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Alteration of fractured cementitious materials

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Abstract

The alteration of cement materials in a fractured repository was investigated by experimental and modelling techniques to predict the long-term evolution of a cementitious repository for the safety assessment of radioactive waste disposal. A flow-through experiment with an artificially fractured cement column sample was carried out, and the evolution of a chemical composition in discharged water and the distribution of mineral components in a solid matrix, which was dominated by the dissolution of portlandite and calcium-silicate hydrate (C-S-H), were observed. A coupling transport and chemical equilibrium calculation code, which includes a thermodynamic incongruent dissolution model of C-S-H, was developed to predict the alteration of the fractured cement materials. The advection transport of a component in a solution within a crack and the diffusion of a component in a solid matrix were modelled in the calculations. With the proposed model, the possible alteration of cement materials along a crack was described.

Keywords: Radioactive waste; Crack; Leaching; Calculation code; Calcium silicate hydrate (C-S-H)

1. Introduction

Cement material, a potential waste packaging, backfilling and construction material for the disposal of radioactive waste, is expected to provide both physical and chemical containments. Under a high-pH condition provided by leaching the components of cement hydrates, solubility is low and sorption distribution ratio is high for many radionuclides; thus, the release of radionuclides from radioactive waste is restricted. Also, the physical properties of cement materials, such as a low permeability and a low diffusivity in matrices, can reduce the migration of radionuclides from a cementitious repository. Under geological conditions, cement materials are altered by some reactions; for example, dissolution into groundwater and secondary mineral formation caused by chemical components in groundwater. The containment properties of cement materials are affected by the alteration reactions. Also, leached high-pH solution with alkaline components from cement materials affects the physical and chemical properties of bentonite, which is foreseen to be used as a buffer material in geological repository systems [1,2], and surrounding rocks. Therefore, for the long-term safety assessment of radioactive waste disposal, it is necessary to develop a series of predictive calculation models of the long-term evolution of a cementitious repository system. The $CaO–SiO_2–H_2O$ system is suggested to be responsible for the high-pH condition in cements and is important in discussing the high-pH chemical condition in the long-term assessment of a repository environment [3,4].

In the past performance assessment studies in Japan, the evolution of cement materials was discussed using only a homogeneous porosity transport model [2]. CRACK and CRACK2 computer programs were developed to predict radionuclide release via fractures [5]. These programs can be used to calculate the evolution of a fractured cementitious repository, considering the flux of groundwater concentrated within fractures. Brodersen examined the precipitation of calcite from calcium bicarbonate solution passing through cracks in concrete and the leaching behaviour of components from cementitious materials [6]. It was observed that calcite is mostly precipitated on the surface of the cracks [7,8] and fills the cracks, and it was suggested that the produced thin layers of low-porosity calcite act as a diffusion barrier limiting contact between cement and solution. Brodersen

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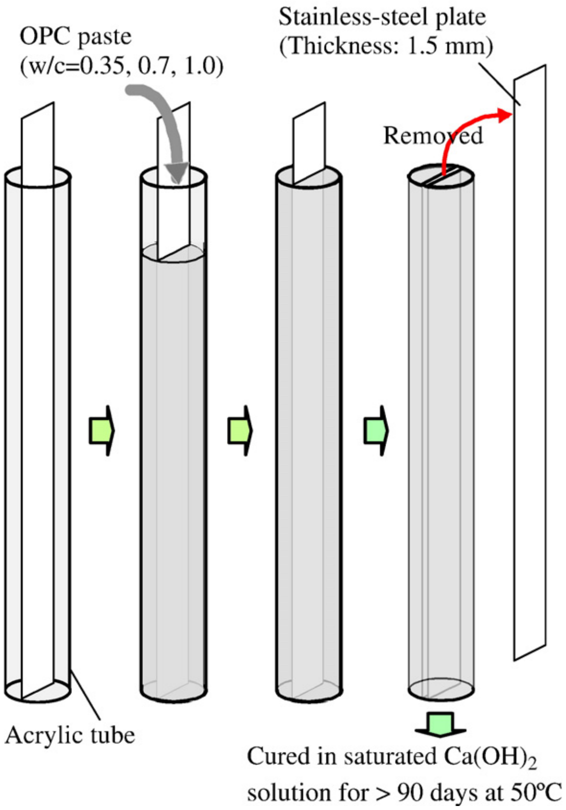


Fig. 1. Preparation of artificially fractured cement column sample.

Table 1
Chemical composition of OPC used in this study

Chemical composition/wt.%							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
21.2	5.2	2.8	64.2	1.5	2.0	0.3	0.5

simulated the obtained experimental results using the CRACK2 computation model; however, the dissolution of the calcium-silicate hydrate (C-S-H) phase, which is one of the principle components in cementitious materials, was not included in the model and the leaching of silicic acid was disregarded [6]. The leaching of the C-S-H phase could dominate the chemistry of a cementitious repository even in the case of early leaching in groundwater after closure and particularly under high Ca-leaching conditions; therefore, it is very important to include the dissolution of the C-S-H phase into the discussion on the alteration of fractured cementitious materials in a repository system.

