Scientific paper

Calcite Precipitation at Cement–Bentonite Interface. Part 1: Effect of Carbonate Admixture in Bentonite

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Abstract

Calcium leaching from cementitious materials into bentonite is a key process for the long-term alteration of cement–clay interfaces of engineered barrier systems. Strong chemical gradients between cement and clay drive the precipitation of minerals such as calcium silicate hydrate (C–S–H) and calcite. To analyze the mineralogical and porosity evolution at the cement–clay interface, composite specimens consisting of cement paste and bentonite mixed with various amounts of sodium carbonate were subjected to immersion and chloride migrations tests and were investigated by electron probe micro-analysis (EPMA), thermogravimetry/differential thermal analysis (TG-DTA), and X-ray diffraction (XRD) after 4–20 months of immersion. The results show that adding sodium carbonate to the bentonite enhanced the formation of calcite in the form of a surface layer on the cement paste. This suggests pore clogging at the interface and implies the existence of a threshold amount of carbonate addition above which pore clogging occurs. This is the first of two papers; the accelerated evolution of the samples in the presence of an electrical field is discussed in the second paper.

1. Introduction

The safe management and disposal of waste in general and specifically of toxic and radioactive waste is of critical importance for maintaining a safe and sustainable society (Lang-Lenton León 2001). The designs of waste repositories vary depending on the type of waste and the national regulations; however, the design should always follow international standards for safe disposal (IAEA 2011).

In the case of radioactive waste, the majority of designs utilize significant quantities of cement-based materials for constructing access galleries, storage cells, concrete plugs, and engineered barriers as well as for backfilling voids (Glasser and Atkins 1994; Metcalfe and

Walker 2004). In many design concepts, clay materials such as bentonite are also used to seal access galleries and engineered barriers (Pusch 1992; Metcalfe and Walker 2004; Sugita *et al.* 2007). Furthermore, deep geological repositories are sometimes located in clay host rock (Alexander and McKinley 2007).

Because of the large geochemical differences between cement and clay, the long-term evolution of clay–cement interfaces is an active area of research (Gaucher and Blanc 2006; Gaucher *et al.* 2009; Savage 2013; Marty *et al.* 2015; Luraschi *et al.* 2020). The chemical gradient can cause the dissolution of primary minerals in both materials and induce the precipitation of secondary minerals near the interface. Mineralogical changes induce changes in porosity, transport parameters, and mechanical properties, and can therefore compromise or enhance the functionality of clay and cement materials.

Early experimental studies on clay–cement contacts utilized batch experiments to investigate the evolution of clay powder or compacted clay samples in alkaline solutions (Gaucher and Blanc 2006). More recently, experimental investigations have focused on examining the interactions between hardened cement/mortar/concrete and compacted clay, including mass transport processes across the cement–clay interface (Dauzères *et al.* 2010; Fernández *et al.* 2016; Yamaguchi *et al.* 2016; Balmer *et al.* 2017; Luraschi *et al.* 2020).

Long-term in-situ experiments in underground research laboratories (URLs) on cement–clay interactions have also been conducted, for example in Mol (Belgium) (Read *et al.* 2001), Tournemire (France) (Tinseau *et al.* 2006; Gaboreau *et al.* 2011), Bure (France) (Gaboreau *et al.* 2012), Grimsel (Switzerland) (Fernández *et al.* 2017) and Mont Terri (Switzerland) (Jenni *et al.* 2014; Mäder *et al.* 2017). These long-term experimental studies have

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revealed the precipitation of secondary minerals such as calcium silicate hydrate (C–S–H), magnesium silicate hydrate (M–S–H), calcite (Gaboreau *et al.* 2012; Fernández *et al.* 2017; Mäder *et al.* 2017), and gypsum (Gaboreau *et al.* 2012) near the cement–clay interface and corresponding reduction in porosity. Previous laboratory and field experiments have revealed that the typical extensions of porosity changes at cement–clay interfaces were a few hundred micrometers to a few millimeters in a few years (Jenni *et al.* 2014; Luraschi *et al.* 2020). Longer experiments with interaction times greater than 10 years showed detectible porosity changes up to 1–2 cm from the interface (Gaboreau *et al.* 2020, 2011). Larger changes were common in the cement material. While porosity was often reduced near the interface, porosity further away from the interface increased owing to the dissolution of hydrated cement phases. However, unambiguous conclusions regarding the mechanism of pore clogging have not yet been identified to date.

