



## Modelling thermo-hydro-mechano-chemical interactions for nuclear waste disposal

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**Abstract:** A fully coupled thermo-hydro-mechano-chemical (THMC) formulation is described in this paper. Special attention is paid to phenomena likely to be encountered in clay barriers used as engineered barriers in the disposal of nuclear radioactive 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 kinetics- and equilibrium-controlled reactions are incorporated. The formulation is implemented in a numerical code. An application is presented concerning the performance of a large-scale in-situ heating test simulating high-level radioactive waste repository conditions.

**Key words:** coupling analysis; thermo-hydro-mechano-chemical (THMC) analysis; radioactive waste; engineered barriers; bentonite; cation exchange

## 1 Introduction

Prospective designs of deep geological repositories for high-level radioactive waste generally include an engineered barrier around waste canisters. Often, compacted swelling clay is the main component of those barriers that will be subsequently subjected to temperature increases due to heat emitted by the waste and hydration from water coming from the adjacent rocks. As a result, a number of interacting thermal, hydraulic, mechanical and chemical phenomena arise that have a series of impacts on the performance and long-term reliability of the barrier. A rational assessment of the barrier behaviour requires the application of thermo-hydro-mechano-chemical (THMC) formulations to perform the required coupled numerical analyses.

Although a number of coupled thermo-hydro-mechanical (THM) formulations and the corresponding numerical codes have been available for some time [1–4],

coupled THMC formulations have lagged behind. Only recently a number of proposals were put forward in this field [5–8]. The research has now reached such a state that, through the incorporation into efficient computer codes, it is possible to perform coupled THMC numerical analyses to deal with extremely complex engineering problems.

In this paper, a fully coupled THMC formulation is briefly described that allows the performance of numerical analyses considering the thermal, hydraulic, mechanical and chemical behaviours and their interactions. The formulation takes into account the possibility that the material is partly saturated. Therefore, the term “hydraulic” should be interpreted in a wide sense, i.e. including both liquid and gas flow phenomena. Although the formulation is general, special attention is paid to the phenomena (especially chemical phenomena) that are likely to occur in swelling clay in an engineered barrier for nuclear waste isolation. To demonstrate that the tool developed is now capable of performing fully coupled THMC analysis involving practical engineering problems, the formulation is applied to the analysis of a large-scale in-situ heating test simulating nuclear radioactive waste repository conditions.

## 2 Theoretical formulation

### 2.1 THM formulation

The THM formulation presented here is based on the proposed one in Ref.[1] applied to clay. The formulation uses a multi-phase and multi-species conceptual model. The porous medium is assumed to be made up of three phases: solid, liquid and gas. The main part of the solid phase is an inert mineral that does not dissolve but may contain precipitated species. The liquid phase contains water, dissolved air and dissolved chemical species, and the gas phase is made up of dry air and water vapour. Note that dry air is considered as a single species in spite of the fact that it is a mixture of gases.

Using the compositional approach, the formulation is based on the establishment of balance equations for each species: mineral, water and air, instead of using the phases. Thus, the contributions of phase changes automatically vanish. Variables in this paper may include a subscript or a superscript. The subscripts refers to different phases (“s” for solid, “l” for liquid and “g” for gas), while the superscript indicates the species (“w” for water and “a” for dry air).

The solution to a coupled THM problem is required to meet simultaneously the following balance equations:

(1) Balance of solid:

$$\frac{\partial}{\partial t}[\rho_s(1-\phi)] + \nabla \cdot \mathbf{j}_s = 0 \quad (1)$$

(2) Balance of water mass:

$$\frac{\partial}{\partial t}(\rho_l \phi) + \nabla \cdot \mathbf{j}_l = f^w \quad (2)$$

(3) Balance of internal energy:

$$\frac{\partial}{\partial t}[E_s \rho_s(1-\phi) + E_l \rho_l \phi] + \nabla \cdot (\mathbf{i}_c + \mathbf{j}_{E_s} + \mathbf{j}_{E_l}) = f^Q \quad (3)$$

