NUMERICAL EVALUATION OF CALCIUM LEACHING FROM CEMENTITIOUS MATERIALS IN CONTACT WITH BENTONITE

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ABSTRACT: The use of concrete with bentonite is being investigated as a barrier material for the radioactive nuclear waste in Japan. Because such waste contains materials with long half-lives, the barrier must remain stable for several tens of thousands of years, which is far longer than the lifetimes of conventional infrastructures under normal use. Here, it is important to investigate the effect of interaction between concrete and bentonite. In this study, a unified approach that can be used for both concrete and bentonite is developed in order to simulate the long-term durability of cementitious composites considering the influence of surrounding bentonite on the degradation process of concrete. To predict the calcium leaching, a multi-phase equilibrium of calcium ions and their transport are formulated on the basis of thermodynamics. For the bentonite, the proposed equilibrium formulation considers the absorbed ions as well as the exchanged ions as the bound ions. The relation was determined based on the experimental results for block sample of compacted dense bentonite. The proposed model is verified by comparing to experimental results that investigate calcium leaching of concrete with bentonite. The analysis revealed that the deterioration of concrete developed rapidly when the bound effect of the surrounding bentonite was taken into account. This is because the pores in the bentonite maintained a low concentration of free calcium ions due to the ion binding effect and the constantly high concentration gradient between the concrete and the surrounding bentonite. In addition, the sensitivity analysis shows that consideration of additional absorbed ions as the bound ions has significant effect on the calcium leaching from concrete with bentonite. They mean that it is important to take into account the effect of bentonite on the degradation process of concrete by the proper model.

KEYWORDS: leaching, concrete, bentonite, engineered barrier, durability, thermodynamics

1. INTRODUCTION

Recently, the performance assessment of the underground nuclear-waste repository has been being discussed in Japan. For the low level radioactive waste, the use of concrete with bentonite is being investigated as a barrier material to isolate the waste from sphere of human activities. The concrete is expected as the barrier having low diffusivity and the bentonite is expected as the barrier having low conductivity. Because such waste contains materials with long half-lives, the barrier must remain stable for several tens of thousands of years, which is far longer than the lifetimes of conventional infrastructures under normal use. Here, it is important to investigate the effect of interaction between concrete and bentonite.

In this study, a multi-phase physicochemical method for simulating the durability of cementitious composites is proposed for predicting the long-term degradation of concrete by calcium leaching

(Maekawa *et al*., 2003; Nakarai *et al*., 2006a, 2006b; Usui *et al*., 2006). In order to consider the influence of surrounding bentonite on the degradation process of concrete, a unified approach that can be used for both concrete and bentonite is developed. To predict the calcium leaching, a multi-phase equilibrium of calcium ions and their transport are formulated on the basis of thermodynamics.

2. MODELING OF CALCIUM LEACHING

2.1 Governing equation

Momentum, energy, and the mass flow of materials must satisfy the laws of conservation. As the governing equation, the following mass conservation equation is applied in terms of the total calcium ions in the pore solution and the solid-phase calcium in the system (Nakarai *et al*., 2006b), in reference to the equation by Gérard *et al*. (2002).

$$\frac{\partial}{\partial t}(\phi \cdot S \cdot C_{ion}) + \frac{\partial C_{bound}}{\partial t} - div J_{ion} = 0 \qquad (1)$$

where, ϕ is the porosity, S is the degree of saturation in the pore spaces, C_{ion} is the molar concentration of calcium ions in the liquid phase [mmol/m^3], C_{bound} is the amount of bound calcium per unit volume [mmol/m^3], and J_{ion} is the flux of calcium ions [mmol/m^2-s].