It is impossible to experimentally assess the very long-term evolution of cement–clay interfaces as part of the engineered barrier system for the lifetime of a deep geological repository. Computer simulations are frequently used to predict the evolution of chemical conditions and material properties in deep geological repositories. Such predictions require a thorough understanding of the chemical reactivity of materials influenced by the transport of reactants (Seigneur *et al.* 2019). Process-based computer models are often used to analyze laboratory and field experiments by testing alternative processes and scenarios. However, experiments can be used to calibrate or validate the assumptions in predictive computer simulations. Following the development of a calcium-leaching model for cement-based materials (Bentz and Garboczi 1992; Buil *et al.* 1992; Yokozeiki *et al.* 2003; Nakarai *et al.* 2006a), reactive transport modeling of cement–clay interactions has been conducted in numerous studies (van der Lee and De Windt 2001; Yokozeiki *et al.* 2004; Nakarai *et al.* 2006b; Berner *et al.* 2013; Kosakowski and Watanabe 2014; Liu *et al.* 2014; Blanc *et al.* 2015; Marty *et al.* 2015). Nearly all numerical models showed strong porosity reduction and even pore clogging in response to the precipitation of secondary minerals, mainly C–S–H and/or calcite, near the cement–clay interface. The main mechanism underlying these changes involves the creation of dissolution fronts on both sides of the interface due to the strong contrast in pH between cement and clay pore waters. In the pore water of cement-based materials, calcium and hydroxide in equilibrium with hydrated cement phases are consumed near the interface by reactions with silicon or carbonate that originates from the clay. The migration of hydroxide from the cement into the clay increases the pH, giving rise to the so-called pH plume, and enhances the dissolution of SiO₂ and clay minerals. These changes,

in turn, result in the release of silica, which also diffuses toward the interface from the clay compartment and contributes to secondary C–S–H formation. In addition, carbonate concentrations are generally higher in clay pore waters with intermediate pH than in those with high pH; hence, calcite formation is observed in the latter. Although the calculated mineralogical evolution qualitatively agrees with experimental data, the calculated clogging times often depend on the discretization of the modeling domain and the parametrization of kinetic control of mineral precipitation/dissolution (Marty *et al.* 2009; Hayek *et al.* 2011, 2012). At the clogging times, the mineralogical alteration depth in the clay barrier from the interface with cement significantly varies, for example, from 1 mm to 20 cm (Marty *et al.* 2009).

Experimental studies reported to date have shown that the precipitation of carbonates, pore structure, and pore size distribution change significantly during concrete carbonation (Patel *et al.* 1985; Ngala and Page 1997; Šavija and Luković 2016). The type of cement material has a strong impact on the consequences of carbonation; it is expected that, as a consequence of carbonation, the porosity of cement paste might change. In their review, Šavija and Luković concluded that the porosity decreases for Portland cement paste and concrete while the porosity increases for blended cement paste as a result of carbonation (Šavija and Luković 2016). Similar observations have been reported for carbonate precipitation in soils (Bronick and Lal 2005). Furthermore, the bio-mediated calcite precipitation method accelerates the precipitation of calcite, and has been used to improve the mechanical properties of soils (Gollapudi *et al.* 1995; De Muynck *et al.* 2010; DeJong *et al.* 2010; Ho *et al.* 2018) and to repair cracks in concrete (Wu *et al.* 2012; Al-Salloum *et al.* 2017; Huynh *et al.* 2019).

