Coupled Thermo-Hydro-Mechanical and Chemical Analysis of Expansive Clay Subjected to Heating and Hydration

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Abstract. A fully coupled formulation combining reactive transport and an existing thermo-hydro-mechanical (THM) code is presented. 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 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 total analytical concentrations (including precipitated minerals) are adopted as basic transport variables and chemical equilibrium is achieved by minimizing Gibbs Free Energy. The formulation has been incorporated in a general purpose computer code capable of performing numerical analysis of engineering problems. A validation exercise concerning a laboratory experiment involving the heating and hydration of an expansive compacted clay is described.

Key words: coupled formulation, reactive transport, THM problem, swelling clays.

1. Introduction

Compacted swelling clays are often envisaged as a 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 of these barriers require, therefore, the performance of fully coupled thermo-hydro-mechanical and chemical (THMC) numerical analyses.

Indeed, in the development of numerical tools to analyze engineering problems involving geomaterials there has been a strong trend towards

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coupled formulations incorporating an increasing number of phenomena. The aim is to account for the full range of interactions between the various processes occurring simultaneously in the same problem. For instance fully coupled thermo-hydro-mechanical (THM) formulations have been put forward in the past by a number of researchers (e.g. Olivella *et al.*, 1994; Gawin *et al.*, 1995; Thomas and He, 1995).

On the geochemical field, reactive transport formulations initially developed for non-isothermal conditions and saturated porous media (e.g. Kirkner and Reeves, 1988; Friedly and Rubin, 1992; Saaltink *et al.*, 1998) has been extended to non-isothermal conditions (e.g. Steefel and Lasaga, 1994) or unsaturated media (e.g. Yeh and Tripathi, 1991). At present, an increasing number of formulations join reactive transport and the thermo-hydraulic (TH) problem in a coupled way (White, 1995; Cheng and Yeh, 1998; Xu *et al.*, 1999). Other approaches exist that couple conservative transport with THM formulations (e. g. Schrefler, 1995; Thomas *et al.*, 2001).

In this paper a fully coupled THMC formulation is described that combines an already existing (Olivella *et al.*, 1994) and operational (Gens *et al.*, 2002) THM approach with the equations of reactive transport in a fully coupled manner. The formulation allows the performance of numerical analyses considering all four aspects of behaviour: thermal, hydraulic, mechanical and chemical and their interactions. The formulation also takes into account the possibility that the material is partially saturated. Therefore, the term hydraulic should be interpreted in a general sense, i.e. including both liquid and gas flow phenomena.

A number of novel features are incorporated in the formulation. For instance the main unknowns of the transport equations are the total analytical concentrations (that includes precipitated minerals concentrations) instead of the more usual aqueous concentrations. Also, chemical equilibrium is solved by minimizing directly Gibbs free energy instead of resorting to the more generally used mass action law. Special attention is paid to the problems of dissolution/precipitation of minerals in local equilibrium. In this type of problems precipitated minerals may appear or disappear according to local conditions causing numerical difficulties that must be tackled in an efficient way. Although the formulation is general, particular consideration has been given to the phenomena (especially chemical phenomena) that are likely to occur in swelling clays used in an engineered barrier for nuclear waste isolation.

The formulation has been incorporated into a computer code and a number of issues concerning numerical implementation are discussed. Finally, the paper presents a validation exercise in which a highly compacted clay is subjected to simultaneous hydration and heating, mimicking in this way

the actions likely to occur in an engineered barrier placed around high level nuclear waste.

2. Mathematical Formulation of the Coupled THMC Problem

2.1. BASES OF THE FORMULATION

The main aim of the paper is the development of a formulation for the reactive transport in an unsaturated deformable porous medium of several chemical species dissolved in the liquid phase but also present in the solid phase. Reactive transport refers to the movement through a porous medium of a number of solute species that can react with other solutes in the same phase (homogenous reactions) or with other species in other phases (heterogeneous reactions). The formulation must also include couplings with the thermal, hydraulic and mechanical problems.

To achieve this, it is assumed that three phases are present in the porous medium: solid, liquid and gas. The basic component of the solid phase is assumed not soluble but not inert as it can adsorb and exchange ions with the solution. Precipitated minerals are also part of the solid phase. Gas phase is made up of dry air and water vapour and the liquid phase contains water, solutes and dissolved air. Note that dry air is considered as a single species in spite of the fact that it is a mixture of gasses. Chemical reactions considered in the formulation include:

- Homogeneous reactions: aqueous complex formation, acid/base and oxidation/reduction.
- Heterogeneous reactions: dissolution/precipitation of minerals and cation exchange.

Local equilibrium is assumed for all the chemical reactions except for dissolution/precipitation of minerals where kinetics can also be considered. The use of one or the other of those two hypothesis must be based on the comparison between rates (or characteristic times) of concentration changes due to reactions and due to transport (Steefel and Lazaga 1994). Local equilibrium is the limiting case for kinetics when transport characteristic times are much higher then those of the chemical reaction. In addition, linear sorption and radioactive decay are also included in the formulation for specific analyses.

2.2. THM FORMULATION

Although the main focus of the paper is on the reactive transport problem, the THM formulation is briefly described for completeness. The approach used here is based on the THM formulation proposed in Olivella *et al*.

(1994) and Olivella (1995) applied to clays (Gens *et al.*, 1998, 2002). Using the compositional approach, the formulation is based on the establishment of balance equations for main mineral, water and air, instead of using phases. Thus, the contributions of phase changes automatically cancel.

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.

Adding the mass balance equations to the equation for energy balance and momentum balance (equilibrium), the governing equations for the THM problem are obtained. More details on the THM formulation are given in Gens *et al.* (1998, 2002).

2.3. TRANSPORT EQUATIONS

The development of the reactive transport equations uses the general approach of Lichtner (1985), Kirkner and Reeves (1988) and Steefel and Lasaga (1994). Starting from the mass balance equation of each one of the species present in the medium, the final independent transport equations are obtained using the restrictions arising from the various reversible chemical reactions (local equilibrium assumption).

Let us consider the reactive transport of N chemical species in a deformable unsaturated 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 moles/Kg of solution and R_i is the total production rate of species i due to chemical reactions, in moles/m^3/s. $\mathbf{j}_i$ is the total flux of species i expresses moles/m^2/s. As in Olivella *et al.* (1994), 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. For simplicity, it is assumed that the mechanical dispersion tensor is the same for all the solutes. This has the advantageous consequence that electrical charge is conserved in the reactive transport equations when chemical reactions are charge balanced (Lichtner, 1985).

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

$$\mathbf{j}_i = \lambda_i \mathbf{j}_i' + \phi S_l \rho_l C_i \dot{\mathbf{u}} \tag{3}$$

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 and $\mathbf{j}_i'$ is the flux of species i with respect to the solid phase. $\mathbf{j}_i'$ is given by:

$$\mathbf{j}_i' = \rho_l C_i \mathbf{q}_l - \mathbf{D}_l \nabla C_i \tag{4}$$

where $\mathbf{q}_l$ is the Darcy's flux and $\mathbf{D}_l$ the hydrodynamic dispersion tensor (molecular diffusion plus mechanical dispersion).

It is now necessary to introduce the reactions in local equilibrium to obtain the set of independent concentrations in the system. If N_x is the number of reversible independent reactions in a system containing N species, the number of independent chemical components is $N_c = N - N_x$ (full details are given in Reed, 1982; Lichtner, 1985; Kirkner and Reeves, 1988). 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 (Steefel and Lasaga 1994):

$$A_i = \sum_{j=1}^{N_c} v_{ij} A_j \quad (i = 1, \dots, N_x) \tag{5}$$

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 (Lichtner, 1985).

The general notation for the chemical reactions used in (5) allows the incorporation of the most relevant geochemical processes (e.g. hydrolysis, complex formation, acid/base reactions, oxidation/reduction reactions, dissolution/precipitation of minerals) into the formulation. Cation exchange reactions can also be written in accordance with (5). Appelo and Postma (1993) introduce this latter type of reaction in the chemical equilibrium problem without algorithm modifications.

Using the properties of reversible reactions (5), it is possible to derive the basic transport equation (details are given in Kirkner and Reeves, 1988; Steefel and Lasaga, 1994):

$$\frac{\partial}{\partial t}(\phi S_l \rho_l U_j) + \nabla \cdot \left(\rho_l U a_j \mathbf{q}_l - \mathbf{D}_l \nabla U a_j + \phi S_l \rho_l U_j \dot{\mathbf{u}}\right) +$$

$$+ \sum_{m=1}^{N_m} \nu_{jm} r_m = 0 \quad (j = 1, \ldots, N_c) \tag{6}$$

$$U_j = C_j + \sum_{i=1}^{N_x} \nu_{ij} X_i \quad (i = 1, \ldots, N_c) \tag{7}$$

$$U a_j = \lambda_j C_j + \sum_{i=1}^{N_x} \nu_{ij} \lambda_i X_i \quad (i = 1, \ldots, N_c) \tag{8}$$

where U_j is the total analytical concentration and $U a_j$ is the total aqueous concentration of the primary species j. C_j and X_i are the concentrations of the primary and secondary species and λ_j and λ_i are the mobilities of the primary and secondary species, respectively. 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-controlled reactions. ν_{jm} is the number of moles of primary species j in a mol of mineral m.

