THM and reactive transport analysis of expansive clay barrier in radioactive waste isolation

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SUMMARY

A fully coupled formulation combining reactive transport and an existing thermo-hydro-mechanical (THM) code is briefly described. Special attention has been given to phenomena likely to be encountered in clay barriers used as part of containment systems of nuclear waste. The types of processes considered in the chemical formulation include hydrolysis, complex formation, oxidation/reduction reactions, acid/base reactions, precipitation/dissolution of minerals and cation exchange. Both kinetically controlled and equilibrium-controlled reactions have been incorporated. The formulation has been implemented in the finite element code CODE_BRIGHT. An application is presented concerning the performance of a large scale *in situ* heating test simulating high-level nuclear waste repository conditions. Copyright © 2006 John Wiley & Sons, Ltd.

KEY WORDS: reactive transport problem; THM formulation; clay barrier; nuclear waste

1. INTRODUCTION

Compacted swelling clays are often envisaged as the main component of engineered barriers for radioactive waste disposal. These barriers are subjected to thermal loading due to the heat emitted by the waste and to hydration from water coming from the adjacent rock. As a consequence of these thermo-hydraulic phenomena, mechanical and chemical changes arise that, in turn, may affect all other aspects of behaviour. A correct understanding and prediction

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of these barriers would require, therefore, the performance of fully coupled thermo-hydro-mechanical and chemical (THMC) numerical analyses.

Although there have been a number of coupled THM formulations proposed and the corresponding numerical codes have been available for some time (e.g. References [1–3]), coupled THMC formulations have lagged behind. Only recently, a number of proposals have been put forward in this field (e.g. References [4, 5]). The research is now reaching a state that, through the incorporation into efficient computer codes, it is possible to perform coupled THMC numerical analyses to tackle engineering problems of a high level of complexity.

In this paper a fully coupled THMC formulation is briefly described that allows the performance of numerical analyses considering all four aspects of behaviour: thermal, hydraulic, mechanical and chemical and their interactions. The formulation takes into account the possibility that the material is partly saturated. The formulation is applied to the analysis of a real large-scale *in situ* heating test simulating nuclear repository conditions.

2. DESCRIPTION OF THE THMC FORMULATION

The main focus of the paper lies on the reactive transport problem. The THM component of the formulation adopted here is based on the THM formulation proposed in Reference [2] applied to clays [6, 7]. The THM formulation is defined by a set of governing balance equations, constitutive equations and equilibrium restrictions. Balance equations apply to mass of water (unknown: liquid pressure, P_l), mass of air (unknown: gas pressure, P_g), internal energy (unknown: temperature, T) and linear momentum (unknown: displacements, $\mathbf{u}$). As an example, the balance equation for the mass of water is expressed as

$$\frac{\partial}{\partial t}(\phi S_l \rho_l w_l^w + \phi S_g \rho_g w_g^w) + \nabla \cdot (\mathbf{j}_l^w + \mathbf{j}_g^w) = f^w \tag{1}$$

where ϕ is the porosity, S_l and S_g the liquid and gas degree of saturation, ρ_l and ρ_g, the liquid and gas densities in kg/m^3 of phase, w_l^w the mass fraction of water in the liquid (close to one in dilute solutions) and w_g^w the mass fraction of water vapour in the gas phase. The term $\phi S_l \rho_l w_l^w$ is the water content in the liquid phase per unit volume and $\phi S_g \rho_g w_g^w$ the water content in the gas phase. $\mathbf{j}_l^w$ and $\mathbf{j}_g^w$ are the mass flux of water in the liquid and gas phases, respectively. The term f^w may represent, in the context of this paper, the water production or loss associated with precipitation or dissolution of minerals. More details on the THM formulation are given in References [6, 7].

To complete the THMC formulation, a number of additional chemical species are considered. The mass continuity of each chemical species is expressed by the reactive transport equation. In addition to the usual homogeneous reactions occurring in the liquid phase (aqueous complex formation, acid/base and oxidation/reduction), heterogeneous reactions that exchange matter between the liquid and the solid phase are also taken into account. The main heterogeneous reactions considered are dissolution/precipitation of minerals and cation exchange. In general the chemical processes are faster than the characteristic times of the THM problem, so it is assumed that chemical equilibrium prevails. Only some dissolution/precipitation processes are assumed to be kinetics-controlled.

