UNCERTAINTY IN THE REACTIVE TRANSPORT MODEL RESPONSE TO AN ALKALINE PERTURBATION IN A CLAY FORMATION

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ABSTRACT

The mineral alteration in the concrete barrier and in the clay formation around long-lived intermediate-level radioactive waste in the French deep geological disposal concept is evaluated using numerical modeling. There are concerns that the mineralogical composition of the surrounded clay will not be stable under the high alkaline pore fluid conditions caused by concrete (pH~12). Conversely, the infiltration of CO_2-rich groundwater from the clay formation into initially unsaturated concrete, at the high temperature (T~70°C) produced from the decay of radionuclides, could cause carbonation, thereby potentially affecting critical performance functions of this barrier. This could also lead to significant changes in porosity, which would affect aqueous diffusive transport of long-lived radionuclides. All these processes are therefore intimately coupled and advanced reactive transport models are required for long-term performance assessment. The uncertainty in predictions of these models is one major question that must be answered. A mass-transfer model response to an alkaline perturbation in clay with standard model values is first simulated using the two-phase non-isothermal reactive transport code TOUGHREACT. The selection of input parameters is thereafter designed to sample uncertainties in a wide range of physico-chemical processes without making a priori assumptions about the relative importance of different feedbacks. This "base-case" simulation is perturbed by setting a parameter to a minimum, intermediate or maximum value or by switching on/off a process. This sensitivity analysis is conducted using grid computing facilities of BRGM (http://iggi.imag.fr).

Our evaluation of the preliminary results suggests that the resaturation and the heating of the near-field will be of long enough duration to cause a limited carbonation through all the width of the concrete barrier. Another prediction is the possibility of self-sealing at the concrete/clay interface. Further research is however required to discuss the effect of such evolution on the desirable performance function of both barriers.

INTRODUCTION

For long-lived intermediate-level radioactive waste type B5.2, the use of concrete as engineering barrier and Callovian-Oxfordian clay as geological barrier at a repository depth of 500 m is considered in the French disposal concept (ANDRA, 2005). Upon emplacement, initially unsaturated concrete is expected to experience coupled processes involving heating, resaturation with groundwater from the clay formation, degassing and geochemical reactions. After the early period of resaturation, solute transport is supposed to be diffusion-controlled because of the extremely low permeability of surrounding clay. These coupled processes may lead to changes in the porosity of the concrete or clay barriers. In the present paper, a fully coupled Thermo-Hydro-Chemical (THC) response of a two-phase mass-transfer model is evaluated and tested by a sensitivity analysis. This study is an extension of a previous model applied to an isothermal and fully saturated concrete/clay interface (Burnol et al, 2005); it investigates the coupled effect of temperature and unsaturated conditions. The system is simulated for a 2000-year period, which covers the most predominant thermal perturbation in the ANDRA disposal concept. The base-case simulation is then perturbed by changing key parameters values or by switching on/off a key process in order to evaluate the uncertainty of predictions.

MODEL DESCRIPTION

Simulations were performed using the two-phase non-isothermal reactive transport code TOUGHREACT (Xu et al., 2001). This code was developed by introducing reactive geochemistry into the framework of TOUGH2 V2 (Pruess et al., 1999).