A possible way to solve equation (6) is taking the concentrations of primary and secondary species C_j and X_i as unknowns. The additional N_x required equations will be supplied by the geochemical model (e.g. mass action law). However, in the present formulation, the total analytical concentrations U_j have been chosen to be the unknowns of the transport equations (6), and $U a_j$ and r_m are considered non-linear functions of U_j. The link between the unknowns U_j and the dependent variables $U a_j$ and r_m is provided by the geochemical model described in next section. 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-controlled reactions. As a consequence of this choice, the initial conditions of the transport equations (6) are expressed in terms of total analytical concentrations U_j, whereas the boundary conditions are expressed in terms of total aqueous concentrations $U a_j$.

2.4. CHEMICAL EQUILIBRIUM MODEL

Most reactive transport formulations use the mass action law to solve the chemical equilibrium equations (e.g. Lichtner, 1985; Kirkner and Reeves, 1988; Steefel and Lasaga, 1994; Saaltink *et al.*, 1998). In this formulation an alternative (though thermodynamically equivalent) approach is used, based

on the minimization of Gibbs Free Energy. This approach has a wider application range extending to highly non-ideal brine systems (Harvie *et al.*, 1987; Greenberg and Møller, 1989). To compute the concentrations of the species in equilibrium, a Newton–Raphson algorithm is applied to the direct minimization of Gibbs Free Energy. Lagrange multipliers are used to incorporate the restrictions of the problem (Harvie *et al.*, 1987).

The minimization problem can be written as

$$\underset{n_j^c, n_i^x}{\text{minimize}} \quad G = \sum_{j=1}^{N_c} \mu_j^c n_j^c + \sum_{i=1}^{N_x} \mu_i^x n_i^x \tag{9}$$

subject to

$$n_j^U = n_j^c + \sum_{i=1}^{N_x} v_{ij} n_i^x \quad (j = 1, \ldots, N_c) \tag{10}$$

$$n_j^c \geqslant 0 \quad (j = 1, \ldots, N_c); \; n_i^x \geqslant 0 \quad (i = 1, \ldots, N_x) \tag{11}$$

where G is Gibbs Free Energy and μ_j^c and μ_i^x are the chemical potentials of the primary and secondary species. n_j^c and n_i^x are the number of moles of the primary and secondary species in a representative elementary volume (REV, as defined in Lichtner, 1985) are the variables to be optimized. n_j^U is the total number of moles of a primary species j in a REV. The number of moles n_j^c, n_i^x and n_j^U are directly related to concentrations C_j, X_i and U_j, respectively.

Therefore, restriction (10) is the number-of-moles equivalent to equation (7). It is important to note that the main unknowns of the transport problem, U_j, can be considered constant in the chemical equilibrium problem. As pointed out before, when chemical reactions are charge balanced the reactive transport equations (6) conserve electrical charge. So, if the initial and boundary conditions of the transport problem are electrically neutral, then the restriction of electric neutrality of the chemical equilibrium problem is automatically satisfied.

The chemical potential of a species k (μ_k) is defined as (Anderson and Crerar, 1993):

$$\mu_k = \left(\frac{\partial G}{\partial n_k}\right)_{P, T, \hat{n}_k} = (\mu_k)^0 + RT \ln a_k \tag{12}$$

Using (12), μ_k is obtained from G once the pressure, temperature and number of moles of the other species in the system (represented by the symbol $\hat{n}_k$) are fixed. $(\mu_k)^0$ is the reference chemical potential that, by definition, depends only on pressure and temperature but not on the composition of the phase where species k is located. The chemical activity of the species k,

a_k, depends on the pressure, temperature and composition of the solution. It is usually given by a model based on thermodynamical theory and experimental observations. Therefore, the computation of the activity depends on the type of chemical system being considered. Pure minerals are a special case of a species with a chemical activity equal to 1 and, therefore, their chemical potentials depend only on pressure and temperature.

Equation (11) ensures that the species' concentration never become negative. It is possible to write these inequality restrictions using the following:

$$n_j^c = (t_j^c)^2 \quad (j = 1, \dots, N_c) \tag{13}$$

$$n_i^x = (t_i^x)^2 \quad (i = 1, \dots, N_x) \tag{14}$$

where t_j^c and t_i^c are auxiliary variables.

The general problem given by equations (9), (10), (13) and (14), can be expressed as a problem of minimization without restrictions by setting up the Lagrangian:

$$L = G + \sum_{j=1}^{N_c} \eta_j \left[n_j^U - n_j^c - \sum_{i=1}^{N_x} v_{ij} n_i^x \right] -$$

$$- \sum_{j=1}^{N_c} \omega_j^c \left[n_j^c - (t_j^c)^2 \right] - \sum_{i=1}^{N_x} \omega_i^x \left[n_i^x - (t_i^x)^2 \right] \tag{15}$$

where η_j, ω_j^c and ω_i^x are lagrangian multipliers corresponding to restrictions (10), (13) and (14), respectively.

The stationary points of the Lagrangian are:

$$\frac{\partial L}{\partial n_j^c} = \mu_j^c - \eta_j - \omega_j^c = 0 \quad (j = 1, \dots, N_c) \tag{16}$$

$$\frac{\partial L}{\partial n_i^x} = \mu_i^x - \sum_{j=1}^{N_c} v_{ij} \eta_j - \omega_i^x = 0 \quad (i = 1, \dots, N_x) \tag{17}$$

$$\frac{\partial L}{\partial \eta_j} = n_j^U - n_j^c - \sum_{i=1}^{N_x} v_{ij} n_i^x = 0 \quad (j = 1, \dots, N_c) \tag{18}$$

$$\frac{\partial L}{\partial \omega_j^c} = n_j^c - (t_j^c)^2 = 0 \quad (j = 1, \dots, N_c) \tag{19}$$

$$\frac{\partial L}{\partial \omega_i^x} = n_i^x - (t_i^x)^2 = 0 \quad (i = 1, \dots, N_x) \tag{20}$$

$$\frac{\partial L}{\partial t_j^c} = -2\omega_j^c t_j^c = 0 \quad (j = 1, \ldots, N_c) \tag{21}$$

$$\frac{\partial L}{\partial t_i^x} = -2\omega_i^x t_i^x = 0 \quad (i = 1, \ldots, N_x) \tag{22}$$

Equations (21) and (22) are the Kuhn–Tucker conditions for the primary and secondary species, respectively. This condition establishes that when the secondary species i is present (t_i^x not equal to zero), its Lagrangian multiplier ω_i^x is zero. On the other hand, if ω_i^x is different from zero, then the secondary species i is not present in the system.

At this point, the number of moles n_j^c, n_i^x and n_j^U are replaced by their respective concentrations C_j, X_i and U_j (given in mols/Kg of liquid phase) in the equations (16)–(22) that define the chemical equilibrium problem. The water species requires special attention because it plays a dual role; on the one hand it participates in the chemical reactions and, on the other hand, it is the solvent of the liquid phase. Although the concentration of water in the liquid phase is a dependent variable, it is necessary to establish its mass balance (Reed, 1982) and its consideration may be important in brines or other concentrated solutions (Olivella et al., 1994). Moreover, if water participates in heterogeneous reactions such as dissolution and precipitation of minerals, it is also necessary to consider the source/sink term of water f^w in equation (1). Since (1) already ensures the conservation of water mass, it is possible to eliminate its concentration C_1 (concentration of primary species 1) as an unknown of the chemical equilibrium problem together with the restrictions associated with this variable.

Another important simplification is to assume that all primary species will always be present in the medium. As a consequence of the Kuhn–Tucker condition (21), the lagrangian multipliers of the primary species ω_j^c are zero and, therefore, they can be eliminated together with equation (21). Thus, any mineral that may disappear from the porous medium must be considered as a secondary species. Moreover, according to equation (16), if $\omega_j^c = 0$ then $\eta_j = \mu_j^c$. By substituting this result in (17), η_j and equation (16) may be eliminated from the problem.

It is possible now to remove the auxiliary variables t_j^c and t_i^x from the problem and prescribe the restrictions (21) and (22) algorithmically (Harvie et al., 1987) by writing them again in (11) as inequality restrictions. In the (22) Kuhn–Tucker condition, it is possible to substitute the concentration X_i for the auxiliary variable t_i^x. Now, concentration X_i is an unknown of the problem together with C_j and ω_i^x.

Using the considerations above, the chemical equilibrium problem reduces to

$$\mu_i^x - \sum_{j=1}^{N_c} v_{ij}\mu_j^c - \omega_i^x = 0 \quad (i=1,\dots,N_x) \tag{23}$$

$$U_j = C_j + \sum_{i=1}^{N_x} v_{ij}X_i \quad (j=2,\dots,N_c) \tag{24}$$

$$C_j > 0 \quad (j=2,\dots,N_c) \tag{25}$$

$$X_i \geqslant 0 \quad (i=1,\dots,N_x) \tag{26}$$

$$\omega_i^x \sqrt{X_i} = 0 \quad (i=1,\dots,N_x) \tag{27}$$

It should be noted that equality does not appear in (25) because the primary species are always assumed to be present in the system. In fact, in the current version of the formulation, only pure precipitated minerals can disappear from a part of the porous medium. When this occurs, equation (23) leads to (details can be found in Harvie *et al.*, 1987):

$$\omega_i^x = -RT \ln(\Omega_i) \tag{28}$$

where Ω_i is the saturation state of mineral i, given by

$$\Omega_i = \frac{\prod_{j=1}^{N_c} a_j^{v_{ij}}}{K_i} \tag{29}$$

using the fact that the activity of the pure mineral is $a_i = 1$. a_j is the activity of the primary species and K_i is the equilibrium constant of the reaction (solubility product). K_i is given by

$$\ln K_i = \frac{(\mu_i^x)^0}{RT} - \sum_{j=1}^{N_c} v_{ij} \frac{(\mu_j^c)^0}{RT} \tag{30}$$

where $(\mu_j^c)^0$ and $(\mu_i^x)^0$ are the reference chemical potentials of the primary and secondary species, respectively.