In this study, the alteration of cement materials in a fractured repository was investigated by developing a calculation code, which includes the incongruent dissolution/precipitation model of the C-S-H phase [9]. An artificially fractured column-shaped hardened cement sample in which a simple crack was introduced was prepared and used in a flow-through leaching experiment using distilled water to observe the dissolution of the C-S-H system. The evolutions of the mineral composition in a solid phase and the chemical composition in a liquid phase have been investigated with regard to leaching of selected cement minerals and cement-derived elements (Ca, Si). The incongruent dissolution of the C-S-H phase was successively observed. A coupling transport and chemical equilibrium calculation code was developed to predict the alteration behaviour of the fractured cement sample on the basis of observations. The advection of components in a solution in a crack and the diffusion of components in a cement matrix were modelled in the calculations.

2. Experimental

The simplified transport in a crack in cement materials was investigated in this study. Artificially fractured cement column samples were prepared, as shown in Fig. 1. Ordinary Portland cement (OPC) was hydrated in acrylic tubes with a diameter of 10 or 14 mm and a length of 200 mm, in which a stainless-steel plate with a thickness of 1.5 mm was inserted. Then the steel plate was removed from the tubes and a single parallel-walled artificial crack was introduced into the cement column samples. The cement samples were hydrated with water/cement clinkers (w/c) of different mixing ratios of 0.35, 0.7 and 1.0 to give a series of diffusivities in the solid. To prevent bleeding (separation of water at the top of the paste) in the samples at high w/c ratios of 0.7 and 1.0, the water and cement clinker were mixed continuously for 3 h at w/c = 0.7 or repeatedly for 10 h (mixed for 3 min every 30 min) at w/c = 1.0 before setting in the tubes. This procedure is similar to the method employed by Haga et al., who prepared hardened cement hydrates with a relatively large porosity, where pores are homogeneously distributed in the

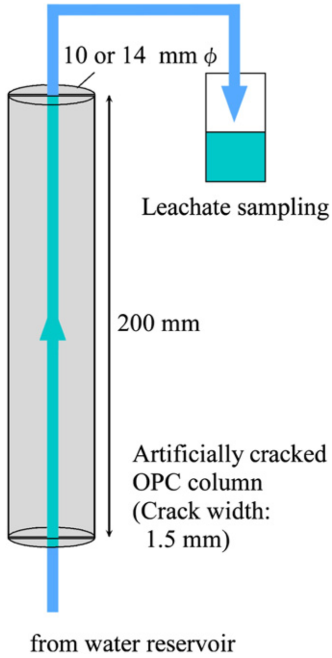


Fig. 2. Experimental design of flow-through leaching experiments.

Table 2
Experimental conditions

Exp. ID	OPC35	OPC70	OPC100
Water/cement at hydration	0.35	0.70	1.0
Density/g cm^{-3}	1.9	1.6	1.3
Diameter of column/mm	10	14	14
Aperture/mm	1.5	1.5	1.5
Flow rate/cm^3 h^{-1}	2.5	2.5	2.4
Darcy flow rate/m s^{-1}	4.6×10^{-5}	4.5×10^{-5}	4.5×10^{-5}
Porosity[a]/%	15	40	52
Effective diffusion coefficient[b]/m^2s^{-1}	2×10^{-12}	5×10^{-11}	9×10^{-11}

[a] Measured by mercury intrusion porosimetry.

[b] The effective diffusion coefficient within the initial solid matrix was determined by fitting calculations using the measured calcium concentration in the discharged water.

samples at w/c ratios of 0.6, 0.8 and 1.0 [10]. Then the hydrated materials were cured in a saturated $Ca(OH)_2$ solution (to minimise leaching of calcium) at 50 °C (to enhance hydration [11] and reduce effects of unhydrated phases) for more than 90 days. The chemical composition of the OPC used in this study is shown in Table 1.

The setup for the flow-through leaching experiments is shown in Fig. 2. Distilled water flowed through the artificial crack at a constant rate of 2.5 cm^3 h^{-1} (Darcy flow rate: 4.5×10^{-5} m s^{-1}) at room temperature. The experimental conditions are summarised in Table 2. The table also shows the porosity of the solid matrix of equivalent cement samples prepared separately, measured by mercury intrusion porosimetry. The solid samples were analysed by X-ray diffraction (XRD) and the presence of portlandite, monosulphate, katoite and C-S-H gel was observed, as shown in Fig. 3 (initial OPC). No crystallised C-S-H mineral was observed in the OPC sample cured at 50°C; thus, the effect of aging temperature is assumed to be negligible in this study.