Current state-of-the-art developments regarding the understanding of chemical and pore-scale processes that control the precipitation in porous media have been summarized recently in two review papers (Putnis 2015; Stack 2015). These reviews highlighted some key advances, including the detailed study on calcite precipitation in small pores, which was conducted using a hydrogel with a diffusive transport setup (Nindiyasari *et al.* 2014), where the importance of pore size on the precipitation process was demonstrated. Currently, however, the more complex interplay between pore size, surface charges, solute transport, and precipitation kinetics remains poorly understood. In addition, although fundamental investigations of simple systems have been conducted using both experimental and numerical techniques (Tartakovsky *et al.* 2008; Katz *et al.* 2011; de Anna *et al.* 2014; Chagneau *et al.* 2015; Poonoosamy *et al.* 2016; Prasianakis *et al.* 2017), the processes in complex media, which are composed of many different mineral phases with a broad range of pore sizes, are still not well understood.

Table 1 Outline of composite specimens.

Specimen	Cement paste		Bentonite			Dry density
	Type of cement	W/C	Type of bentonite	Type of carbonate	Carbonate/ dried bentonite	
BL	Ordinary Portland cement (OPC)	0.60	Na-type (Kunigel V1)	—	0	$1.6 \times 10^3 \text{ kg/m}^3$
NC1				Na_2CO_3	1.0 %	
NC4				Na_2CO_3	4.0 %	

Table 2 Chemical compositions of cement and bentonite (wt%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cl	ig.loss	Insol.
Cement	21.28	5.09	3.15	65.36	1.01	2.01	0.32	0.41	0.25	0.14	0.10	0.006	0.84	0.10
Bentonite	70.7	13.8	1.49	2.30	2.26	0.29	2.56	0.33	0.20	0.05	0.08	<0.001	5.12	-

*ig.loss=loss of ignition, insol.=insoluble residue

The main objectives of the present study are 1) to improve the fundamental understanding of calcite precipitation at cement–clay interfaces by accelerating the precipitation and 2) to investigate the possibility of complete clogging of interfacial porosity by the addition of carbonate to a bentonite mixture. Such experimental data improve system understanding and allow validation of computer simulations for the long-term evolution of cement–clay interfaces. In this first study, we conducted experiments using cement–bentonite composite specimens immersed in water in a laboratory. We investigated the effect of adding sodium carbonate to pure bentonite by immersion tests in order to enforce calcite precipitation. After 4, 10, and 20 months, the degradation of the cement paste and bentonite was investigated postmortem using several experimental techniques to determine the progress of mineral alteration fronts and changes in porosity. Acceleration of ionic migration using electromigration methods is discussed in the second paper (Nakarai *et al.* 2021).

2. Material and methods

The experimental setup follows the experimental protocol for cement–clay interaction prescribed by the Radioactive Waste Management Funding and Research Center (RWMC 2008) in Japan. The RWMC investigated the evolution of cement–bentonite samples in immersion tests and reported the results of immersion tests for 10 and 20 months (RWMC 2010, 2011). In this study, we investigated the effect of adding varying amounts of sodium carbonate to bentonite (see **Table 1**). A reference sample without carbonate (samples BL), identical to the previous investigations, was also prepared.

2.1 Composite specimen consisting of bentonite and cement paste

For the immersion tests, composite specimens consisting of cement paste and bentonite materials were prepared. **Table 1** summarizes the material properties and the mixing ratio of sodium carbonate admixtures to the weight of dried bentonite (%) and **Fig. 1** shows the experimental configuration and sample dimensions. As alteration for the limited immersion test periods should be observed only in the surface layers at the interface (Jenni *et al.* 2014; Luraschi *et al.* 2020), the small

specimens were prepared.

The cement used in this experiment was ordinary Portland cement (OPC) without any admixtures and was specifically supplied by the Japan Cement Association (JCA) for research purposes. The chemical composition of the cement, based on the Japanese standard JIS R 5202 (2005), is listed in **Table 2**.

The high water-to-cement ratio of 0.60 for producing the cement paste samples resulted in high porosity, large pores (Cook and Hover 1999) and high diffusivity and

(a) Immersion test for detailed analysis (full model).

(b) Immersion test for the chloride migration test (half model).

(c) Chloride migration tests.