When a mineral i is present ($X_i > 0$), the solution will be saturated with respect to this mineral implying that $\Omega_i = 1$ and $\omega_i^x = 0$. The Kuhn–Tucker condition (27) is thus naturally satisfied.

A solution can never be supersaturated with respect of a mineral in local equilibrium, i.e. $\Omega_i \leqslant 1$. This indicates that it is necessary to add the physical restriction:

$$\omega_i^x \geqslant 0 \tag{31}$$

2.5. DEGREES OF FREEDOM RESULTING FROM THE FORMULATION

An important feature of the formulation concerns the treatment of the dissolution/precipitation processes, especially in those cases where a particular mineral may disappear from part of the domain. In the formulations based on the mass action law the process must be specifically removed from the system of the equations in that part of the domain. Rubin (1983), Lichtner (1985) and Saaltink *et al.* (1998) discuss in some detail this moving boundary problem.

When the process is removed from the system of equations, the number of unknowns of the problem (N_u) is consistent with the number of degrees of freedom (N_f) computed according to the Gibbs' phase rule (Bethke, 1996; Steefel and MacQuarrie, 1996): $N_u = N_f = N_c - N_\Phi + 2$, where N_c is the number of primary species (as defined in this paper) and N_Φ is the number of phases of the system (liquid, minerals and gases in equilibrium with the solution). The two additional degrees of freedom correspond to temperature and pressure.

The formulation presented in this paper provides an alternative for solving the reactive transport problem as defined by the transport equation (6) and the chemical equilibrium equations (23)–(27) and (31). The unknowns of the transport equations (6) are now the concentrations of the total primary species, U_j, and the unknowns of the optimization scheme that defines the chemical equilibrium problem are the concentrations of the primary and secondary species, C_j and X_i, respectively together with the Lagrangian multipliers for the precipitated minerals in local equilibrium, ω_i^x.

An important characteristic of the algorithm described lies in restriction (26). When a mineral disappears in a particular zone of the domain, the restriction is simply activated. Using this algorithm, the number of degrees of freedom is constant and it does not depend on the presence or absence of the precipitated minerals in equilibrium, although the total number does not coincide now with the minimum degrees of freedom computed according to thermodynamic rules ($N_u = N_c + 1 > N_f$). The constancy of the number of degrees of freedom throughout the domain is very advantageous from the point of view of numerical implementation. The formulation is therefore well adapted to problems with highly dynamic appearance/disappearance of minerals as in the validation exercise presented in Section 4.

3. Numerical Implementation

In this section, a number of features related to the numerical implementation of the reactive transport formulation presented earlier are described. The main objective is to use the Newton–Raphson method to solve the non-linear system of equations that results from the discretization of the

transport equations. Those equations can be discretized by the Finite Element method using the procedures reported in Olivella *et al.* (1996). To apply the Newton–Raphson method, the following derivatives are required:

$$\frac{\partial Ua_j}{\partial U_k} = \lambda_j \frac{\partial C_j}{\partial U_k} + \sum_{i=1}^{N_x} v_{ij} \lambda_i \frac{\partial X_i}{\partial U_k} \quad (j = 2, \dots, N_c)$$

$$\frac{\partial r_m(C_j, X_i)}{\partial U_k} = \sum_{j=2}^{N_c} \frac{\partial r_m}{\partial C_j} \frac{\partial C_j}{\partial U_k} + \sum_{i=1}^{N_x} \frac{\partial r_m}{\partial X_i} \frac{\partial X_i}{\partial U_k} \quad (m = 1, \dots, N_m)$$

(32)

where U_k is the total analytical concentration of the k primary species. As the dependent variables Ua_j and r_m are known functions of the primary and secondary species concentrations (C_j and X_i, respectively), what is in fact required is the following tangent matrix:

$$\left(\frac{\partial C_j}{\partial U_k}, \frac{\partial X_i}{\partial U_k} \right) \quad \text{para} \begin{cases} j = 2, \dots, N_c \\ i = 1, \dots, N_x \\ k = 2, \dots, N_c \end{cases}$$

(33)

that provides the derivatives of the concentrations of the primary and secondary species with respect to the total analytical concentrations of the primary species.

The tangent matrix in (33) is obtained differentiating the equations of the chemical equilibrium problem with respect to U_k. Once the chemical equilibrium problem is solved and the minerals in equilibrium with the solution are known, the following equations can be established:

a) For primary species:
Differentiating the local mass balance equations (using the definition of total analytical concentration):

$$U_j = C_j + \sum_{i=1}^{N_x} v_{ij} X_i \Rightarrow \frac{\partial U_j}{\partial U_k} = \delta_{jk} = \frac{\partial C_j}{\partial U_k} + \sum_{i=1}^{N_x} v_{ij} \frac{\partial X_i}{\partial U_k}$$

(34)

where δ_{jk} is Kronecker's delta:

$$\delta_{jk} = \begin{cases} 1 \text{ if } j = k \\ 0 \text{ if } j \neq k \end{cases}$$

(35)

b) For secondary species:

Differentiating Kuhn–Tucker's condition (27):

$$\omega_i^x \sqrt{X_i} = 0 \Rightarrow \sqrt{X_i} \frac{\partial \omega_i^x}{\partial U_k} + \frac{\omega_i^x}{2\sqrt{X_i}} \frac{\partial X_i}{\partial U_k} = 0 \Rightarrow \frac{\partial \omega_i^x}{\partial U_k} = -\frac{\omega_i^x}{2X_i} \frac{\partial X_i}{\partial U_k}$$

(36)

Differentiating equation (23):

$$\mu_i^x - \sum_{j=1}^{N_c} v_{ij}\mu_j^c - \omega_i^x = 0 \Rightarrow \frac{\partial}{\partial U_k}\left(\mu_i^x - \sum_{j=1}^{N_c} v_{ij}\mu_j^c\right) - \frac{1}{RT}\frac{\partial \omega_i^x}{\partial U_k} = 0 \quad (37)$$

Substituting the result of (36) into (37):

$$X_i \frac{\partial}{\partial U_k}\left(\mu_i^x - \sum_{j=1}^{N_c} v_{ij}\mu_j^c\right) + \frac{\omega_i^x}{2RT}\frac{\partial X_i}{\partial U_k} = 0 \quad (38)$$

It is possible to apply equation (38) in three different ways depending on the type of species considered:

b.1) For aqueous secondary species, where $\omega_i^x = 0$ and $X_i \neq 0$, the following expression is obtained:

$$\frac{\partial}{\partial U_k}\left(\mu_i^x - \sum_{j=1}^{N_c} v_{ij}\mu_j^c\right) = 0 \Rightarrow \frac{1}{X_i}\frac{\partial X_i}{\partial U_k} - v_{i1}\frac{1}{a_w}\frac{\partial a_w}{\partial U_k} - \sum_{j=2}^{N_c} v_{ij}\frac{1}{C_j}\frac{\partial C_j}{\partial U_k} = 0 \; (39)$$

where a_w is the chemical activity of water (solvent of the liquid phase). In this formulation water is primary species 1 ($a_w = a_1$). Equation (39) corresponds to the linearized mass action law.

b.2) For pure minerals present in the system where $\omega_i^x = 0$ and $X_i \neq 0$, and if, furthermore, its chemical potential μ_i^x is constant, the following results:

$$\frac{\partial}{\partial U_k}\left(\mu_i^x - \sum_{j=1}^{N_c} v_{ij}\mu_j^c\right) = 0 \Rightarrow v_{i1}\frac{1}{a_w}\frac{\partial a_w}{\partial U_k} + \sum_{j=2}^{N_c} v_{ij}\frac{1}{C_j}\frac{\partial C_j}{\partial U_k} = 0 \quad (40)$$

that corresponds to the linearization of the solubility product.

b.3) For minerals not present in the system, where $\omega_i^x \neq 0$ and $X_i = 0$, then:

$$\frac{\partial X_i}{\partial U_k} = 0 \quad (41)$$

In equations (39) and (40), it was assumed that the chemical activities of the aqueous species a_j and a_i are given by:

$$a_j = m_j \gamma_j = \frac{C_j}{w_l^w}\gamma_j, \quad a_i = m_i \gamma_i = \frac{X_i}{w_l^w}\gamma_i \quad (42)$$

where m_j and m_i are the concentrations of the species of the primary and secondary species, respectively expressed in mol/kg H_2O and γ_j and γ_i
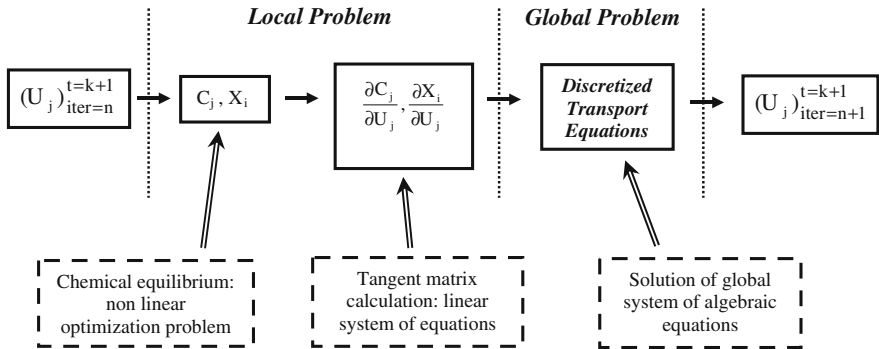
Local Problem   **Global Problem**

$(U_j)^{t=k+1}_{iter=n}$ → C_j, X_i → $\dfrac{\partial C_j}{\partial U_j}, \dfrac{\partial X_i}{\partial U_j}$ → *Discretized Transport Equations* → $(U_j)^{t=k+1}_{iter=n+1}$

Chemical equilibrium: non linear optimization problem

Tangent matrix calculation: linear system of equations

Solution of global system of algebraic equations

Figure 1. Numerical implementation of the reactive transport problem into a finite element code.

their respective activity coefficients. Concentrations C_j and X_i are given in mol/kg of liquid. For simplicity, in this development the water mass fraction in the liquid w_l^w and the activity coefficients, γ_j and γ_i, were assumed constant. Therefore, their derivatives with respect to U_k are neglected.

