INTEGRATED THERMODYNAMIC MODELING APPROACH FOR PREDICTING LONG-TERM PERFORMANCE OF CONCRETE/BENTONITE ENGINEERED BARRIER SYSTEMS IN A GEOLOGICAL REPOSITORY FOR RADIOACTIVE WASTE DISPOSAL

Yogarajah ELAKNESWARAN*, Toyoharu NAWA* , Tsutomu SATO*, Ryo NAKABAYASHI*
Nicolas C. M. MARTY**
Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, JAPAN*
BRGM, 3 Avenue C. Guillemin, F-45060 Orleans, Cedex 2, FRANCE**

ABSTRACT**:** In the context of global warming, nuclear energy contribute a significant part of our energy production without CO_2 emissions. The safe operation of nuclear power plants and managing the nuclear facilities is growing importance in the nuclear industry. The advances in concrete and bentonite play an important role in creating cost efficient and durable structures in nuclear facilities. Cementitious materials are extensively used for encapsulation, back filling, and grouting purposes in deep geological repository for long-lived radioactive wastes. Bentonite is an important component of engineered barrier systems of high-level radioactive waste. Therefore, material issues are important in the entire process of nuclear waste management. A key consideration in the nuclear waste management is the development of a highly durable waste package that ensures the long-term performance of these materials and the isolation of radionuclides. The long-term performance of concrete/bentonite barrier system has been investigating for safe disposal of radioactive waste, however remains poorly understood. A considerable amount of research has been carried on the degradation of concrete and bentonite materials in geological repository. However, to the best knowledge of authors, very few models exist to predict the long-term performance of these materials under coupling different degrading mechanisms. In this study, an integrated thermodynamic model has been developed to predict the long-term performance of concrete/bentonite barrier system under coupling multi-species transport and dissolution. The simulation results give many details regarding the mineralogical changes and ionic concentration in concrete/bentonite systems. Some of the important parameters have been identified on the degradation of concrete and bentonite materials. The proposed integrated thermodynamic model needs long-term experimental validation in the context of safety assessment of the system. The comparison of the simulated results to natural analogues seems more realistic.

KEYWORDS: Thermodynamic model, multi-ionic transport, radioactive waste

1. INTRODUCTION

A rapid growing world population suggests the important role of nuclear power in the future for demand of more electricity. Further, nuclear power is a key element in world energy strategies concerning the availability of energy sources and climate changes. However, the managing the nuclear waste is major socio-political and environmental challenges. Unlike to other waste, nuclear waste contains components that are unstable due to decay of radioactive elements. Therefore, it requires many approaches to protect both human and environment from the radiation. An isolation of nuclear waste from the appropriate environment and allow the radioactive constituents to decay is the currently accepted method to manage the nuclear waste. Internationally different kinds of radioactive waste are being or planned to be disposed in different types of geological repository (Metcalfe, *et al.*, 2004). The deep geological repository concepts extensively use cementitious and bentonite materials. These materials behave as physical and chemical barrier to radionuclides migration over the long-term. The potential variation of chemical and physical properties of these materials with time is an important factor to maintain the performance over the time scale required. Further, concrete-bentonite interaction is one of the important phenomena to evaluate the long-term performance the barrier system.

An important requirement for the nuclear waste disposal system is to provide the reasonable assurance of safety that the waste can be disposed safely under range of anticipated repository conditions. This requires a good understanding of the underlying process affecting the performance of disposal system. This understanding can be incorporated into models to predict the performance of both the disposal system and its components with time. Several modeling studies have been carried out to predict the performance the barrier system (Marty, *et al.*, 2009; Metcalfe, *et al.*, 2004). More research works are needed to couple different degradation mechanisms on the prediction of the performance.

1.1 Objectives

The primary objective of this study is to develop an integrated thermodynamic model for the prediction of long-term performance of concrete/bentonite barrier system. The developed model uses the phase-equilibrium, surface complexation, ion exchange, and multi-component diffusion modules in PHREEQC (Parkhust, 1999) to consider various chemical behaviors involved in the degradation. A sensitive analysis on important parameters which affecting the performance of barrier system is conducted.