The amount of discharged water and the pH and concentrations of Na, K, Ca, Si, Al and S were measured during the flow-through leaching experiments for 142 days. After the flow-through leaching experiments, the cement columns were cut into pieces of 5 mm length and some of the sliced column samples were grinded and analysed by XRD and differential thermal analysis (DTA) to identify and quantify their average mineral composition. The cross section of the column samples was analysed by scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDXA) to observe the distribution of components in a cement matrix.

3. Modelling

A coupling transport and chemical equilibrium calculation code, coupled chemical equilibrium-mass transport code for fractured media (CCT-F), was developed to predict the alteration behaviour of fractured cement materials. All thermodynamic modelling calculations were carried out using the thermodynamic database HATCHES [12] Ver. NEA14.

The mineral composition of the OPC hydrate was derived by an approach based on that described by Glasser et al. [13] with some modifications. Glasser et al. calculated the equilibrium phase distribution by considering the phases of $Ca(OH)_2$, C-S-H, hydrotalcite and monosulphate [13]. As shown in Fig. 3, the OPC hydrate was composed of portlandite, C-S-H gel ettringite, and a small amount of certain minerals after the flow-through leaching experiments. And the amount of portlandite was measured by DTA. Thus, we calculated the mineral composition in the OPC hydrate by an approach [9] in this study as follows:

Step 1. The mineral assembly in the OPC hydrate was described with portlandite ($Ca(OH)_2$), C-S-H, hydrotalcite and ettringite.

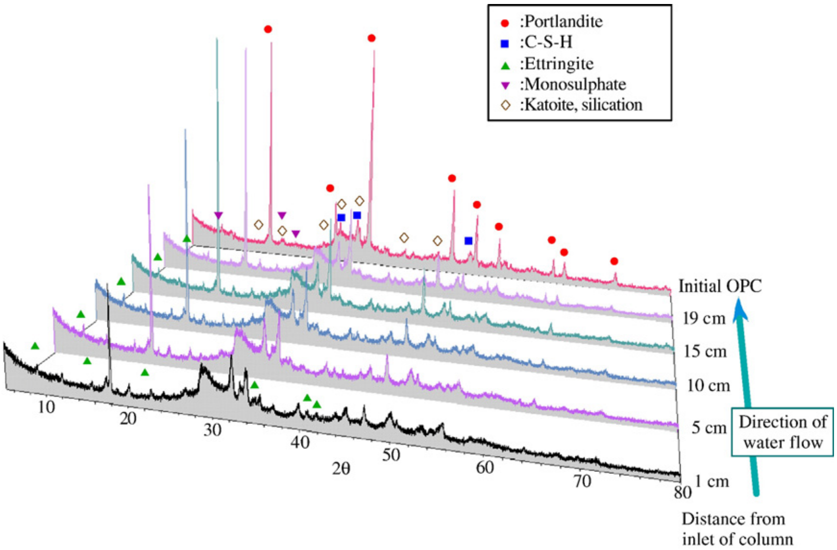


Fig. 3. XRD patterns of cement solid matrix (OPC100).

Table 3
Calculated mineral composition of OPC hydrate [mol kg^{-1}]

Hydrotalcite	Ettringite	C-S-H gel (1.755 $CaO.SiO_2.1.755\ H_2O$[a])	$Ca(OH)_2$
0.052	0.30	2.6	2.6

[a] The formula of C-S-H is given by the C-S-H incongruent dissolution/precipitation model [9].

Step 2. MgO was assumed to be completely incorporated into hydrotalcite. The inventory of Al_2O_3 was adjusted accordingly.

Step 3. SiO_2 was assumed to be taken up by the C-S-H gel with Ca/Si = 1.755 [9], and C-S-H was described using the model proposed by Sugiyama and Fujita [9].

Step 4. The amount of portlandite was estimated by the DTA of the OPC hydrate sample used in the OPC dissolution experiment in this study.

Step 5. The remaining CaO was assumed to be taken up by ettringite, which was observed by XRD after a flow-through experiment (Fig. 3). The remaining Al_2O_3 was assumed to be amorphous alumina gel or taken up by some phases (e.g., C-A-S-H gel), although excess Al is not included in the following modelling calculations.

The chemical composition of the OPC used in this study is shown in Table 1 and the mineral composition of the OPC hydrate calculated by the above-mentioned method is shown in Table 3. The $CaO–SiO_2–H_2O$ system is considered to be responsible for the high-pH condition in cements [3,4], and Sugiyama and Fujita showed that the equilibrium of the OPC hydrate with water could be well described dominantly by the dissolution of the C-S-H system [9]. In the leaching experiments described later, aluminium concentration in the leachate was very low (~10^{-5} mol dm^{-3}, as shown in Fig. 5), suggesting that the dissolution of calcium aluminate phase was very small when it coexisted with portlandite and C-S-H. Then the OPC was simply described as the assembly of portlandite and C-S-H gel in this modelling study for reducing the load of calculation.