Let us consider the reactive transport of N chemical species in a multiphase porous medium. The transport of every one of those species can be expressed as

$$\frac{\partial}{\partial t}(\phi S_l \rho_l c_i) + \nabla \cdot \mathbf{j}_i = R_i \quad (i = 1, \ldots, N) \tag{2}$$

where c_i is the concentration of species i in mol/kg of solution and R_i is the total production rate of species i due to chemical reactions, in mol/m^3/s. $\mathbf{j}_i$ is the total flux of species i, in mol/m^2/s. As in Reference [2], this flux is considered as the sum of advective and non-advective fluxes. Advective flux is, in turn, the sum of the movement of the liquid phase with respect to the solid phase (governed by the generalized Darcy's law) and of the solid phase with respect to the reference configuration. The non-advective flux is the product of molecular diffusion and mechanical dispersion.

In order to make Equation (2) valid for all species, including those in the solid phase, it is convenient to express the total flux $\mathbf{j}_i$ as

$$\mathbf{j}_i = \lambda_i(\rho_l C_i \mathbf{q}_l - \mathbf{D}_l \nabla c_i) + \phi S_l \rho_l c_i \dot{\mathbf{u}} \tag{3}$$

where λ_i is the mobility of species i. λ_i is 1 if the species is in the liquid phase and 0 if it is in the solid phase. $\dot{\mathbf{u}}$ is the solid phase velocity, $\mathbf{q}_l$ is the Darcy's flux and $\mathbf{D}_l$ the hydrodynamic dispersion tensor (molecular diffusion plus mechanical dispersion).

If N_x is the number of reversible independent reactions in a system containing N species, the number of independent chemical components is $N_c = N - N_x$ [8]. It is now possible to classify the system in N_c primary species and N_x secondary species. Reversible reactions between the two types of species are expressed as [9]

$$A_i = \sum_{j=1}^{N_c} v_{ij} A_j \quad (i = 1, \ldots, N_x) \tag{4}$$

where A_j and A_i are the chemical formulas of the primary and secondary species, respectively, and v_{ij} the number of moles of the primary species j in a mol of the secondary species i. It should be noted that the classification of the species into primary and secondary ones is not unique [8].

Using the properties of the reversible reactions (4), it is possible to derive the basic transport equations [8, 9]:

$$\frac{\partial}{\partial t}(\phi S_l \rho_l U_j) + \nabla \cdot (\rho_l Ua_j \mathbf{q}_l - \mathbf{D}_l \nabla Ua_j + \phi S_l \rho_l U_j \dot{\mathbf{u}}) + \sum_{m=1}^{N_m} v_{jm} r_m = 0 \quad (j = 1, \ldots, N_c) \tag{5}$$

$$U_j = C_j + \sum_{i=1}^{N_x} v_{ij} X_i \quad (i = 1, \ldots, N_c) \tag{6}$$

$$Ua_j = \lambda_j C_j + \sum_{i=1}^{N_x} v_{ij} \lambda_i X_i \quad (i = 1, \ldots, N_c) \tag{7}$$

where U_j is the total analytical concentration and Ua_j is the total aqueous concentration of the primary species j. C_j and X_i are the concentrations of the primary and secondary species, respectively. λ_j and λ_i are the mobilities of the primary and secondary species. r_m is the rate of precipitation or dissolution of mineral m under kinetics conditions and N_m is the number of

minerals in kinetics conditions. v_{jm} is the number of moles of primary species j in a mol of mineral m.

In the present formulation, the total analytical concentrations U_j are the unknowns of the transport equation (5), and Ua_j and r_m are considered non-linear functions of U_j. This type of unknown exhibits the interesting property of being independent of chemical equilibrium. Total analytical concentration changes in time are exclusively due to transport and kinetics reactions.

The link between the unknowns U_j and the dependent variables Ua_j and r_m is expressed by the geochemical model. In this formulation, an approach based on the direct minimization of Gibbs free energy is used [10]. To compute the concentrations of the species in equilibrium, a Newton–Raphson algorithm is applied to the direct minimization of Gibbs free energy and Lagrange multipliers are used to incorporate the restrictions of the problem. The implementation is well adapted to problems with highly dynamic appearance/disappearance of minerals as in the case presented in next section.