Equations (34) and (39)–(41) define a linear system of equations the unknowns of which are the derivatives of the concentrations of the primary and secondary species with respect to the total analytical concentrations of the primary species, i.e. the components of the tangent matrix (33). This matrix will be used in the solution of the non-linear equations system of the reactive transport problem using the Newton–Raphson method.

In the numerical implementation of the present formulation, the computation of the (non-linear) chemical equilibrium and the calculation of the (linear) tangent matrix are performed *locally* for every node of the finite element mesh before the *global* assembly of the system for the whole mesh. Figure 1 shows the scheme for a Newton–Raphson iteration (iter $= n + 1$) for time $t = k + 1$ to obtain the global unknowns of the problem,$(U_j)^{t=k+1}_{iter=n+1}$, from the values of the unknowns of the previous iteration $(U_j)^{t=k+1}_{iter=n}$. The resulting formulation is able to accommodate the various associations of minerals into a single set of equations allowing an efficient implementation in finite element codes.

4. Validation Exercise

4.1. DESCRIPTION OF THE CASE

A research programme involving the testing of specimens of bentonite under simultaneous heating and hydration (FEBEX, 1997) has been performed at CIEMAT (Madrid, Spain) as part of the FEBEX project. There is considerable information, obtained independently, on the parameters
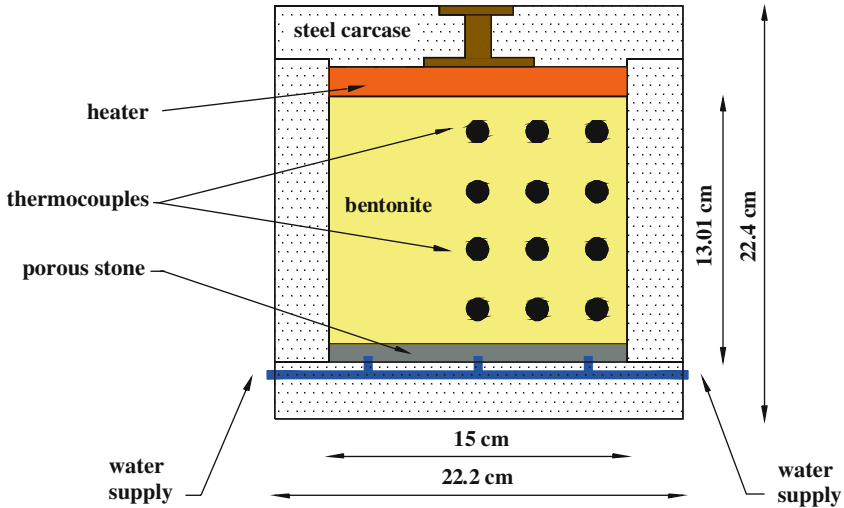
Figure 2. Layout of the test.

required by the modelling. Comprehensive chemical characterization of the clay mineral, interstitial water and hydration water has also been performed (FEBEX, 2000). Temperatures were measured throughout the test. Degree of saturation, porosity and chemical composition of the water were observed in small specimens obtained after dismantling the tests. Those experiments provide, therefore, a useful case for validating the formulation above.

In the test selected for analysis (Cuevas *et al.*, 1996; FEBEX, 1997), a cylindrical sample of swelling clay was compacted one-dimensionally in a rigid steel cell and subjected to heating and hydration from the two opposite sides of the cylinder (Figure 2). The inner dimensions of the cell are: diameter 15 cm and height 13 cm. Hydration is performed through the lower porous stone under a 1 MPa constant water pressure. On the upper part of the specimen, a heater applies a constant $100°C$ temperature. This boundary temperature was achieved gradually over a period of 5 h. The initial conditions of the bentonite were as follows: dry density $1.62 \, g/cm^3$ and water content 11.2%. This results in an initial porosity of 0.4 and an initial degree of saturation of 0.44.

Thermocouples installed inside the specimen (Figure 2) measure the evolution of temperatures during the test. Hydration and heating were maintained for 109 days. After cooling, the cell was dismantled and the final distributions of water content, porosity, aqueous concentrations, pH and adsorbed cation concentrations were measured.

A fully coupled THMC numerical analysis of this experiment has been performed applying the formulation described above. In the modelling,
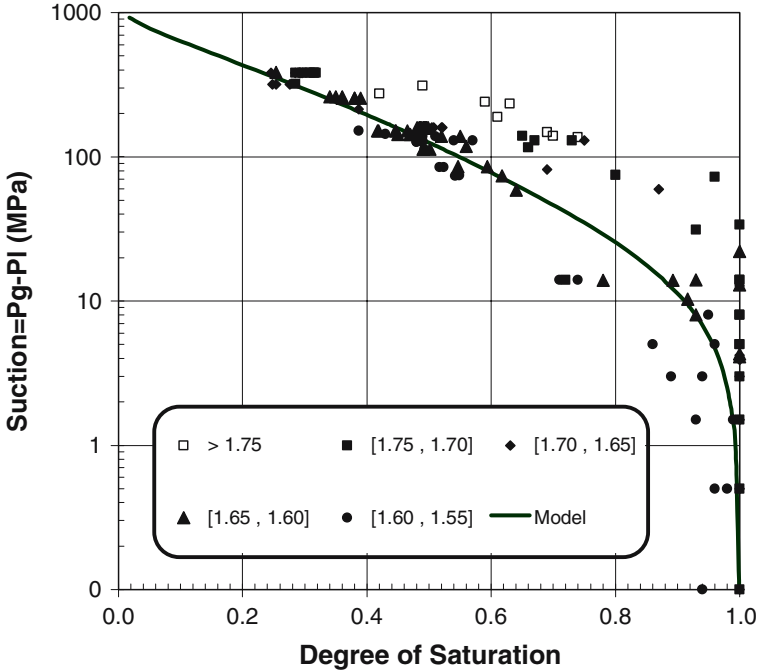
Figure 3. Adopted retention curve compared with experimental results. The different symbols refer to the various dry densities of the specimens tested.

only the bentonite specimen has been considered, represented by a one-dimensional mesh 13 cm long divided in 50 equal-size elements. This guarantees a Peclet number lower than 2 for transport problems. In the thermal problem, the following heat dissipation boundary condition has been applied:

$$Q^* = h_0(T - T_0) \tag{43}$$

where Q^* denotes the lateral heat loss of the bentonite sample.

Although a single coupled THMC analysis has been performed, the THM and reactive transport results are discussed separately in the following sections.

4.2. THM APPROACH AND RESULTS

The constitutive relationships required to define the THM behaviour of the bentonite are presented in Gens *et al.* (1998, 2002). Only the most relevant and modified ones are specifically discussed in this section.

For the retention curve, usually a critical element in THM modelling, a modified form of van Genuchten (1980) expression is used:

$$\frac{S_l - S_{lr}}{S_{ls} - S_{lr}} = S_e = \left[1 + \left(\frac{P_g - P_l}{P_0 \frac{\sigma}{\sigma_0}}\right)^{\frac{1}{1-\lambda}}\right]^{\lambda} \left[1 - \frac{P_g - P_l}{P_s}\right]^{\lambda_s}, \quad P_g - P_l \geqslant 0 \quad (44)$$

where λ_s, P_s (in MPa), λ, σ_0 (in N/m) and P_0 (in MPa) are material parameters. The surface tension σ (in N/m) dependency on temperature was obtained based on the values of surface tension given in Custodio and Llamas (1983):

$$\sigma = 0.03059 \exp\left(\frac{252.93}{273.15 + T}\right) \text{N/m} \quad (45)$$

The modification is required for matching the actual bentonite behaviour at high suction values (FEBEX, 2000). The parameters adopted to define this law have been based on tests carried on samples at different dry densities (Figure 3). They are: $P_0 = 18$ MPa, $\sigma_0 = 0.072$ N/m, $\chi = 0.2$, $\chi_s = 1.5$, $P_s = 1000$ MPa, $S_{lr} = 0.01$ and $S_{ls} = 1$. In the analysis the gas pressure was fixed at $P_g = 0.1$ MPa (atmospheric). Consequently, from the adopted retention curve, an initial liquid pressure of $P_l = -165$ MPa was obtained corresponding to the initial degree of saturation $S_1 = 0.44$.

Intrinsic permeability controls the rate of progress of hydration. In the analysis an exponential relationship with porosity was used:

$$\mathbf{k} = k_0 \exp[a(\phi - \phi_0)]\mathbf{I} \quad (46)$$

It was based on the experimental data shown in Figure 4 (FEBEX, 2001). The corresponding parameters are $k_0 = 3.7 \times 10^{-21} \text{m}^2$, $a = 25$ and $\phi_0 = 0.40$. Another parameter concerning the hydraulic problem is the tortuosity for vapour diffusion, estimated as $\tau = 0.8$. Indeed the same tortuosity value has been used for the reactive transport equations.

