Development of a reactive transport code MC-CEMENT ver. 2 and its verification using 15-year *in situ* concrete/clay interactions at the Tournemire URL[†]

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ABSTRACT: Highly alkaline environments induced by cement-based materials are likely to cause the physical and/or chemical properties of the bentonite buffer materials in radioactive waste repositories to deteriorate. Assessing long-term alteration of concrete/clay systems requires physicochemical models and a number of input parameters. In order to provide reliability in the assessment of the long-term performance of bentonite buffers under disposal conditions, it is necessary to develop and verify reactive transport codes for concrete/clay systems. In this study, a PHREEQC-based, reactive transport analysis code (MC-CEMENT ver. 2) was developed and was verified by comparing results of the calculations with *in situ* observations of the mineralogical evolution at the concrete/argillite interface. The calculation reproduced the observations such as the mineralogical changes in the argillite limited to within 1 cm in thickness from the interface, formation of $CaCO_3$ and CSH, dissolution of quartz, decrease of porosity in the argillite and an increase in the concrete. These agreements indicate a possibility that models based on lab-scale (~1 year) experiments can be applied to longer time scales although confidence in the models is necessary for much longer timescales. The fact that the calculations did not reproduce the dissolution of clays and the formation of gypsum indicates that there is still room for improvement in our model.

Because of the extended time and large space scales involved, safety assessments for the geological disposal of radioactive waste are complex. An implementer conducts the assessment and submits it to the regulator as a part of the application for obtaining a license to construct and operate a repository. The regulator is required to review the assessment efficiently and effectively. The Nuclear Safety Research Center of Japan Atomic Energy Agency, being responsible for supporting the regulatory activities, focuses research activities on features, events and processes that are highly correlated with the results of the safety analysis. The long-term alteration of cement-bentonite systems is one of the main issues that need to be considered.

Highly alkaline environments induced by cement-based materials are likely to cause the physical and/

or chemical properties of the bentonite buffer materials in radioactive waste repositories to deteriorate. Assessing long-term alteration of concrete/clay systems requires physico-chemical models and a number of input parameters. In our previous studies, alkaline alteration of bentonite (Nakayama *et al.*, 2004; Yamaguchi *et al.*, 2007, 2008) and diffusive mass transport in micropores in cement based materials (Yamaguchi *et al.*, 2009a) were empirically investigated and modeled. In order to provide reliability in the long-term assessment of bentonite buffer performance under disposal conditions, it is necessary to develop and verify reactive transport codes for concrete/clay systems.

For that purpose, multi-purpose codes such as PHREEQC (Parkhurst & Appelo, 1999), PHAST (Parkhurst *et al.*, 2000), TOUGHREACT (Xu & Pruess, 2001) and QPAC (Quintessa, 2010) have been used (Gaucher *et al.*, 2004; Luna *et al.*, 2006; Itälä *et al.*, 2011; Savage *et al.*, 2010). In order to meet more specific purposes, various codes such as PRECIP (Noy, 1998), HYTEC (van der Lee *et al.*, 2003), RAIDEN 3 (Watson *et al.*, 2004), CRUNCH (Maher *et al.*, 2006), ALLIANCE (Montarnal *et al.*, 2007), MCD (Appelo & Wersin, 2007) and MC-BENT (Yamaguchi *et al.*, 2007) have also been developed and used.

The code MC-BENT, one of those codes for specific purposes, is a PHREEQC-based, coupled mass-transport/chemical-reaction code developed for assessing changes in hydraulic conductivity of the bentonite buffer accompanied by changes in mineralogy and porosity. Because MC-BENT was developed for alkaline alteration of clays, it was neither suitable for calculating redox reactions such as dissolution of pyrite, nor for the calculation of the diffusion of ions in cement based materials for which much lower diffusivity is anticipated than in compacted clays.

Because the computer codes will be used in safety assessments of geological disposal that involves long time scales, they need to be verified for use in the calculations. Data on the alteration of compacted bentonite that can be used for the verification is scarce. Yamaguchi *et al.* (2007) used the observation of alteration of compacted Na-type montmorillonite in high pH solutions reported by Ichige & Mihara (1998) to verify MC-BENT. Yamaguchi *et al.* (2008) used the result of a hydraulic conductivity test for a sand-bentonite mixture with a $Ca(OH)_2$ solution at 80ºC reported by RWMC (2002). Watson *et al.* (2009) used the

results of a laboratory experiment investigating the effects of cementitious water diffusing through bentonite. Because the safety assessments of geological disposal involve much longer periods than these laboratory observations, it is necessary to test the code with data of alteration phenomena over longer periods. It is, however, generally difficult to observe mineralogical alteration in the time scale of a laboratory experiment and to define conditions that natural or engineered analogous materials have experienced for longer time periods. Such data are scarce as reviewed by Dauzères *et al.* (2010) although efforts (Yamaguchi *et al.*, 2012) were made to obtain data on simpler systems for the verification.

In this study, a new code, MC-CEMENT ver. 2, was developed and verified by comparing results of the calculations with *in situ* observations of the concrete/argillite interactions over 15 years at a borehole at the Tournemire Underground Research Laboratory.