Thermal and hydrological processes

The modeled system represents a vertical section which includes waste canister packages with a radius of 3 m, surrounded by a 2-m wide concrete barrier and by a portion of Callovian-Oxfordian clay (Figure 1). A one-dimensional radial grid of 164 elements is performed with MESHMAKER, with the horizontal axis of the excavated drift as axis of symmetry (Figure 1).
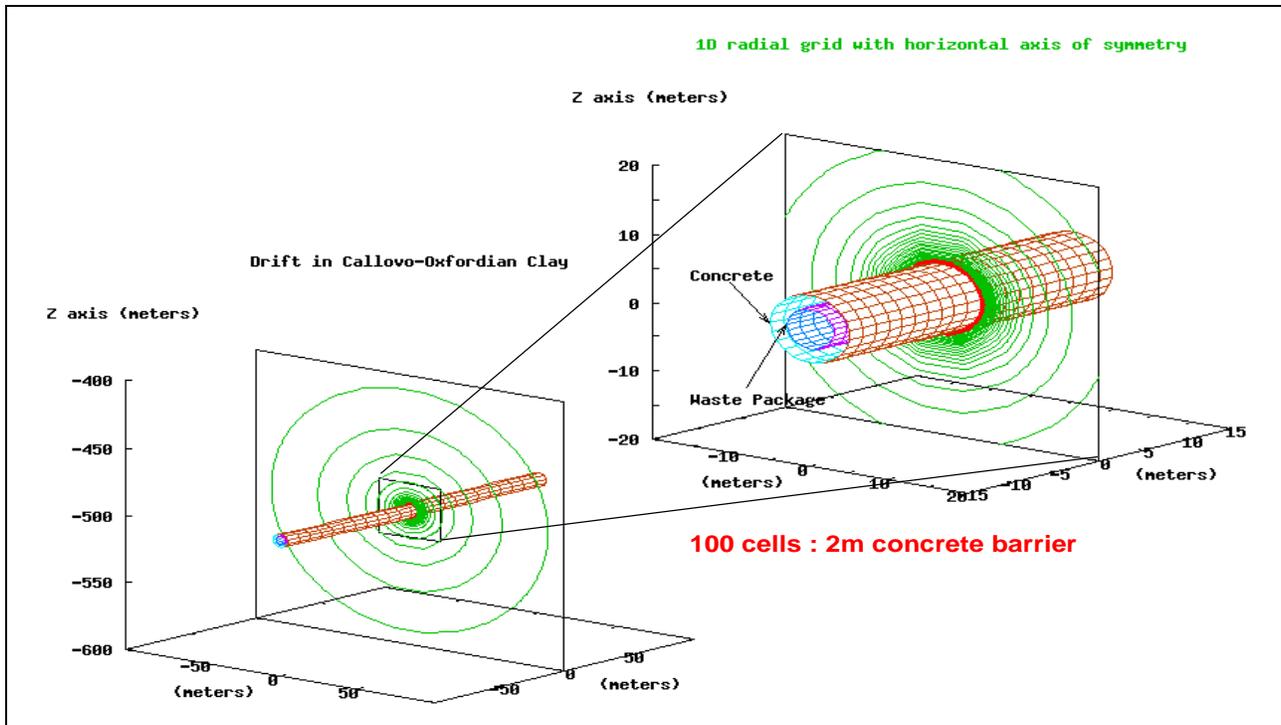
Figure 1. ANDRA design of a deep repository in clay (500m) for long-lived intermediate-level radioactive waste
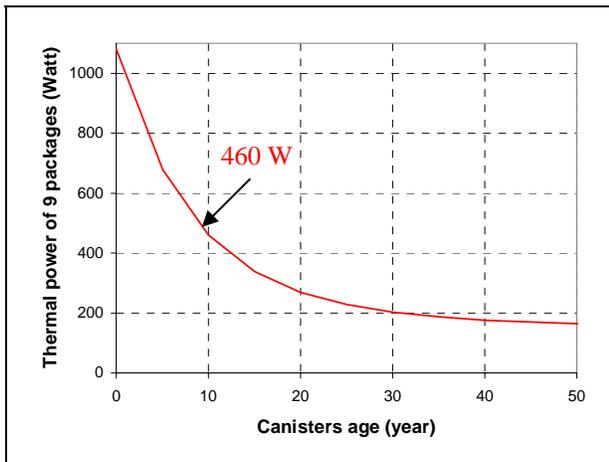
Figure 2. Residual thermal power of 9 packages B5.2

Because of the length of the drift (270 m, Figure 1), the modeled system represents an infinite linear string of identical waste packages and an additional element of infinite volume represents constant boundary conditions. The dimensioning, the power of the canisters at the time of deposition (460 W after 10 years, see Figure 2), the thermal properties of the engineered barrier are factors that control the temperature which must not exceed 70°C in the ANDRA concept for the B5.2 waste. The initial conditions in the concrete barrier are assumed to be 50°C temperature, 1 atm pressure and 70% gas saturation. In clay, the initial conditions are assumed to be 25°C, 5 MPa (representing hydrostatic conditions at a disposal depth of 500 m) and fully water saturated, which are the same as the boundary conditions. The hydrological and thermal properties of both media listed in Table 1 and 3 define the base-case simulation. Note that Van Genuchten formulation for the relative permeability and the capillary pressure is used (Figure 3).