The porosity of the cementitious materials is calculated in the microstructure model based on the process of hydration hydrate by inputting basic information such as mix proportion, material properties and environmental conditions (Maekawa *et al*., 1999, 2003). The saturation of the cementitious materials is calculated in the moisture model based on the hydration and the pore structure that are calculated in the system (Maekawa *et al*., 1999, 2003). The porosity and the saturation of the

bentonite are calculated from input data (Usui *et al*., 2006). The bound calcium, denoted by C_{bound}, is physicochemically bound and not related to mass transport. For the cementitious composites, C_{bound} is equilibrated with the calcium in the solid phase, C_{solid}, which is present mainly in the cement hydrates of C-S-H gel and calcium hydroxide. For the ordinary soil materials, the amount of bound calcium is assumed to be zero. When the target soil material has the capacity to sorb ions such as mineral clays, the sorbed ions are treated as bound calcium. For bentonite, the binding of calcium ions is also taken into account. The relation between the liquid and bound calcium is determined below.

2.2 Modeling of phase equilibrium of calcium

2.2.1 Phase equilibrium in cementitious material

For the cementitious materials, an isotherm correlation rooted in the model described by Buil *et al*. (1992) is used to uniquely determine the amount of calcium in the solid phase from a given concentration of liquid phase calcium ion (Nakarai *et al*., 2006a; Usui *et al*., 2006).

$$C_{Solid} = f(C_{ion}) = A \cdot \left\{ C_{CSH} \cdot \left(C_{ion}/C_{satu} \right)^{1/3} \right\} + B$$

$$A = \begin{cases} -\dfrac{2}{x_1^3} C_{ion}^{\ 3} + \dfrac{3}{x_1^2} C_{ion}^{\ 2} & (0.0 \leq C_{ion} \leq x_1) \\ 1 & (x_1 < C_{ion}) \end{cases} \qquad (2)$$

$$B = \begin{cases} 0 & (0.0 \leq C_{ion} \leq x_2) \\ \dfrac{C_{CH}}{\left(C_{satu} - x_2 \right)^3} \cdot \left(C_{ion} - x_2 \right)^3 & (x_2 < C_{ion}) \end{cases}$$

where, C_{satu} is the saturated liquid phase calcium ion concentration [mmol/l], x_1 is the concentration of calcium ion when the rapid transition of C-S-H gel into silica gel begins [mmol/l], and x_2 is the concentration of calcium ion when the calcium hydroxide has completely dissolved and the

dissolution of C-S-H gel begins [mmol/l]. In this study, $x_1 = 3.0$ mmol/l and $x_2 = (Csatu - 0.7)$ mmol/l are adopted (Figure 1).
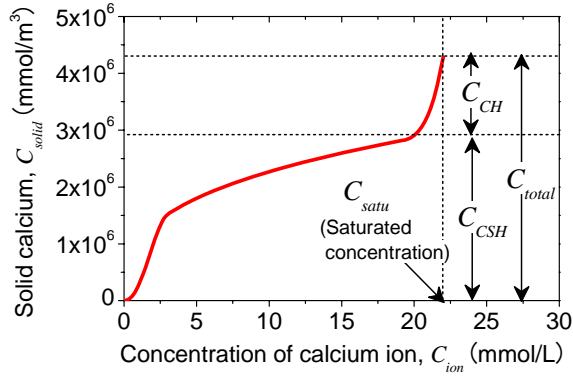

Figure 1. Equilibrium relation of calcium in cementitious material

The parameters in the phase equilibrium (i.e. the amount of calcium and the saturated concentration of calcium ions) are defined not through experiments but by computation. All are calculated as time-dependent variables in order to take into account the influence of mix proportion, ambient conditions, hydration, and degradation due to calcium leaching. The total amount of calcium in the solid phase of the cementitious composite is determined from the chemical composition of the mixture. The amount of calcium hydroxide in the cement paste is determined stoichiometrically using the chemical equations in the multi-component hydration model (Maekawa *et al.*, 1999). The concentration of saturated calcium ions in the liquid phase equates to the concentration of saturated calcium hydroxide in the pore solution in this study.

2.2.2 Phase equilibrium in bentonite
As for the thermodynamic equilibrium of calcium in the bound ion and free ion in the liquid phases in the bentonite, an isotherm correlation was investigated by the experiments (Usui *et al.*, 2006). Two kinds of samples of the bentonite were prepared; non-compacted powdery samples and compacted

cylindrical samples (1.6Mg/m³). The two kinds of samples were immersed in the calcium chloride solution having different concentration under 20 °C, respectively (Figure 2). The solution was stirred every day to make the concentration uniform. After the checking the stability of concentration, the concentrations of free calcium ion and sodium ion in the solution were measured by using the inductively coupled plasma emission spectrometry. Figure 3 shows the example of change in the ion concentration of calcium and sodium in the solution. The concentration of calcium took longer time for the stability that of sodium.

