DESCRIPTION OF THE RADIOLOGICAL DECONTAMINATION BY ELECTRO-MIGRATION IN SATURATED CONCRETE: A MULTI SPECIES APPROACH.

F. Frizon, P. Thouvenot
CEA Cadarache, DEN/DED/SEP/LETD
Build 352, 13108 St Paul-lez-Durance Cedex, FRANCE

J. P. Ollivier, S. Lorente
Laboratoire Matériaux et Durabilité des Constructions, INSA-UPS, Department of Civil Engineering, National Institute of Applied Sciences
135 Avenue de Rangueil, 31077 Toulouse, FRANCE

ABSTRACT

A numerical model was developed in order to describe the electromigration of radioelements through contaminated concrete. The transport of several ionic species across a saturated sample of material, is described by the Nernst-Planck relation. The multi species approach provides a better understanding of the phenomena involved: it stresses the need to know, as precisely as possible, the material characteristics and the history of the contamination. The approach also sheds lights on the way the radionuclide (cesium 137) is carried away from a concrete sample during a decontamination simulation.

INTRODUCTION

The decontamination of materials is a major concern among the nuclear power industry, as part of the studies on decommissioning and dismantling nuclear facilities. Among these materials, the concrete is by itself a specific field of research: the penetration of radioelements may occur from several millimeters up to few centimeters from the material surface, due to the concrete porosity.

Several methods have been tested in order to remove the contaminants from the concrete surface: chemical extraction methods, mechanical techniques… Decontamination by electro-migration (also called electrokinetics) is very promising because it allows treating concrete structures, which are deeply contaminated, without strongly damaging the material itself. An electric field, in combination with a lixiviant solution, is applied to the contaminated structure. The radioelements are therefore carried away from the concrete. The method reduces the cost of treatment in decreasing the solid waste volume. The technique is similar to the one used in the removal of chloride ions from concrete in order to reduce the corrosion. It is also applied successfully to the remediation of soils.

This work focuses on the cesium decontamination (isotope 137) which is the radionuclide featuring the highest diffusivity, among the major contaminants found in concrete (1). Electrokinetics methods are based on the Nernst - Planck equation. The latter is usually written for the considered element in the pore solution. Studies dealing with ionic penetration (chloride) through concrete under an electrical field have shown that this description is not

sufficient (2). The authors propose a new approach of the problem, which accounts for the interactions between the different ionic species present in the pore solution and the cesium ion. The transport of each ionic species through the saturated porous medium is described by the Nernst - Planck equation where the electrical field holds both for the outside potential difference and the liquid-junction potential (electrical field between the ionic species in the pore solution). In addition, the conservation equations, written for each species, take into account the interactions between the species and the solid phase.

We present in this paper some preliminary results obtained using the multi species approach. The ionic distribution in the concrete sample during diffusion and decontamination tests is discussed, in addition to the estimation of the time necessary to extract cesium from a contaminated sample, in a specific example.

MULTI SPECIES APPROACH

The transport of ions through a porous medium is described by the Nernst-Planck equation (Eq. 1). This equation indicates that the diffusion of an ionic species is due to the concentration gradient of the species (molecular diffusion) but also to an electrical diffusion term, which accounts for the interactions between the ions. It is noteworthy that if the electrical diffusion is neglected, then the Nernst-Planck equation becomes identical to the first Fick's law of diffusion.

In this paper, the cement-based material is assumed to be saturated; in addition, the convection phenomenon is neglected. The Nernst-Planck relation is therefore given by Eq. 1, where the ionic transfer is unidirectional.

$$J_i(x,t) = -D_i \left[\frac{\partial c_i(x,t)}{\partial x} + z_i c_i(x,t) \frac{F}{RT} E(x,t) \right] \qquad (Eq.\ 1)$$

where, for each ionic species i, J_i represents the flux [mol/(m^2.s)], D_i the intrinsic effective diffusion coefficient [m²/s], c_i the concentration in the bulk solution [mol/m^3], z_i the valence of ionic species, x the space position [m], t the time [s], F the Faraday constant [96484.6 C/mol], R the ideal gas constant [8.3143 J/(mol. K)], T the absolute temperature [K], E(x,t) the local electric field [V/m].

Based on the works published by Tang (3) and Truc et al. (4), we assumed that the non-ideality of the solution has negligible effects on the ionic fluxes.