Geochemical processes

The chemical system includes 12 aqueous components, 32 minerals and 1 gas. The mineralogy of both simulated media (concrete and clay) is based on previous studies (Gaucher et al, 2004). All the dissolution and precipitation reactions are assumed to proceed at local equilibrium because of the considered large time scale and large uncertainties in kinetic rate constants. The temperature dependence of thermodynamic equilibrium constants for all phases (solid, aqueous and gaseous phases) are automatically calculated by TOUGHREACT using a polynomial expression incorporated in a supported thermodynamic database converted from the PHREEQC database decribed in Gaucher et al. (2004). The list of the potential secondary phases (clay, cement and zeolites phases) is given for the base-case simulation (Figure 4); this list will be modified during the sensitivity analysis by inhibiting the precipitation of one phase. The initial compositions in pore water in concrete at 50°C and in clay at 25°C are consistent with experimental data (Table 2). We imposed fixed geochemical conditions at the outer model boundary. The coupled transport and geochemical equations were solved using the Sequential Non-Iterative method.
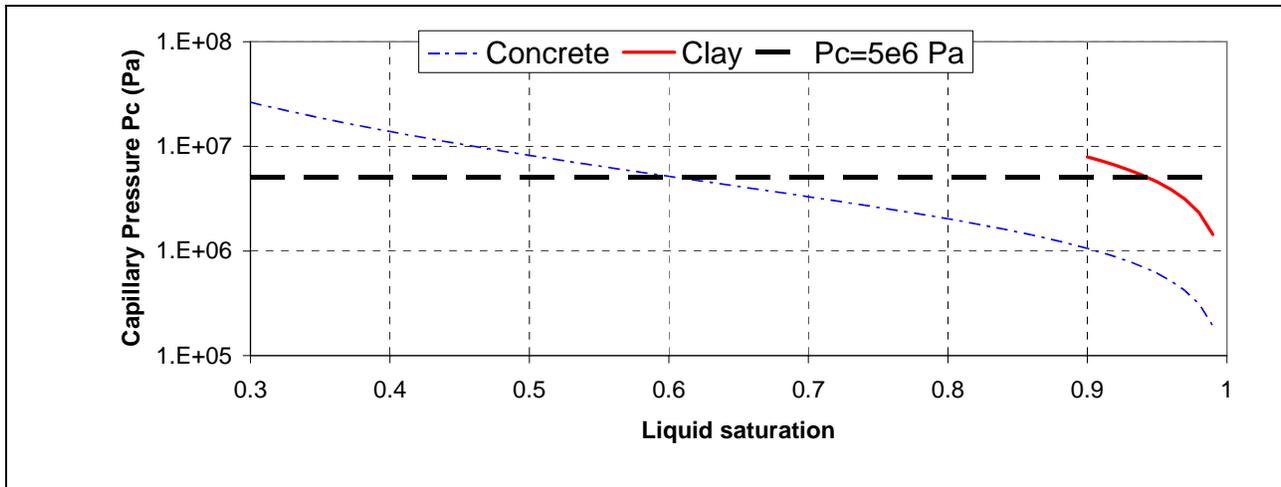
Figure 3. Van Genuchten function of concrete and clay capillary pressure used in the base-case simulation

Figure 4. Initial and secondary mineral phases considered in the base-case simulation

Table 1. Hydraulic and thermal properties (base-case)

Properties	Concrete	Clay
Van Genuchten Po (Pa)	2×10^6	15×10^6
Van Genuchten m	0.317	0.317
Specific Heat (J/kg K)	917	817
Permeability (m^2)	1.77×10^{-19}	10^{-20}
Porosity	0.2	0.144

Table 2. Initial composition of concrete and clay pore waters (total aqueous concentration in molal)

Species	Concrete	Clay
pH	11.7	7.6
'Ca++'	0.1883E-01	0.1484E-01
'Mg++'	0.1418E-07	0.1309E-01
'Na+'	0.2022E-01	0.3192E-01
'Cl-'	0.1011E-01	0.3030E-01
'SiO2(aq)'	0.2654E-05	0.9976E-04
'HCO3-'	0.8881E-05	0.6775E-03
'SO4--'	0.1583E-03	0.3180E-01
'K+'	0.1011E-01	0.4168E-02
'Al+++'	0.6675E-05	0.1489E-07

RESULTS AND DISCUSSION

Base-Case Simulation

First, we used the base-case setup discussed above to simulate the reactive transport model response to the alkaline and thermal perturbation.