The amount of total bound calcium was calculated by subtracting the amount of free ion from the total amount of calcium in each solution. The amount of cation-exchanged calcium ion was calculated from the amount of the leached sodium ion. Figure 4 shows the results of the experiments and the proposed model for total bound calcium. In the computation of calcium leaching, the amount of calcium per unit volume is used;

$$C_{bound} = 10 \cdot (1 - \phi) \cdot \gamma \cdot c_{bound} \qquad (3)$$

where, γ is the density of bentonite [kg/m³] and c_{bound} is the amount of bound calcium per 100g obtained from the experiments [meq/100g].
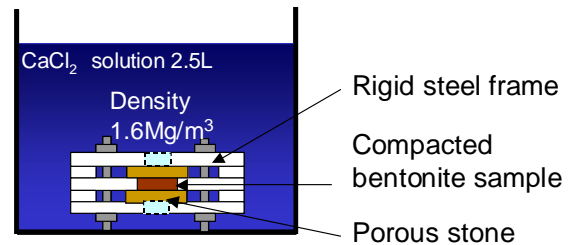

Figure 2. Experiment of compacted bentonite sample for phase equilibrium modeling
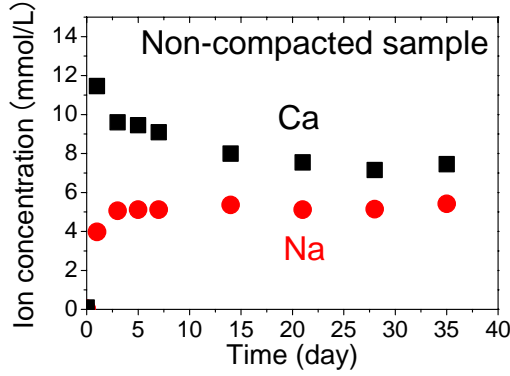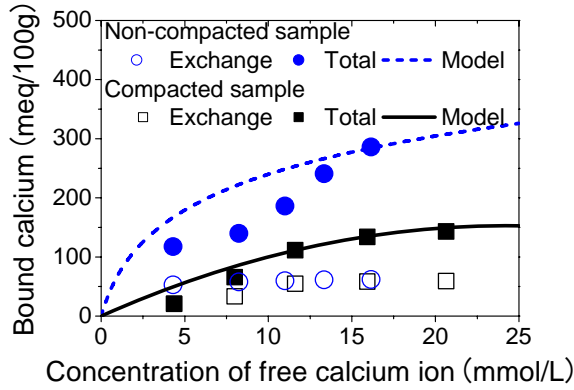
Figure 3. Change in ion concentrations

Figure 4. Equilibrium relation of calcium in bentonite

The amounts of cation-exchanged calcium ion calculated from sodium ion were almost same in the two experiments and they are close to the amount of typical cation exchange capacity (CEC) of the same kind of Na-bentonite (Maeda *et al.*, 1998). On the other hand, the total amounts of bound calcium were larger than the amount of cation-exchanged calcium ion. This means that bentonite has the additional capacity to sorb ions due to other effect such as surface complexation mechanism (Baeyens and Bradbury, 1997). The total amount of bound calcium in the compacted sample was smaller than that in the non-compacted sample. This is because the compacted sample does not have enough space to absorb the additional calcium ion. The validity of the phase equilibriums for the modeling will be discussed by using sensitivity analysis later.