Fig. 1 Schematic diagrams of the cells for investigating the cement–bentonite interaction (left: cross section view, right: longitudinal cross section view).

decreased the degradation resistance of the cement paste (Bentz and Garboczi 1992). Cement and water were mechanically mixed at 30 °C. Before casting, the cement paste was allowed to rest in a bag for several hours at 30 °C: in the first 2–3 h, the cement paste was mixed every hour, and then mixing was done every 30 minutes until bleeding from the segregation disappeared. After casting, cylindrical specimens ($\phi 20$ mm $\times$ 70 mm) of cement paste were cured in hot water at 50 °C for 28 days to ensure mature cement hydration. After curing, the specimens were cut in 10 mm thick disks for the immersion tests. The chemical composition of the cement used is shown in **Table 2**.

The bentonite used in this study was Kunigel-V1, a Japanese sodium-type bentonite. The chemical composition of Kunigel-V1, as reported in the literature (Ito *et al.* 1993), is summarized in **Table 2**. In terms of mineralogy the bentonite included montmorillonite (47 wt%), quartz (37.5 wt%), plagioclase (4.1 wt%), analcime (3.3 wt%), calcite (2.4 wt%), dolomite (2.0 wt%), and pyrite (0.6 wt%) (Ito *et al.* 1993).

Three types of bentonite samples were prepared: pure bentonite (BL) and bentonite samples mixed with 1 % and 4 % sodium carbonate (Na_2CO_3) (NC1 and NC4, respectively) relative to the dried bentonite weight. The addition of carbonate in such amounts can provide sufficient carbonate to allow for pore clogging near the interface in a short time. In the case of carbonate–bentonite samples (NC1 and NC4), powdered chemicals were used for preparing mixtures. The mixtures were prepared such that the bentonite and sodium carbonate were homogeneously mixed. Then, the bentonite mixtures were statically compacted using a compressive machine. The dry density of the bentonite samples was found to be $1.6 \times 10^3 \text{ kg/m}^3$, which is around the designed value for the radioactive repository (Masuda *et al.* 1999).

For the immersion test, composite specimens with bentonite samples between two cement paste samples were prepared by Taiheiyo Consultant Co. Ltd. (**Fig. 1(a)**). First, a shaped cement paste sample was placed on one side of the acrylic resin cells with an inner diameter of 20 mm and length of 30 mm. Then, the compacted bentonite sample was positioned on the cement paste, and finally, another cement paste sample was placed on the top of the cell.

Furthermore, chloride migration tests were conducted after the immersion tests at Hiroshima University. For these tests, additional specimens were prepared (**Fig. 1(c)**) after immersion (**Fig. 1(b)**) as half models of the above specimens (**Fig. 1(a)**). The half model consisted of a 5 mm-thick bentonite disc that was set on top of a 10 mm-thick cement paste disc (**Fig. 1(b)**). The full model consisted of a 10 mm-thick bentonite disc sandwiched between two 10 mm-thick discs of cement paste (**Fig. 1(a)**). The different diameters of discs were necessary because of size limitations associated with some experimental equipment.

2.2 Immersion tests of the composite specimen

Before the actual immersion, the composite specimens were vacuum-saturated with deionized water. This leaches the alkalis in the initial cement pore solution and transforms the cement from the initial “Stage I” state (Berner 1992), which is characterized by high alkali concentrations and a pH of > 13 , into a “Stage II” state (Berner 1992), where the pH is buffered at ~ 12.5 by the existence of portlandite. During the pre-saturation procedure, the saturation of bentonite without cracking was visually checked from homogenous color changes of the specimens. Finally, the composite specimen was placed in 50 mL of deionized water for the immersion tests (see **Fig. 1**), which gave a liquid-to-solid ratio of approximately 5.3 by volume. The measured pH after 10 months of immersion test was 12.70 (RWMC 2010).

For bentonite, negatively charged species can only enter part of the pore space; they are repelled from negatively charged clay surfaces and cannot enter mono- or bi-hydrated clay interlayers (Van Loon *et al.* 2007). The fraction of the so-called anion accessible porosity depends on the type of bentonite, its compaction, and the ionic strength of the solution. For high compaction, the fraction of anion accessible porosity might become very small, as most water is present in the interlayers. In this study, Kunigel-V1 was compacted to a dry density of $1.6 \times 10^3 \text{ kg/m}^3$. For this density, the total porosity can be approximated to be 0.4 and the anionic porosity value to be 0.08 (0.2 of the total porosity) (Ishidera *et al.* 2008). If negatively charged carbonate complexes are excluded from the interlayer water of montmorillonite after re-saturation, the added sodium carbonate for the 4 % mixture exceeds its solubility limit (30.7 g/100 g water at 25 °C) for the (anion) accessible porosity. For the samples with 1 % carbonate addition, the sodium carbonate is completely dissolved.