Spatial evolution of temperature

A maximum temperature around 70°C at the canister-concrete interface is reached about 10 years after waste emplacement (Figure 5). This prediction is consistent with the ANDRA design (2005). At the concrete-clay interface (X=5m in Figure 5), the maximum temperature is about 65°C. After 2000 years, the difference between the calculated temperature and the ambient temperature (25°C) is less than 5°C.
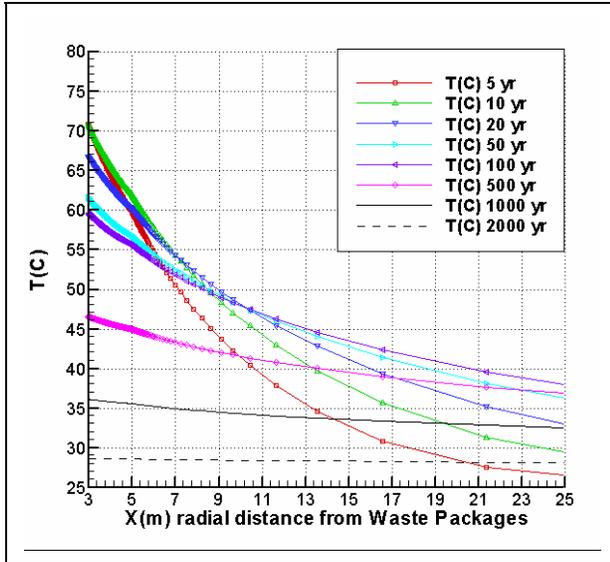
Figure 5. Spatial evolution of the temperature around the waste packages

Concrete resaturation time

Because of the ventilation during the emplacement period, the concrete barrier will be initially only partially water-saturated and with a lower pressure than in surrounding clay. The clay pore water will be therefore driven to the concrete under both hydraulic pressure and capillary pressure gradients. The period necessary to reach complete resaturation is predicted to last 1800 years after emplacement (Figure 6). This resaturation time depends on many parameters (permeability, capillary pressure of concrete/clay) and affects the possibility of gas phase diffusive transport.
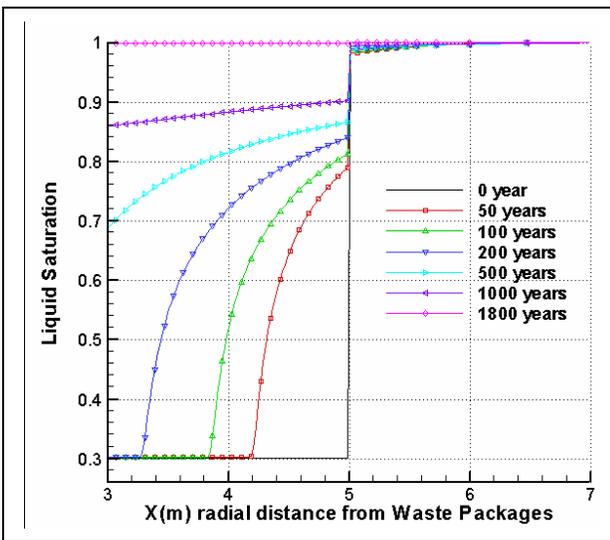
Figure 6. Spatial evolution of the liquid saturation in the concrete barrier (3m<X<5 m)

Carbonation of concrete

During the early period of resaturation concrete, the high CO_2 partial pressure in surrounding clay pore will be redistributed by gas phase diffusive transport. The high pH of concrete will cause the solubilization following the reaction $CO_2(g) + 2OH^- \rightarrow CO_3^{--} + H_2O$ (Figure 7).
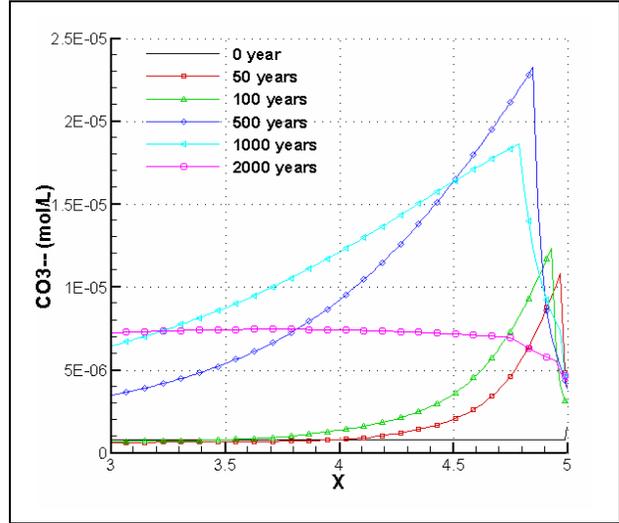
Figure 7. Spatial evolution of CO_3^{--} and Ca^{++} in concrete (3m<X<5 m)