REACTIVE TRANSPORT ANALYSIS CODE MC-CEMENT VER.2

MC-CEMENT ver.2 solves the flow and the reactive transport in porous media. The finite differential method (FDM) is applied in MC-CEMENT ver. 2 for discretization. PHREEQC ver. 2.18 (Parkhurst & Appelo, 1999) and HST3D ver. 2 (Kipp Jr., 1997) are used for chemical reaction and mass transport analysis, respectively. The sequential non-iterative approach (SNIA) is used to couple chemical reactions and mass transport. A model of diffusive mass transport in micropores in cement-based materials (Yamaguchi *et al.*, 2009a) was incorporated to take low diffusivity in cement based materials into account. The code sequentially calculates the groundwater flow, heat transfer, mass transport, geochemical reactions, changes in properties such as porosity and effective montmorillonite dry density, and changes in parameters for mass transport such as hydraulic conductivity and diffusivity. Space-dependent mass transport parameters such as diffusivity, hydraulic conductivity and porosity and their changes with time as a result of dissolution and formation of minerals can be calculated by the code. The minimum threshold porosity was set to 0.5% (0.005) to avoid abortion of the calculation accompanied by the clogging of the pores with secondary minerals.

IN SITU OBSERVATIONS AT TOURNEMIRE 15 YEAR-OLD DM BOREHOLE

An *in situ* engineered analogue of a concrete/ argillite interface (Fig. 1) which has undergone 15 years of interaction at the IRSN Tournemire Underground Research Laboratory (URL, Aveyron, France) has been characterized by IRSN (Tinseau *et al*., 2006; De Windt *et al*., 2008; Gaboreau *et al*., 2011; Techer *et al*., 2012). Mineralogical and chemical evolution (Tinseau *et al*., 2006) and spatial distribution of porosity (Gaboreau *et al*., 2011) were analysed. Precipitation of gypsum, recrystallization of mixed-layer clays, K-feldspars overgrowth etc. were observed. These mineralogical changes were limited in the argillite to within 1 cm

in thickness from the interface (Fig. 2). Clogging of the porosity was observed in the argillite while the porosity increased in the concrete, where newly formed CSH and $CaCO_3$ were observed.

CONDITIONS OF THE CALCULATION

The mineralogical evolution at the concrete/ argillite interface was simulated by MC-CEMENT ver. 2 in a unidimensional system by separating the interface into calculation cells of 1, 2 or 5 mm thickness as shown in Fig. 3. The boundary conditions were Dirichlet. The time step used in the calculation was 32 min, which enabled to complete a calculation simulating the alteration over 15 years within regular working hours. The
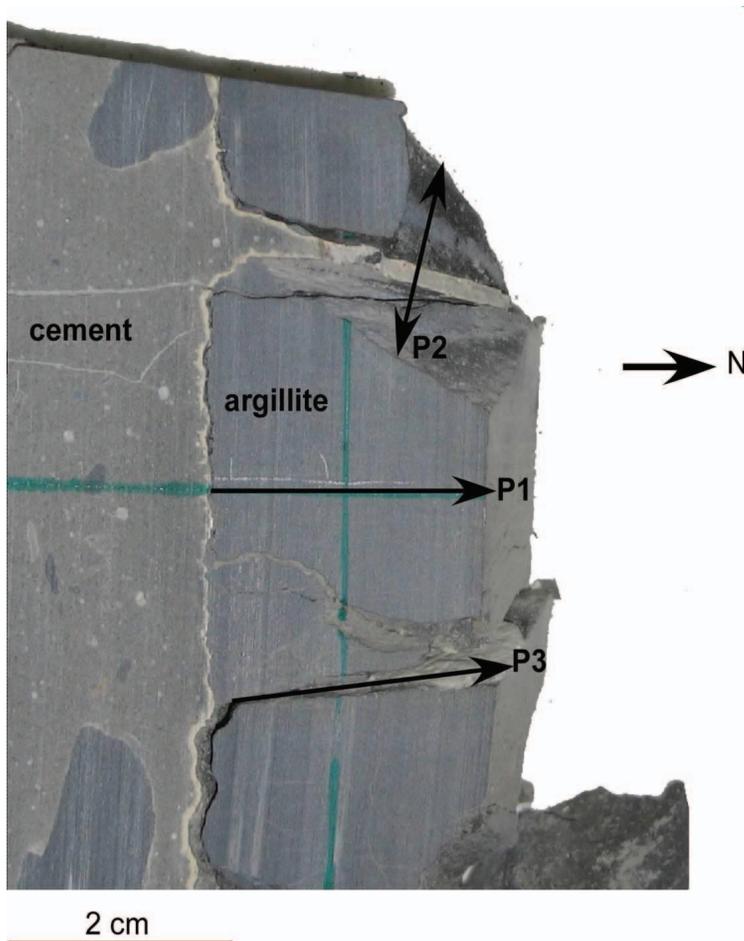