Sugiyama and Fujita [9] proposed a thermodynamic incongruent dissolution/precipitation model of C-S-H, assuming a binary nonideal solid solution of $Ca(OH)_2$ and SiO_2. In this model, the log K values of the model end members of the solid solution are given as functions of the Ca/Si ratio of C-S-H system.

$$\log K_s = \frac{1}{1+y}\cdot\log K_{s0} - \frac{1}{1+y}\cdot\log\frac{1}{1+y} + \frac{y}{(1+y)^2} \times\left[A'_{s0} + A'_{s1}\left(\frac{1-y}{1+y}\right) + A'_{s2}\left(\frac{1-y}{1+y}\right)^2\right] \tag{1}$$

$$\log K_c = \frac{y}{1+y}\cdot\log K_{c0} - \frac{y}{1+y}\cdot\log\frac{y}{1+y} + \frac{y}{(1+y)^2} \times\left[A'_{c0} + A'_{c1}\left(\frac{1-y}{1+y}\right) + A'_{c2}\left(\frac{1-y}{1+y}\right)^2\right] \tag{2}$$

(y = Ca/Si of C-S-H)

$$\text{at Ca/Si} \le 0.461, \quad \log K_s = \log K_{s0} - \log(1+y)$$

$$\text{at } 1.755 \le \text{Ca/Si}, \quad \log K_s = -7.853, \qquad \log K_c = 22.81$$

$$\log K_{s0} = -2.710, \ \log K_{c0} = 22.81 \ [12]$$

The empirical parameters (A_{ij}) given by Sugiyama and Fujita [9], which were calculated using the available solubility data [14–18], are shown in Table 4. (Note that the model can consider the dissolution of portlandite coexisting with C-S-H gel at high Ca/Si ratios (1.755 ≤ Ca/Si). The dissolution of C-S-H system at Ca/Si ≥ 1.755 is described with constant log K values of log K_s = −7.853 and log K_c = 22.81, which means portlandite coexists with C-S-H gel (Ca/Si = 1.755) [9].) This model can predict the equilibria of the incongruent dissolution and precipitation with a continuous change in the Ca/Si ratio of the solid phase by a series of calculations, in which the quantities of the dissolved/precipitated end members are calculated stepwisely, so that the quantities and compositions of the solid and liquid phases, and the conditional solubility constants used in the subsequent step can be estimated [9]. CCT-F contains the geochemical code HARPHRQ [19] for calculating the chemical equilibrium, and the C-S-H model [9] is employed and added to calculate the incongruent dissolution and precipitation iteratively.

To calculate the mass transport in the fractured media, a quasi-two-dimensional advection/dispersion/diffusion model that is similar to the model described by Chambers [5] is employed in CCT-F. Fig. 4 shows a schematic representation of the model considered in this study. In this model, the following are assumed.

i. Transport in the crack is dominated by only advection and dispersion. Diffusion within the crack is not included; thus, the gradient of aqueous concentration across the crack is neglected.
ii. Transport within the cement solid matrix is constrained to be diffusive and perpendicular to the direction of the crack. Haga et al. [10] showed that diffusive transport dominates the leaching of calcium from the surface of a hardened cement solid. The planes of symmetry in the middle of the solid matrix represent a no-flow boundary. Diffusive transport in the matrix parallel to the crack is neglected.
iii. Transport from the matrix into the crack is described as diffusion on the surface of the crack (y = 0).
iv. Components are lost from the system only via the crack.

Table 4
Fitted values of empirical parameters [9]

End member	SiO_2			$Ca(OH)_2$		
A_{ij}	A'_{s0}	A'_{s1}	A'_{s2}	A'_{c0}	A'_{c1}	A'_{c2}
Ca/Si ≤ 0.833	−18.623	57.754	−58.241	37.019	−36.724	164.17
Ca/Si > 0.833	−18.656	49.712	25.033	36.937	−7.8302	−50.792

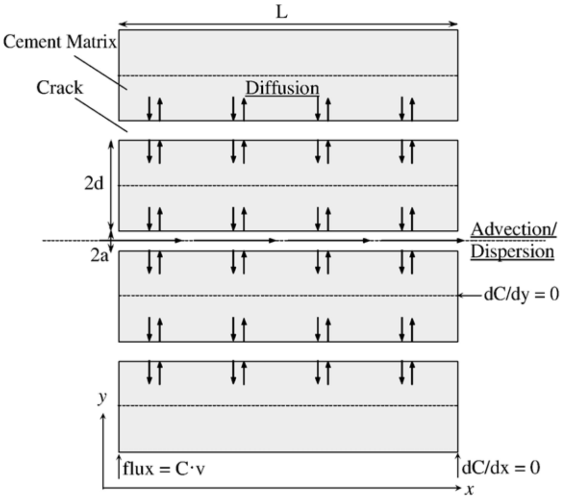


Fig. 4. Schematic representation of transport model in fractured cement materials.