This solubilization will cause in turn the following carbonation of concrete by dissolution of portlandite and precipitation of calcite : $CO_3^{--} + Ca(OH)_2(s) \rightarrow CaCO_3 + 2OH^-$ (Figure 8).
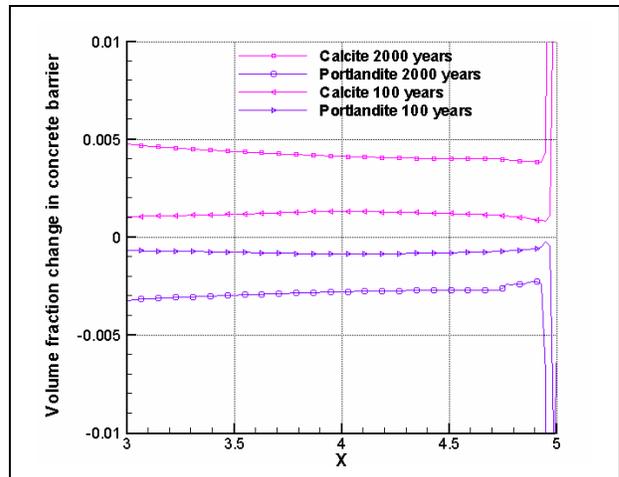
Figure 8. Dissolution of portlandite and precipitation of calcite in concrete (3m<X<5 m)

It can been seen in Figure 8 that this carbonation process is however limited, with a maximum change in portlandite volume fraction within 2000 years of -0.003, i.e. about 10% of the initial value. This process of degassing of CO_2 and therefore the carbonation

process will be increased by the heating due to the waste packages (Figure 9). These processes will be discussed in the following sensitivity analysis.
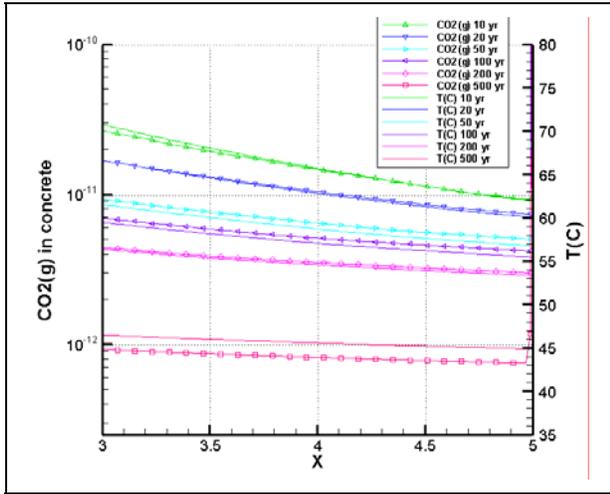
Figure 9. $CO_2(g)$ in   volume   fraction   and temperature in concrete (3m<X<5 m)

Porosity change

The carbonation process described above causes only a slight decrease of porosity (about –0.3%) at the canister-concrete interface. It can be seen that the major porosity change occurs in response to the pH gradient at the concrete-clay interface (Figure 10).
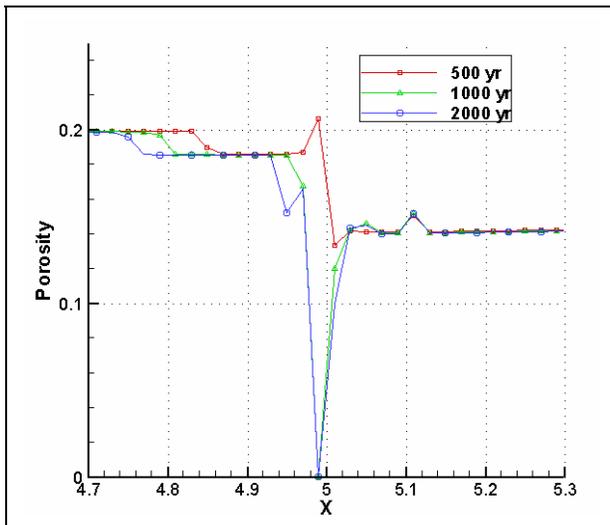
Figure 10. Spatial evolution of porosity at concrete-clay interface (base case)