Electrical field

The local electrical field E(x,t) has two different origins: an external electrical field applied by electrodes when it comes to electrokinetics problems, but also a diffusion potential induced by the movement of ions.

The ionic flux is indeed linked to the ion concentration and its gradient by the diffusion coefficient (see Eq. 1). The value of this coefficient depends on the ionic species. The higher the diffusion coefficient, the higher the ionic flux. The second term in the Nernst-Planck equation tends to balance the latter statement. Electrical interactions occur between the ions in solution, as they are electrically charged species. The diffusion potential induced, also called

liquid junction potential, tends to slow down the ions with the highest diffusion coefficient, while the ionic species with the lowest diffusivity are accelerated.

For sake of simplicity, the variables x and t are from now on omitted, e.g. $E(x,t)$ is then written E. The electrical field E can be evaluated from the electrical balance given by Eq. 2 (5). In this equation, j is the current density imposed from outside during a decontamination test.

$$j = \frac{I}{A} = F \sum_{i=1}^{n} z_i J_i \qquad \text{(Eq. 2)}$$

Then, combining together Eq. 1 with Eq. 2, we obtain the expression of the electrical field (Eq. 3).

$$E = -\frac{RT}{F} \frac{\dfrac{j}{F} + \sum_{i=1}^{n} z_i D_i \dfrac{\partial c_i}{\partial x}}{\sum_{i=1}^{n} (z_i)^2 D_i c_i} \qquad \text{(Eq. 3)}$$

Note that in the case of a diffusion problem, where $j = 0$, Eq. 3 gives directly the value of the liquid junction potential.

We can rewrite Eq. 1 into Eq. 4:

$$J_i = -D_i \left[\frac{\partial c_i}{\partial x} - z_i c_i \frac{\dfrac{j}{F} + \sum_{i=1}^{n} z_i D_i \dfrac{\partial c_i}{\partial x}}{\sum_{i=1}^{n} (z_i)^2 D_i c_i} \right] \qquad \text{(Eq. 4)}$$

Interactions between the ionic species and the solid

Previous researches have shown that interactions exist between the ionic species and the solid (6). The total ion concentration is therefore the sum of the bound ion concentration and the free ion concentration. The latter only, is involved when it comes to estimate the penetration depth of a given ionic species.

The mass balance, written at the scale of the material, is given by Eq. 5:

$$\frac{\partial c_{Ti}}{\partial t} = -\frac{1}{p} \frac{\partial J_i}{\partial x} \qquad \text{(Eq. 5)}$$

We now replace c_{Ti}, the total ion concentration, by Eq. 6:

$$c_{Ti} = \frac{1-p}{p} \rho Cb_i + c_i \qquad \text{(Eq. 6)}$$

where p is the porosity of the material,

ρ is the density of dry material [kg/m^3],

Cb_i is the quantity of ion i bound per mass of dry material [mol/kg].

We obtain then Eq. 7, which is the continuity equation of the ionic species i.

$$p \frac{\partial c_i}{\partial t} + (1-p)\rho \frac{\partial Cb_i}{\partial t} = -\frac{\partial}{\partial x}\left[D_i \frac{\partial c_i}{\partial x} + z_i D_i c_i \frac{F}{RT} E \right] \qquad \text{(Eq. 7)}$$

The solution of Eq. 7 is the concentration profile of the ion through the porous medium at a given time.

Overall, the relation between the binding of a species on a cement-based material and the free amount of the same ion is given by Eq. 8.

$$Cb_i = \alpha c_i{}^\beta \quad \text{where } \alpha \text{ and } \beta \text{ are empirical constant parameters} \qquad \text{(Eq. 8)}$$

This equation is known as the Freundlich isotherm. In the case of the cesium binding, experiments have shown that the relation is linear (6). Therefore, $\beta = 1$. This relation is computed into the code by considering that the interactions between cesium and the cement-based material are instantaneous and reversible.