The transport of aqueous species in the crack is described by the following advection/dispersion equation:

$$D_{e,f}\cdot\frac{1}{x^l}\cdot\frac{\partial}{\partial x}\left(x^l\frac{\partial C(x,0,t)}{\partial x}\right)-v\cdot\frac{\partial}{\partial x}\left(\frac{C(x,0,t)}{x^l}\right)$$
$$=\phi\cdot R_d\frac{\partial C(x,0,t)}{\partial t}-S(x,t), \qquad (3)$$

where

C	concentration of aqueous species,
t	time,
l	spatial coordinates (0: rectangular, 1: cylindrical, 2: spherical),
v	velocity of flow in crack,
ϕ	porosity,
R_d	retardation factor,
$D_{e,f}$	effective diffusion constant including dispersion in crack ($\alpha\cdot v$, α: dispersion length), and
S	source term, which is given by

$$S(x,t)=D_{e,m}\cdot\left.\frac{\partial C(x,y,t)}{\partial y}\right|_{y=0}+S_{eq}(x,t), \qquad (4)$$

$D_{e,m}$	effective diffusion constant in matrix and
S_{eq}	source term given by chemical equilibrium calculation within crack.

The first term on the right-hand side of Eq. (4) denotes the flux into the solid matrix from the crack.

The transport of aqueous species within the matrix is described by the following one-dimensional diffusion equation.

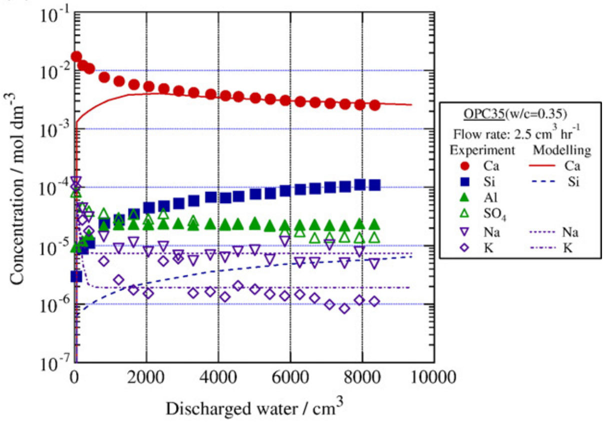
$$D_{e,m}\cdot\frac{\partial^2 C(x,y,t)}{\partial y^2}=\phi\cdot R_d\frac{\partial C(x,y,t)}{\partial i}-S_{eq}(x,y,t) \qquad (5)$$

The second term of the right-hand side of Eq. (5) is the source term given by chemical equilibrium calculation within matrix.

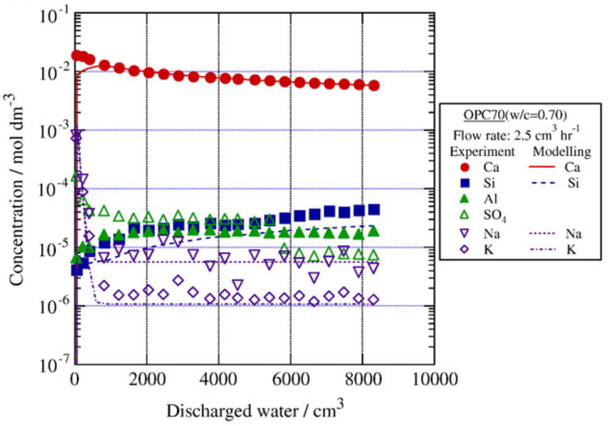
Note that transport within the cement solid matrix is assumed to be diffusive and perpendicular to the direction of the crack *(y*-axis); therefore, this model is referred to as a quasi-two-dimensional advection/dispersion/diffusion model. Eq. (5) is combined with Eq. (3) via the concentration $C(x,0,t)$ term for the surface of the crack ($y=0$). The quasi-two-dimensional advection/dispersion/diffusion model is coupled with the chemical equilibrium calculation including the incongruent C-S-H dissolution/precipitation model [9].

The evolution of the hydraulic properties of the cement solid matrix due to the leaching of components is also considered in

(a) OPC35



(b) OPC70



(c) OPC100

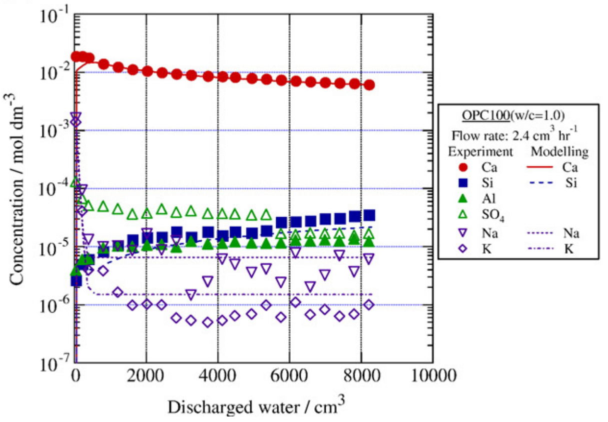


Fig. 5. Measured composition of discharged water. (a) OPC35, (b) OPC70 and (c) OPC100.