There is even an occlusion of the porosity, i.e. a volume fraction change equal to the porosity after 900 years. To further understand the reactions that cause this drastic change, the major volume fraction changes of minerals are plotted after 2000 years. It can be seen that most of the change in porosity is

caused by precipitation of torbermorite (Figure 11), which has a very high molar volume (301 cm^3/mol). The other major reaction paths in concrete are (1) hydrogarnet and portlandite dissolution and (2) monosulfoaluminate → ettringite. In clay, the major paths are (3) dolomite → calcite and (4) montmorillonite-Ca + quartz → illite + saponite-Ca. These reactions paths are very similar to the reactions identified at 25°C by Lagneau (2002) and Gaucher et al. (2004).
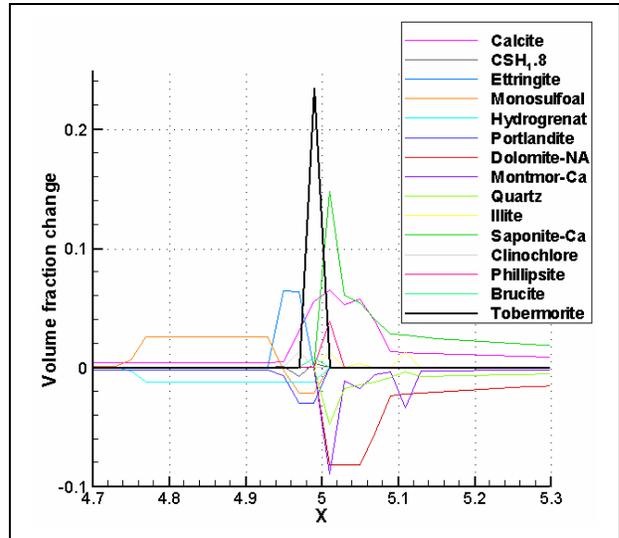
Figure 11. Volume fraction change at concrete/clay interface after 2000 years (base-case)

Sensitivity Analysis

Parameters for sensitivity analyses were selected to examine uncertainties in a wide range of physico-chemical processes without making a priori assumptions about the relative importance of different feedbacks. The base-case simulation was perturbed by setting a parameter to a minimum, intermediate or maximum value or by switching on/off a key process (Table 3). The feedback of the porosity on the diffusion coefficient (e.g. Archie Law) is not considered in this preliminary study.

Inhibition of tobermorite precipitation

Because tobermorite precipitation has been identified in the base-case simulation as a key process for the porosity change, the previous simulations are repeated without allowing this phase to form.

Carbonation prediction

There is no carbonation when an initial fully water-saturated condition is imposed in the concrete. Figure 12 shows that the carbonation in concrete is indeed caused by the gas phase diffusive transport of CO_2. This process increases with increasing temperature as shows the comparison of Figure 8 and Figure 13.

Table 3. Parameter values (grey shading denotes settings in the base-case scenario)