Regarding the thermal problem, the values adopted for the thermal conductivities for the saturated and dry states of the bentonite are $\lambda_{sat} = 1.15$ W/m/K and $\lambda_{dry} = 0.47$ W/m/K (FEBEX, 2000). So, thermal conductivity of the medium depends on degree of saturation and is given by (Gens *et al.*, 1998, 2002):

$$\lambda = \lambda_{dry}\left(1.0 - \sqrt{S_l}\right) + \lambda_{sat}\sqrt{S_l} \text{ W/m/K} \quad (47)$$

The internal energy of the solid phase (in J/kg) is computed using:

$$E_s = E_s^0 T + \frac{c_p}{2} T^2 \quad (48)$$

where $E_s^0 = 732.5$ J/kg/°C and $c_p = 1.38$ J/kg/°C^2 (FEBEX, 2000).

Finally, regarding the mechanical constitutive law, a thermo-elastoplastic model for unsaturated soils (Gens, 1995) has been used. It is an

extension of the Barcelona Basic Model, (BBM) (Alonso *et al.*, 1990) incorporating temperature effects. Parameters were adjusted for the initial dry density of $1.62\,g/cm^3$ based on the final distribution of porosities of the test. This exercise is not therefore a check on the performance of the mechanical model.

During the performance of the test involved only temperatures were measured. Figure 5 shows the observed and computed distributions of temperatures at various times using $h_0 = 204\,W/m^2/K$ and $T_0 = 293.15\,K$. In fact, temperature reaches equilibrium early on in the test with only minimal changes afterwards.

In Figure 6 the distributions of degree of saturation at various times are presented. Comparison with observations is of course only possible with the observed values at the end of the test. It can be noted that drying has occurred close to the heater whereas the degree of saturation has increased near the hydration end. The changes in porosity presented in Figure 7 are the result of the combined hydration and heating action. The bentonite shrinks near the heater while it undergoes swelling at the opposite end. Overall, the sample volume remains practically constant. Again comparisons are performed with the porosity values obtained at the end of the experiment.
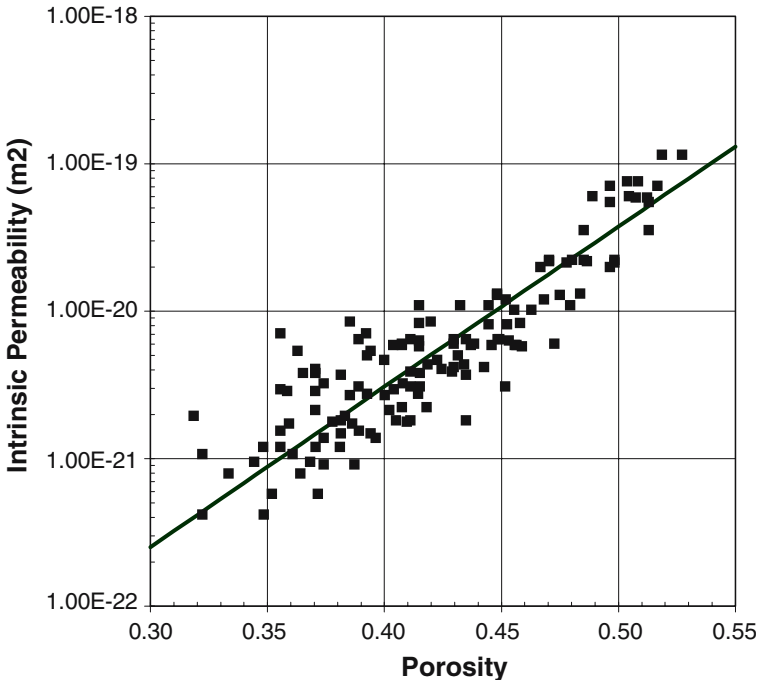
Figure 4. Intrinsic permeability used in the analysis compared with experimental results.

On the whole, it is probably fair to state that the numerical model is capable of reproducing in a satisfactory manner the observed experimental results of the THM problem.

4.3. REACTIVE TRANSPORT ANALYSIS

According to the geochemical characterization studies of the bentonite (FEBEX, 2000), the main processes that take place in the water-bentonite system are dissolution/precipitation of carbonates, sulphates, halite and chalcedony as well as cation exchange. It is also assumed that the geochemical system is in equilibrium with the atmospheric gaseous CO_2 at a partial pressure of $10^{-3.5}$ atm. This hypothesis is difficult to check directly but it has a significant influence on the evolution of the main geochemical variables of the system.

The main exchangeable cations are calcium, magnesium, sodium and potassium (denoted respectively by CaX_2, MgX_2, NaX and KX, where X^- represents the exchange site in the clay mineral. For exchangeable cations, an approximate thermodynamic formulation (Gaines–Thomas) was used based on selectivity coefficients. This formulation allows the inclusion of exchange reactions in the chemical equilibrium problem (Appelo and Postma, 1993). In this simplified formulation, the sum of concentrations of exchangeable cations compensates the excess of negative electrical charge in the clay, represented by the CEC (cation exchange capacity). A clay with large CEC shows large concentrations of exchangeable cations
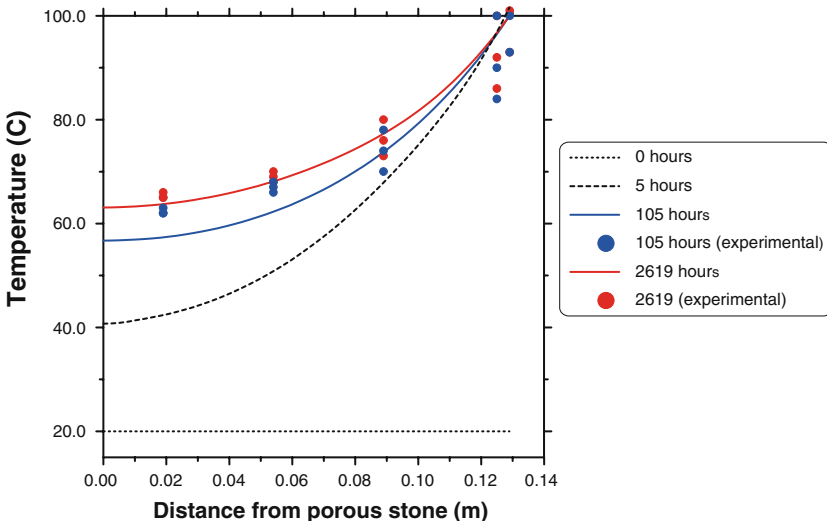
Figure 5. Distributions of temperatures inside the specimen at various times. Computed and observed results.
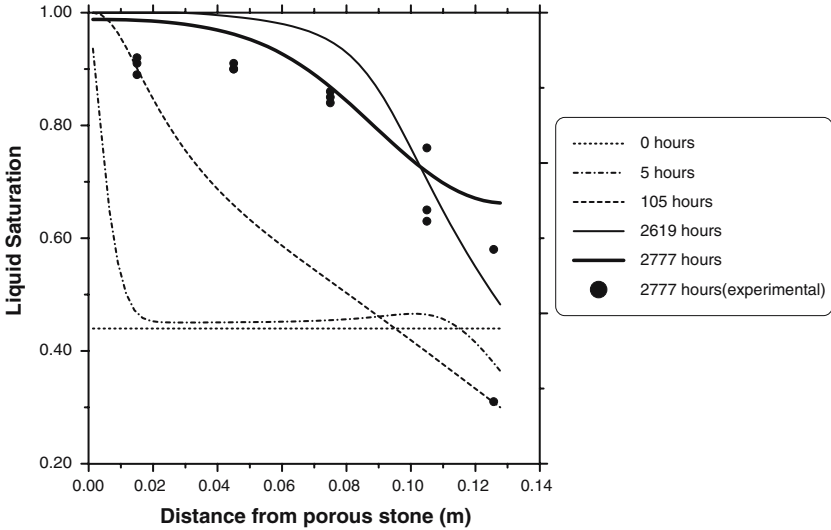
Figure 6. Distribution of degree of saturation inside the specimen at the end of the test. Computed and observed results.
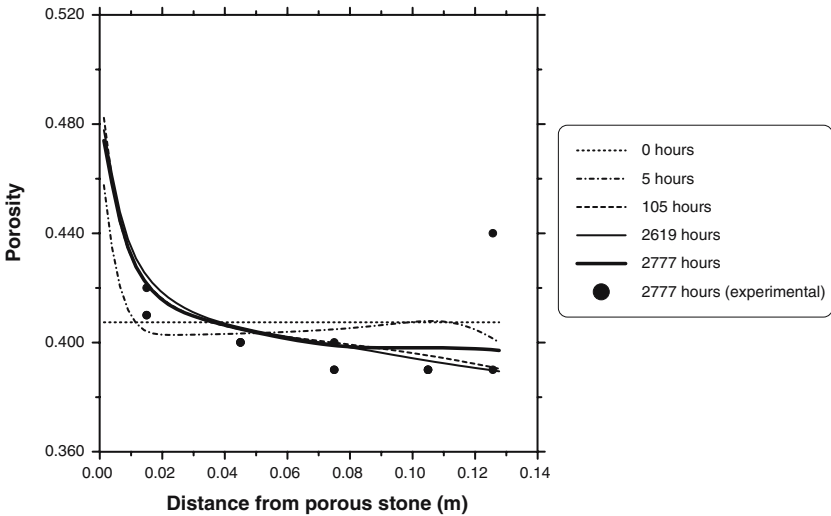

Figure 7. Distribution of porosity inside the specimen at the end of the test. Computed and observed results.

and therefore the charge is not balanced in the pore water (Fernández, 2004; Leroy and Revil, 2004), however the system (clay + pore water is electrically neutral.