(4) Equilibrium:

$$\nabla \cdot \boldsymbol{\sigma} + \mathbf{b} = \mathbf{0} \quad (4)$$

where  $\phi$  is the porosity;  $\rho_i$  ( $i = s, l$ ) is the density;  $\mathbf{j}_i$  ( $i = s, l$ ) is the total mass flux;  $\boldsymbol{\sigma}$  is the stress tensor;  $\mathbf{b}$  is the body forces vector;  $E_i$  ( $i = s, l$ ) is the specific internal energy;  $\mathbf{j}_{E_i}$  ( $i = s, l$ ) is the energy flux due to mass motion;  $f^w$  and  $f^Q$  are the sink/source terms for water mass and energy, respectively; and  $\mathbf{i}_c$  is the conductive heat flux, which is governed by Fourier's law:

$$\mathbf{i}_c = -\lambda \nabla T \quad (5)$$

where  $\lambda$  is the coefficient of thermal conductivity.

Note that no gas component is explicitly used as desaturation of clay during tests does not occur or is minimal.

Using the definition of material derivative:

$$\frac{D_s(\cdot)}{Dt} = \frac{\partial(\cdot)}{\partial t} + \frac{d\mathbf{u}}{dt} \nabla(\cdot) \quad (6)$$

Eq.(1) becomes

$$\frac{D_s \phi}{Dt} = \frac{1}{\rho_s} \left[ (1-\phi) \frac{D_s \rho_s}{Dt} \right] + (1-\phi) \nabla \cdot \frac{d\mathbf{u}}{dt} \quad (7)$$

Now the balance equation of solid (Eq.(7)) can be eliminated by introducing it into the water mass balance equation (Eq.(2)). Making use again of the definition of material derivative, the following equation can be obtained:

$$\phi \frac{D_s \rho_w}{Dt} + \frac{\rho_w}{\rho_s} (1-\phi) \frac{D_s \rho_s}{Dt} + \rho_w \nabla \cdot \frac{d\mathbf{u}}{dt} + \nabla \cdot (\rho_w \mathbf{q}_l) = 0 \quad (8)$$

Water flow is controlled by Darcy's law:

$$\mathbf{q}_l = -K_l (\nabla p_l - \rho_w \mathbf{g}) = -\frac{k}{\mu_l} (\nabla p_l - \rho_w \mathbf{g}) \quad (9)$$

where  $K_l$  is the liquid permeability, and  $k$  is the intrinsic permeability. Liquid permeability depends on temperature through the variation of water viscosity, and the intrinsic permeability depends on porosity.

The formulation must be completed with a number of constitutive laws that describe various phenomena under consideration. The main ones correspond to the flow of heat by conduction, the advective flow of water and the mechanical constitutive law for mechanical behaviour.

### 2.2 Chemical formulation

Now 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), the reactions that exchange matter between the liquid phase 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 the chemical equilibrium prevails. Only some dissolution/precipitation processes are assumed to be kinetics-controlled. The transport equations describe the mass continuity of each chemical species in the porous medium. In the chemical equilibrium problem, a relationship among the species concentrations is

established that allows a reduction in the degrees of freedom of the reactive transport problem [9].

Considering the reactive transport of  $N$  kinds of chemical species in a deformable unsaturated porous medium, the transport of each species can be expressed as

$$\frac{\partial}{\partial t}(\phi S_i \rho_i c_i) + \nabla \cdot \mathbf{j}_i = R_i \quad (i = 1, 2, \dots, N) \quad (10)$$

where  $c_i$  is the solution concentration of specie  $i$  ( $\text{mol} \cdot \text{s/kg}$ );  $R_i$  is the total production rate of specie  $i$  due to chemical reactions ( $\text{mol} \cdot \text{m}^{-3}/\text{s}$ ); and  $\mathbf{j}_i$  is the total flux of specie  $i$  ( $\text{mol} \cdot \text{m}^{-2}/\text{s}$ ), which is considered as the sum of advective and non-advective fluxes in Ref.[1]. 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 consequence of molecular diffusion and mechanical dispersion. For simplicity, it is assumed that the mechanical dispersion tensor is the same for all solutes. This has an advantageous consequence that electrical charge is conserved in the reactive transport equations when chemical reactions are charge-balanced [10].