2.3 Chloride migration tests of the cement paste specimen

After 4 months of immersion tests for the half-models shown in **Fig. 1(b)**, the cement paste samples were carefully prepared for the chloride migration tests as illustrated in **Fig. 1(c)**. All surfaces, except the interface with bentonite in the former immersion tests, were coated with acryloyl-modified acrylic resin. This allows one-dimensional in-diffusion tests with NaCl solution (3 % in mass) for 48 h from the surface affected by the contacted bentonite.

2.4 Experimental methods

After 4, 10, and 20 months of the immersion tests, test cells for detailed analysis were selected (**Fig. 1(a)**). The specimens were dismantled and cut into smaller samples using a diamond saw, as illustrated in **Fig. 2(a)**. The sub-samples were analyzed by electron probe micro-analysis (EPMA), thermogravimetry/differential thermal analysis (TG-DTA), and X-ray diffraction (XRD). In addition, for TG-DTA and XRD measure-

ments, powder samples of the interface surface layers with 1 mm thickness for the cement paste and 2 mm thickness for the bentonite were prepared. The sample thickness was chosen based on the thickness of the alteration zone measured by EPMA.

After completing the chloride migration tests, the specific specimens were also cut into smaller samples, as shown in **Fig. 2(b)**. EPMA measurements were conducted on the cross section indicated in **Fig. 2(b)** to qualitatively investigate chloride migration.

Each measurement was conducted using one sample from the specimens, although it was not sufficient to capture the variability among samples. As significant inconsistency among the results (e.g. unbalanced alteration between two cement–bentonite interfaces, unstable progress of degradation with time) for each sample was not observed, the experiments are well suited to capture the basic processes responsible for porosity change at the interface and to improve understanding on the effect of adding carbonate to the bentonite.

(1) EPMA measurement

Chemical element mapping on cross sections of the composite specimens was conducted using a JXA-8200 (JEOL Ltd., Japan) electron probe microanalyzer. The polished plain surface was coated with carbon (25–30 nm thick) as the conductive material. The acceleration voltage was 15 kV and the pixel size was $40\ \mu\text{m} \times 40\ \mu\text{m}$, with a counting interval of 40 ms. A standard published by JSCE (JSCE 2005) has been referred.

(2) XRD analysis

Mineral contents on the surface layer of the cement paste were qualitatively analyzed by XRD using an X'Pert

PRO (PANalytical, Netherlands) diffractometer. The measurement conditions were as follows: X-ray source Cu-K α , tube voltage 40 kV, tube current 45 mA, scanning range $2\theta = 5^\circ$ to 60° , step width 0.017° , and a measurement time for one step of 0.2 s.

(3) Thermal analysis

Samples from the surface layer of the cement paste and the surface and inner layers were prepared for TG-DTA using a Thermo plus evo2 TG8121 (Rigaku, Japan). The change in weight was measured from room temperature to 1000°C with the temperature ramped up at a rate of $10^\circ\text{C}/\text{min}$ under nitrogen gas flow. The temperature ranges for calculating the amounts of calcium hydroxide ($\text{Ca}(\text{OH})_2$) and calcium carbonate (CaCO_3) were determined from the measured DTA curves. The determined ranges were approximately $410\text{--}470^\circ\text{C}$ for $\text{Ca}(\text{OH})_2$ and $510\text{--}710^\circ\text{C}$ for CaCO_3 .

3. Experimental results and discussion

The results of calcium elemental mapping on cross sections of the composite specimens after 20 months of immersion are shown in **Fig. 3**. Some cracks are visible in both the cement paste and bentonite. These artifacts are probably caused by drying as a necessary part of the sample preparation process, because there were no mineralogical alternations observed in or around the cracks. In the cement paste adjacent to the interfaces, a decrease in the calcium content is observed. The extension of the calcium-depleted zone is inversely correlated to the amount of premixed carbonate in the bentonite. For a sample with a high premixed carbonate content, the width of the calcium-depleted surface layer is smaller.