3. EXAMPLE OF APPLICATION

3.1. The FEBEX in situ heating test

A large-scale *in situ* heating test is being performed at the Grimsel Test Site, an underground research laboratory located in the Swiss Alps. The rock in the site is mainly granite. The test tries to reproduce the main features of the current Spanish concept for deep underground disposal of high-level radioactive waste [11].

The test layout (Figure 1) consists in placing two heaters at the end of a drift of 2.28 m diameter and 70.4 m length specially bored for this purpose. The diameter and length of the heaters (0.9 and 4.54 m, respectively) corresponds to the actual dimensions of the canister
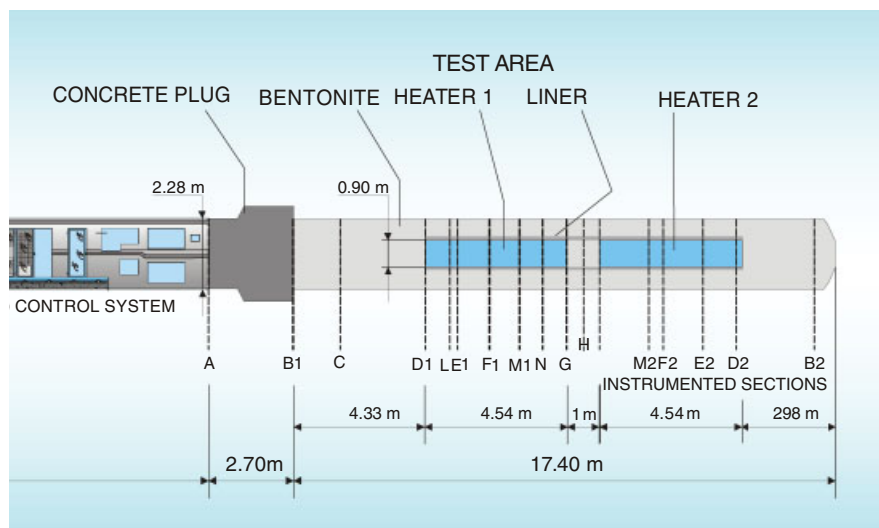

Figure 1. Lay out of the Febex *in situ* heating test.

envisaged for radioactive waste storage. The heaters are placed in the axis of the drift at a 1 m distance from each other.

The space between the drift and the heaters is filled by blocks of compacted bentonite with a smectite content in the range of 88–96%. The test is heavily instrumented with measurements of temperatures, relative humidity (equivalent to total suction), pore pressures, displacements, and stresses.

The test schedule involves switching on the heaters an applying increasing power until the temperature reaches a value of 100°C at some point in the bentonite. From that moment on, the power of the heaters is constantly adjusted in order to keep the maximum temperature in the bentonite barrier at the 100°C mark. The test was run in this way for 5 years until one of the heaters was switched off and dismantled. The experiment continues with the other heater without a planned finishing date. In the numerical simulation, a very fine one-dimensional finite element mesh was adopted that guarantees a Peclet number less than 2 for the transport problem, an important consideration when using a Galerkin-based finite element formulation.

## 3.2. Features of analysis and chemical model

Only a brief overview of the analysis characteristics will be given. More information is reported in References [7, 11]. The numerical computations have been carried out using the fully coupled THMC version of CODE_BRIGHT. Radial symmetry has been assumed resulting in a 1-D axisymmetric analysis that is quite appropriate for examining the behaviour of the bentonite barrier and immediate adjacent rock.

After a short initial period of applying increasing power to the heaters, a constant 100°C temperature has been applied to the contact between the heater and the buffer, in correspondence with the test protocol. Although the full heating test has lasted for 5 years, the analysis has been run up to 100 years to check and predict long-term THMC conditions. The rock thermal, hydraulic and mechanical boundary conditions have been based on the results of the comprehensive site investigation carried out at the site.
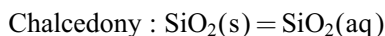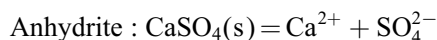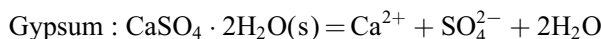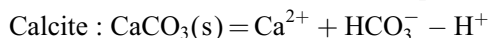
The initial conditions of the bentonite were as follows: dry density $1.7\,\mathrm{g/cm^3}$ and water content 14.4%. This results in an initial degree of saturation of 0.65 and an initial suction of 115 MPa. Both the bentonite (solid phase and interstitial water) and the hydration water were subjected to a full chemical characterization. The thermo-hydro-mechanical parameters were determined in an independent laboratory testing programme.