SIMULATIONS

Numerical Aspects of the Code

We describe in this section the way we computed the set of equations constituted by equations 3, 4 and 7 for a system of n ionic species.

$$
\begin{bmatrix} J_1 \\ \vdots \\ J_i \\ \vdots \\ Jn \end{bmatrix} = -\begin{bmatrix} D_1 \frac{\partial c_1}{\partial x} + z_1 D_1 c_1 \frac{F}{RT} E \\ \vdots \\ D_i \frac{\partial c_i}{\partial x} + z_i D_i c_i \frac{F}{RT} E \\ \vdots \\ D_n \frac{\partial c_n}{\partial x} + z_n D_n c_n \frac{F}{RT} E \end{bmatrix} = MAT. \begin{bmatrix} \frac{\partial c_1}{\partial x} \\ \vdots \\ \frac{\partial c_i}{\partial x} \\ \vdots \\ \frac{\partial c_n}{\partial x} \end{bmatrix} + \begin{bmatrix} z_1 c_1 D_1 \dfrac{j/F}{\sum_j z_j{}^2 D_j c_j} \\ \vdots \\ z_i c_i D_i \dfrac{j/F}{\sum_j z_j{}^2 D_j c_j} \\ \vdots \\ z_n c_n D_n \dfrac{j/F}{\sum_j z_j{}^2 D_j c_j} \end{bmatrix} \qquad \text{(Eq. 9)}
$$

with

$$MAT = \begin{bmatrix} D_1\left(-1+\dfrac{z_1{}^2 c_1 D_1}{\sum\limits_j z_j{}^2 D_j c_j}\right) & \cdots & D_1\dfrac{z_1 z_i c_1 D_i}{\sum\limits_j z_j{}^2 D_j c_j} & \cdots & D_1\dfrac{z_1 z_n c_1 D_n}{\sum\limits_j z_j{}^2 D_j c_j} \\ \vdots & \ddots & & & \vdots \\ D_i\dfrac{z_i z_1 c_i D_1}{\sum\limits_j z_j{}^2 D_j c_j} & \cdots & D_i\left(-1+\dfrac{z_i{}^2 c_i D_i}{\sum\limits_j z_j{}^2 D_j c_j}\right) & \cdots & D_i\dfrac{z_i z_n c_i D_n}{\sum\limits_j z_j{}^2 D_j c_j} \\ \vdots & & & \ddots & \vdots \\ D_n\dfrac{z_n z_1 c_n D_1}{\sum\limits_j z_j{}^2 D_j c_j} & \cdots & D_n\dfrac{z_i z_n c_n D_i}{\sum\limits_j z_j{}^2 D_j c_j} & \cdots & D_n\left(-1+\dfrac{z_n{}^2 c_n D_n}{\sum\limits_j z_j{}^2 D_j c_j}\right) \end{bmatrix}$$

The conservation equation is given by Eq. 7.

$$\begin{bmatrix} p+(1-p)\rho\dfrac{\partial Cb_1}{\partial c_1} & 0 & \cdots & \cdots & 0 \\ 0 & \ddots & & 0 & \vdots \\ \vdots & & p+(1-p)\rho\dfrac{\partial Cb_i}{\partial c_i} & & \vdots \\ \vdots & 0 & & \ddots & 0 \\ 0 & \cdots & \cdots & 0 & p+(1-p)\rho\dfrac{\partial Cb_n}{\partial c_n} \end{bmatrix} \cdot \begin{bmatrix} \dfrac{\partial c_1}{\partial t} \\ \vdots \\ \dfrac{\partial c_i}{\partial t} \\ \vdots \\ \dfrac{\partial c_n}{\partial t} \end{bmatrix} = -\begin{bmatrix} \dfrac{\partial J_1}{\partial x} \\ \vdots \\ \dfrac{\partial Ji}{\partial x} \\ \vdots \\ \dfrac{\partial J_n}{\partial x} \end{bmatrix}$$

(Eq. 10)

All variables are computed in their dimensionless form in order to provide a good stability to the numerical computations.

$$x^* = \frac{x}{L_0} \qquad t^* = \frac{D_0}{L_0{}^2}t \qquad c^* = \frac{c}{c_0} \qquad D^* = \frac{D}{D_0} \qquad j^* = \frac{jL_0}{Fc_0 D_0} \qquad \text{(Eq. 11)}$$

The variables noted with the mark * are in dimensionless form. D_0, L_0, c_0 are constant, respectively equal to the largest diffusion coefficient, the characteristic length of the system (thickness of the concrete or mortar sample) and the highest concentration.

The numerical scheme is based on a finite difference method with explicit scheme (7). Four different species are taken into account: sodium, potassium, cesium and hydroxide.