2.3 Modeling of calcium ion transport

When both diffusion and advection are considered, the flux of calcium ions transported in a porous media takes the following form (Maekawa *et al.*, 2003).

$$J_{ion} = -D_{eff} \cdot \nabla C_{ion} + \phi \cdot S \cdot \mathbf{u} \cdot C_{ion} \qquad (4)$$

where, D_{eff} is the effective diffusion coefficient of calcium ion [m²/s], $\mathbf{u}^{T} = [ux\ uy\ uz\ ]$ is the velocity vector of a calcium ion transported by a solution flow [m/s]. The transport properties of ions in porous materials, such as concrete and soils, depend on their pore structures. The effective diffusion coefficient is defined by considering the properties of the pore structures in the concrete and the bentonite. In this study, the pore structure is computationally characterized by the porosity, the degree of saturation and the parameters representing the effects of geometry and electric charge on the surface of the pores.

For calculating the effective diffusion coefficient in the concrete, tortuosity and constrictivity are defined (Atkinson and Nickerson, 1984). In this study, tortuosity is defined in terms of porosity, and constrictivity by the pore radius (Nakarai *et al.*, 2006a).

$$D_{eff} = \phi \cdot S \cdot \frac{\delta}{\Omega} \cdot D_{ion} \qquad (5)$$

where, Ω is the tortuosity, δ is the constrictivity, D_{ion} is the diffusion coefficient of a calcium ion in bulk liquid phase [m²/s]. The tortuosity factor expresses the increased length of the actual ion transport pathway according to the tortuosity of the pores. Since the change of porosity and pore radius of cement paste is calculated in the pore structure

model based on the hydration and degradation, the change of the effective diffusion coefficient is automatically taken into account. The diffusion coefficient of the calcium ions is obtained from Einstein's theorem.

For calculating the effective diffusion coefficient in the bentonite, two parameters representing the reduction of diffusivity by effects of geometory and electric interaction are defined as below (Usui *et al*., 2006).

$$D_{eff} = \phi \cdot S \cdot G \cdot w_{el} \cdot D_{ion} \qquad (6)$$

where, G is the parameter representing the effect of the geometry of the pores and w_{el} is the parameter expressing the effect of the electric interactions between ions and electric charge of the montmorillonite. The parameter for the geometry is determined based on the experimental results investigating the effective diffusion coefficient of HTO (Mihara, 2000). Since HTO is electroneutral, the effect of the electric interactions on the diffusivity can be eliminated. The parameter for the electric interaction is determined as 1.5 by considering the increase in the diffusivity caused by the surface diffusion (Sato, 1999).

3. VERIFICATION

3.1 Calcium leaching from cement paste

The experiments for investigating calcium leaching from cement paste having different water-to-cement ratio (Haga, *et al*., 2005) are simulated in order to verify the proposed model. In the experiment, four kinds of cement paste specimens were prepared. The water-to-cement ratios of them were 0.4, 0.6, 0.8 and 1.0. After casting, they were cured in the water under 50°C for 56 days. Then, the block-shaped specimens were submerged in deionized water under 20°C to

accelerate calcium leaching. The water-to-solid ratio was 1000. After 3, 7, 28, and 91 days of immersion, the distribution of remaining calcium in the specimen was measured by using electron probe microanalysis. Figure 5 compares the deterioration depth of cement paste between the experiment and the analysis by the proposed model. Here, the deterioration depth is the length from the surface of deterioration zone where the amount of calcium is decreased. This figure showed applicability of the proposed model for calcium leaching from cement paste.
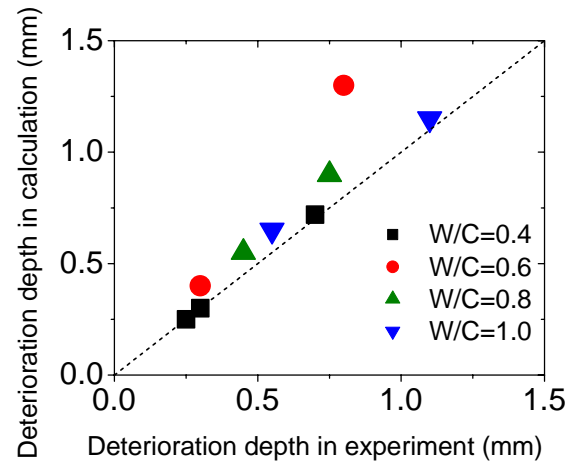