FIG. 1. Picture of the concrete/argillite interface. The P1 perturbation was studied in this paper.
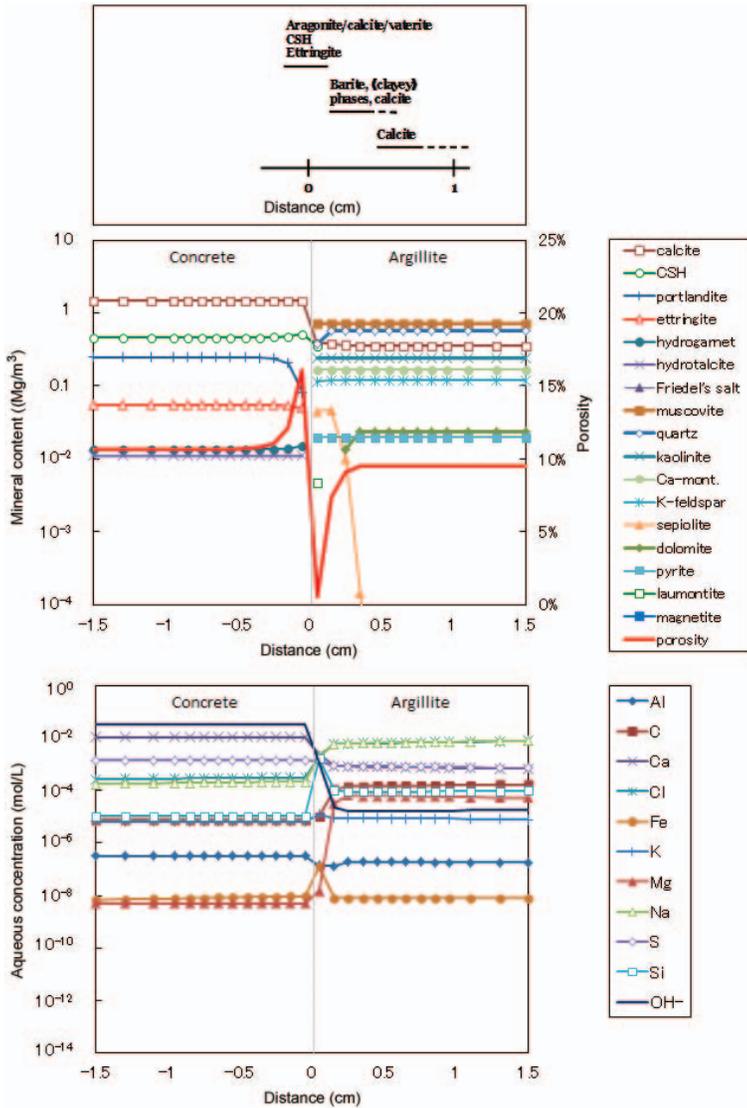
FIG. 2. Schematic distribution of the secondary phases observed in the argillite matrix (upper, Tinseau *et al.*, 2006), and distribution of minerals (middle) and aqueous concentrations (lower) after 15-year interaction calculated by MC-CEMENT ver.2 (Case 1).
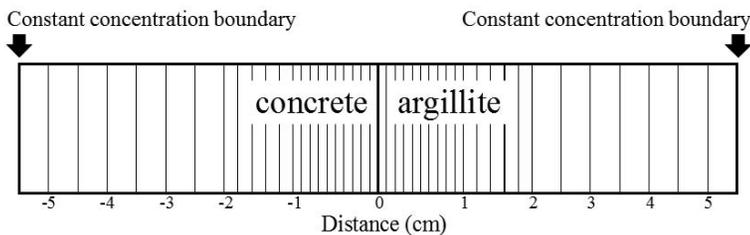

FIG. 3. Unidimensional heterogeneous discretization of the concrete/argillite interface in our calculation.

minimum separation of 1 mm was determined to make the Neumann number less than unity. The constant temperature of 15ºC (De Windt *et al.*, 2008) was used because of small daily and annual fluctuations, typically 0.1º and 2.2º, respectively. The porosity was 13% for the concrete and 9.5% for the argillite (De Windt *et al.*, 2008) determined for unaltered samples. The argillite and the concrete were assumed to be saturated based on the observation by Tinseau *et al.* (2006). Only diffusive transport was considered, ignoring advective transport based on the observations at Tournemire (Patriarche *et al*, 2004). The effective diffusivity was coupled with the porosity. The model reported by Yamaguchi *et al.* (2007) was used for the argillite and that of Yamaguchi *et al.*

TABLE 1. Mineral model used in analysis. Initial compositions are shown in wt.%.

