between the clay layers, the movement of these ions causes the electro-osmosis. Because sodium is the easiest exchangeable cation in the cation-exchange series[3], the retardation will be very low. The total mobility of Na should be corrected for the contribution of the electro-osmosis in order to apply the Einstein relation (R is set to 1). The corrected mobility of $2.10\ 10^{-9}\ m^2/Vs$ gives a diffusion coefficient of $5.47\ 10^{-11}\ m^2/s$ and compares well with the value of $6.55\ 10^{-11}\ m^2/s$. This latter value was obtained from a pure diffusion experiment conducted in parallel because no diffusion data for Na were available (Figure 9). The pure diffusion experiment was performed in the same sense as the electromigration experiment without applying a potential.

Figure 9: Distribution profile of Na-22 after 24 hrs in a pure diffusion experiment

Lower electrical fields means less acceleration and hence a lower convection velocity. The dispersion coefficients obtained, D(fit), are of the same magnitude as the diffusion coefficients, D(ref). However they remain overestimated.

Recalling equation 11 for the dispersion coefficient and taking into account that for cations $V_c^t = V_c^a$:

$$D^a = D_m^a + aV_c^t$$

eq. 18

the D^a and V_c^a are obtained from the curve fitting. In order to calculate the apparent diffusion coefficient we only need the dispersion length 'a'. For Boom Clay the dispersion length was reported as a=0.1cm[26]. Introducing this parameter in the equation gives erroneous results. E.g., for Sr-85, a D_m^a of **-3.85 10⁻¹¹ m²/s** is found. This implies that the dispersion length should be smaller.

An estimation can be made for the dispersion length if we put D(fit), D(ref) and the corresponding V_c^a into the equation and calculate the dispersion length. For Sr-85 we obtain a dispersion length of 0.016cm. Doing so for the other elements we can specify a range for the dispersion length: 0.01<a<0.1cm.

If we want to calculate the diffusion coefficient from the dispersion coefficient it is necessary to have a better estimate of the dispersion length. To achieve this we have to perform electromigration experiments at different voltages. From the relationship between the dispersion coefficient and the convection velocity, both the dispersion length and the diffusion coefficient can be calculated.

The parameters obtained from the first experimental series can not be used in this respect due to the physical changes which took place during the experiment.

6. Conclusions

During a diffusion experiment one has to avoid perturbations of the clay core to have a representative experiment. During electromigration some extra perturbations as pH gradients, changes in the ionic strength, dewatering, Joule heating, can occur.
The current experimental set-up with the automatic neutralisation at low voltages reduces these perturbations to a minimum.

The feasibility of the electrokinetic method to determine the diffusion coefficient of ionic species is demonstrated. There are two ways to extract the diffusion coefficient from an electromigration experiment.

A first way is based on the Einstein relation. From the displacement of the distribution profile the velocity is obtained. The velocity is composed of two components, electromigration and electro-osmosis. Only the electromigration velocity is necessary to calculate the diffusion coefficient. The electro-osmotic velocity is experimentally determined by the displacement of HTO. To determine the contribution of the electro-osmotic velocity to the total velocity of the species, the retardation has to be taken into account. For non-sorbed elements (anions) there is no retardation and the correction is made straightforward. For retarded species (cations) the retardation factor is necessary. But for retardation factors >10, the electro-osmotic velocity can be neglected. Only for weak retarded species the retardation factor is necessary to correct for the electro-osmosis.

From curve fitting the dispersion coefficient and the convection velocity are obtained. Due to the high convection velocity, the dispersion coefficient deviates significantly from the diffusion coefficient and can not be set equal as can be done in percolation and flow-through experiments. To obtain a correct diffusion coefficient the dispersion length is necessary. A dispersion length of 0.1 cm, as reported for Boom Clay, is too large and should be re-evaluated.

7. Experiments in progress

$\Rightarrow$ Electromigration of I-131 to complete the experimental series in paragraph 5.2.2.

$\Rightarrow$ Migration of C-14 labelled organic matter.
The different species present in organic matter will have different behaviour in an electric field and can be studied separately.

$\Rightarrow$ Migration of Si-32.
Electromigration is used to study the speciation of the Si-species.

$\Rightarrow$ Pure diffusion experiments for HTO, I^-, Na^+, Ca^{2+}, CO_3^{2-}...
Pure diffusion tests are performed to obtain diffusion coefficients needed to validate the electromigration results.

8. Future work

◊ Evaluation of the dispersion length
  ⇒ Electromigration experiments at different voltages.

◊ More thorough evaluation of the electro-osmotic velocity
  ⇒ HTO migration experiments at different voltages.

◊ Optimisation of the set-up
  ⇒ design of a new cell allowing cooling,
  ⇒ automation (automatic data-acquisition),
  ⇒ automatic measurement of the activity.

◊ Blank test for a thorough physico-chemical analysis of the clay core.

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