Figure 5. Comparison of deterioration depth of cement paste

3.2 Interaction between cement paste and bentonite

In order to verify the proposed model, the experiment for investigating the effect of interaction between the cement paste and the bentonite on the calcium leaching (Shibata and Sakamoto, 2005) is simulated. In the experiment, the specimen of the cement paste was set between two specimens of bentonite as shown in Figure 6. The diameters of specimens were 30mm and the thickness of each specimen was 10mm. The water-to-cement ratio of the cement paste was 100%. The drying density of the bentonite was 1.2Mg/m^3. After the flow examination for 6 months, the specimens were

sealed for 6 months. Then, the distribution of the calcium was measured on the cross section by using the electron probe X-ray microanalysis. The experimental results showed the significant decrease in the calcium at the surface of the cement paste in contact with the bentonite as shown in Figure 6.

The results of the calculation were shown in Figure 7. The bound calcium ratio was calculated by dividing the amount of the bound calcium by the amount of the bound calcium in the sound part of the cement paste. The distribution of the residual solid calcium in the cement paste as the bound calcium is important indicator for assessing the degree of the deterioration caused by leaching since the decrease in solid calcium causes the decrease in the material performance such as strength and permeability. The proposed model could well predict the calcium leaching in the experiment. In order to investigate the influence of the modeling of the bound calcium, the sensitivity analytical were also performed. In the case of the calculation ignoring the bound calcium in the bentonite, the deterioration caused by leaching is very small. In the case of the calculation using the equilibrium model for the non-compacted bentonite (Figure 4), the amount of the calcium leached from cement paste and the bound calcium in the bentonite became large. These results indicate that the modeling of the equilibrium relation between free and bound calcium for the target compacted bentonite is important since the amount of bound calcium has significant effect on the calcium leaching of the cement paste in contact with the bentonite.
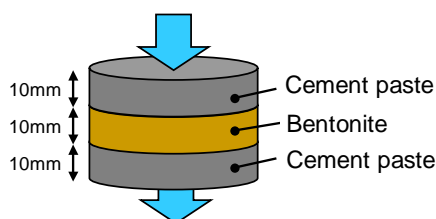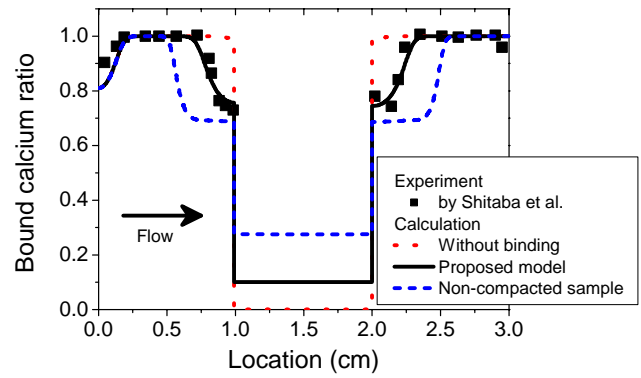

Figure 6. Outline of experiment

Figure 7. Interaction between cement paste and bentonite

4. SIMULATION OF LONG-TERM DURABILITY OF CONCRETE WITH BENTONITE

The long-term durability associated with calcium leaching of the concrete barrier in the underground nuclear-waste repository is investigated by using proposed model. In this study, three calculations were performed in order to investigate the influence of the surrounding environmental condition. The three surrounding materials were the compacted bentonite, the hypothetical bentonite without the binding capacity and the deionized water. The water-to-cement ratio of the concrete was 45%. The drying density of the bentonite was 1.6 Mg/m^3. Figure 8 shows the outline of the analysis.