Fig. 3 Calcium element mapping (wt%) measured by EPMA on the specimens (cement paste–bentonite–cement paste) after 20 months. (Left: BL-20M; Center: NC1-20M; Right: NC4-20M).

This observation will be discussed later in the paper considering pore clogging.

For a detailed quantitative analysis, longitudinal profiles for selected elements across the alteration zones at the interfaces were constructed from the EPMA measurements (**Fig. 4**). The profiles for the initial element contents in the cement paste and bentonite were interpolated from unaltered material compositions after 4 months of interaction (dashed lines in **Fig. 4**). The profiles of aluminum, magnesium, and iron show fewer changes and the detailed measurements are included in the **Appendix**.

The results of XRD (**Fig. 5** and **Appendix**) and TG-DTA (**Fig. 6**) on the cement side show an increase in portlandite and calcite in the surface layers of cement paste specimens as the amount of carbonate admixture is increased. For sample BL (no carbonate admixture), the portlandite was completely dissolved and no calcite was

present after 20 months, while for sample NC4 (4 % carbonate admixture), both portlandite and calcite are present.

Figure 7 shows the measured XRD patterns from the bentonite surface layer within the range between 26° and 31° for the initial and final specimens in this study. The XRD patterns for all specimens are given in the **Appendix**. Samples BL and NC1 showed evidence of smectite dissolution after 20 months, while C–S–H seems to have precipitated. Sample NC4 shows no significant change that can be related to the change in mineralogy.

3.1 Mineralogical evolution at interface of reference sample without carbonate admixture

In the case of BL, high and continuous diffusion across the interface caused strong changes not only in calcium but also in sodium, silica, and sulfate. Calcium leaching

Fig. 4 Longitudinal profiles of main chemical compositions measured by EPMA.

decreased the calcium content in the cement side and increased the calcium in the bentonite side (Fig. 4(a)). Calcium leaching causes portlandite to quickly disappear at the surface of the cement paste (Figs. 5 and 6). The degraded depth of cement paste with time, defined by the calcium-leached depth from the interface in Fig. 4(a), is plotted in Fig. 8. The calcium-leached depth was obtained from the area showing clear drop of calcium concentration measured by EPMA. The depth of the calcium-depleted zone increased in proportion to the square root of time, similar to other immersion tests of cement paste in solutions (Carde *et al.* 1997; Haga *et al.* 2005; Choi and Yang 2013). Square-root dependency is typically found in processes that are controlled by diffusive transport, for example, for reaction fronts originating from cement/clay interaction (Kosakowski and Berner 2013; Kosakowski *et al.* 2014) and for the progress of carbonation fronts (Papadakis *et al.* 1989; Richardson 2002; Ta *et al.* 2016).

In addition, in the calcium-leached area of the cement paste, sulfur content was depleted and sulfur accumulated at the leaching front (Fig. 4). This observation can be explained by the release of sulfate from ettringite/monosulfate decalcification and re-precipitation at the leaching front because of high pH, similar to what is observed during carbonation (Kobayashi *et al.* 1990).

In the bentonite, the calcium increase corresponded to

Fig. 5 Changes in XRD intensities of minerals at the surface layer of cement paste specimens before and after immersion tests (dotted lines show results before, and solid lines show results after the tests).

the decrease in sodium content, which suggests cation exchange (Sposito *et al.* 1983). Furthermore, silica dissolution at the surface layer of bentonite was observed (Fig. 4). The dissolution of quartz and clay minerals is known to be accelerated at high pH (Palandri and Kharaka 2004).

The XRD measurements from the bentonite surface layer (Fig. 7) suggest that the dissolution of smectite in bentonite is caused by the high pH front progressing into bentonite from the cement side. The increase in pH in bentonite is supported by the formation of C-S-H detected on the clay surface. This observation is consistent with other experimental studies (Dauzeres *et al.* 2010; Fernández *et al.* 2016) and numerical modeling (De Windt *et al.* 2004; Kosakowski and Berner 2013).