Input Data for the Model: Physical Parameter

Based on the numerical procedure described in the preceding section, we can simulate diffusion, migration and decontamination tests. The principle of these tests is sketched on Figure 1.
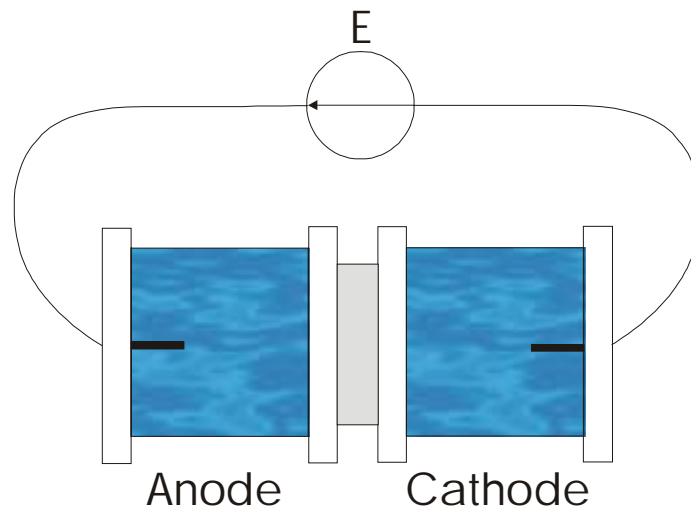
Fig. 1. Principle of diffusion and migration tests.

A saturated concrete specimen is placed between two compartments containing two different salt solutions. During an accelerated penetration test or a decontamination test, an external electrical field is applied between the anode and the cathode. This external current does not exist when it comes to a diffusion test.

The input parameters needed to compute the set of equations 3, 4 and 7 are of three kinds: those describing the sample, the ions and the pore solution. The parameters chosen in this paper are listed in the following tables.

Table I. Parameters Defining the Mortar Sample.
(the binding isotherm values are given for cesium ion)

Open porosity p	0.14
Dry density ρ [kg/m^3]	2200
Thickness of the sample [cm]	1 to 3
Surface of exposed mortar [cm^2]	70
Binding isotherm	α=0.16 10^{-3} β=1 (6)

Table II. Intrinsic Diffusion Coefficients.

Ion	Intrinsic diffusion coefficient [m²/s] *
Na$^+$	1.5 10^{-12}
K$^+$	2 10^{-12}
Cs$^+$	2.2 10^{-12}
OH$^-$	7 10^{-12}

*The intrinsic diffusion coefficients are chosen in agreement with the ones provided by Truc (8). The cesium coefficient is obtained using the same method.

Table III. Initial Ionic Concentrations in the Pore Solution.

Ion	Pore Solution Concentration (mol/m^3)**
Na$^+$	25/200
K$^+$	80/500
OH$^-$	105/700

** The first values of pore solution are similar to the one given by Schmidt and Rostasy (9), the second to those given by Diamond in high alkalinity case (10).

The ionic concentrations in the two compartments surrounding the sample depend on the type of simulation. In every case, these parameters are maintained constant. It is noteworthy that it is also the case during the experiments as the anolyte and catholyte are regularly changed in order to consider that the boundary conditions are in steady state. The cesium in the pore solution comes from a cesium hydroxide.

Results

We present in this section some results of interest. The concentration profiles of cesium are plotted on Figure 2 after a 100 days test. We decided to simulate a basic case of diffusion (meaning that the external current is zero) in order to point out the influence of the initial conditions. In the two examples proposed, the sample is saturated, according to the very first assumption that was made in this work. The initial concentration of the ions is yet totally different (cf. Table IV), except for the cesium: in each example it is zero in the pore solution.

Table IV. The Simulation Data of Figure 2.

Duration of the Simulated Test [days]	100
Nodes	51
Time Step [s]	300
Thickness of the Sample [cm]	3
Exposed Surface [cm²]	70

Data for Schmidt-Rostasy Pore Solution

Ion	Anodic Solution Concentration [mol/m^3]	Cathodic Solution Concentration [mol/m^3]
Na$^+$	25	25
K$^+$	80	80
Cs$^+$	500/250	0
OH$^-$	605/355	105