2. DESCRIPTION OF THE MODELS

In this study, a geochemical transport code PHREEQC was used to perform all the calculations reported below (Parkhust, 1999). The speciation, sorption, exchange, and multi-ionic transport processes were calculated based on the built-in models in PHREEQC and thermodynamic data. The thermodynamic properties of various minerals and aqueous species were collected from the BRGM database (THERMODDEM) (Blanc, *et al.*, 2010a, 2010b). It is available at http://thermoddem.brgm.fr.

2.1 Phase-equilibrium model

This model is used to define the amount the pure phases that can react reversibly with an aqueous phase to achieve equilibrium. The pure phases will dissolve or precipitate to achieve the equilibrium or will dissolve completely. The equilibrium reactions are expressed by mass-action equations (Appelo, *et al.*, 2009). In general, pure-phase equilibrium can be written as:

$$K_p = \prod_i \left(\gamma_i c_i\right)^{n_{i,p}} \qquad (1)$$

where K_p is the thermodynamic equilibrium constant for the phase p, γ_i is the activity coefficients of ion i, c_i is the concentration of ion i, and $n_{i,p}$ is the stoichiometric coefficient of ion i in the phase p. The activity coefficients are calculated according to the extended Debye-Huckel equation (Appelo, *et al.*, 2009):

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + b_i I \tag{2}$$

where A and B are the temperature dependent coefficients, and a_i and b_i are ion-specific fit parameters. Ionic strength, I, can be described as:

$$I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \tag{3}$$

where z_i is the charge number of ion i. The calculations can be carried out using PHREEQC. The input data include the name of the phase (defined by chemical reaction, equilibrium constant and standard heat of reaction), the specified saturation index, and the amount of the phases present in moles. In this study, the phase-equilibrium model was applied for thermodynamic equilibrium reactions between phases of concrete and bentonite, and pore solution as well as equilibrium reactions between phases of concrete and exposure solution.

2.2 Surface complexation model

The adsorption of ions on the charged surface is often modeled as surface complexation reactions. A generalized two-layer surface complexation model, which includes electrostatic interactions between adsorbing species and surface sites, built-in PHREEQC has been incorporated to consider the effect of surface charge on the ionic transport (Dzombak, *et al.*, 1990). In the model, all specifically adsorbed ions are assigned to a surface layer and all non-specifically adsorbed ions are assigned to diffuse layer. A Gouy-Chapman theory is assumed for ionic distribution in the diffuse layer. Further, the model assumes that the activity of surface species is numerically equal to their concentration. The surface charge is caused by ionization of all surface sites through proton exchange reactions as well as surface coordination reactions with cations and anions. The surface charge density is the amount of charge per area of the surface materials (Dzombak, *et al.*, 1990):

$$\sigma = \frac{F}{AS}\left[\left(\equiv SiOH_2^+\right) + \left(\equiv SiOM^+\right) - \left(\equiv SiO^-\right) - \left(\equiv SiA^-\right)\right] \tag{4}$$

where F is Faraday constant (96,485 C/mol), A is specific surface area (m^2/g), S is solid concentration (g/l), $\equiv SiOH_2^+$ and $\equiv SiO^-$ are adsorption densities of protons and hydroxyl ions (mol/l), and $\equiv SiOM^+$ and $\equiv SiA^-$ are adsorption densities of specifically adsorbed cations and anions (mol/l). According to Gouy-Chapman theory (for a symmetrical electrolyte with valence Z), the surface charge density (σ_d (C/m^2)) is related to surface potential (ψ_0 (V)) by:

$$\sigma_d = \left(8000 \varepsilon \varepsilon_0 RTc\right)^{\frac{1}{2}} \sinh\left(\frac{ZF\psi_0}{2RT}\right) \tag{5}$$

where R is the universal gas constant, T is the absolute temperature (K), ε is the dielectric constant of water (dimensionless), ε_0 is the permittivity of free space ($8.854 * 10^{-12}$ C/V.m), and c is the molar electrolyte concentration. The surface charge of the surface is balanced by the excess charge in the diffuse layer through:

$$\sigma + \sigma_d = 0 \tag{6}$$

This model was used to characterize the charged surface/pore solution interface.

