

---

# Reactive transport modeling of interaction processes between claystone and cement

L. De Windt, D. Pellegrini\*, J. van der Lee

*Ecole des Mines de Paris (EMP/CIG) - 35 rue Saint-Honoré - 77305 Fontainebleau - France*  
*\* Institut de protection et de sûreté nucléaire (IPSN/DES) - BP6 - 92265 Fontenay-aux-Roses  
France*

---

**Abstract:** The disposal of radioactive wastes in clayey formations may require the use of large amounts of concrete and cement. The chemical interactions between these industrial materials and the host rock are modeled with the reactive transport code HYTEC for time scales and a geometry representative of disposal projects. The pH evolution, a key parameter in element mobility, is studied more specifically. It depends on several interdependent processes: i) diffusion of highly alkaline cement pore solution, ii) strong buffering related to important mineral transformations both in the cement and in the clay, and iii) cation exchange processes, beyond the zone of intense mineral transformations. In addition, precipitation of secondary minerals may lead to a partial or complete clogging of the pore space, almost stopping the propagation of the high pH plume. In a second step, preliminary results on the migration of strontium and uranium in these strongly coupled systems are presented as an example of transport parameter derivation.

## 1. CONTEXT AND SPECIFICITIES OF THE STUDY

Claystone is being investigated in several countries as one of the type of rock formation that could possibly host an underground repository for radioactive wastes. The design of an underground repository often includes large amounts of cementitious materials. These materials could be used as a barrier in the case of intermediate level wastes (ILW) to minimize corrosion of steel containers and radionuclide migration, and also for supporting the cavities (drifts, disposal vaults...). For purposes of safety assessment, these positive features have to be balanced with the potentially negative effects of cement degradation on the performances of the geological barrier in the near field. The porewater chemistry of cements is indeed characterized by high amounts of alkaline and hydroxyl ions. The migration of the cement porewater into the surrounding media leads to a so-called alkaline plume. Accordingly, local destruction of the claystone minerals as well as substantial modification of pore water chemistry, radionuclide retention and solubility properties may occur.

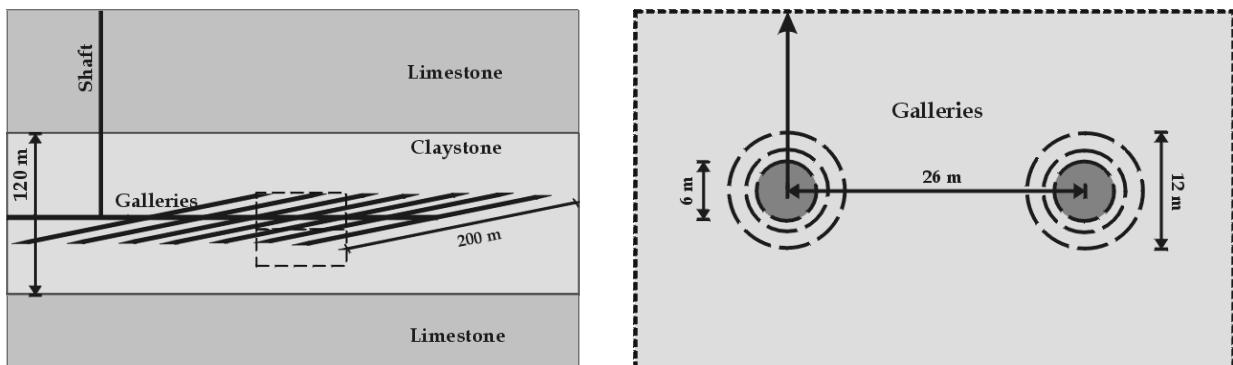
In this context, pH is the key parameter to follow since: i) it gives an indication of the alkaline plume extension, ii) it is a global indicator of the numerous mineralogical transformations, and iii) the sorption and the solubility of many actinides and fission products significantly change with pH. Furthermore, the propagation of the alkaline plume and the modification of both cement and clay geochemistry are strongly coupled. In particular, a partial or complete sealing of the poral space may occur due to the precipitation of large amount of secondary minerals. It is thus necessary to model the system evolution as a whole with reactive transport codes able to take into account the feedback of chemistry on porosity and transport