the calculation code. The component minerals in the solid are leached from the surface of the solid into the solution within the crack. In this model, it is considered that the porosity of the solid matrix increases as the component minerals are dissolved and leached from the solid. This is described by the following equations:

$$\phi(t) = 1 - (1 - \phi(0)) \cdot \frac{V_{\text{solid}}(t)}{V_{\text{solid}}(0)} \tag{6}$$

$$V_{\text{solid}}(t) = \sum_{i:\text{solids}} \text{CS}_i(t) \cdot v_{\text{mol}_i} \tag{7}$$

where

ϕ porosity,
CS molarity of component mineral,
v_{mol} molar volume of component mineral ($v_{\text{mol Ca(OH)}_2} = 0.0331$ dm^3 mol^{-1}, $v_{\text{mol SiO2}} = 0.0273$ dm^3 mol^{-1}).

The initial porosity ϕ (0) was measured by mercury intrusion porosimetry and is given in Table 2. In the developed code, the diffusion coefficient in the altered surface region of the solid matrix is calculated using a simple formula.

$$D(t) = D(0) \cdot \frac{\phi(t)}{\phi(0)} \tag{8}$$

Then the flux caused by diffusion in the matrix is given as

$$J(t) = -D(t) \cdot \frac{\partial C}{\partial y}\bigg|_{y=0} = -D(0) \cdot \frac{\phi(t)}{\phi(0)} \cdot \frac{\partial C}{\partial y}\bigg|_{y=0}. \tag{9}$$

Therefore, as the porosity of the solid matrix increases owing to the dissolution of component minerals, the effective diffusion coefficient increases and the leaching of a component into the crack is enhanced.

4. Results and discussion

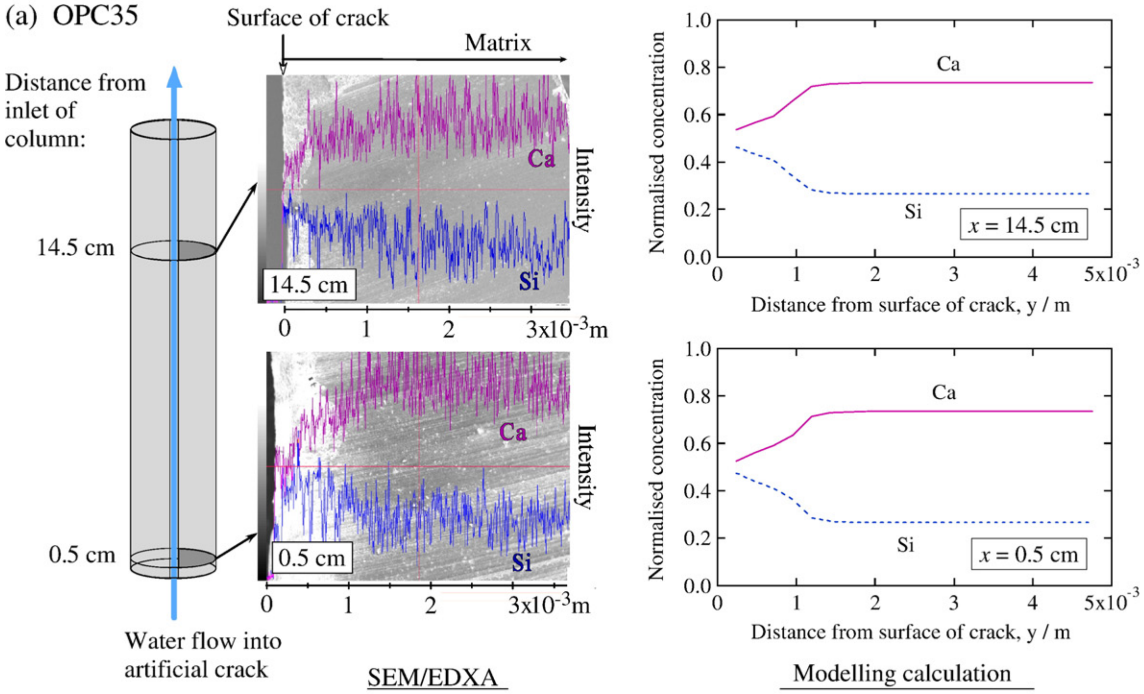
The XRD patterns of the divided solid samples are shown in Fig. 3, which are for the sample OPC100 as an example. Portlandite, ettringite and C-S-H gel were observed, but the presence of calcite was not clearly identified in all samples after the flow-through experiments. These results indicate that the effect of carbonation is minimised in the flow-through experiments and can be neglected. This is not further discussed in this paper.