Minerals (abbrev.)	Chemical formula	– Model 1 –		– Model 2 –	
		Concrete	Argillite	Concrete	Argillite
Na-montmorillonite*	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	0	0	0	0
Kaolinite (AS_2H_2)*	$Al_2Si_2O_5(OH)_4$	0	10.9	0	10.9
Ca-montmorillonite*	$Ca_{0.17}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	0	7.6	0	7.6
Muscovite*	$KAl_2AlSi_3O_{10}(OH)_2$	0	32.1	0	32.1
K-feldspar	$KAlSi_3O_8$	0	5.4	0	5.4
Dolomite	$CaMg(CO_3)_2$	0	1.1	0	1.1
Pyrite	FeS_2	0	0.9	0	0.9
Quartz	SiO_2	0	0	0	0
Quartz (sand)**	SiO_2	0	26.0	0	26.0
Calcite	$CaCO_3$	67.0	16.0	67.0	16.0
Portlandite	$Ca(OH)_2$	6.9	0	6.9	0
Monosulfate (AFm)	$3CaO·Al_2O_3·CaSO_4·12H_2O$	1.5	0	1.5	0
Ettringite (AFt)	$3CaO·Al_2O_3·3CaSO_4·H_2O$	1.5	0	1.5	0
Hydrotalcite (HT)	$4MgO·Al_2O_3·10H_2O$	0.5	0	0.5	0
Sodium oxide	Na_2O	0	0	0	0
Potassium oxide	K_2O	0	0	0	0
C-S-H (1.8)	$Ca_{1.8}SiO_{3.8}$	22.8	0	22.8	0
C-S-H (1.5)	$Ca_{1.5}SiO_{3.5}$	0	0	0	0
C-S-H (1.3)	$Ca_{1.3}SiO_{3.3}$	0	0	0	0
C-S-H (1.1)	$Ca_{1.1}SiO_{3.1}$	0	0	0	0
C-S-H (1.0)	$CaSiO_3$	0	0	0	0
C-S-H (0.9)	$Ca_{0.9}SiO_{2.9}$	0	0	0	0
C-S-H (0.833)	$Ca_{0.833}SiO_{2.833}$	0	0	0	0
C-S-H (0.6)	$Ca_{0.6}SiO_{2.6}$	0	0	0	0
C-S-H (0.4)	$Ca_{0.4}SiO_{2.4}$	0	0	0	0
Analcime	$NaAlSi_2O_6·H_2O$	0	0	0	0
Hydrogarnet (C_3AH_6)	$3CaO·Al_2O_3·6H_2O$	0	0	0	0
Laumontite	$CaAl_2Si_4O_{12}·4H_2O$	0	0	0	0
Gypsum	$CaSO_4·2H_2O$	0	0	0	0
Friedel's salt	$3Ca·Al_2O_3·CaCl_2·10H_2O$	0	0	0	0
Brucite	$Mg(OH)_2$	0	0	0	0
Sepiolite	$Mg_4Si_6O_{15}(OH)_2·6H_2O$	0	0	0	0
Katoite (C_3ASH_4)	$Ca_3Al_2(SiO_4)(OH)_8$	0	0	0	0
Gibbsite	$Al(OH)_3$	0	0	0	0
Pyrophyllite (AS_4H)	$Al_2Si_4O_{11}·H_2O$	0	0	0	0
Siderite	$FeCO_3$			0	0
Wüstite	FeO			0	0
Magnetite	Fe_3O_4			0	0
Hematite	Fe_2O_3			0	0

* The kinetic dissolution model for montmorillonite (Yamaguchi *et al.*, 2007) is applied.
** The kinetic dissolution model for quartz (Yamaguchi *et al.*, 2007) is applied.

(2009a) for the concrete. MC-CEMENT ver. 2 cannot use a diffusion coefficient for each species.

Our regular mineral model (Model 1, Table 1) (Yamaguchi *et al*., 2008) was applied to the concrete/argillite system. Compositions of primary minerals were assumed based on De Windt *et al*. (1999, 2008). Dolomite, muscovite, K-feldspar and Ca-montmorillonite were considered as the primary minerals of argillite (Case 1). In order to reproduce the formation of gypsum observed *in situ*, another mineral model (Model 2, Table 1) developed by Otsuka *et al*. (2008), including iron minerals, was tested, expecting that the formation of iron minerals would promote the dissolution of pyrite, the release of sulfur into the porewater and the formation of gypsum (Case 2). In order to promote the dissolution of clay minerals observed *in situ*, hypothetical initial contents of Na_2O and K_2O in the concrete were also tested (Case 3). The hypothetical initial contents, 0.55 wt.% Na_2O and 0.28 wt.% K_2O, correspond to the concentration of NaOH of 4 mol l^{-1} and that of KOH of 2 mol l^{-1} in the initial concrete porewater, assuming instantaneous dissolution. The kinetic dissolution of clay minerals such as Ca-montmorillonite, muscovite and kaolinite was assumed by applying the model for the dissolution rate of montmorillonite (Yamaguchi *et al*., 2007). The sources of the thermodynamic data were described by Yamaguchi *et al*. (2008) and Otsuka *et al*. (2008). Although MC-CEMENT ver. 2 solves cation exchange reactions of montmorillonite, they were not calculated because, under Ca-rich conditions with concrete, Ca-type montmorillonite was not likely to change to Na-type. The porewater compositions shown in Table 2 were used as initial conditions and as boundary conditions. The composition of the concrete porewater is one calculated by equilibrating water with the concrete. The composition of the argillite porewater is quite different from those reported in Tinseau *et al*. (2006) and in Beaucaire *et al*. (2008), but a simplified one for the modelling purpose (De Windt *et al*., 2008).