After several transformations, the final form of the reactive transport equations is

$$\frac{\partial}{\partial t}(\phi S_i \rho_i U_j) + \nabla \cdot [\rho_i (Ua)_j \mathbf{q}_i - \mathbf{D}_i \nabla (Ua)_j + \phi S_i \rho_i U_j \dot{\mathbf{u}}] + \sum_{m=1}^{N_m} \nu_{jm} r_m = 0 \quad (j = 1, 2, \dots, N_c) \quad (11)$$

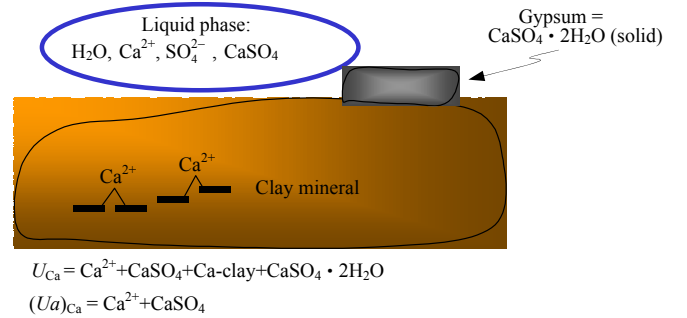
$$U_j = C_j + \sum_{i=1}^{N_x} \nu_{ij} X_i \quad (i = 1, 2, \dots, N_c) \quad (12)$$

$$(Ua)_j = \lambda_j C_j + \sum_{i=1}^{N_x} \nu_{ij} \lambda_i X_i \quad (i = 1, 2, \dots, N_c) \quad (13)$$

where  $U_j$  is the total analytical concentration;  $(Ua)_j$  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;  $\lambda_j$  and  $\lambda_i$  are the mobility of the primary and secondary species, respectively;  $r_m$  is the rate of precipitation or dissolution of mineral  $m$  under kinetics conditions;  $N_m$  is the number of minerals under kinetics conditions;  $\nu_{jm}$  is the mole number of primary species  $j$  in a mol of mineral  $m$ ;  $N_c$  is the number of primary species; and  $N_x$  is the number of secondary species.

In the present formulation, the total analytical concentration  $U_j$  in Eq.(11) is unknown, and  $(Ua)_j$  and  $r_m$  are considered as nonlinear functions of  $U_j$ . The link between the unknown  $U_j$  and the dependent variables

$(Ua)_j$  and  $r_m$  is the chemical equilibrium model described in Ref. [9]. This type of the unknown exhibits an interesting property of being independent of chemical equilibrium. The changes of total analytical concentration with time are exclusively due to transport and kinetics reactions. Figure 1 illustrates the meanings of these variables in a particular example. The total analytical concentration for the calcium,  $U_{\text{Ca}}$ , takes into account its presence in the liquid phase as dissolved  $\text{Ca}^{2+}$  and  $\text{CaSO}_4$ , in the solid phase as precipitated gypsum, and in the clay mineral as exchangeable cation. The aqueous concentration,  $(Ua)_{\text{Ca}}$ , only considers the calcium in the liquid phase.