Data for Diamond Pore Solution

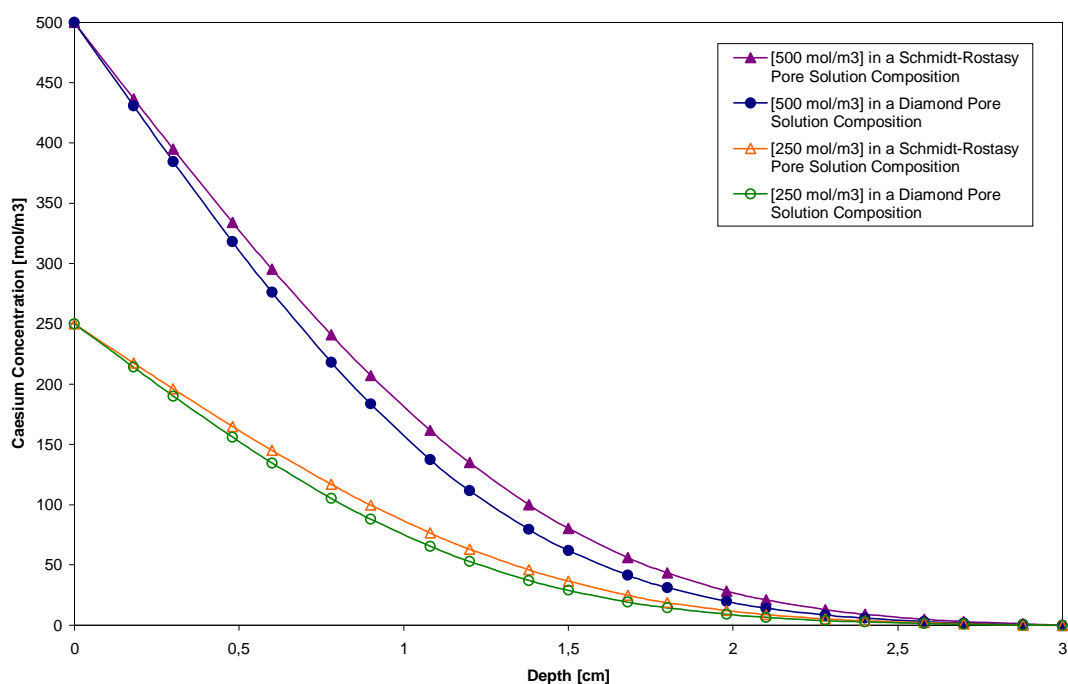| Ion	Anodic Solution Concentration [mol/m^3]	Cathodic Solution Concentration [mol/m^3]
Na$^+$	200	200
K$^+$	500	500
Cs$^+$	500/250	0
OH$^-$	1200/950	700

Fig. 2. Simulation of Cesium Diffusion into Mortar for various Concentrations in anodic Compartment.

Note that we chose intentionally to present examples with high cesium concentrations. We are dealing here with a new description of the decontamination problem (the multi-species approach) rather than an actual estimation of the amount of radioelement that might be carried away from the concrete sample.

After a hundred days, the steady state is still not reached. Nevertheless, since the penetration depth is very close to the material thickness, Figure 2 shows that a hundred days is the time necessary to cross the sample in this example. At first sight, the initial conditions do not seem to have any influence on the transport of the radioelement. Yet, the shape of the concentration profiles is rather different. The quantity of cesium that reached half of the sample is 80 mol/m^3 when the pore solution concentration is based on Schmidt and Rostasy's data and the cesium concentration is 500 mol/m^3 in the compartment, while at the same abscissa, it is 61 mol/m^3 in a pore solution such as Diamond's one. The average difference between the amounts of cesium in the two cases is of 9%, which is far from negligible. This result shows that a high level of alkalinity in the compartments and the porous medium tends to slow down the penetration of cesium, because of the electrical field generated between species of the same charge. In addition, this first example stresses how the knowledge of the initial ionic concentration is important, in order to predict the distribution of radionuclides through the concrete wall.

We focus now on the example of an electrokinetic decontamination. The data used for the simulation are listed in Table V, the sorption process is assumed to be irreversible in this case. A 12 V potential drop (4V/cm) is applied to accelerate the migration of the cesium toward the outside. It is worth to point out (Figure 3-a) that after two days the all amount of cesium has left the 3 cm thick concrete sample. Furthermore, the cesium amount is a linear function of time. Again, the initial concentration of cesium is high compared to the level that is actually measured in situ.