The selected primary species are H_2O, Ca^{2+}, K^+, Na^+, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, H^+, $SiO_2(aq)$, NaX. They are all in the liquid phase except adsorbed sodium, NaX, where X^- stands for the clay mineral. The secondary species, in equilibrium with the primary ones, are: OH^-, CO_3^{2-}, $CO_2(aq)$, $CaCO_3(aq)$, $CaHCO_3^+$, $CaSO_4(aq)$, $CaCl^+$, $MgSO_4(aq)$, $MgHCO_3^+$, $MgCl^+$, $NaHCO_3(aq)$, $NaSO_4^-$, $NaCl(aq)$, KSO_4^- and $HSiO_3^-$.

A total cation exchange capacity, $CEC = 86.2\,\mathrm{meq/100\,g}$ of solid has been used. The exchangeable cations are also secondary species and are controlled by the following reactions:

$$CaX_2 = Ca^{2+} + 2NaX - 2Na^+$$

$$MgX_2 = Mg^{2+} + 2NaX - 2Na^+$$

$$KX = K^+ + NaX - Na^+$$
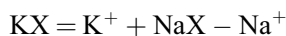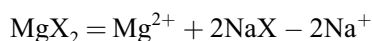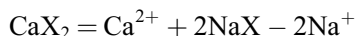
Finally, the phases in equilibrium with the solution of the liquid phase are:

$$\text{Calcite}: CaCO_3(s) = Ca^{2+} + HCO_3^- - H^+$$

$$\text{Gypsum}: CaSO_4 \cdot 2H_2O(s) = Ca^{2+} + SO_4^{2-} + 2H_2O$$

$$\text{Anhydrite}: CaSO_4(s) = Ca^{2+} + SO_4^{2-}$$

$$\text{Chalcedony}: SiO_2(s) = SiO_2(aq)$$

$$\text{Carbonic gas at } 10^{-3.5} \text{ atm}: CO_2(g) = HCO_3^- - H_2O + 2H^+$$

As a result of these assumptions, the number of unknowns per node was 13: one being the temperature, one the liquid pressure, one the displacement and the remaining 10 the primary chemical species (excluding water).

3.3. Results of the THMC analysis

Only a small selection of results will be shown here. They have been chosen to demonstrate the capabilities of the formulation and to point out some of the significant THMC features of the problem. THM results are given for three points of the buffer: one near the heater, one in the central part of the barrier and one closer to the rock (external buffer).

Figure 2 shows the variation of temperature at those points. Close to the heater the temperature is maintained at 100°C. At the other two points there is, after the initial transient
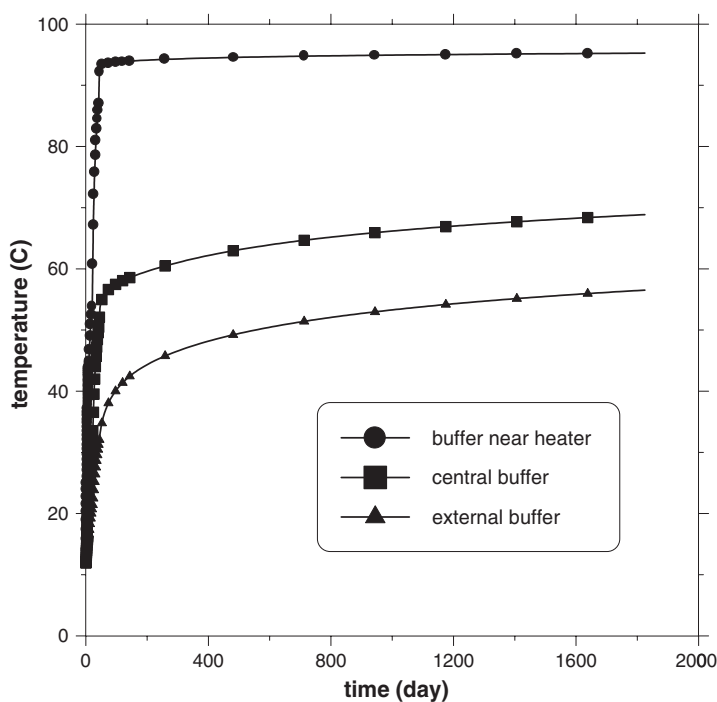