parameters. The present paper provides such a modeling study. Care has been taken to approach time scales and geometrical design which are consistent with the sets of

hypotheses developed in feasibility studies of underground repositories for radioactive waste. All simulations of this paper are based on an extensive literature review (not detailed here) with respect to experiments and natural analogues related to cement/clay interactions. An approach for the derivation of transport parameters is currently developed by coupling migration of elements and cement-clay interactions. Preliminary results on the migration of strontium and uranium in these strongly coupled systems are presented in the last section of the paper.

## 2. SYSTEM AND MODEL DESCRIPTION

The studied system is a simplified representation for the near field of an ILW repository in a deep argillaceous formation, derived from the various repository design studied at present time. The chosen properties of the host rock formation are those of stiff clays such as can be found in France and Switzerland (see for instance [1]). The clay is strongly indurated and has a rather low porosity (15 %). Diffusion is assumed to be the predominant migration vector with an average pore diffusion coefficient of  $10^{-10}$  m<sup>2</sup>/s. The waste disposal design consists of long horizontal tunnels (100 m long, 6 m in diameter, 20 m between two tunnels) perpendicular to handling drifts (Fig. 1). For simplification purposes, it is assumed that the tunnels are entirely filled with cement, i.e. the same type of cement is used for the wastes and the engineered barrier. In accordance with field observations, the excavation damaged zone (EDZ) is defined as a strongly fractured zone (1-m thick) and a disturbed transition zone (1-m thick), with higher porosities and pore diffusion coefficients than the undisturbed clay rock. Given the symmetry of the system, a cross section including two tunnels at mid-length is considered for the simulations. The temperature is fixed to be 20 °C representative of thermal conditions for intermediate level wastes.



**Figure 1.** Simplified geometry of the repository site and cross section used for the simulations.

As it was assumed by De Windt et al. [2], the cement is close to a Portland Cement (pH = 13.3, K-Na-OH fluid in equilibrium with CSH1.8, portlandite and ettringite). The cement stands for a reactive geochemical zone in itself and is not considered to be a constant boundary condition. The claystone mainly contains clay minerals (illite, interstratified illite/smectite) with cation exchange properties, but also quartz, calcite and dolomite. In our modeling, Ca-montmorillonite stands for the smectitic part of the claystone. The porewater has a pH of 7.7 with sodium, chloride and sulfate as major ions. Porewater is in equilibrium with the minerals and the exchangeable ions. The cation exchange capacity is 20 meq/100g, Ca being the dominant exchangeable cation. At in situ pH, the proton concentration contained in the clay was estimated to be at least 10 % as in [3] and [4]. Due to a lack of kinetic data, all simulations are based on the local equilibrium assumption. Nevertheless, some expected kinetic effects are included by fine-tuning the precipitation and dissolution behavior, e.g. preventing some clay minerals from precipitating.

HYTEC [5], based on the geochemical code CHESS [6], is used to simulate reactive transport in saturated porous media in one or two dimensions. Convective/dispersive and diffuse transport can be simulated for solutes and colloids. A wide range of processes such as aqueous chemistry, redox, dissolution/precipitation, surface complexation and ion exchange can be modeled at equilibrium or with kinetic control. In addition, HYTEC is strongly coupled, i.e. the hydrology (flow and diffusion) may change when mineral precipitation or dissolution changes the local porosity [7]. Several well-known thermodynamic databases are available for the code. For the present study, the EQ3/6 (V8-R6) dataset was selected [8]. It was enriched with experimental data for ion exchange constants [9] and for calcium silicate hydrates denoted hereafter by CSH. Three discrete CSH species of increasing Ca/Si ratio were introduced: CSH0.8, CSH1.1 and CSH1.8.