Figure 9 shows the calculated deterioration depth of the concrete from the surface. Here, the deterioration depth was determined as the length of the part where the decrease in the solid calcium was observed. The analytical results showed that the degradation depth became large by considering the bound effect of the bentonite. Especially, the acceleration of the calcium leaching by the bound effect in the bentonite was large at early stage and the degradation depth for the bentonite with bound effect was almost as large as the depth for the

deionized water. Figure 10 and 11 show the distribution of the concentration of the free calcium ion and the amount of the bound calcium after 1,000 years, respectively. In the case of the bentonite with binding capacity, the pore water in the bentonite maintained a low concentration of free calcium ions (Figure 10) and the constantly high concentration gradient at the surface of the cement paste (Figure 11).
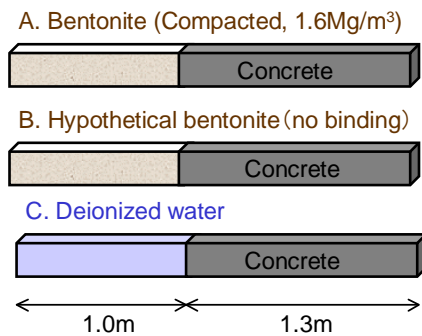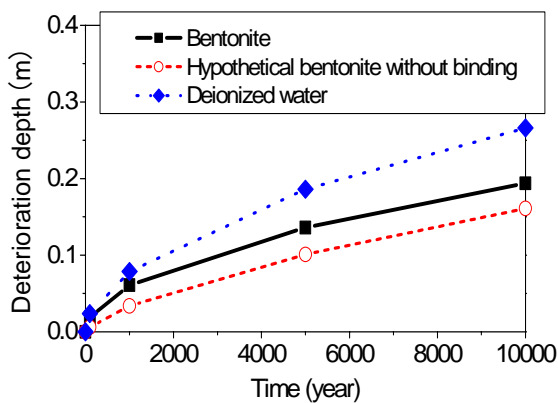

Figure 8. Outline of analysis
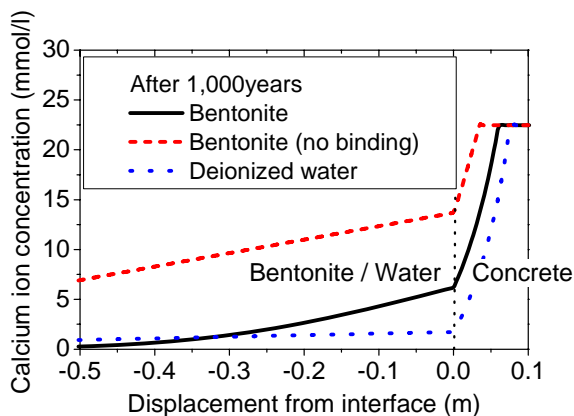

Figure 9. Change of deterioration depth
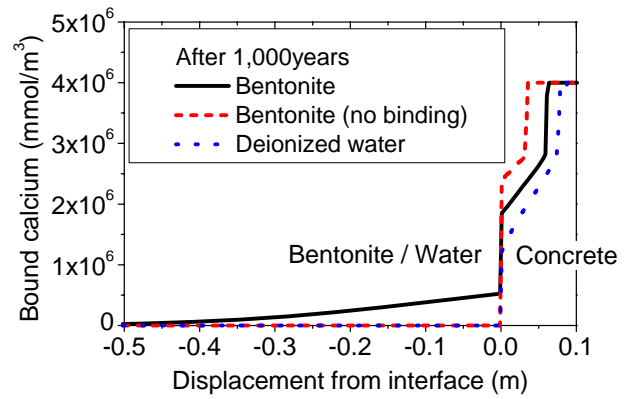

Figure 10. Distribution of calcium ion

Figure 11. Distribution of bound calcium

5. CONCLUSIONS

The unified modeling for both the concrete and the bentonite was proposed for predicting the long-term durability by the calcium leaching of the concrete with the bentonite. The multi-phase equilibrium of calcium ions and their transport are formulated on the basis of thermodynamics. For the bentonite, the proposed equilibrium formulation considers the bound ions due to ion exchange and absorption on its microstructure and it was determined based on the experimental results. The proposed model was verified by comparing to experimental results that investigate the interaction between the concrete and the bentonite. The analysis revealed that the deterioration of concrete developed rapidly when the bound effect of the surrounding bentonite was taken into account. This means that it is very important to take into account the effect of bentonite on the degradation process of concrete.

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