Figure 2. Variation of temperature with time (5 years) at three points of the bentonite barrier.
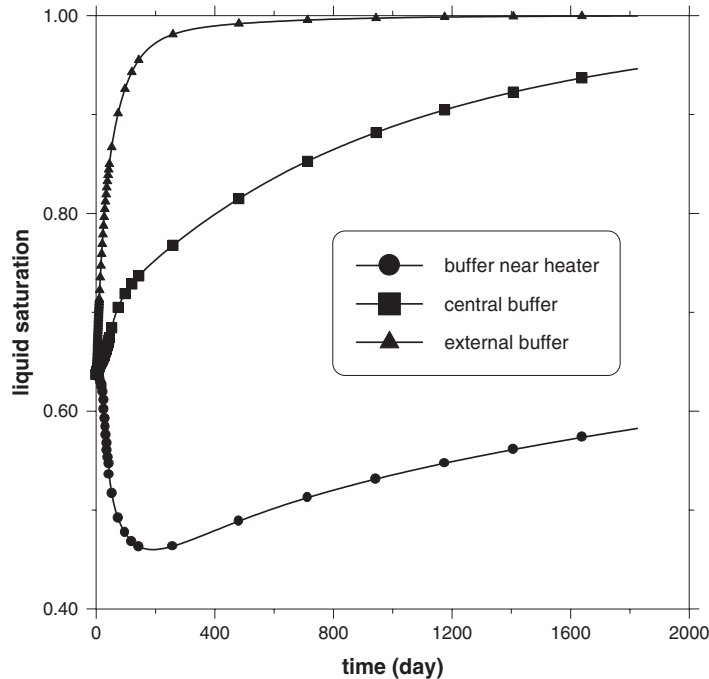
Figure 3. Variation of degree of saturation with time (5 years) at three points of the bentonite barrier.

period, a gentle temperature rise over time. Figure 3 shows the evolution of degree of saturation for the first 5 years. It can be observed that there is a strong drying close to the heater followed by a milder hydration afterwards. The part of the barrier close to the rock becomes quickly saturated, but the central part is still unsaturated after 5 years. In fact, the long-term calculations (Figure 4) indicate that more than 35 years would be required to achieve complete barrier saturation. More information on the THM results is given in Reference [7].

Figure 5 presents the ionic strength distribution in the buffer and in the rock at various times up to 100 years. Naturally the ionic strength in the granitic water is much lower than that of the bentonite water. It can be noted that the diffusion process is slow, after 100 years the solutes have only penetrated about 8 m in the rock. The ionic strength near the heater increases because of evaporation but the value reached is not very high.