Parameter/Property	Low	Intermediate	High	Switch
Water diffusion coefficient(m²s⁻¹)	1e-11	1e-10	-	
Thermal conductivity (W/mK)				
Concrete (at 0.3 water saturation)	1	1.5	2	
Clay (at full water saturation)	-	1.3	2	
Porosity in clay	0.1	0.144	-	
Gaseous diffusive transport in concrete				On/Off
Initial fully water-saturated conditions in concrete				On/Off
Initial water saturation in concrete		0.3	0.5	
Isothermal conditions (°C)	25		50	On/Off
Tobermorite precipitation				On/Off
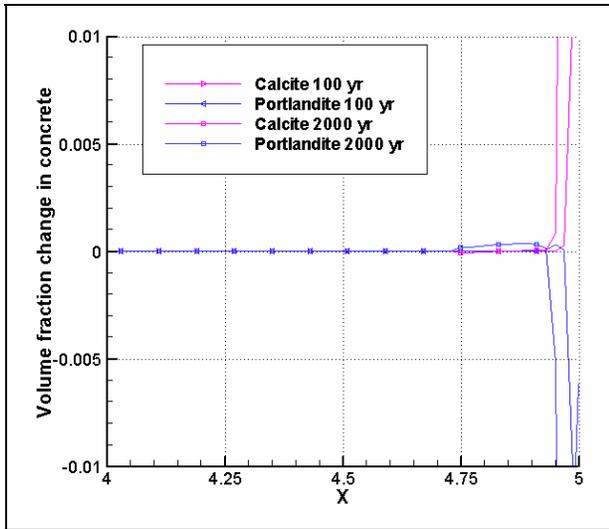
Figure 12. Volume fraction change of portlandite and calcite without gaseous diffusive transport
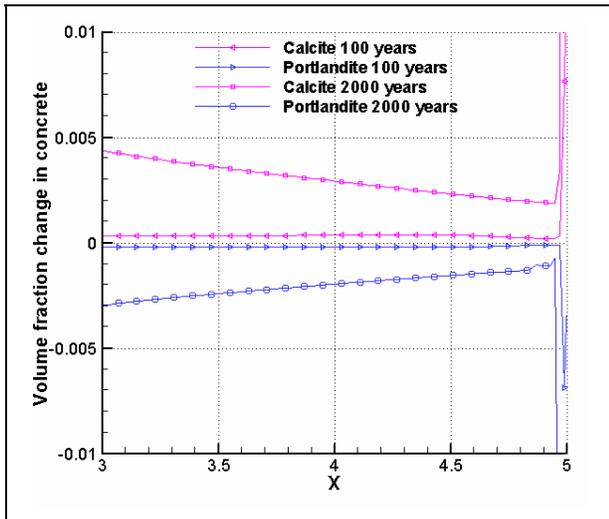
Figure 13. Carbonation process in concrete with isothermal conditions (25°C)

Uncertainty in predicted porosity change

In order to evaluate the uncertainty of prediction of porosity change at the interface, the changes of all simulations of Table 3 are plotted in Figure 14.
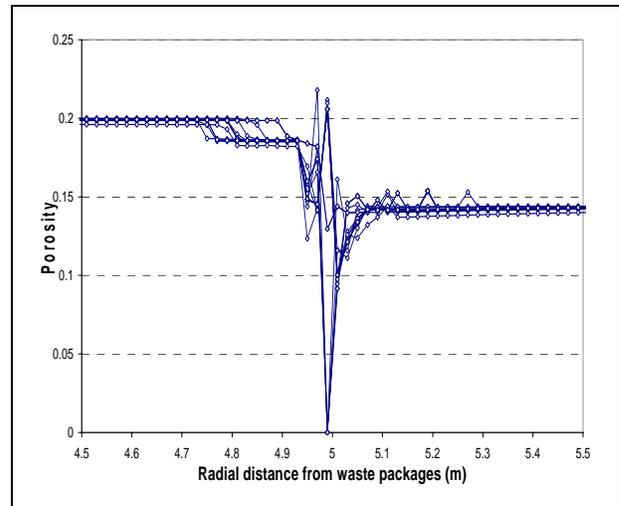
Figure 14. Porosity at the interface concrete/clay after 2000 years for all simulations

It can be seen that the change of porosity after 2000 years depends on many parameters and particularly at the first node in concrete (X=4.99, Figure 14), where the sealing occurred in the base-case.

CONCLUSIONS

The two-phase non-isothermal base-case standard simulation presented in this paper reveals significant coupled thermal, hydrological and chemical processes (THC) : a limited carbonation along the entire width of the concrete barrier and a possible drastic change of the porosity at the concrete/clay interface before 2000 years. A first sensitivity analysis shows that the resaturation and the heating

will be large enough and of long enough duration to cause a limited carbonation in all concrete. On the other hand, the change in porosity is maximum at the concrete/clay interface but the extent of this change depends on many parameters. Therefore, these results should be considered as preliminary. The effect of mineral precipitation under kinetic constraints, rather than local equilibrium, will deserve further investigation. The detailed impact of different parameter perturbations, both individually and simultaneously, in this highly coupled problem will be the subject of further research.

ACKNOWLEDGMENT

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