The multi species description helps to understand the kinetic of decontamination. The hydroxide ions with the highest diffusion coefficient and the highest concentration, control the process. Initially, the cesium concentration is of 500 mol/m^3 in the porous medium. The cesium ions leave the sample to the left. After 12 hours, one fourth of the material is free of ions. The slope of the right part of the curves is, in each case (12h, 24h, 36h), characteristic of a decontamination front. When the lasting of the test increases, this slope tends to become smoother until the highest value of cesium concentration in the sample diminishes before the radionuclide leaves totally the material. For example, when the test is of 36 hours, the peak value in cesium is 350 mol/m^3 .
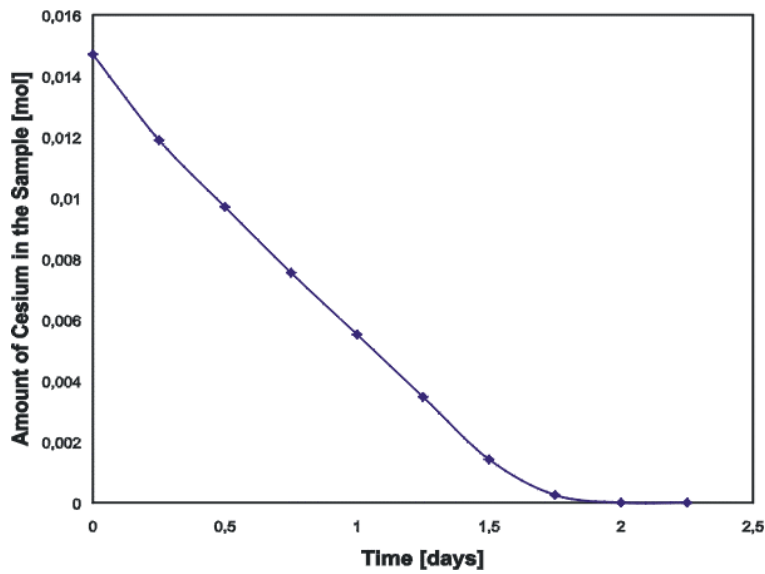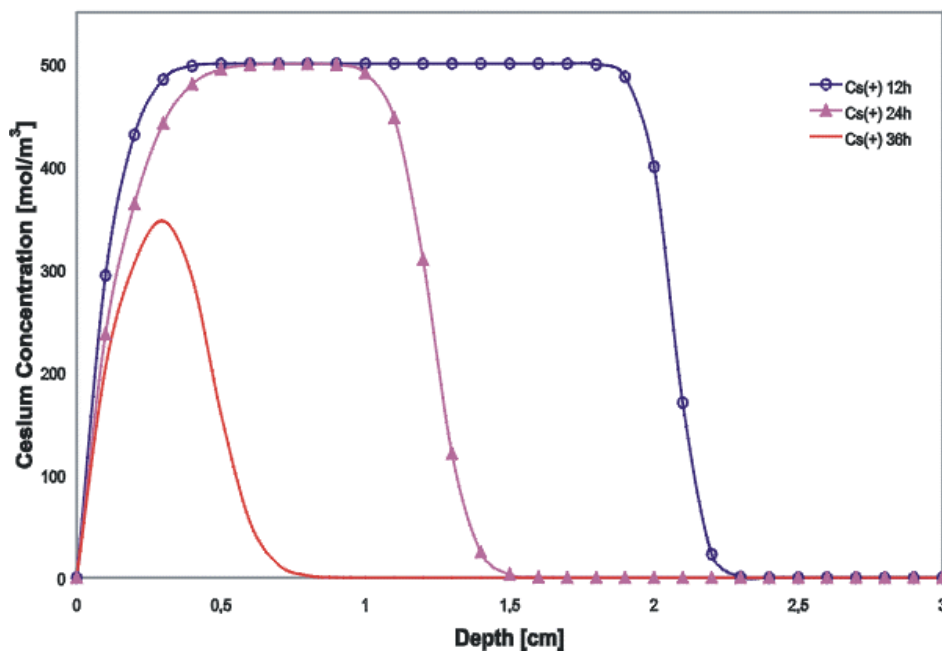

Fig. 3. Simulation of Cesium Decontamination with Diamond Pore Solution Composition under an External Applied Field of 4 V/cm.

Table V. Simulation Data of Figure 3.