The computed concentrations for some of the individual cations can be examined in Figures 6 and 7. The tendency is towards a dilution of the aqueous species in the barrier, specially, at shorter times, near the rock (Figure 6). Concentrations in the rock increase progressively due to diffusion. The exchangeable cations in the buffer clay do not vary much (Figure 7). There are some initial changes due to the impact of heating but the final cation content in the solid phase after 100 years is rather similar to the initial one. It should be stressed, however, that there is some uncertainty over the details of cation exchange processes at elevated temperature.
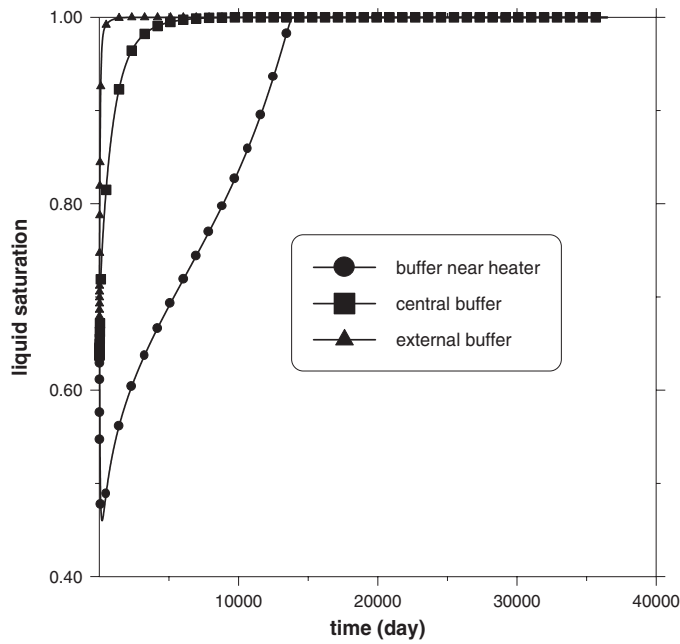
Figure 4. Variation of degree of saturation with time (100 years) at three points of the bentonite barrier.
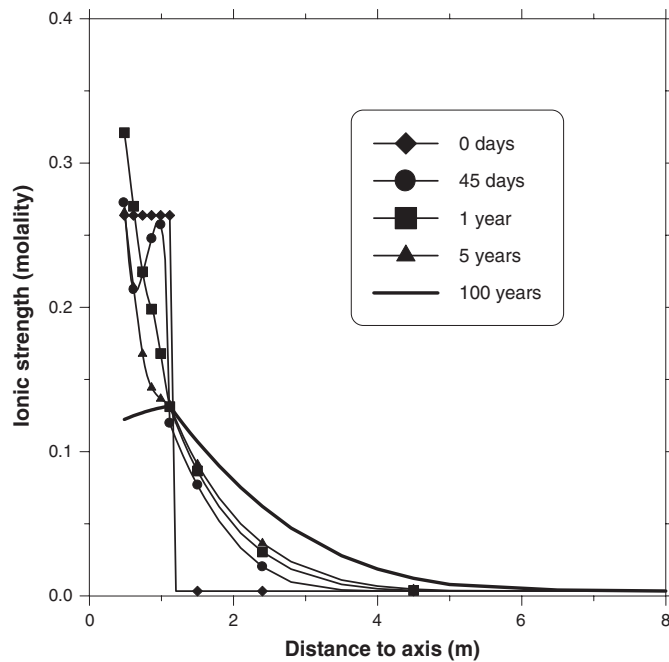

Figure 5. Distribution of ionic strength in the bentonite barrier and rock at various times.
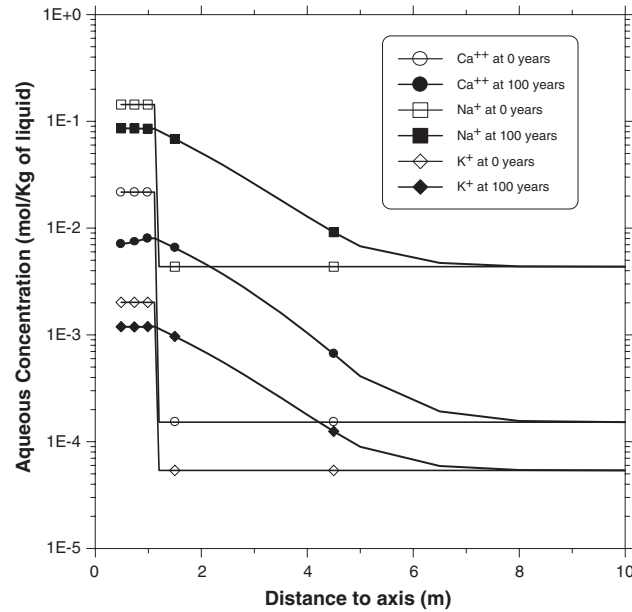
Figure 6. Distribution of the aqueous concentration of cations Ca^{2+}, Na^+ and K^+ in the bentonite barrier and rock at various times.
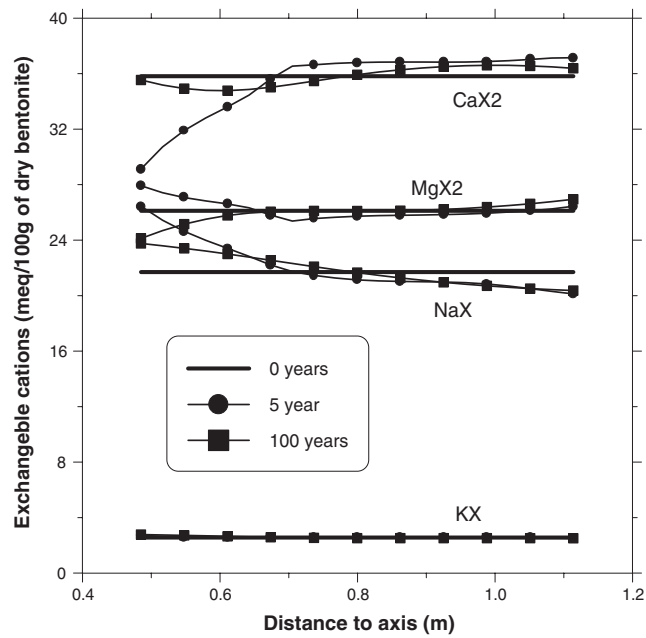