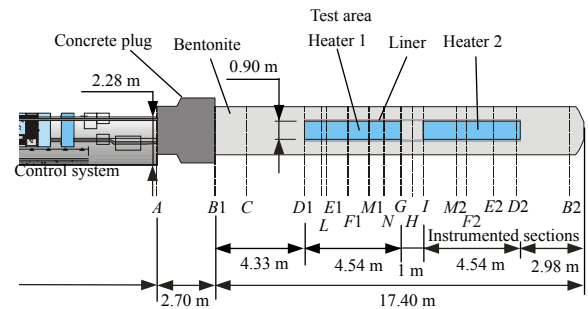


**Fig.1** Illustration of the definition of calcium concentrations in a specific geochemical system.

### 3 Example of application

#### 3.1 A large-scale in-situ heating and hydration 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 involved 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 (Fig.2) consists of two heaters at the end of a drift of 2.28 m in diameter and 70.4 m in length especially bored for this purpose. The diameter and length of the heaters (0.9 and 4.54 m, respectively) correspond to the actual dimensions of the canister envisaged for radioactive waste storage. The heaters are placed in the axis of the drift at a 1 m distance from each other.



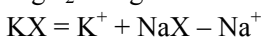
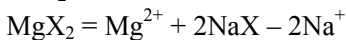
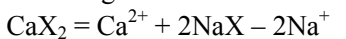
**Fig.2** Layout of the large-scale in-situ heating and hydration test.

### 3.2 Characteristics of analysis

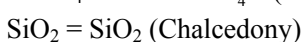
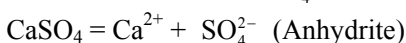
Numerical computations were carried out using the fully coupled THMC version of CODE\_BRIGHT. Radial symmetry was assumed, resulting in a 1D axisymmetric analysis that is quite appropriate for examining the behaviour of bentonite barrier and immediate adjacent rock. More information was reported in Refs.[8, 11, 12].

After an increasing power was provided to the heaters for a short period, a constant temperature of 100 °C was achieved at the interface between the heater and the buffer, in correspondence with the test protocol. Although the full heating test has lasted for five years, the analysis was run up to 100 years to check and predict long-term THMC conditions. The rock thermal, hydraulic and mechanical boundary conditions were based on the results of comprehensive site investigation carried out. The initial conditions of the bentonite were as follows: a dry density of 1.7 Mg/m<sup>3</sup> and a water content of 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 THM parameters were determined by an independent laboratory testing programme.

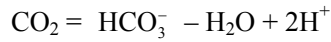
The selected primary species are H<sub>2</sub>O, Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, H<sup>+</sup>, SiO<sub>2</sub> (aqueous), NaX. They are all in the liquid phase except adsorbed sodium NaX, where X<sup>-</sup> stands for the clay mineral. The secondary species, in equilibrium with the primary ones, are: OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, CO<sub>2</sub> (aqueous), CaCO<sub>3</sub> (aqueous), CaHCO<sub>3</sub><sup>+</sup>, CaSO<sub>4</sub> (aqueous), CaCl<sup>+</sup>, MgSO<sub>4</sub> (aqueous), MgHCO<sub>3</sub><sup>+</sup>, MgCl<sup>+</sup>, NaHCO<sub>3</sub> (aqueous), NaSO<sub>4</sub><sup>-</sup>, NaCl (aqueous), KSO<sub>4</sub><sup>-</sup> and HSiO<sub>3</sub><sup>-</sup>. A total cation exchange capacity CEC=86.2 meq/(100 g) of solid is used. The exchangeable cations are also secondary species and are controlled by the following reactions:



Finally, the phases in equilibrium with the solution of the liquid phase are



Carbonic gas at 10<sup>-3.5</sup> atm is



As a result of these assumptions, the number of the unknowns per node is 13: one is temperature, one is liquid pressure, one is displacement, and the others are about primary chemical species (excluding water).

### 3.3 Results of the THMC analysis

A selection of results is shown in this section. They are 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 from three points of the buffer: one near the heater, one in the central part of the barrier, and one close to the rock (external buffer).