2.3 Ion exchange model

The reaction among cations sorbed on the charged surface and in the solution is called cation exchange. Ion exchange model is built-in PHREEQC with considering mass-action equation and mole-balance equation for exchange sites (Appelo, *et al.*, 2009). Ion exchange reactions are simulated as ion association reactions in the form of half reactions. For exchange of Ca^{2+} for Na^+ can be written as:

$$1/2Ca^{2+} + Na - X \leftrightarrow 1/2Ca - X_2 + Na^+ \tag{7}$$

$$K_{Ca\backslash Na} = \frac{\left[Ca - X_2\right]^{0.5}\left[Na^+\right]}{\left[Ca^{2+}\right]^{0.5}\left[Na - X\right]} \tag{8}$$

The Equation (7) is spilt two half reaction:

$$Ca^{2+} + 2X^- \leftrightarrow CaX_2 \tag{9}$$

$$Na^{+} + X^{-} \leftrightarrow NaX \tag{10}$$

where X^- indicates the exchanger surface, and CaX_2 and NaX are exchangeable cations. The use of equivalent fraction of exchangeable cations for activities in Equation (7) is known as Gaines-Thomas convention (Appelo, *et al.*, 2009). The main input data to PHREEQC for performing these calculations are the chemical equation for mole-balance and mass-action expressions, and equilibrium constant and its temperature dependence.

2.4 Multi-component diffusion model

The ions in a solution have an effect from the co-existing ions. Thus, diffusion coefficients of cations, anions, and neutral species in a solution have different values. However, most of the models to calculate the ionic transport into concrete or bentonite assume the same diffusion coefficient for all the species. Further, the ionic diffusion into concrete or bentonite materials depends on the existence of electrical double layer, however, this well-known feature has not included in the current models. The multi-component diffusion (MCD) module available in PHREEQC can be used to simulate the ionic transport in concrete and bentonite materials because it accurately simulates the multi-component diffusion through free solution as well as through diffuse double layer (DDL). The basic theory for calculating MCD for all species is described elsewhere (Appelo, *et al.*, 2007). The multi-component diffusion equation is as follows:

$$J_i = -D_{w,i}\left[\frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)}+1\right]\frac{\partial c_i}{\partial x} + D_{w,i} z_i c_i \; \frac{\sum_{j=1}^{n} D_{w,j} z_j \left[\frac{\partial \ln(\gamma_j)}{\partial \ln(c_j)}+1\right]\frac{\partial c_j}{\partial x}}{\sum_{j=1}^{n} D_{w,j} z_j^2 c_j} \tag{11}$$

where J_i is the flux of a species i (mol/m^2/s), c_i is the concentration of ion i, γ_i is the activity coefficients of ion i, $D_{w,i}$ is the tracer diffusion coefficient of ion i (m^2/s), z_i is the charge number of ion i, and the subscript j is introduced to show that these species are for the potential term. The above Equation (11) can be used in the free solution as well as in the DDL; only the concentrations of ions differ in the free solution and the DDL. The MCD can be incorporated in PHREEQC with the keyword "–multi_d". The MCD module calculates fluxes for all species separately in the charged free solution and in the DDL, and then sums them up for the interface between two cells. In the proposed model, the MCD model was applied with other models that take into account the phase–equilibrium, surface complexation, and ion-exchange reactions.

3. SYSTEM CONFIGURATION FOR THE SIMULATION

A concrete contact with bentonite was considered for the simulations. Geometry of the analysis is illustrated in Figure 1. The thickness of concrete and bentonite was fixed to 1 m, and the spatial discretization is shown in Figure 1. One side of concrete was considered to be directly contact with groundwater and other side of the concrete contacted with bentonite. A one-dimensional transport coupled with chemical reactions was considered in the model. In the analysis, chemical reactions and multi-ionic transport were calculated simultaneously. The schematic description of the multi-ionic transport and chemical reactions process in the concrete/bentonite system is illustrated in Figure 2. The integrated model allows predicting the spatial and time variation of minerals compositions and pore water concentrations. It was assumed that the pore volume of concrete and bentonite materials filled with pore solution. The transport of ions through concrete and bentonite materials was considered a pure diffusion process in a saturated medium with interconnected porosity. Initial and final boundary conditions were set to the constant groundwater concentration and zero flux respectively. The exposure groundwater was in equilibrium with concrete before it enters into the pore solution. Thus, the concentration of the exposed solution changes with thermal equilibrium. Changes in the porosity during the simulation were calculated from the changes of volume of the minerals. The simulation will be stopped when the re-calculated porosity falls below the porosity limit (0.01). It was assumed that the concrete/bentonite system in the isothermal conditions at 25 °C and the effects of carbonation is ignored in this investigation. The simulation was carried out over a period of 500 years.