Duration of the Simulated Test [hours]	12/24/36	Ion	Cathodic Solution Concentration [mol/m³]	Pore Solution Concentration [mol/m³]	Anodic Solution Concentration [mol/m³]
Nodes	301	Na^+	30	25	25
Time Step [s]	60	K^+	0	80	80
Thickness of the Sample [cm]	3	Cs^+	0	500	0
Exposed Surface [cm²]	70	OH^-	30	605	105

The multi species approach provides also information on the behavior of the other ionic species studied here: sodium, potassium and hydroxide. The data are still the ones listed in Table V, the test is one day. The results are plotted in Figure 4-a in terms of ionic fluxes. The ionic fluxes are here chosen positive when the ions move from the cathode to the anode. The hydroxide flux is constant all over the sample. Figure 4-b must be seen as a picture of the ionic repartition into the material. Since there is no source of cesium in the anodic compartment, the radioelement leaves the sample the way we described previously. Whereas, due to the boundary conditions in the anolyte, we notice an accumulation of sodium and potassium in the material. The hydroxide ions penetrate the sample from the surface (cathodic compartment) to the core of the sample. It modifies strongly the composition of the pore solution, changing the equilibrium between the solid phase and the pore solution. This last result illustrates how the electrokinetics remediation may create new phase equilibrium and, hence, modify the mineralogical phase of the cement-based materials.

CONCLUDING REMARKS

Electromigration is a new method of nuclear decontamination. Interesting results are expected because the method was already applied to related situations such as soil remediation for example. The numerical tool that we developed aims to describe the transportation of the radionuclides through contaminated concrete in order to predict later the efficiency of electrokinetics, in terms of lasting of experiments. We showed that the initial ionic concentration has non-negligible effects on the radioelement distribution in a concrete sample. The results provided during a decontamination test under a 4 V/cm external electrical field helps to understand the way the radionuclide is extracted from the porous medium, but also, drives our attention to the new phases equilibrium that may occur. In conclusion, the multi-species approach of electrokinetics is not only a description tool but also an important part in the design of the decontamination process.
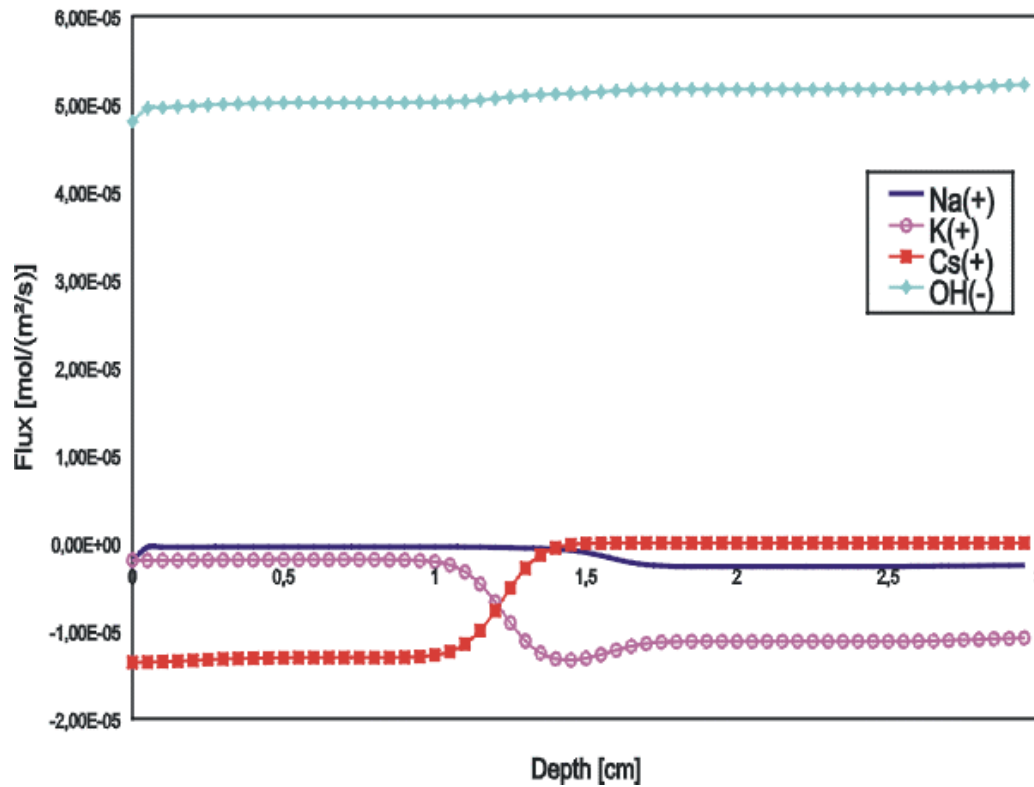
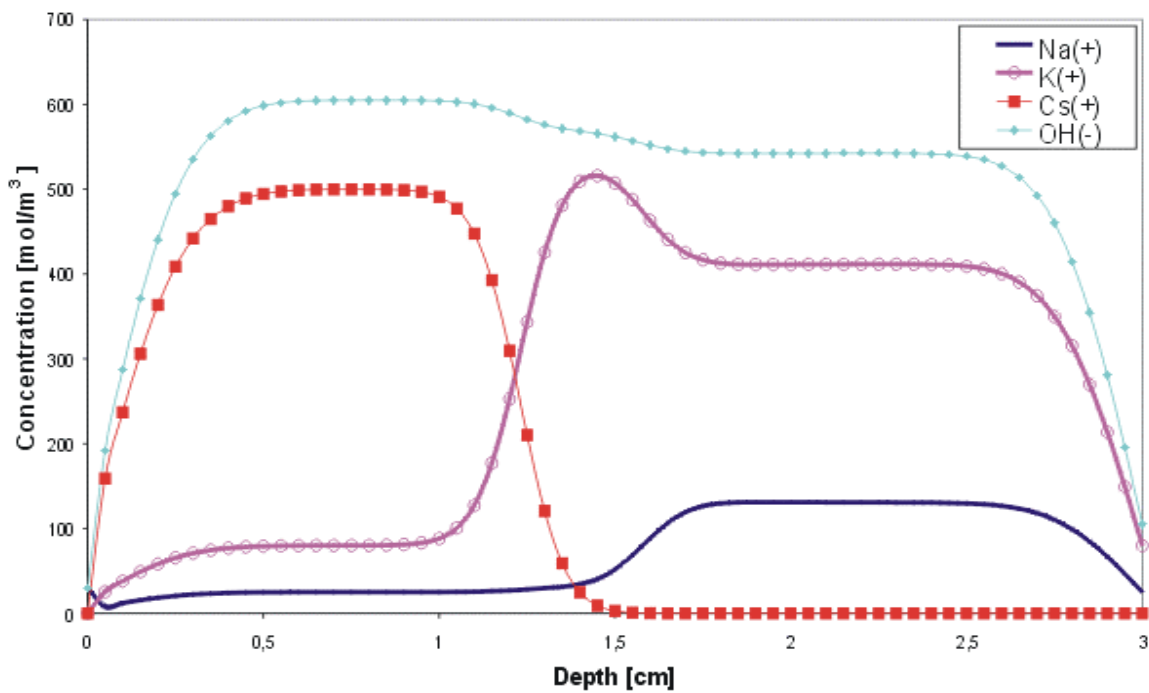**Fig. 4. Simulation of a Decontamination Process with a Schmidt – Rostasy's Pore Solution Composition, under an External Electrical Field of 4V/cm.**