Table I shows the initial conditions of the reactive transport problem (FEBEX, 2000). The concentration values in mol/kg of liquid represent the

Table I. Initial conditions for geochemical modelling

Dissolved and precipitated minerals or exchangeable cations	Percentages of solid (for minerals) or percentage of *CEC* (for exchangeable cations)	mol/kg of liquid (at 11.2% water content)
$CaSO_4$	0.14	0.09178
NaCl	0.13	0.19841
$CaCO_3$	0.6	0.53518
SiO_2	0.038	0.056453
CaX_2	41	1.57777
MgX_2	31	1.19295
NaX	25	1.92411
KX	3	0.23089

initial conditions for a water content of 11.2%. A cation exchange capacity of $CEC = 86.2$ meq/100 g of solid has been considered (Cuevas *et al.*, 1996).

Table II summarizes the geochemical model adopted (Fernández and Rivas, 1999). All species present in the system are written in terms of the primary species through the corresponding chemical reactions. The B-dot model (Wolery, 1992) was used for the computation of the activity coefficients of the aqueous species in dilute solution and its database for obtaining the equilibrium constants of the chemical reactions. The selectivity coefficients for the Gaines–Thomas convention adopted here are: $K_{Na\backslash Ca} = 0.293$, $K_{Na\backslash K} = 0.115$, $K_{Na\backslash Mg} = 0.339$ (FEBEX, 2000). Those values are consistent with those found in the literature for this type of reactions (Appelo and Postma, 1993).

The initial conditions of the reactive transport problem in terms of total analytical concentration of the primary species are defined from the initial concentrations of Table I and the reactions shown in Table II. For the carbonic gas in equilibrium with the system at $10^{-3.5}$ atm, an initial free mass of 1 mol/kg of liquid is considered so that it is never exhausted. The total analytical concentrations of the primary species are consequently given by

$$U_{Ca} = C_{CaCO_3} + C_{CaSO_4} + C_{CaX_2} = 2.20473 \, \text{mol/kg}$$

$$U_K = C_{KX} = 0.23089 \, \text{mol/kg}$$

$$U_{Na} = C_{NaCl} - 2C_{CaX_2} - 2C_{MgX_2} - C_{KX} = -5.57392 \, \text{mol/kg}$$

$$U_{Mg} = C_{MgX_2} = 1.19295 \, \text{mol/kg}$$

$$U_{Cl} = C_{NaCl} = 0.19841 \, \text{mol/kg} \tag{49}$$

$$U_{SO_4} = C_{CaSO_4} = 0.09178 \, \text{mol/kg}$$

Table II. Geochemical model for the bentonite

Primary species	H_2O, Ca^{2+}, K^+, Na^+, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, H^+, $SiO_2(aq)$, NaX
Aqueous secondary species	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^-, $HSiO_3^-$
Exchangeable cations as secondary species	$CaX_2 = Ca^{2+} + 2NaX - 2Na^+$ $MgX_2 = Mg^{2+} + 2NaX - 2Na^+$ $KX = K^+ + NaX - Na^+$
Equilibrium phases	halite: $NaCl(s) = Na^+ + Cl^-$ calcite: $CaCO_3(s) = Ca^{2+} + HCO_3^- - H^+$ gypsum: $CaSO_4.2H_2O(s) = Ca^{2+} + SO_4^{2-} + 2H_2O$ anhydrite: $CaSO_4(s) = Ca^{2+} + SO_4^{2-}$ chalcedony: $SiO_2(s) = SiO_2(aq)$ carbonic gas a $10^{-3.5}$atm: $CO_2(g) = HCO_3^- - H_2O + 2H^+$

$$U_{HCO_3} = C_{CaCO_3} + C_{CO_2(g)} = 1.53518\,\text{mol/kg}$$
$$U_H = -C_{CaCO_3} + C_{CO_2(g)} = 0.46482\,\text{mol/kg}$$
$$U_{SiO_2} = C_{SiO_2} = 0.056453\,\text{mol/kg}$$
$$U_{NaX} = C_{NaX} + 2C_{CaX_2} + 2C_{MgX_2} + C_{KX} = 7.69644\,\text{mol/kg}$$

Establishing chemical equilibrium using those values of initial total analytical concentrations at the initial temperature of 20 °C, the chemical composition of the bentonite at a water content of 11.2% is obtained (Table III). Under those conditions, all halite is dissolved in the liquid phase and will remain so throughout the test. Initially there is no anhydrite either because at 20 °C, gypsum is the more stable sulphate mineral.

Hydration was performed using distilled water, therefore, it is assumed that the water infiltrating into the specimen has a total aqueous concentration equal to zero for all primary species, i.e. it is pure water with a pH=7. This means that one of the main processes occurring in the bentonite will be the dilution of pore water.

The main mechanisms for the dissolved species considered in the modelling are advection and molecular diffusion. It was considered that mechanical dispersion is not significant in solute transport. Advection is more important at the start of the test, when the clay is still very dry and hydration occurs at a high rate. As saturation is approached, molecular

diffusion becomes more important and for long times, it is the only relevant transport mechanism.

The coefficient of molecular diffusion was adjusted using the distribution of aqueous species in the bentonite obtained at the end of the test from chemical analysis of the water extracted from the pores. Special attention was paid to the Cl^- anion, since it is a conservative solute in terms of total aqueous concentration (the halite never precipitates during the test).

Figures 8 and 9 show the agreement achieved regarding the aqueous concentrations of the ions. In the formulation, the hydrodynamic dispersion tensor $\mathbf{D}_l$ (equation 4) is given by the contributions of molecular diffusion (Fick's law) and mechanical dispersion:

$$\mathbf{D}_l = \phi \rho_l \tau S_l D_m^{\text{solute}} \mathbf{I} + \rho_l \mathbf{D}_l' \tag{50}$$

where $\mathbf{D}_l'$ is the mechanical dispersion tensor (Bear, 1972) and the molecular diffusion coefficient used is given by

$$D_m^{\text{solute}} = (D_m)^o \exp\left[\frac{-q}{R(273.15 + T)}\right] \tag{51}$$

Table III. Chemical composition of the bentonite (pore water, exchangeable cations and minerals) at the initial 11.2% water content and 20°C

Pore water	(Total aqueous concentration in mol/kg of liquid)
Ca^{2+}	0.0271558
K^+	0.0022669
Na^+	0.1634601
Mg^{2+}	0.0268753
Cl^-	0.1984100
SO_4^{2-}	0.0374574
HCO_3^-	0.0004657
SiO_2	0.0001375
pH	7.68
Exchangeable cations	**(meq/100 g of solid)**
CaX_2	35.5779
KX	2.56057
NaX	21.9414
MgX_2	26.1200
Minerals	**(% of solid)**
halite	0
calcite	0.59955
gypsum	0.10473
anhydrite	0
chalcedony	0.03789

where parameters in equation (51) are $(D_m)^\circ = 5 \times 10^{-6}\,m^2/s$ and $q = 24530\,J/mol$. In this formulation, $(D_m)^\circ$ and q are the same for all aqueous species. The tortuosity τ for the medium (equation 50) was estimated as $\tau = 0.8$ (the same value was used for vapour and aqueous species). In fact the values obtained from the adjustment are consistent with the experimental values determined independently for this material (Martín *et al.*, 2000; FEBEX, 2000).
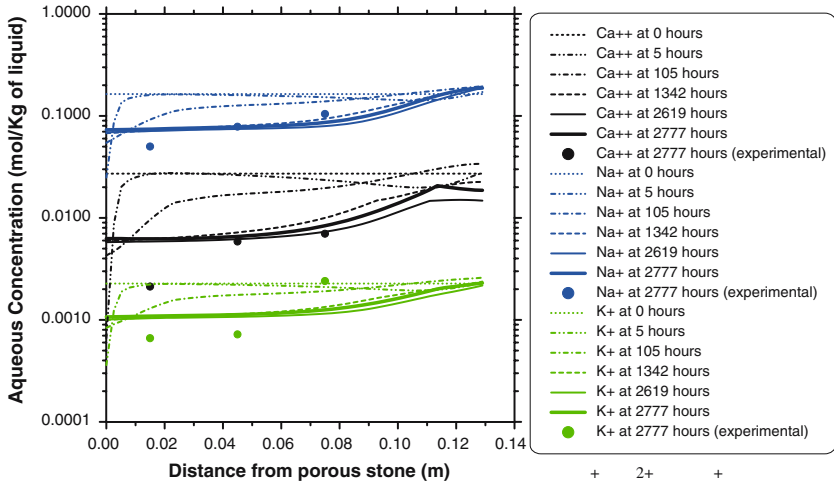

Figure 8. Distribution of the aqueous concentration of cations Na^+, Ca^{2+} and K^+ inside the specimen. Computed results and observed values at the end of the test.
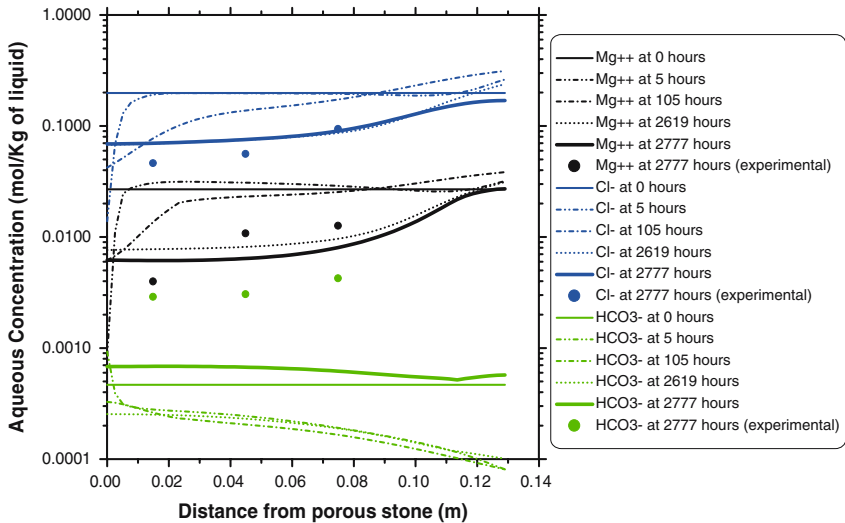
Figure 9. Distribution of the aqueous concentration of ions Mg^{2+}, Cl^- and HCO_3^- inside the specimen. Computed results and observed values at the end of the test.