The measured aqueous compositions of the discharged water are shown in Fig. 5 as functions of time. In the case of OPC35 (w/c = 0.35, Fig. 5(a)), the initial calcium concentration in the discharged solution was approximately 2×10^{-2} mol dm^{-3}, suggesting that portlandite dissolved and leached from the cement solid, and reached equilibrium. Sodium and potassium concentrations in the early phase of the experiments were approximately 1×10^{-4} mol dm^{-3} and had little effect on the solubility of portlandite. For all cases in the experiments, low sodium and potassium concentrations ($< 2 \times 10^{-3}$ mol dm^{-3}) were observed under the experimental conditions (the flow rate and the amount of OPC hydrate). Also, much of sodium and potassium may have leached out into the curing solution at the sample preparation (Fig. 1). As the amount of discharged water increased, calcium concentration decreased and silica concentration increased with time. This is due to the incongruent dissolution of C-S-H with decreasing Ca/Si ratio.

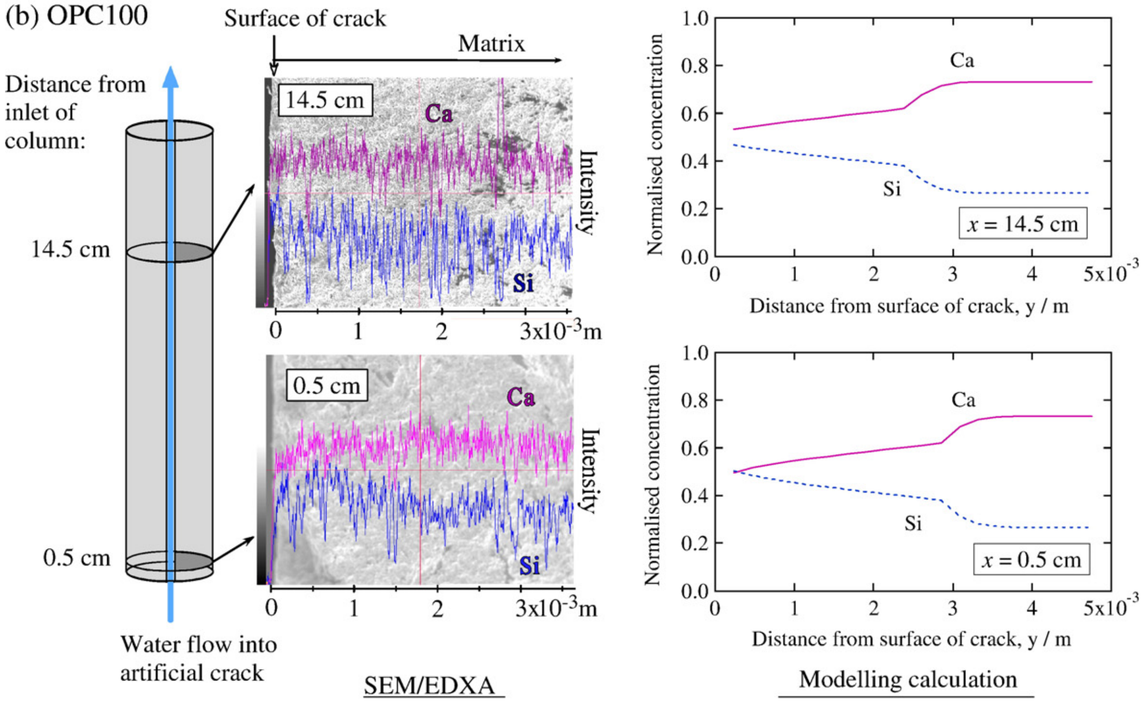
In the cases of OPC70 (Fig. 5(b)) and OPC100 (Fig. 5(c)), the measured calcium concentration in the discharged solution in the initial phase of the experiments was approximately 2×10^{-2} mol dm^{-3}, and the calcium concentration during the flow-through leaching experiment was higher than that for OPC35. These suggest that the leaching rate of calcium from the cement solid matrix is higher in the cases of OPC70 and OPC100 than in the case of OPC35 because of the higher porosity of the solid and the higher diffusion coefficient in the matrix (Table 2). The diffusivity of cement hydrates increased as the porosity of the solid increased.

The effective diffusion coefficient within the initial solid matrix, $D(0)$, was estimated by a series of sensitivity analysis to fit the measured calcium concentration in the discharged water and is shown in Table 2. The estimated $D(0)$ values were comparable to those obtained in the study of Haga et al. [10], in which the dependence of the diffusion coefficient of calcium in the hardened OPC solid matrix on porosity was calculated, and the intrinsic diffusion coefficients of caesium, strontium and iodine in the water-saturated Portland cement matrix measured by Atkinson and Nickerson [20]. The calculated calcium and silica concentrations in the discharged water shown in Fig. 5 were compared with the experimentally measured values. The agreement between the calculated and measured calcium and silica concentrations was reasonably good for all cases, although the measured silica concentrations were slightly higher than the calculated values and the calculated calcium concentrations in the early phase were lower than the measured values particularly for the case of OPC35. There is a certain scatter in the thermodynamic data of the C-S-H system [9,21] and the observed discrepancy for the silica concentrations can be explained within the uncertainty. The observed discrepancy between the experimental and modelling data for the initial calcium leaching behaviour could be explained as follows: In the modelling calculation, the transport from the solid matrix into the crack is described as the diffusion of dissolved species in the pore solution in the matrix, but calcium may have been also transported into the solution within the crack by the dissolution of the component minerals (C-S-H gel and portlandite) on the surface of the crack in the leaching experiments. And it may have been followed by an increase crack width. For the case of OPC35, the rate of transport by diffusion was low in the initial phase since the initial diffusion coefficient was very low ($\sim 2 \times 10^{-12}$ m^2 s^{-1}, as shown in Table 2); therefore, the effect of the direct transport by dissolution on the surface may have been observed more distinctly in this case than in the other cases. The contribution of the dissolution of the matrix on the surface of the crack and the possibility of an increase in crack width should be discussed further using experimental data in future studies.