REFERENCES

1. K.S. DICKENSON *et al.*, "Demonstration recommendations for accelerated testing of concrete decontamination methods", DOE, (1995).
2. J.Z. ZHANG and N.R. BUENFELD, "Presence and possible implications of a membrane potential in concrete exposed to chloride solution", Cement and Concrete Research **27** (6), pp. 853-859, (1997).
3. L. TANG, "Concentration dependence of diffusion and migration of chloride ions. Part2. Experimental evaluations", Cement and Concrete Research **29**, pp. 1469-1474, (1999).
4. O. TRUC, J.P. OLLIVIER, L.O. NILSSON, "Numerical simulation of multi-species transport through saturated concrete during a migration test - MsDiff code", Cement and Concrete Research **10**, pp. 1581-1592, (2000).
5. J.S. NEWMAN, "Electrochemical systems", New Jersey, (1991).
6. C. RICHET, "Etude de la migration des radioéléments dans les liants hydrauliques-Influence du vieillissement sur les mécanismes et la cinétique des transferts.", Universite de Paris XI Orsay, 267 p, (1992).
7. W.F. AMES, "Numerical methods for partial differential equations.", New York: Academic Press, (1977).
8. O. TRUC, "Prediction of Chloride Penetration into Saturated Concrete - Multi-Species Approach., in Laboratoire Matériaux et Durabilité des Constructions.", Institut National des Sciences Appliquées: Toulouse (France), 210 p, (2000).
9. F. SCHMIDT and F.S. ROSTASY, "A method of calculation of the chemical composition of the concrete pore solution.", Cement and Concrete Research **23,** pp.1159-1168, (1993).
10. S. DIAMOND, "Effects of two danish flyashes on alkali contents of pore solutions of cement-flyash pastes.", Cement and Concrete Research. **11,** pp. 383-394, (1981).