In order to test the improvement of the currently developed code, MC-CEMENT ver. 2, from the previous code, MC-BENT, a calculation was performed under the same conditions as the previous calculation presented at the XIV International Clay Conference (Yamaguchi *et al*., 2009b) (Case 4). The four calculation cases are summarized in Table 3.

RESULTS AND DISCUSSION

Case 1

Figure 2 shows the schematic distribution of the secondary phases observed in the argillite matrix (Tinseau *et al*., 2006) and the distributions of minerals after 15 years of interaction calculated by MC-CEMENT ver. 2. Calculated distributions of aqueous concentrations are also shown to better understand the mineral content, although no actual porewater compositions for comparison are available. The calculation reproduced observations such as the mineralogical changes in the argillite limited to within 1 cm in thickness, formation of $CaCO_3$ and CSH, dissolution of quartz, decrease in porosity

TABLE 2. Chemical compositions of initial porewaters used in the calculation. These compositions were also used as the constant concentration for the boundary conditions.

Components	Concrete porewater (mol l^{-1})	Argillite porewater (mol l^{-1})
H (H^+)	$10^{-12.52}$	$10^{-8.2}$
Na	7.04×10^{-5}	1.3×10^{-2}
K	6.30×10^{-6}	0
Ca	9.5×10^{-3}	0
Mg	2.01×10^{-10}	0
C (CO_3^{2-})	7.8×10^{-6}	0
Cl	1.68×10^{-4}	1.3×10^{-2}
S (SO_4^{2-})	2.24×10^{-5}	2.10×10^{-4}
Si	1.1×10^{-5}	0
Al	1.7×10^{-4}	0

TABLE 3. Summary of the conditions of four calculation cases.

	Case 1	Case 2	Case 3	Case 4
Mineral model	Model 1	Model 2[*]	Model 1	Model 1
Initial contents of Na_2O and K_2O in the concrete (wt.%)	0	0	0.55 and 0.28**	0
Code	MC-CEMENT ver.2	MC-CEMENT ver.2	MC-CEMENT ver.2	MC-CEMENT ver.2 and MC-BENT
pH of initial pore-water of concrete and constant boundary condition	12.52	12.52	12.52	13.4

* Model 2 allows formation of iron minerals such as siderite, wustite, magnetite and hematite.
** Na_2O content range of $0.028-0.55$ and K_2O content range of $0.014-0.28$ were also applied.

of the argillite and an increase in the concrete. These agreements indicate the possibility that models based on lab-scale (~1 year) experiments can be applied to longer time scales, although confidence in the models is necessary for much longer time scales.

Figure 4 shows the calculated evolution of the minerals and aqueous concentrations over 15 years at the interface. In the concrete, the calculation

shows the dissolution of portlandite and increase in the porosity after 1 year. No significant evolution of the concrete porewater can be seen. In the argillite, the calculation shows concentrations of C, K, Ca, Si, Mg, Al and Fe after the 1st calculation step of 6×10^{-5} years or 32 min. Dissolution of dolomite and formation of sepiolite and hydrotalcite finished in 0.15 year. Formation of CSH and laumontite, dissolution of quartz and decrease in the porosity
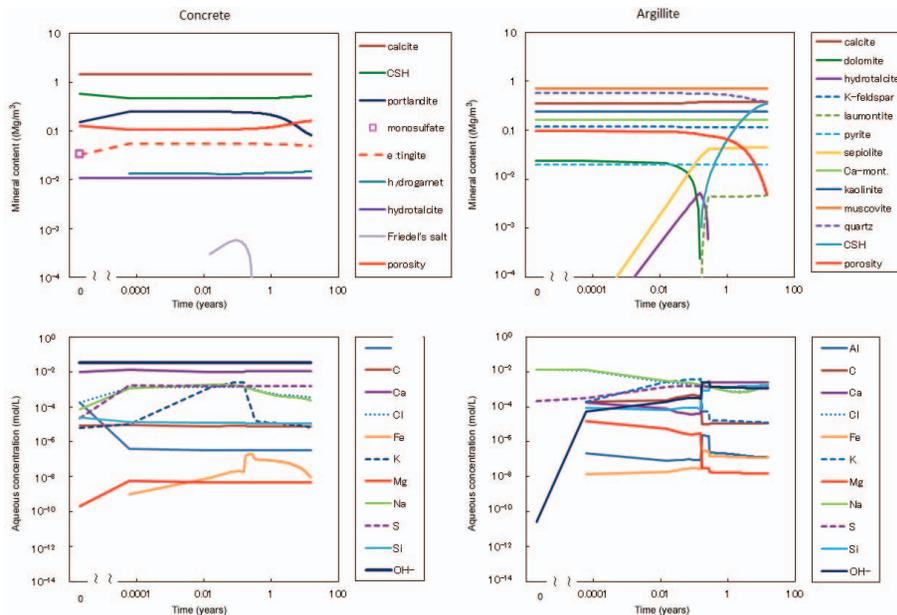

FIG. 4. Calculated evolutions of the minerals (upper) and aqueous concentrations (lower) over 15 years at the interface, at -0.05 cm in the concrete (left) and at $+0.05$ cm in the argillite (right).

occurs afterwards. The changes in minerals accompany abrupt changes in the aqueous concentrations at around 0.2 year.