The calcium and silicon concentrations at the cross sections of the divided solid samples of OPC35 and OPC100 analysed using SEM/EDXA are given in Fig. 6. For the case of OPC35, calcium leached from the surface and the Ca/Si ratio of the solid decreased in the surface region. For the case of OPC100, the distribution of calcium in the solid matrix was not clearly observed, suggesting that calcium leaches from a deep region owing to the high diffusion coefficients in the matrix of OPC100 (Table 2). The calculated calcium and silicon concentrations in the matrix normalised to the total calcium and silicon concentration in the initial cement solid are also shown and were compared with experimental results in Fig. 6. The calculation model could qualitatively predict the distribution of calcium and silicon in the solid matrix. The profiles of the $Ca(OH)_2$ concentration parallel to the direction of the crack determined by DTA are shown in Fig. 7. Although the predicted profiles of $Ca(OH)_2$ concentration are higher than the measured profiles, the experimental results were reasonably predicted by the



(a) OPC35



(b) OPC100

Fig. 6. Ca and Si concentration profiles at cross sections of leached OPC samples. (a) OPC35 and (b) OPC100.

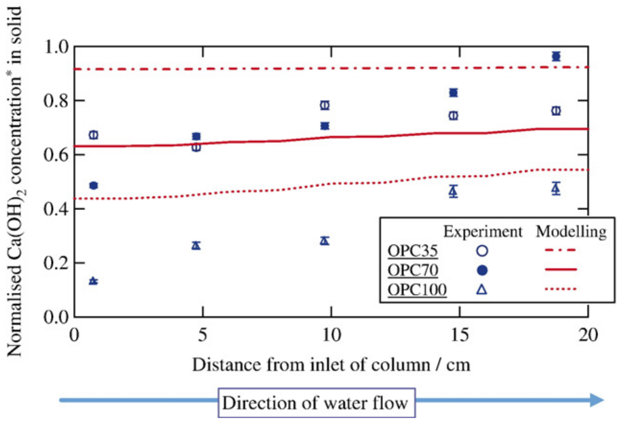


Fig. 7. Profile of amount of portlandite parallel to direction of crack. * Concentration of $Ca(OH)_2$ in matrix normalised to $Ca(OH)_2$ concentration in initial cement solid.

calculation model, considering the uncertainties of the thermodynamic data for the C-S-H system. The discrepancy between the experimental and modelling data could be reduced by considering the dissolution on the surface of the crack discussed above. Also, the consideration of kinetics could improve the model. The CCT-F code assumes that the dissolution of the component in the pore of the cement sample reaches equilibrium; however, in certain cases, particularly under higher-flow-rate conditions, it appears that the component in the hardened cement might not have reacted to equilibrium with the pore solution in the time frame given by the experimental flow-rate condition. A more detailed discussion could be made if data on the kinetics and the diffusion transport in the solid matrix were available for future studies.

Further studies should also be carried out to determine the effects of calcium aluminate phases and a groundwater composition on the alteration of the fractured cement system. In this study, the cement system was simplified as the assembly of portlandite and C-S-H gel, and the leaching of these minerals was investigated. Calcium aluminate phases should be included to make the modelling more realistic. Also, in reality, groundwater contains chemical constituents (e.g., sulphate, carbonate, and magnesium), which react to form secondary minerals or reduce pH. The model and CCT-F code could be further improved by integrating the results of future studies.

5. Conclusions

The alteration of cement materials in a fractured system was investigated. A flow-through leaching experiment using an artificially fractured OPC column sample and distilled water as leachate was carried out, and the composition of the discharged solution and the distribution of components in the solid matrix were analysed.

A coupling transport and chemical equilibrium calculation code were developed. The notable feature of this code is that the incongruent dissolution/precipitation model of C-S-H is included in the chemical equilibrium calculation and a quasi-two-dimensional transport model is coupled with this. In the developed code, the transport in the cracks is described by only advection and dispersion, and the transport within the cement solid matrix is constrained to be diffusive and perpendicular to the direction of the crack. With the proposed model, the measured composition of the discharged solution was reasonably well predicted and the possible alteration of cement materials along a crack was described. This model is a useful tool for discussing the alteration of a fractured cementitious repository system.

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