It can be noted that the concentrations of all aqueous species (except HCO_3^-) have reduced during the test due to the entrance of distilled water (Figures 8 and 9). The only exception is the HCO_3^- anion that exhibits a significant increase on cooling. This is due to the solution of calcite at this stage due to its enhanced solubility at lower temperatures. The computed increase is however insufficient to match the observed test results.

Figure 10 shows that the bentonite pH (both computed and measured values) varies little during the test. The values lie practically always between 7.5 and 8.5, due to the presence of calcite and the assumed equilibrium with carbonic gas. This is an important result because it guarantees the thermodynamic stability of the clay fraction (FEBEX, 2000). A moderate increase of pH is predicted on cooling due again to the solution of calcite that entails a corresponding consumption of H^+, according to

$$CaCO_3(s) + H^+ \rightarrow Ca^{2+} + HCO_3^- \tag{52}$$

A parallel increase in Ca^{2+} is not computed because its concentration is also influenced by cation exchange phenomena.

Regarding the exchangeable cations of the clay (Figure 11), there is also a reasonable correspondence between experimental and computed concentration values except near the heater. The reason for this lack of agreement in the region with temperatures above $70\,^{\circ}C$ are unclear at present but they may be due, at least in part, to shortcomings of the cation exchange model at high temperatures. In the model it has been assumed that the equilibrium constants for cation exchange and the CEC do not depend on temperature.
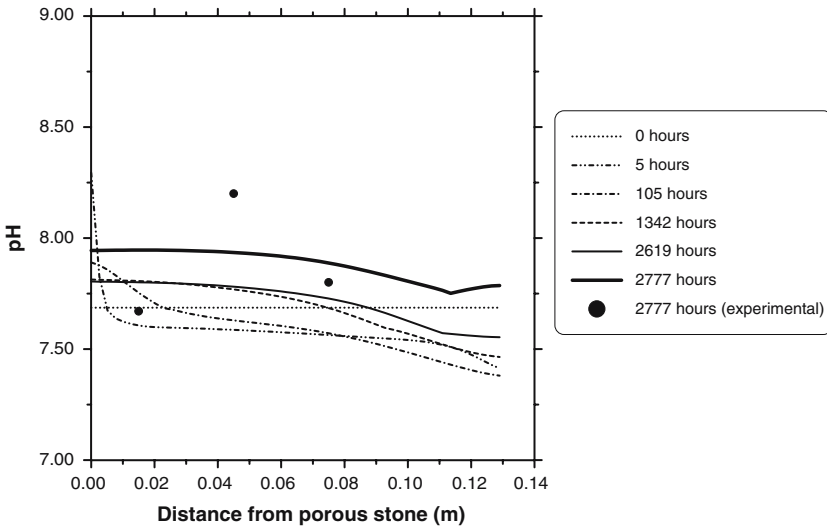

Figure 10. Distribution of pH inside the specimen. Computed results and observed values at the end of the test.
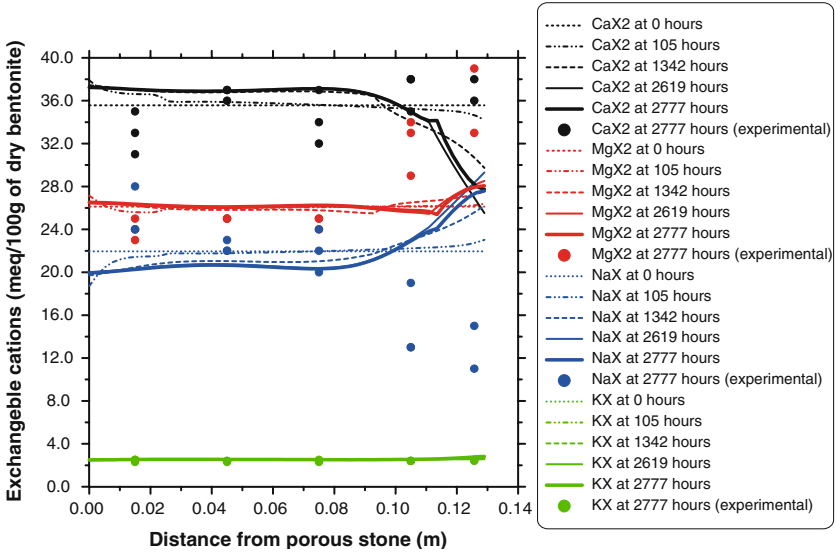
Figure 11. Distribution of the exchangeable cations CaX₂, MgX₂, NaX and KX inside the specimen. Computed results and observed values at the end of the test.
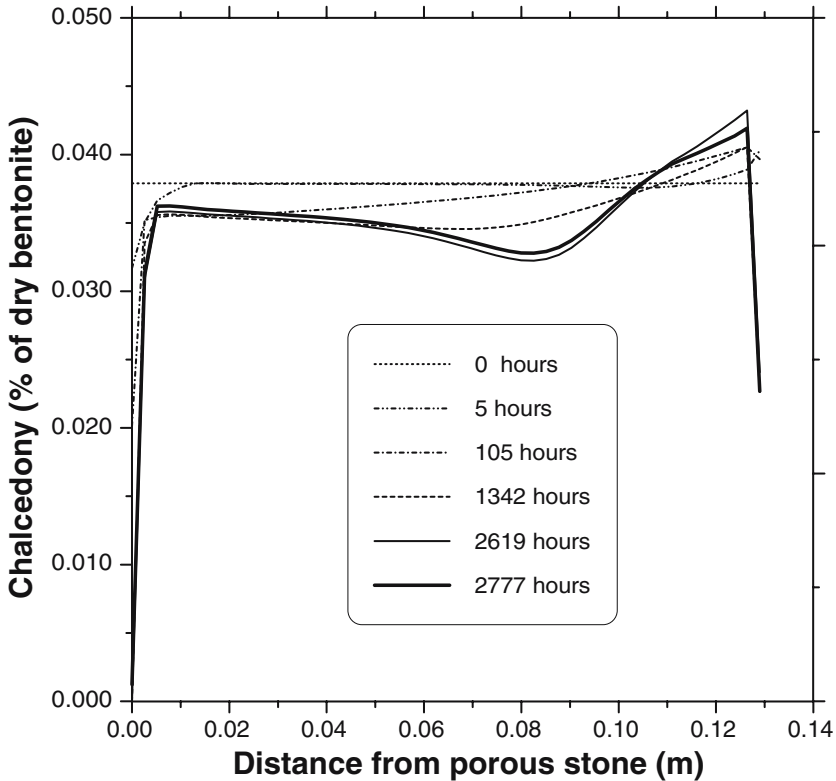

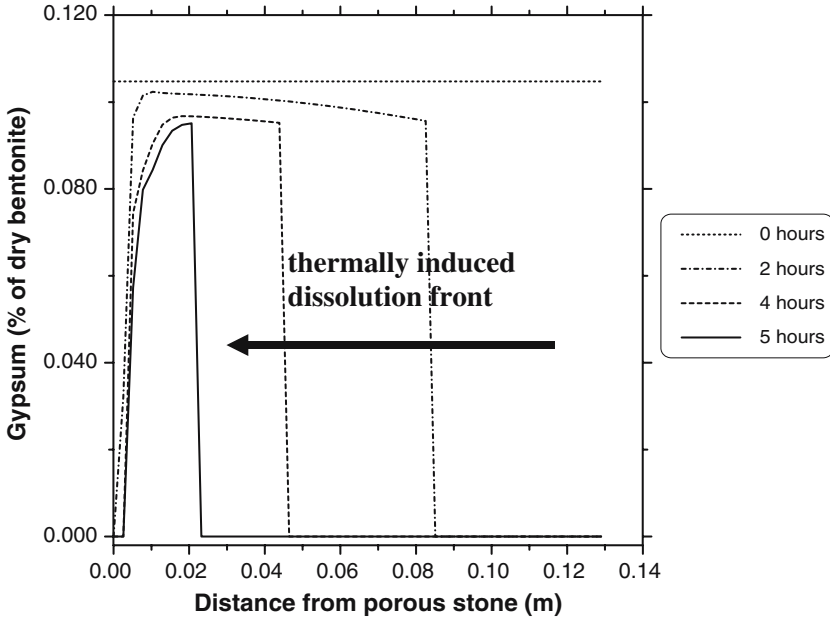*Figure 12.* Distributions of chalcedony in the sample. Computed results.

Figure 13. Computed distributions of gypsum in the specimen during the heating phase.