Tinseau *et al*. (2006) reported that SEM photomicrographs show the blue centimetric zone characterized by intense precipitation of honeycomb neoformed clays and calcite. Our calculation shows the formation of sepiolite over a 3 mm range, which might correspond to the honeycomb neoformed clays; however, sepiolite is also called 'mountain leather' and its morphology is often string-like (Wada, 1992).

Our calculation did not reproduce the dissolution of clays and the formation of gypsum which indicates that there is still room for improvement in our model.

Case 2

The results of the calculations in which the formation of iron minerals were allowed in order to reproduce the formation of gypsum are shown in Fig. 5. Unfortunately, the formation of gypsum was not reproduced by the calculation. Although the formation of magnetite significantly decreased the concentration of iron in the porewater, the concentration of sulfur did not increase. It might be necessary to consider the contribution of dissolved oxygen to dissolve pyrite, to increase the concentration of sulfate in the porewater significantly and thus to form gypsum in the calculation. If anhydrite ($CaSO_4$) is considered in place of gypsum ($CaSO_4 \cdot 2H_2O$), it might be formed
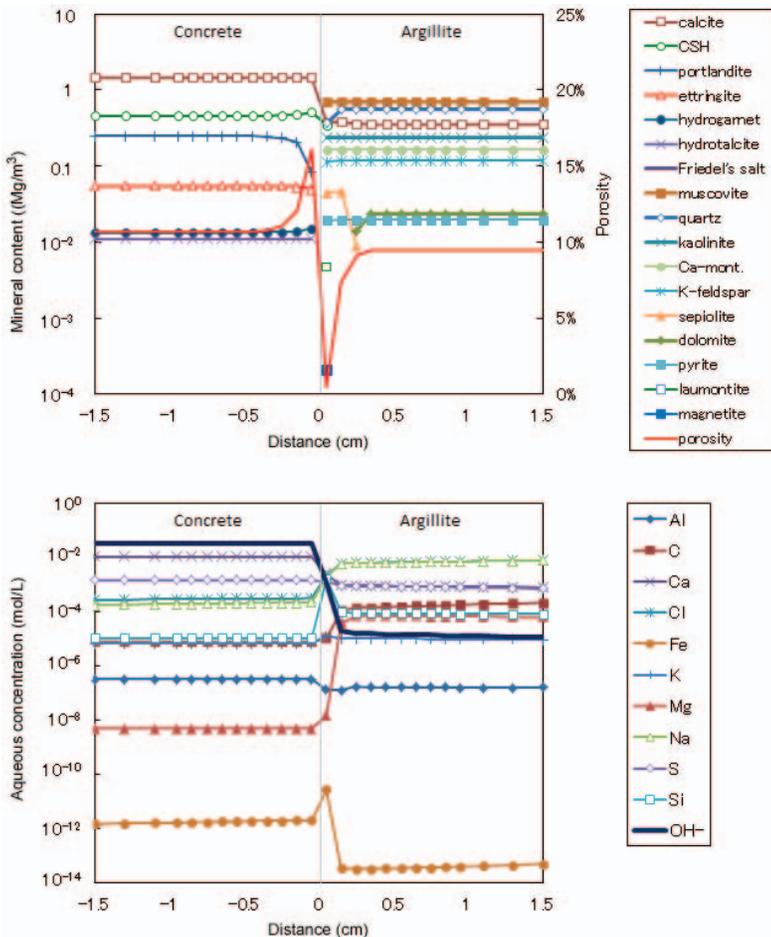

FIG. 5. Spatial distribution of minerals (upper) and aqueous concentrations (lower) after 15-year interaction calculated by MC-CEMENT ver.2 allowing formation of some iron minerals (Case 2).

in the model calculation. We did not try this because our mineral model had been verified with the experimental observation, including the formation of gypsum (Yamaguchi *et al.*, 2008).

Case 3

In order to promote the dissolution of clay minerals observed *in situ*, hypothetical hyperalkaline initial porewater compositions resulting from the dissolution of Na_2O and K_2O in cement clinker were also tested. The results are shown in Fig. 6. Although the concentration of OH^- in the argillite porewater became higher than in Case 1, which resulted in more dissolution of quartz and dolomite,

the clay minerals did not dissolve. To make matters worse, the porosity decreased significantly in the concrete at -0.05 cm and increased in the argillite at 0.15 cm, which disagreed with the observations.