### 3. PH CONTROLLING PROCESSES

One of the most problematic issues in cement/rock interactions is to select secondary minerals which will be allowed to precipitate in the simulations. A rather large variability of those secondary minerals is found in the literature according to the temperature, the nature of the cement, the initial rock-forming minerals and the hydrogeological characteristics [10, 11]. Precipitation of CSH, hydroxides and carbonates is almost always observed. When clay minerals such as illite and smectite are present, ion exchange will occur and influence the overall geochemistry. In the case of young cements, as assumed in this study, the high porewater content in potassium may induce the precipitation of illite and /or the illitization of the smectitic clay minerals. Finally, precipitation of zeolites, sheet silicates and K-feldspars are less plausible at low temperature but were nevertheless observed in some cases. Our modeling approach was therefore to let all these minerals precipitate progressively during the reactions. Table 1 summarizes the successive mineralogical assumptions.

**Table 1.** Mineralogical hypotheses considered in the simulations

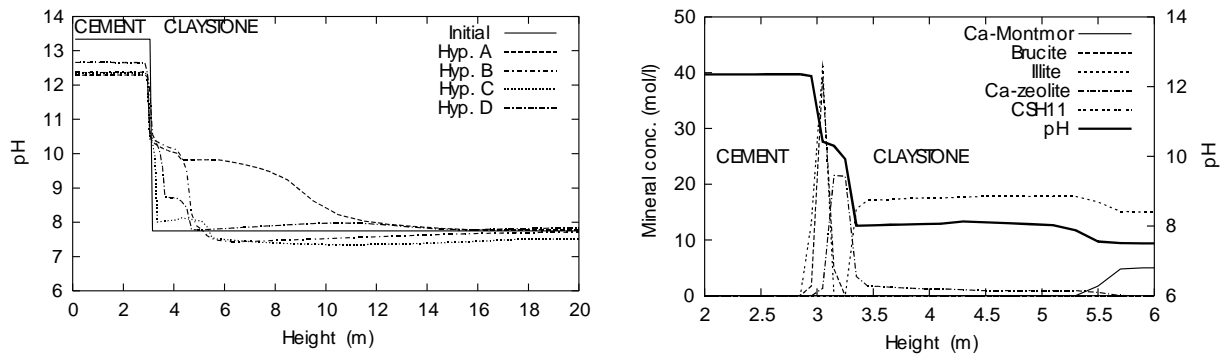
	Non clay minerals (*)	Clay minerals
<b>Hyp. A</b>	CSH	smectite & illite = dissolution only
<b>Hyp. B</b>	CSH + ion exchange	smectite & illite = dissolution only
<b>Hyp. C</b>	CSH + zeolites	smectite = dissolution only, illite = equil.
<b>Hyp. D</b>	CSH + zeolites + K-feldspar + sepiolite	smectite = dissolution only, illite + kaolinite = equilibrium

(\*) Carbonates, hydroxides and oxides are in equilibrium in all hypotheses.