Table 1 Ground water composition (JNC, 2000)

Chemical composition	
pH	8.5
Eh (mV)	-281
Element	**Concentration (mol/l)**
Na	$3.6*10^{-3}$
K	$6.2*10^{-5}$
Ca	$1.1*10^{-4}$
Mg	$5.0*10^{-5}$
B	$2.9*10^{-4}$
P	$2.9*10^{-6}$
F	$5.4*10^{-5}$
Cl	$1.5*10^{-5}$
SO_4	$1.1*10^{-4}$
NO_3	$2.3*10^{-5}$
CO_3	$3.5*10^{-3}$
Si	$3.4*10^{-4}$

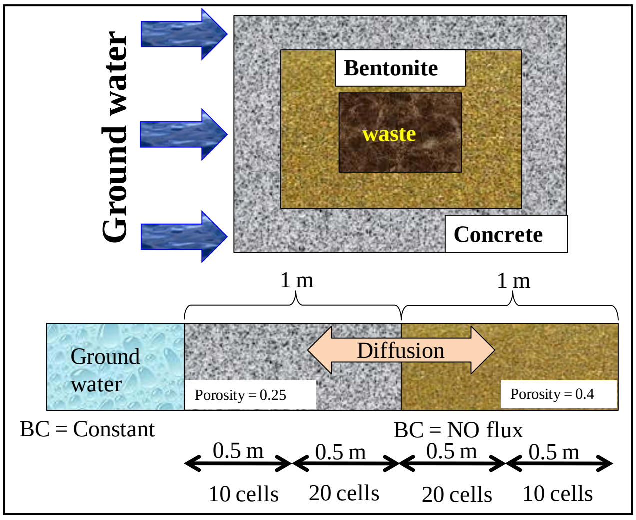

Figure 1 Conceptual model for concrete/bentonite barrier system.

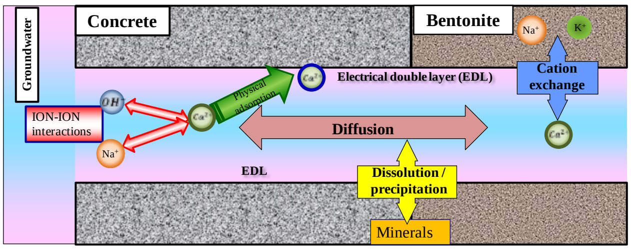

Figure 2 Schematic diagram of the processes in concrete and bentonite materials.

4. CHARACTERISTICS OF THE MATERIALS

Physical and chemical properties of concrete and bentonite materials are needed in advance as the input data to the model. In the simulations, ordinary Portland cement concrete and Kunigel V1 were considered for concrete and bentonite materials respectively. The degradation of concrete depends on the type of external solution. As illustrated in Figure 1, the concrete is in contact with groundwater during the exposure period of 500 years. The chemical composition of groundwater used in the simulation is given in Table 1. The initial amount of minerals in the materials is needed to run the model. The mineralogical composition of concrete is given in Table 2, and it is considered as a matured concrete. Aggregates (both fine and coarse) were assumed to be chemically inert and to have no accessible porosity. Thus, transport of ions through concrete results from the transport process in the cement matrix. The assumed porosity for the concrete is equal to the porosity of hydrated cement paste. It is equal to 0.25 (Elakneswaran, *et al.*, 2009). The ionic concentration in the pore solution of concrete is shown in Table 3. The mineral composition of Kunigel V1 bentonite is shown in Table 4. The porosity of the bentonite assumed to be equal to 0.4, and it is initially filled with pure water. In this study, THERMODDEM database was used for the thermodynamic properties of aqueous species and the minerals phases (Blanc, *et al.*, 2010a, 2010b). The thermodynamic properties of minerals considered in this simulation are tabulated in Table 7. Further, the simulation considers multi-species transport in the concrete/bentonite system. Thus, each species has different diffusion coefficients in the free water at different temperatures (Mills, *et al.*, 1989). The self-diffusion coefficients of ions used in the simulation are summarized in Table 5.