3.2 Minerological evolution at interface of samples with carbonate admixture

(1) Changes in cement paste

The addition of sodium carbonate to bentonite altered the mineral evolution of the cement samples. The extent of calcium depletion and other changes in Figs. 4–6 and 8 was significantly smaller for samples with additional sodium carbonate.

With the addition of 1 % sodium carbonate (NC1), the

Fig. 7 Changes in XRD intensities of minerals at the surface layer of bentonite specimens before and after immersion tests (dotted lines show results before, and solid lines show results after the tests).

Fig. 6 Changes in the amounts of Ca(OH)_2 and CaCO_3 measured by TG-DTA at the surface layer of cement paste

decrease in the calcium concentration on the cement paste and its increase in on the bentonite were much smaller than those without carbonate (**Fig. 4(a)**). These observations indicate reduced diffusive fluxes across the interface owing to partial pore clogging caused by calcite precipitation at the interface. However, the progress of calcium leaching from cement paste was not stopped and was also proportional to the square root of time after 4 months (**Fig. 8**). The XRD (**Fig. 5** and **Appendix**) and TG-DTA (**Fig. 6**) results show that mineral changes at the surface of cement paste in the cases with sodium carbonate added to bentonite depended on the amount of carbonate added. For samples NC1 (less carbonate mixing), portlandite continuously dissolves with rates decreasing proportionally to the square root of time (**Fig. 6**). Calcite precipitation occurred within less than 4 months and no significant changes were observed later.

In samples with 4 % sodium carbonate addition (NC4), the degraded depth did not change after 4 months, as shown in **Figs. 4** and **8**. Relatively large changes at the interface were observed in the first measurements (4 months). The distinctive changes were the increase in sodium content and the decrease in sulfate content in the surface layer of the cement paste (**Fig. 4**), and more than half of the portlandite dissolved quickly (**Figs. 5** and **6**). Large amounts of calcite were precipitated for NC4 during the first 4 months. The amount of calcium necessary for calcite precipitation was close to the amount of calcium released by portlandite dissolution; this strongly indicated the proposed carbonation reaction. Although secondary mineral precipitations such as feldspar after ettringite/monosulfate dissolution seem possible by the increases in sodium and silicon, XRD patterns did not detect any additional minerals except calcite (**Fig. 5**).

(2) Changes in bentonite

In the initial samples, there were no significant differences visible for samples with and without an admixture of sodium carbonate. After immersion tests for 20 months, mineralogical alterations were clearly observed in BL and NC1, while NC4 did not show any significant changes (**Fig. 7** and **Appendix**). In the case of BL, the smectite peak disappeared and C-S-H was detected. In

the case of NC1, the smectite peak also disappeared and the peaks at $\sim 28.5^\circ$ were shifted to lower angles related to zeolite or feldspar. These observations indicate the dissolution of smectite in bentonite and the precipitation of secondary minerals associated with calcium leaching from cement paste. During sample collection after the immersion tests, hardened bentonite mixtures were observed in BL and NC1. This implied a change in the structure of bentonite by cementation with secondary mineral precipitation.

(3) Effect of amount of carbonate mixture

Maximum potential amounts of calcite precipitation in the surface layer of the cement paste specimen were calculated (**Fig. 9**). We assumed that all premixed carbonate in bentonite was consumed to generate CaCO_3 in this 1-mm layer during immersion tests. The calcite contents of the original bentonite were not considered because calcite precipitation in the cement paste of BL and changes in the calcite peak in bentonite mixtures were not observed by TG-DTA and XRD.

The relationship between the amount of calculated potential and measured CaCO_3 is plotted in **Fig. 9**. For NC1 (low carbonate admixture), the measured CaCO_3 almost agrees with the calculated potential amount. This indicates that the admixed carbonate was completely used to precipitate CaCO_3 in the surface layer of the cement paste. For the NC4 case (high carbonate admixture), the measured amount was much smaller than the calculated potential amount. This and the existence of portlandite after 4 months implies that only part of the carbonate was used to form calcite. In combination with the observation that the evolution of the system stopped completely after 4 months, it can be assumed that the calcite precipitation in case NC4 clogged the pore space and prevented the migration of remaining carbonate into the cement sample. Furthermore, the measured amount of 20 % calcite can be interpreted as a threshold value necessary to clog the pore space. The amount necessary to clog the pore space is specific for this cement, as porosity (pore size distribution) and composition in terms of hydrated cement minerals influence the amount of

Fig. 8 Depth of degradation cause by calcium leaching from the interface in cement paste.