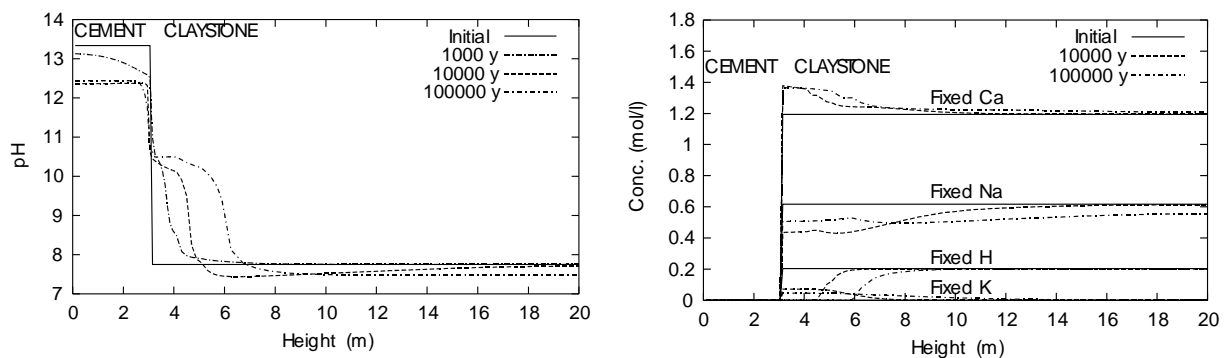
Profiles of pH along the vertical axis are given in Figure 2 after 10000 years. In the cement, close to the interface, the pH quickly falls from 13.3 to 12.6, due to diffusion-driven removal of sodium and potassium ions. In agreement with experiments [12], pH is then buffered by the dissolution of portlandite and CSH1.8, successively. At the interface, the high pH plume from cement is strongly buffered at a value of around 10 for all hypotheses. Further from the interface, the extension of the (reduced) alkaline plume is more hypothesis dependent. The rate and intensity of the pH plume depend on the reactions occurring at the interface. The second graph of Figure 2, representative for hypothesis C, shows the origin of this buffering, i.e., mineral dissolution and precipitation. CSH1.1 precipitates abundantly at the interface at the expense of primary cement and claystone minerals. The transformation of dolomite in calcite and brucite (or hydrotalcite) also contributes to pH buffering as pointed out by the experimental work of Adler et al. [13]. A second zone of pH buffering is located at the front of the transformation of montmorillonite in illite and Ca-zeolite. This last type of minerals is less stable than CSH at the interface where pH and calcium contents are higher. The illitization is favored by the flux of potassium ions. At some distance from the interface: hydroxyl ions

diffuse and disturb the porewater chemistry (hypotheses A and B), without provocation of significant mineral transformations.

Another noticeable result, illustrated in Figure 3, is that the ion exchange process (hypothesis B) represents a second source of pH buffering. The alkaline plume not only increases the concentration of hydroxyls but also of other ions, notably calcium and potassium. Most of these ions are fixed by the clay minerals according to an exchange reaction with sodium ions and protons. Protons in solution neutralize hydroxyl ions, and the pH remains relatively low as long as the stock of exchangeable protons is not totally depleted.

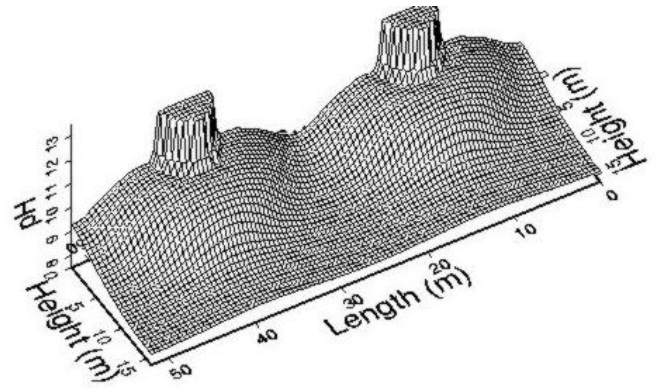
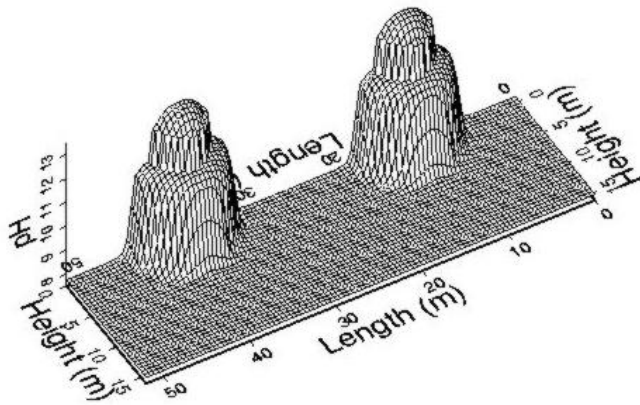


**Figure 2.** Evolution after 10000 y. Longitudinal pH profile for the different hypotheses and content of some relevant minerals for hypothesis C.