Table 2 Mineralogical composition of concrete (Elakneswaran, *et al.*, 2009)

Element	Volume fraction (%)
C-S-H:1.6	11.17
Portlandite	3.86
Monosulfoaluminate	0.92
Ettringite	0.45
Aggregates	83.6

Table 3 Pore solution composition of concrete (Jacques, *et al.*, 2010)

Chemical composition	
pH	13.8
Element	Concentration (mol/l)
Na	$6.82*10^{-2}$
K	$1.61*10^{-1}$
Ca	$1.58*10^{-3}$
Mg	$1.93*10^{-9}$
Cl	$1.4*10^{-3}$
SO_4	$2.81*10^{-4}$
Al	$1.38*10^{-5}$
CO_3	$8.25*10^{-5}$
Si	$3.4*10^{-5}$

Table 4 Mineralogical composition of bentonite (JNC, 2000)

Element	Volume fraction (%)
Analcime	2.63
Calcite	1.60
Amorphous silica	33.22
Dolomite	1.51
Na-Montmorillonite	31.09
Pyrite	0.22
Quartz	29.72

Table 5 Self-diffusion coefficients of ions in free water at 25 °C (Mills, *et al.*, 1989)

Ions	Diffusion coefficient * 10^{-9} (m^2/s)
Al^{3+}	0.548
Ca^{2+}	0.792
CO_3^{2-}	0.923
Cl^-	2.033
Fe^{2+}	0.715
K^+	1.957
Mg^{2+}	0.706
Na^+	1.334
NO_3^-	1.903
OH^-	5.280
SO_4^{2-}	1.065

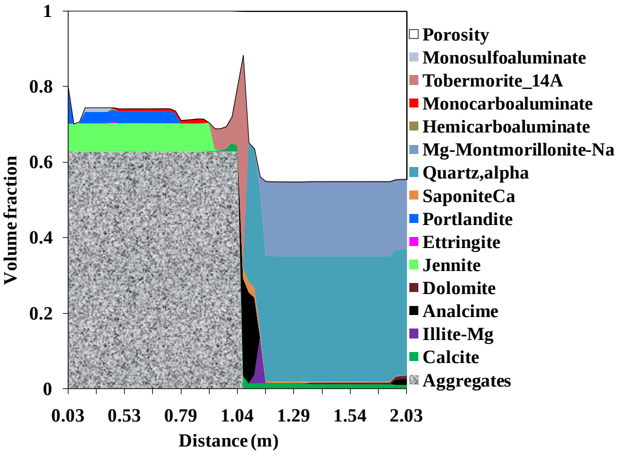

Figure 3 Representation of the distribution of the minerals after 500 years of groundwater transport and concrete/bentonite interactions. The simulation considers thermodynamic equilibrium and multi-component diffusion only.

5. MODELING RESULTS

Figure 3 shows the simulation results for distribution of solid phases after 500 years of groundwater transport through concrete/bentonite barrier system. Figure 4 shows the ionic concentration profiles in the pore water of concrete and bentonite. The coupled thermodynamic reactions between solid phases and aqueous solution, and multi-component diffusion of ions were taken into account in the model. Figure 3 indicates the reorganization of internal microstructure of concrete and bentonite materials due to chemical reactions and ionic diffusion. The calculation results show that the precipitation of secondary cement hydrates (Monocarboaluminate and hemicarboaluminate) in the concrete due to dissolution of monosulfoaluminate and the diffusion of carbonate ions. Further, C-S-H:1.6 is changed to more stable phase of jennite. Portlandite is completely dissolved near concrete/bentonite interface and forms high pH. Thus, the diffusion of hydroxyl ions in the bentonite is responsible for the dissolution of bentonite minerals (e.g. montmorillonite and amorphous silica) and the precipitation of new secondary minerals (e.g. Sapponite and illite). As can be seen in Figure 3, amorphous silica is completely dissolved in bentonite, and the altered montmorillonite lead to precipitation of secondary analcime at the interface. The dissolution of main minerals in concrete and bentonite lead to increase the porosity of the materials. However, the porosity at the interface of concrete/bentonite is significantly reduced by the precipitation of tobermorite. As indicated in the Figures 3 and 4, concrete/bentonite interaction plays an important role on the precipitation or dissolution of minerals and change of pore water concentration at the interface.