In Case 1, Ca^{2+} and OH^- diffused into the argillite and formed CSH, which resulted in a decrease of the porosity. In Case 3 on the other hand, the hyperalkaline porewater (K-Na-OH) diffused into the argillite, dissolved minerals and increased the porosity. Dissolved Si diffused isotropically and formed CSH in the concrete by combining with $Ca(OH)_2$, which resulted in a porosity decrease in the concrete. In the argillite, the dissolved Si formed sepiolite over a 2−7 mm range and decreased the porosity. The difference in
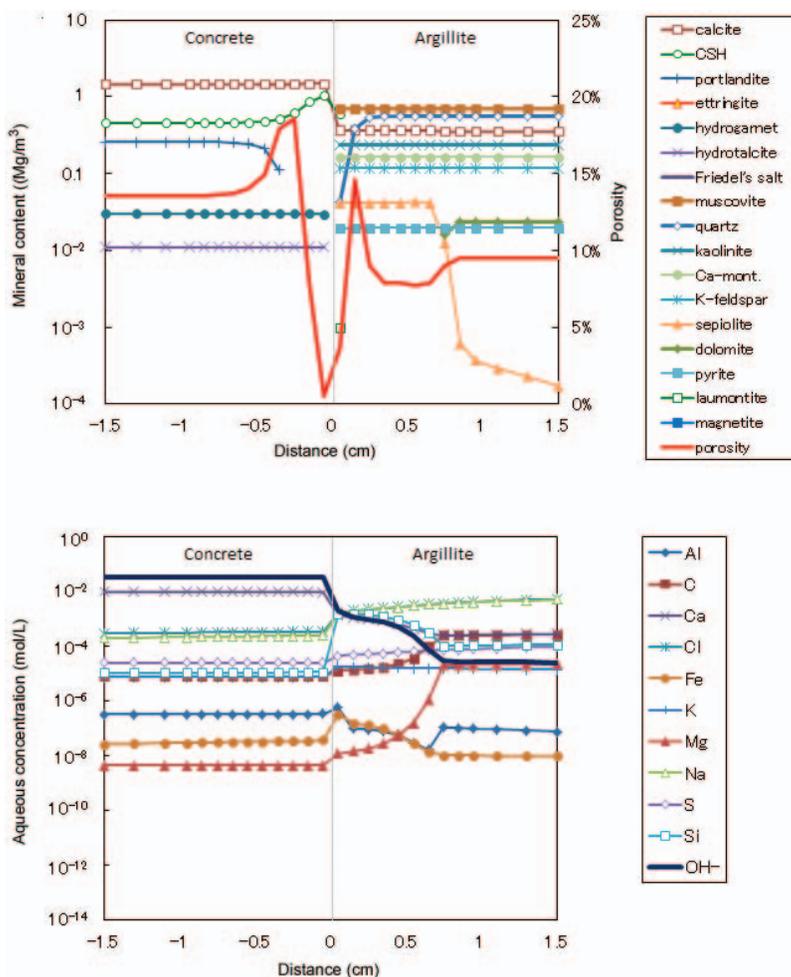

FIG. 6. Spatial distributions of minerals (upper) and aqueous concentrations (lower) after 15-year interaction calculated by MC-CEMENT ver.2 assuming Na_2O and K_2O contents in the concrete (Case 3).
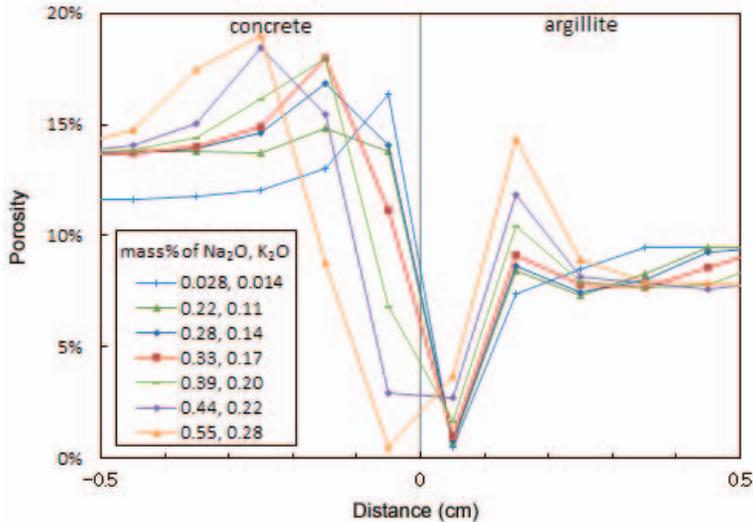
FIG. 7. Spatial distributions of the porosity after 15-year interaction calculated by MC-CEMENT ver.2 assuming variable Na_2O and K_2O contents in the concrete (Case 3).

the evolution of the porosity between Case 1 and Case 3 is systematically demonstrated in Fig. 7 in which the evolution of the porosity was calculated with varying $(Na, K)_2O$ content. The higher $(Na, K)_2O$ contents resulted in mineralogical alteration over a wider range and a drastic change in the porosity in the concrete at 0.05 cm from >15% down to zero. It is inappropriate to consider $(Na, K)_2O$ content in the concrete in this calculation because it resulted in the reverse evolution of the porosity. It may, however, be worthwhile to consider the $(Na, K)_2O$ content and cation exchange reactions together.