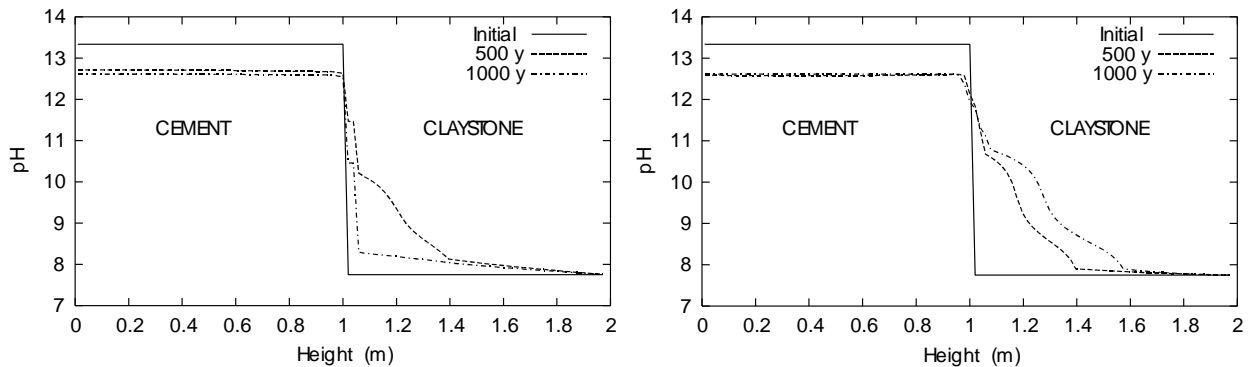
**Figure 3.** Propagation of the alkaline plume and modification of the exchangeable ions population over a period of 100000 years in case of hypothesis B.

It is expected that the impact of pH fronts from the parallel tunnels and the dispersion of chemical elements are more correctly modeled in two dimensions. Two-dimensional pH distributions have been calculated around the two tunnels after 250 and 10000 years (Fig. 4) in case of hypothesis A where pH is relatively poorly buffered. The borders of the first distribution in Figure 4 correspond to the EDZ zone. Mass transport is indeed relatively fast in this disturbed zone. After 10000 years, there is a small overlap of the pH plumes coming from the two parallel tunnels.



**Figure 4.** Two-dimensional pH distributions around the two parallel tunnels: after 250 years and 10000 years for hypothesis A.

Important precipitations of calcite or minerals with high molar volume (CSH and zeolites) may lead to the complete clogging of the pore space at the cement/claystone interface, slowing down, or even stopping, further geochemical evolution of the system [14, 7]. In the context of this study, some preliminary calculations have been made with HYTEC. Figure 5 shows the profiles of pH obtained with and without feedback of chemistry on porosity and diffusion for hypothesis C. At the beginning, the two pH profiles are very similar. But after 1000 years, the porosity and the diffusion coefficient drop rapidly within the claystone close to the interface. The two subsystems, cement and claystone, become isolated from each other. Consequently, the diffusion of the high pH plume is significantly reduced and the pH can be fully controlled by the minerals.