The strong uncertainties lie in the parameters and models on the estimation of mineralogical distribution and pore water concentration. Therefore, sensitive analyses were performed under different parameters or models. The simulation results shown in Figures 3 and 4 indicate that the mineralogical distribution and pore water composition are mainly controlled by the self-diffusion coefficients of ions. In order to understand the effect of self-diffusion coefficient of ions on the mineralogical distribution, the simulation was performed with classic diffusion (all ionic species were assumed to have the same diffusion coefficient of $1.7*10^{-9}m^2/s$) instead of multi-ionic diffusion, and the other modeling parameters were similar to the previous calculation. The simulation result of mineral evolution of solid phases is shown in Figure 5. As can be seen, simulated results by assuming a single diffusion coefficient for all species show qualitatively and quantitatively different mineralogical distribution with respect those obtained when using multi-ionic diffusion (Figure 3). The classic diffusion leads to more alteration front at concrete/bentonite interface. Furthermore, porosity at the interface is increased due to dissolution of bentonite minerals. As comparing Figures 3 and 4, incorporating classic diffusion into the model overestimate the porosity and dissolution of montmorillonite, and underestimate the precipitation of secondarily formed tobermorite at the concrete/bentonite interface. It can be emphasized that the use of classic diffusion method in the model is not sufficient to predict the performance of concrete/bentonite barrier system.

Cation exchange is considered one of the processes that control the cation availability in the pore water and during transport. The ion exchange characteristics of montmorillonite are incorporated in the model through cation exchange reactions. The ions in the pore water of bentonite react to equilibrium with exchanger sites of montmorillonite at all times. The cation exchange capacity (CEC) of montmorillonite and the Gaines-Thomas selectivity coefficients for various ions that compete for the exchanger site are given in Table 6. To evaluate the influence of cation exchange reaction of montmorillonite on the mineralogical distribution of the phases, the ion exchange model for montmorillonite was coupled with thermodynamic and multi-component models for the system. The simulated mineral evolution of solid phases after 500 years of groundwater transport and concrete/bentonite interactions is shown in Figure 6.

It can clearly be seen that the simulated result by incorporating cation exchange reactions of montmorillonite show different mineralogical distribution than those shown in Figure 3 especially at the concrete/bentonite interface. Porosity clogging is appeared at the interface due to large amount of secondarily formed tobermorite and chabazite. It can be inferred that the inclusion of cation exchange reactions of minerals is important for very accurate prediction of the performance of concrete/bentonite barrier system.

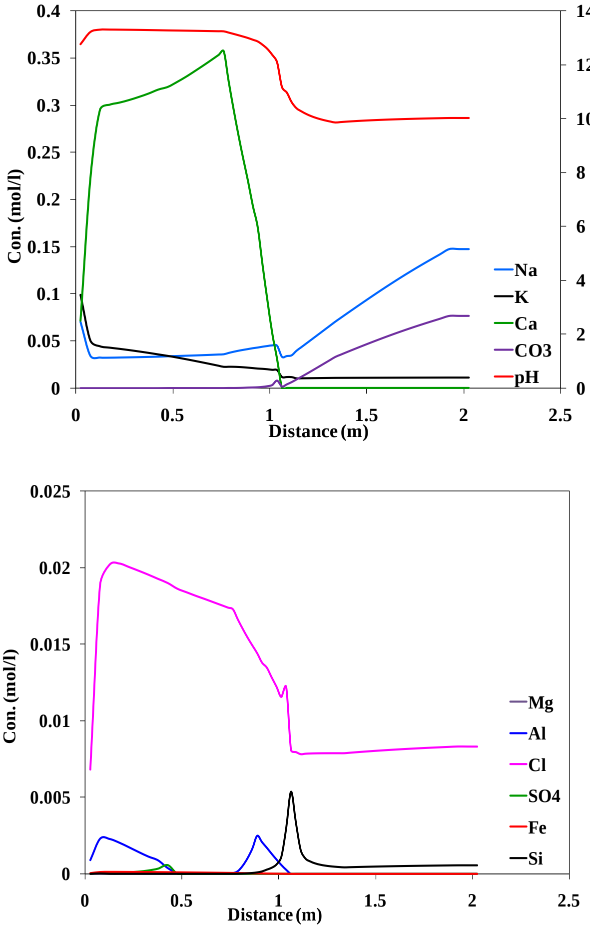

Figure 4 The concentration of ions in the pore solution after 500 years of groundwater transport and concrete/bentonite interactions. The simulation considers thermodynamic equilibrium and multi-diffusion only.