Fig. 9 Relationship between potential and measured amounts of CaCO_3 .

calcite needed to fill the pore space.

3.3 Post transport properties of cement paste contacted with bentonite

The hypothesis of pore clogging is supported by the results of chloride migration tests. The diffusive flux across the interface for the different samples can be demonstrated with the help of the chloride profiles shown in **Fig. 10**. Chloride diffusion across the interfaces (exposed surface) was clearly observed in the BL and NC1 cases. A similar extension of chloride penetration depth for BL and NC1 indicates that transport across the interface is similar, although the mineralogical evolution of the interface is not identical. This is in line with the observation of the continuous progress of calcium leaching shown in **Fig. 8**. For sample NC4, considerably less chloride crossed the surface. The significant reduction in mass flux can therefore support the hypothesis of pore clogging by rapid calcite precipitation. This also agrees with the constant degraded depth after 4 months observed in **Figs. 4** and **8**. The effect of heterogeneity of the microstructure should be discussed using long-term experimental results in the future.

4. Conclusions

In this study, the cement–bentonite interface reaction with a focus on calcite precipitation was investigated on composite specimens of cement paste and compressed bentonite/carbonate mixtures. To accelerate the calcite precipitation at the interface, sodium carbonate was premixed into the bentonite.

Our experimental results revealed that premixed carbonate in bentonite indeed promotes calcite precipitation in the surface layer of the cement paste in contact with bentonite if the initial amount of premixed carbonate is sufficiently high. When the carbonate content was too low, alteration still progressed at a slower rate after calcite precipitation and the transport property of the cement paste did not change. Conversely, a sufficiently high carbonate content resulted in less alteration, a stable composition, and significant reduction of post chloride migration after the early reaction. This suggests pore clogging at the interface, thus implying the existence of a threshold amount of carbonate for pore clogging.

The first samples taken after 4 months already sug-

gested a completely clogged interface for high carbonate admixture samples. Therefore, our measurements did not provide detailed insight into how fast calcite precipitation and pore clogging occurred. We suspect that the clogging had to occur very quickly, as alterations near the interface were very small.

Owing to the small number of samples, the influence of material heterogeneity on interface evolution and clogging conditions could not be determined in this study. However, the analysis shows consistency in terms of mass balance and allows the research to clearly quantify the effect of carbonate addition to bentonite, such that our results can be considered representative in terms of interface evolution and processes that drive porosity clogging.

To determine the feasibility of premixed carbonate to engineered barrier systems for surface and deep geological disposal of radioactive waste, field studies are needed that investigate the properties and the long-term stability of such clogged interfaces under the influence of changes in mechanical loading, thermal pulse or chemical gradients. As pore structure of cementitious materials is one of the key factors controlling pore clogging, microstructure analysis using scanning electron microscopy (SEM), atomic force microscope (AFM), X-ray and neutron tomography, and other methods should also be conducted in future studies. Selective application of the premixed carbonate should be additionally discussed as an effective method for thick bentonite barriers.

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Fig. 10 Mapping of chloride profiles after migration tests.

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Appendix A:

Chemical composition profiles measured by EPMA are shown in **Fig. A1** in addition to main chemical composition shown in **Fig. 4**.

Fig. A1 Longitudinal chemical composition profile measured by EPMA

Appendix B:

All measured XRD intensities of minerals are summarized here. **Figs. B1** and **B2** show XRD intensities measured at the surface layer of cement paste and bentonite specimens, respectively.

Fig. B1 Changes in XRD intensities of minerals at the surface layer of cement paste specimens before and after immersion tests.

Fig. B2 Changes in XRD intensities of minerals at the surface layer of bentonite specimens before and after immersion tests.