**Figure 5.** Profiles of pH with and without feedback of chemistry on porosity and diffusion (hypothesis C).

#### 4. RADIONUCLIDES MIGRATION

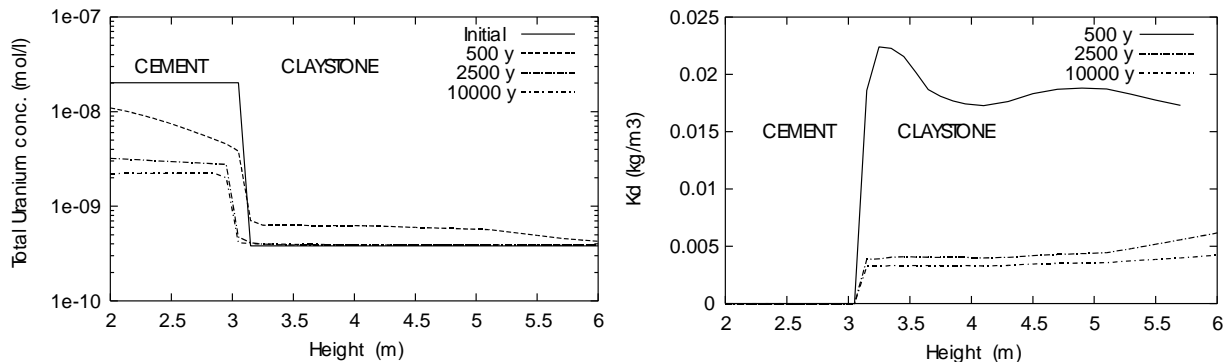
The modeling of the interactions between cement and concrete and the argillaceous host rock aims at estimating the evolution in time of the containment properties of the multi-barriers system. In this context, two types of modeling are considered:

- *type I*: calculation of intrinsic solubility limits and Kd values backing up on the results of modeling of cement/claystone interactions,
- *type II*: full mechanistic modeling which explicitly introduces radionuclides in the calculation with ad hoc assumptions on radionuclide inventory, canister failure, migration pathway, etc.

As a preliminary example, the solubility of uranium has been calculated according to the first approach over the entire domain for hypothesis A using the NEA thermodynamic database [15]. As shown in Figure 6, there is initially a difference of two orders of magnitude between the theoretical maximum solubility of uranium in cement and claystone porewaters. The solubility limit is progressively lessened inside the cement in parallel to the pH drop. Uranium solubility is controlled by the balance between complexation with hydroxyl ligands and the precipitation of U(IV) minerals (coffinite, uraninite). Indeed, reducing conditions constantly prevail after the closure of the repository and the permanent arrival of calcium ions from the cement depletes the claystone porewater in carbonate ligands due to calcite precipitation.

The second type of modeling is illustrated through a simplified calculation of strontium migration in the conservative hypothesis of an early waste package failure just after the resaturation of the near field. Although the entrapment of strontium in cement matrix is effective [12], it seems that the sorption of strontium on preexistent CSH minerals is relatively low [16]. Accordingly, in first approximation, it was assumed that claystone was the principal source of strontium retention in the multi-barriers system. Since, the mechanism of strontium sorption proceeds through ion exchanges in claystone, the calculations were performed in relation with hypothesis B. Strontium is continuously fixed by the clay minerals, but the

competitive effect with calcium ions diffusing from cement is quickly operational and leads to a significant decrease of the  $K_d$  (Fig. 6). The simulation also indicates that the solubility of Sr is controlled by precipitation of carbonate minerals (strontianite or solid solution with calcite), or in some cases by co-precipitation with CSH.



**Figure 6.** Modification of the solubility limit of uranium (hypothesis A) and of the calculated  $K_d$  value of strontium during the first 10000 years (hypothesis B).

## 5. CONCLUSIONS AND PERSPECTIVES

After 10000 years, the pH is always strongly buffered and important mineral transformations occur at the interface, both in cement and host rock, over several decimeters. Even beyond the zone of intense mineral transformations, the pore water chemistry is disturbed due to an attenuated but continuous flux of hydroxyl ions. Four interdependent mechanisms control the pH profile in the whole system: diffusion of the alkaline plume, mineralogical buffering, ion exchange and sealing of the poral space. The alkaline plume significantly disturbs the porewater chemistry and the radionuclide containment properties of the argillaceous barrier. The performances of the cement-claystone barriers system can be assessed by the fully coupled reactive transport code HYTEC for realistic time scales and field-scale geometries. The modeling of strongly coupled geochemical processes and radionuclides migration is not only technically feasible, but represents a relevant alternative to the traditional  $K_d$  and solubility limit approach. Nevertheless, these modeling results are still preliminary. Research is ongoing to better assess the effect of geochemical processes on the hydrology and porosity changes, notably to understand the importance of kinetics and the fractured structure of the EDZ zone. The modeling, which combines the migration of elements and the cement-clay interactions, is developed in parallel.