Figure 3 shows the variation of temperature at those points. Close to the heater, the temperature is maintained at about 100 °C. At the other two points there is, after the initial transient period, a gentle temperature rise with time. Figure 4 shows the evolution of degree of saturation for the first five years. It can be observed that there is a strong drying close to the heater, followed by a milder hydration. The part of the barrier close to the rock becomes quickly saturated, but the central part is still unsaturated after five years. More information about THM results is given in Refs. [8, 12].

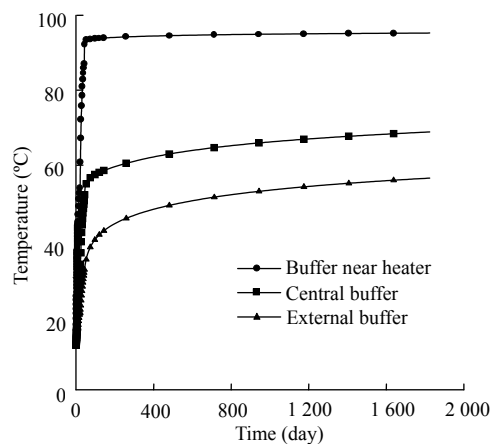
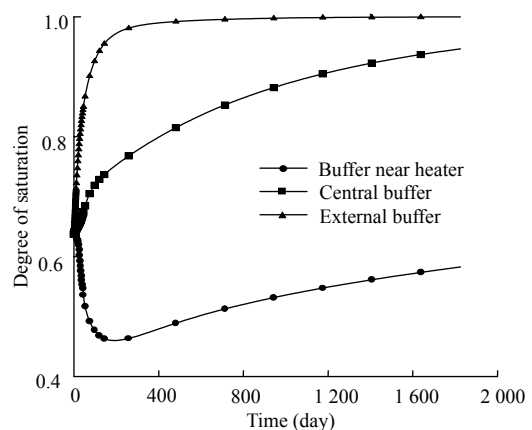
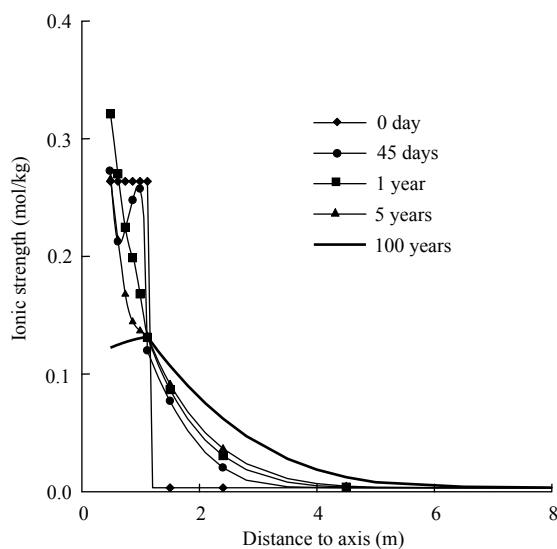


Fig.3 Variation of temperature with time at three points of the bentonite barrier.

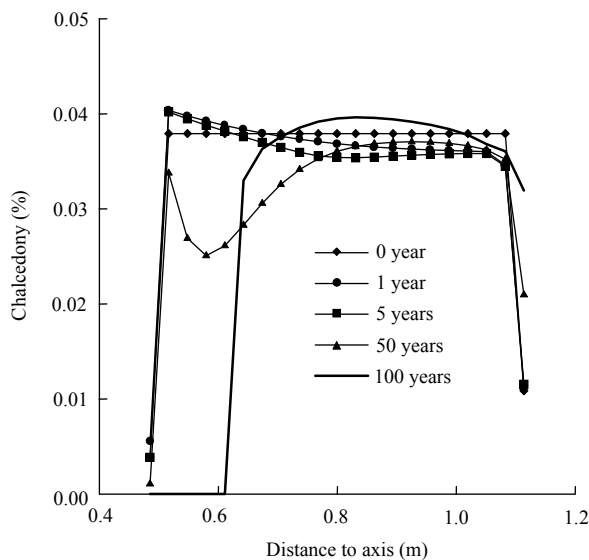


**Fig.4** Variation of degree of saturation with time at three points of the bentonite barrier.

Figure 5 presents the ionic strength distribution in the buffer and 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, and 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. To show the type of results concerning the behaviours of precipitated minerals, Fig.6 is presented with 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. By contrast, near the heater there is initially some precipitation due to water evaporation induced by heating. However, in the long