Figure 7. Distribution of exchangeable cations concentration in the bentonite barrier at various times.
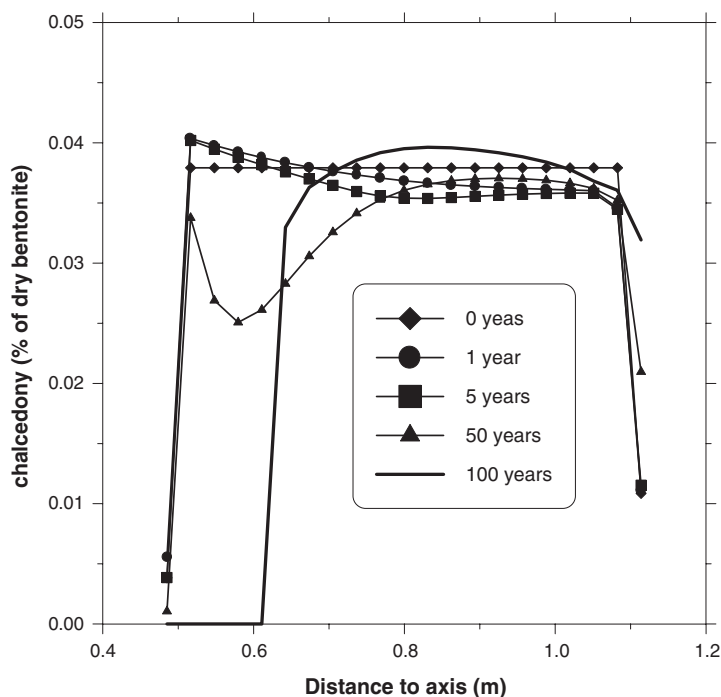
Figure 8. Distribution of chalcedony concentration in the bentonite barrier at various times.

To show the type of results concerning the behaviour of precipitated minerals, Figure 8 is presented showing the distribution of chalcedony concentration at various times. It can be noted that the mineral is dissolved at the two ends of the barrier. Near the rock the mineral dissolves because of the entry of very dilute granitic water. In contrast, near the heater there is initially some precipitation due to water evaporation induced by heating. However, in the long term, the mineral disappears from the inner zone of the barrier due to the higher solubility of the chalcedony leading to an increase in the concentration of $SiO_2(aq)$. This originates a molecular diffusion transport that leads to the development of a dissolution front (clearly visible in the 100 years results) that travels towards the cooler outer part of the barrier.

4. CONCLUSIONS

The paper has presented a very general and fully coupled THMC formulation that incorporates a significant number of THM processes and homogeneous and heterogeneous chemical reactions. The formulation has been incorporated into a computer code (CODE_BRIGHT) in order to perform numerical analysis. An example of application has been briefly described involving the simulation of a quite complex case: a large-scale *in situ* heating test that simulates the conditions of a repository for high-level nuclear waste. It can be concluded that, using the computational tool presented, the performance of coupled THMC analysis or real engineering problems is already a feasible proposition.

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