Observing the computed evolution of the other minerals, it can be observed in Figure 12 that, according to the model, chalcedony is dissolved at both ends of the specimen. In the zone close to the porous stone (hydration end) there is a tendency towards the dilution of SiO(aq) due to hydration with distilled water. In the heater zone, chalcedony exhibits a higher solubility, increasing the concentrations of SiO_2(aq) and generating a flow of this solute by molecular diffusion towards the cooler zones of the sample. This process tends to develop a dissolution front of chalcedony that travels towards the hydration end (colder section) until all chalcedony is dissolved in the hot zone. The limited duration of the test prevents observing the full development of this phenomena.

Sulphates exhibit an evolution somewhat more complex than other minerals. Gypsum is the sulphate mineral more stable at low temperatures, but above $50\,^{\circ}C$ gypsum loses water and becomes anhydrite:

$$CaSO_4 \cdot 2H_2O(s) \rightarrow CaSO_4(s) + 2H_2O \tag{53}$$

Equation (53) generates, during the first hours of the test, a gypsum dissolution front and anhydrite precipitation that starts at the heater end and travels towards the cooler sample sections (Figures 13 and 14).

In Figure 15, it is possible to observe the computed evolution of the anhydrite in the sample. The mineral tends to collect near the heater. This
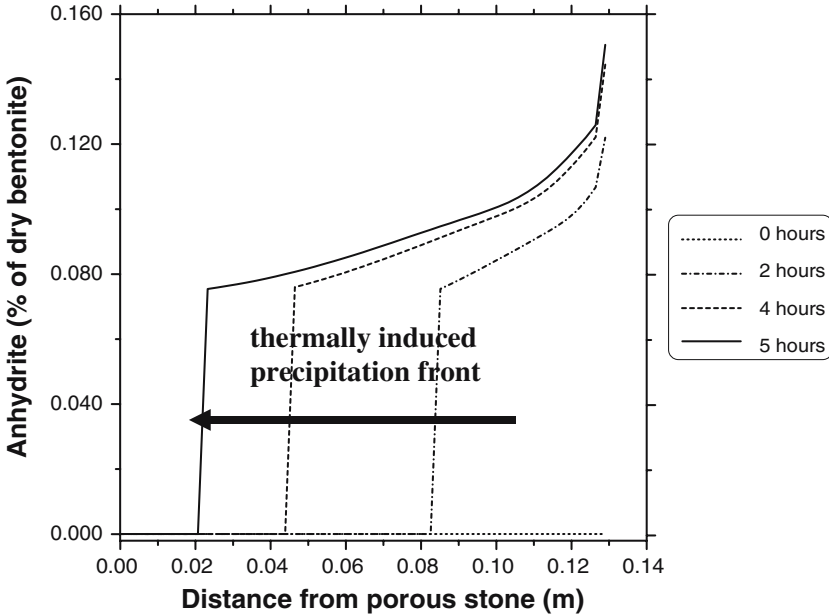
Figure 14. Computed distributions of anhydrite in the specimen during the heating phase.

is a consequence of the evaporation that occurs in that zone. An additional cause lies in the fact that the Ca^{2+} and SO_4^{2-} ions migrate by molecular diffusion towards the hot zones because the minerals that control their concentrations (calcite, gypsum and anhydrite) are more soluble at low temperatures. Figure 16 shows how the SO_4^{2-} distribution favours the migration by molecular diffusion of this anion towards the heater in the zone where anhydrite is present. This result demonstrates that the formulation is capable of simulating the advance of the dissolution front of the anhydrite towards the hot region including the complete dissolution of the mineral in the cool zone (Figure 15).

In other tests performed by CIEMAT in similar cells, scanning electron microscope observations have shown the existence of a thin film of precipitated gypsum (FEBEX, 1997). Using the optical microscope, accumulation of calcite in zones close to the heater was also noted (FEBEX, 1999). These experimental observations are consistent with the results of the model presented. In the analysis, anhydrite accumulated in the heater becomes gypsum during cooling, following the opposite direction of reaction (53).

5. Concluding Remarks

A formulation that generalizes an existing THM code by incorporating the reactive transport equations in an unsaturated deformable porous medium has been presented. The transport and chemical reactions incorporated
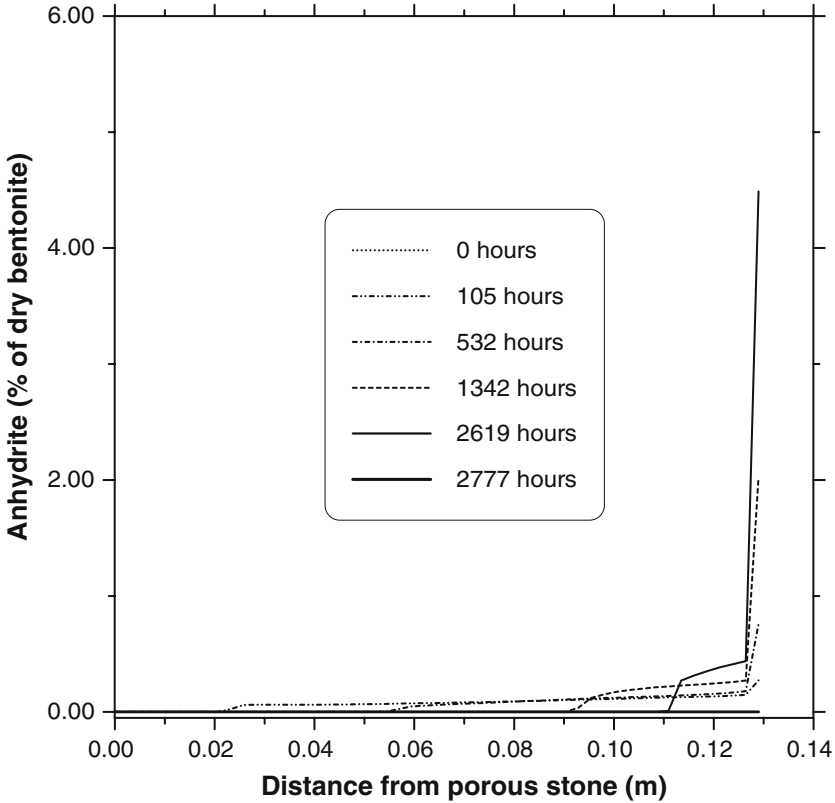
Figure 15. Computed distribution of anhydrite inside the specimen at various times.

are those likely to occur in compacted clay barriers used for isolation of nuclear waste. The formulation is fully coupled allowing, therefore, the examination of the interactions between the various phenomena present in the barrier. The chemical equilibrium equations are solved by ensuring the minimization of Gibbs Free Energy. This approach overcomes the difficulties posed by the possibility of precipitated minerals appearing or disappearing in different parts of the domain. It also allows the use of robust optimization algorithms that contribute significantly to the overall efficiency of the analysis.

A validation exercise involving the simultaneous heating and hydration of a bentonite specimen is described. Encouraging agreement has been found concerning not only THM parameters but chemical variables as well. However, the development of multi-physics models applied to porous media requires more experimental results with simultaneous control of state variables for the thermo-hydro-mechanical and chemical coupled problem. In any case, the numerical tool developed is able to analyze the complex behaviour of clay barriers in a comprehensive manner thereby allowing the
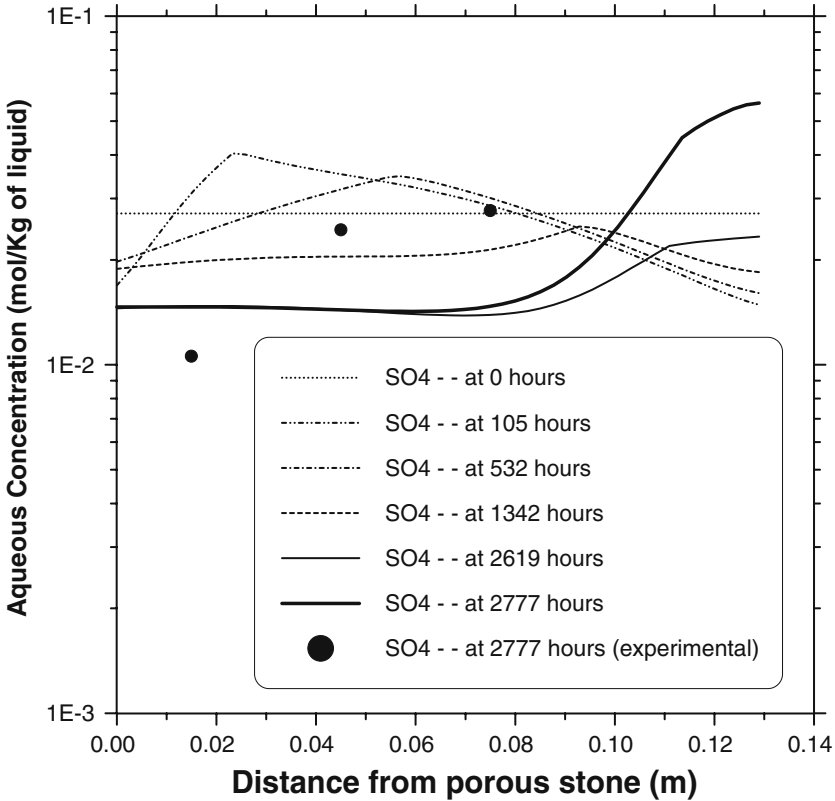
Figure 16. Distribution of the aqueous concentration of SO_4^{2-} inside the specimen. Computed results and observed values at the end of the test.

designer to identify the most significant phenomena to justify subsequent simplifications of the problem for practical applications.

Acknowledegments

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