Case 4

Figure 8 shows our previous calculation using MC-BENT (Yamaguchi *et al.*, 2009b) and the results of the calculation by MC-CEMENT ver. 2 under the same conditions as the previous calculation (Case 4). Although they show similar trends, the range of mineralogical alteration of concrete extended to 7 mm in the previous calculation and 4 mm in the present calculation. The mineralogical alteration is characterized as a decrease in the porosity with the formation of ettringite. This is due to the increase in Ca concentration, accompanied by decreasing OH^- concentration caused by the diffusion of OH^- from the concrete to the argillite. The difference

between the two calculations arose from the fact that MC-CEMENT ver. 2 accounted for the low diffusivity in cement-based materials with a model of diffusive mass transport in micropores (Yamaguchi *et al.*, 2009a). The Case 4 calculation shows an increase in the porosity in the argillite and a decrease in the concrete, which is opposite to the observations. The mineralogical alteration of the argillite extends to 14 mm, which is more emphasized than the Case 3 calculation. This is consistent with the higher concentration of OH^- in Case 4 than in Case 3. Although the concentration of OH^- in the initial concrete porewater was higher in Case 3 ($[NaOH] = 4$ mol l^{-1} and $[K_2O] = 2$ mol l^{-1}) than Case 4, the Case 4 calculations resulted in highly alkaline conditions because pH 13.4 was assumed for the constant boundary condition at the edge of the concrete. This assumption would not be appropriate to reproduce the observed mineralogical alterations although it is useful to demonstrate the effect of the model of diffusive mass transport in micropores in cement based materials.

CONCLUSION

A PHREEQC-based, reactive transport analysis code (MC-CEMENT ver. 2) was developed for the long-term assessment of concrete/clay systems and was verified by comparing the results of the
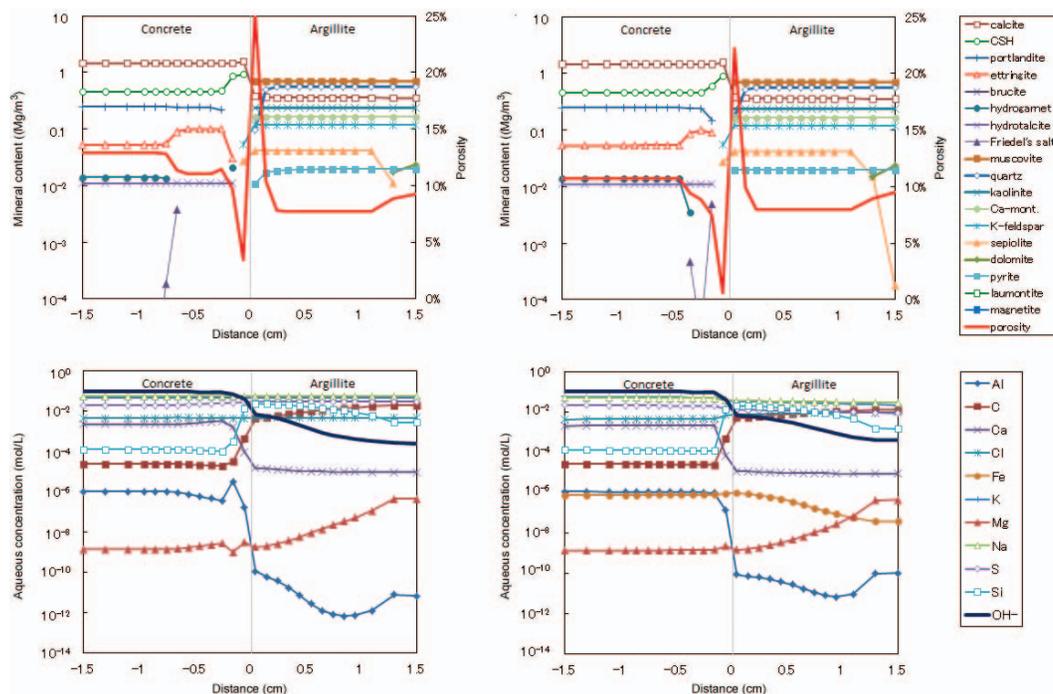
FIG. 8. Spatial distributions of minerals (upper) and aqueous concentrations (lower) after 15-year interaction calculated by MC-BENT (left; Yamaguchi *et al.*, 2009b) and the results of the same calculation by MC-CEMENT ver. 2 (right) (Case 4).

calculations with *in situ* observations of the mineralogical evolution at the concrete/argillite interface at the Tournemire URL. The calculation reproduced the observations such as the mineralogical changes in the argillite limited to within 1 cm in thickness, formation of CaCO₃ and CSH, dissolution of quartz, decrease of porosity in the argillite and an increase in the concrete. These agreements indicate the possibility that the models based on lab-scale (~ 1 year) experiments can be applied to longer time scales. The fact that the calculation did not reproduce the dissolution of clays and the formation of gypsum indicates that there is still room for improvement in our model such as considering dissolved oxygen and cation exchange reactions.

ACKNOWLEDGMENTS

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