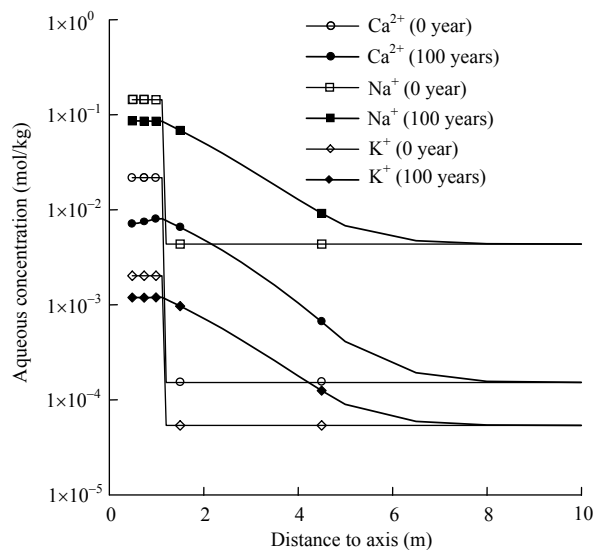
**Fig.5** Distribution of ionic strength in the bentonite barrier and the rock at various times.



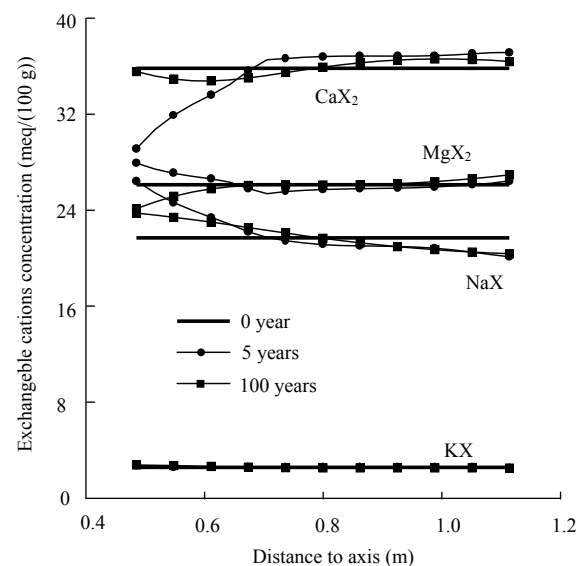
**Fig.6** Distribution of chalcedony concentration in the bentonite barrier at various times.

term, the mineral disappears from the inner zone of the barrier due to the high solubility of the chalcedony, leading to an increase in the concentration of  $\text{SiO}_2$ . This originates a molecular diffusion transport that results in the development of a dissolution front (clearly visible in the results of 100 years) that travels towards the cooler outer part of the barrier.

The computed concentrations for some of the individual cations can be examined in Figs.7 and 8. The tendency is especially towards a dilution of the aqueous species in the barrier at a shorter time near the rock (Fig.7). Concentrations in the rock increase progressively due to diffusion. The exchangeable cations in the buffer clay do not vary much (Fig.8). There are some initial changes due to the impact of heating but the final cation content in the solid phase



**Fig.7** Distribution of the aqueous concentration of cations  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  in the bentonite barrier and the rock at various times.



**Fig.8** Distribution of exchangeable cations concentration in the bentonite barrier at various times.

after 100 years is rather similar to the initial one. It should be stressed, however, that there are some uncertainties over the details of cation exchange processes at high temperatures.

## 4 Conclusions

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

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