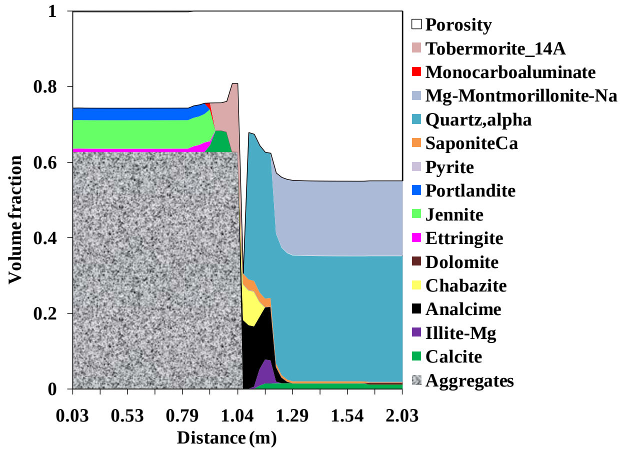

Figure 5 Representation of the distribution of the minerals after 500 years of groundwater transport and concrete/bentonite interactions. The simulation considers thermodynamic equilibrium and classic diffusion only.

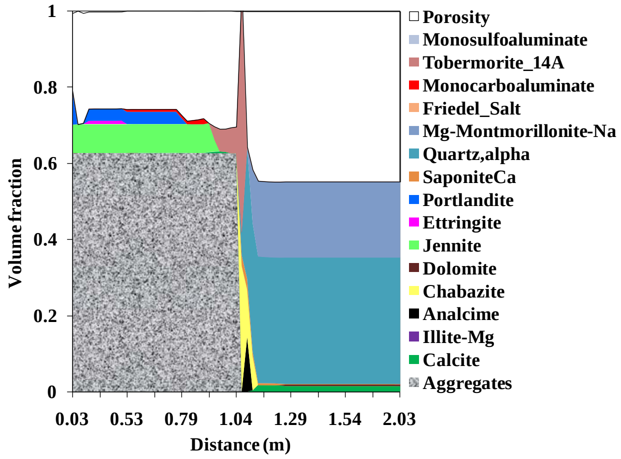

Figure 6 Representation of the distribution of the minerals after 500 years of groundwater transport and concrete/bentonite interactions. The simulation considers thermodynamic equilibrium, multi-diffusion, and ion exchange.

Table 6 Cation exchange parameters for montmorillonite (JNC, 2000)

CEC [meq (100 g)$^{-1}$]	60.1
Gaines-Thomas selectivity coefficients	
2XNa－X_2Ca	0.69
XNa－XK	0.42
2XNa－X_2Mg	0.67

In this study, the influence of self-diffusion coefficient of species and cation exchange mechanism of montmorillonite on mineralogical distribution and concentration of pore water was investigated. However, it has been reported that several other parameters or models, which are sensitive to principal outputs of the simulations (Marty, *et al.*, 2009; Metcalfe, *et al.*, 2004): minerals considered in the simulation, thermodynamic database, dissolution and precipitation kinetics of the minerals, spatial refinement, types of the groundwater, interface chemistry of the minerals, etc. Therefore, a complete sensitive analysis is needed to evaluate the long-term performance of engineered barrier system.

6. CONCLUDING REMARKS

The safe management of nuclear waste is a significant challenge to human ingenuity for sustainable nuclear energy; more precisely, finding a proper solution for radioactive waste disposal over the long-term is a key issue. Models link between theoretical basis of the performance of nuclear waste repository and use this knowledge on safety assessment. This paper describes the performance of concrete/bentonite barrier system by coupling different degradation mechanisms. An integrated thermodynamic model has been developed to understand the degradation of concrete and bentonite materials. Several sensitive parameters or models are identified on mineralogical distribution and pore water composition of concrete and bentonite materials. The self-diffusion coefficient of each ionic species show qualitatively and quantitatively different mineralogical distribution with respect those obtained when using a single diffusion coefficient. Further, incorporation of cation exchange in montmorillonite leads to change the mineral distribution and clog the porosity at the interface. Thus, a proper model development is needed to evaluate the performance of concrete/bentonite barrier system, and it should be validated with long-term experiments.

ACKNOWLEDGEMENTS

The Japan Society for the Promotion of Science, Grants-in-Aid for JSPS fellows Research No: 2100930609, Representative: Prof. T. Sato), is gratefully acknowledged for funding this present research work.