## REFERENCES

1. De Windt L., J. Cabrera and J.-Y. Boisson (1999). Radioactive Waste Containment in Indurated Claystones: Comparison between the Chemical Containment Properties of Matrix and Fractures, *Geological Society of London* 157, 167-181.
2. De Windt L., J. van der Lee and D. Pellegrini (2001). Reactive transport modeling of pH buffering in cement - clay systems, *Water Rock Interaction Proc. (Sardaigne, Italy)*, Balkema Ed., 1315-1318.
3. Cranga M., L. Trotignon, C. Martial and E. Castelier (1998). Simulation of the evolution of a clay engineered barrier by interaction with granitic groundwater: dynamics and characteristics timescales, *Mat. Res. Soc. Symp. Proc.* 506, 629-636.
4. Pearson Jr F.J., H.N. Waber and A. Scholtis (1998). Modelling the chemical evolution of porewater in the Palfris Marl, Wellenberg, Central Switzerland, *Mat. Res. Soc. Symp. Proc.* 506, 789-796.
5. van der Lee J. and L. De Windt (2001). Present state and future directions of modeling geochemistry in hydrogeological systems, *J. Cont. Hydr.* 47, 265-282.
6. van der Lee J. (1998). Thermodynamic and mathematical concepts of CHESSE, *Technical Report LHM/RD/98/39, Ecole des Mines de Paris, Fontainebleau (France)*.
7. Lagneau V. (2000). Influence des processus géochimiques sur le transport en milieu poreux; application au colmatage de barrières de confinement potentielles dans un stockage de déchets en formation géologique, *Ph.D. thesis from Ecole Nationale Supérieure des Mines de Paris*.
8. Wolery T. (1992). EQ3/6. A software package for geochemical modelling of aqueous systems: package overview and installation guide (version 7.0), *Technical Report UCRL-MA-110662 PT I ed., Lawrence Livermore National Laboratory, USA*.
9. De Windt L., J. Cabrera and J.-Y. Boisson (1998). Hydrochemistry of an indurated argillaceous formation (Tournemire site, France), in *Arehart and Hulston (Eds.), Water-Rock Interactions, Taupo (NZ)*, 145-148.
10. Steefel C.I. and P.C. Lichtner (1998). Multicomponent transport in discrete fractures. II : infiltration of hyperalkaline groundwater at Maqarin, Jordan, a natural analogue site, *J. Hydrology* 209, 200-224.
11. Hodgekinson E.S. and C.R. Hughes (1999). The mineralogy and geochemistry of cement/rock reactions: high-resolution studies of experimental and analogues materials, *Geological Society of London* 157, 195-211.
12. Atkins M. and F.P. Glasser (1992). Application of Portland cement-based materials to radioactive waste immobilization, *Waste Manag.* 12, 105-131.
13. Adler M., U. Mader and H. N. Waber (1999). High-pH alteration of argillaceous rock: an experimental study, *Schw. Miner. Petr. Mitt.* 79, 445-454.
14. Lichtner P.C., R. P. Pabalan and C. I. Steefel (1998). Model calculation of porosity reduction resulting from cement-tuff diffusive interaction, *Mat. Res. Soc. Symp. Proc.* 506, 709-718.
15. Wanner H. and I. Forest Eds (1992). Chemical thermodynamics of uranium, Amsterdam: North-Holland.
16. Hietanen R., T. Jaakkola and J.K. Miettinen (1985). Sorption of Cs, Sr, I and C in concrete and sand, *Mat. Res. Soc. Symp. Proc.* 44, 891-898.