REFERENCES

Appelo, C. A. J., & Postma, D. (2009). *Geochemistry, groundwater and pollution*: CRC Press Taylor & Francis Group.

Appelo, C. A. J., & Wersin, P. (2007). Multicomponent Diffusion Modeling in Clay Systems with Application to the Diffusion of Tritium, Iodide, and Sodium in Opalinus Clay. *Environmental Science & Technology, 41*(14), 5002-5007.

Blanc, P., Bourbon, X., Lassin, A., & Gaucher, E. C. (2010a). Chemical model for cement-based materials: Temperature dependence of thermodynamic functions for nanocrystalline and crystalline C-S-H phases. *Cement and Concrete Research*, *40*(6), 851-866.

Blanc, P., Bourbon, X., Lassin, A., & Gaucher, E. C. (2010b). Chemical model for cement-based materials: Thermodynamic data assessment for phases other than C-S-H. *Cement and Concrete Research*, *40*(9), 1360-1374.

Dzombak, D. A., & Morel, F. M. M. (1990). *Surface complexation modelling: Hydrous Ferric oxide*: A Wiley-Interscience Publication.

Elakneswaran, Y., Nawa, T., & Kurumisawa, K. (2009). Electrokinetic potential of hydrated cement in relation to adsorption of chlorides. *Cement and Concrete Research, 39*(4), 340-344.

Jacques, D., Wang, L., Martens, E., & Mallants, D. (2010). Modelling chemical degradation of concrete during leaching with rain and soil water types. *Cement and Concrete Research, 40*(8), 1306-1313.

JNC (2000). *H12:Project to establish the scientific and technical basis for HLW disposal in Japan*: Japan Nuclear Cycle Development Institute.

Marty, N. C. M., Tournassat, C., Burnol, A., Giffaut, E., & Gaucher, E. C. (2009). Influence of reaction kinetics and mesh refinement on the numerical modelling of concrete/clay interactions. *Journal of Hydrology, 364*(1-2), 58-72.

Metcalfe, R., & Walker, C. (2004). *Proceedings of the international workshop on bentonite-cement interactions in repository environments.* Paper presented at the NUMO-TR-04-05.

Mills, R., & Lobo, V. M. M. (1989). *Self-diffusion in electrolyte solutions: a critical examination of data compiled from the literature*: Elsevier Science Publishers B. V.

Parkhust, D. L., Appelo, C. A. J (1999). *A computer program for speciation, batch —reaction, one —dimensional transport and inverse geochemical calculations.*

Table 7 Thermodynamic properties at 25℃ of minerals considered in the simulation (Blanc, *et al.*, 2010a, 2010b)

Minerals	Composition	Log K	Molar volume (Cm^3/mol)
Analcime	$Na_{0.99}Al_{0.99}Si_{2.01}O_6:H_2O$	6.64	96.68
Amorphous silica	SiO_2	-2.70	29.00
Calcite	$CaCO_3$	1.85	36.93
Chabazite	$Ca(Al_2Si_4)O_{12}:6H_2O$	11.52	251.16
C-S-H:1.6	$Ca_{1.60}SiO_{3.6}:2.58H_2O$	28.00	84.68
Dolomite	$CaMg(CO_3)_2$	3.53	64.37
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}:26H_2O$	56.97	710.32
Friedel_Salt	$Ca_4Al_2Cl_2O_6:10H_2O$	74.93	276.24
Illite	$K_{0.85}Mg_{0.25}Al_{2.35}Si_{3.4}O_{10}(OH)_2$	10.25	140.90
Jennite	$Ca_9Si_6H_{22}O_{32}$	147.33	456.40
Monocarboaluminate	$Ca_4Al_2CO_9:10.68H_2O$	80.55	261.96
Monosulfoaluminate	$Ca_4Al_2SO_{10}:12H_2O$	73.08	311.26
Na-Montmorillonite	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	1.32	131.24
Portlandite	$Ca(OH)_2$	22.81	33.06
Pyrite	FeS_2	217.19	23.94
Quartz	SiO_2	-3.74	22.69
Sapponite	$Ca_{0.17}Mg_3Al_{0.34}Si_{3.66}O_{10}(OH)_2$	30.71	136.37
Tobermorite_14A	$Ca_5Si_6H_{21}O_{27.5}$	62.94	351.30