Calcite Precipitation at Cement–Bentonite Interface. Part 2: Acceleration of Transport by an Electrical Gradient

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Abstract
Calcium leaching from cementitious materials in contact with bentonite in nuclear waste repositories can alter the functionality of an engineered barrier system. In this study, we contribute to the fundamental understanding of calcite precipitation at cement–bentonite interfaces by adding carbonate to bentonite. In addition, we accelerate the transport of charged reactants towards the interface using an electrochemical migration method. The carbonate admixture successfully promotes calcite precipitation at the surface of cement paste. The analysis also revealed that the amount of precipitated calcite is not simply correlated to the amount of added carbonate or the applied electrical potential. Experiments in which bentonite pore water contains high initial contents of carbonate exhibit rapid calcite precipitation in a very narrow region at the cement–bentonite interface, resulting in pore clogging. This is the second of two papers; the system evolution without an electrical gradient was discussed in the first paper. This paper is the extended version in English from the authors’ previous works [Watanabe and Nakarai, (2008). “Effect of NaHCO3 in bentonite on calcium leaching from cementitious material.” Proc. of the JCI, 30(1), 717-722. Nakarai, et al., (2010). “Effect of carbonate mixing into bentonite on calcium leaching of cementitious material.” Proc. of the JCI, 32(1), 713-718. (in Japanese)]

1. Introduction
This paper is the second of two papers on pore clogging by calcite precipitation at the contact between cement and clay based materials (Nakarai et al. 2021). Such kind of interfaces exist commonly in engineered underground structures, e.g., tunnels (Kovári 2003; Thomas 2008), radioactive waste disposal (Pusch 1992; Glasser and Atkins 1994; Metcalfe and Walker 2004; Alexander and McKinley 2007; Sugita et al. 2007) or in cemented boreholes (Allan 2000; Kang 2014; Collier et al. 2019). The cement–clay interfaces are characterized by strong geochemical gradients in combination with mass transport in relatively tight materials, which fosters long-term mineral precipitation/dissolution and associated changes of porosity and mass transport across the interface (Gaucher and Blanc 2006). Our goal is to find ways to speed up and control pore clogging at the interface. A completely clogged interface suppresses mass transfer across the interface, which would be advantageous for many applications, e.g., as an effective transport barrier in (radioactive) waste disposal.

In the first paper, we described 20 months immersion tests for cement–bentonite/carbonate composite specimens (Nakarai et al. 2021). Calcite precipitation at the interfaces was promoted by adding carbonate to the bentonite mixture. When the carbonate content was high enough, the cement–bentonite interface showed less alteration expect for significant calcite precipitation and considerable reduction of post chloride migration after the early reaction. These findings in the first paper suggested pore clogging at the interface, thus implying the existence of a threshold amount of carbonate for pore clogging.

Experimental investigations on the cement–clay interfaces often use composite specimens consisting of cement/mortar/concrete and compacted clay (Sugiyama and Tsuji 2008; Dauzeres et al. 2010; Shafizadeh et al. 2015; Fernández et al. 2016; Yamaguchi et al. 2016; Balmer et al. 2017) same as the first paper. More recently, long-term in-situ experiments in underground research laboratories (URL) on the cement–clay interfaces have also been conducted (Read et al. 2001; Gaboreau et al. 2012; Mäder et al. 2017). Generally, the experimental investigation of cement–clay interactions are limited by the slow evolution of these systems as a result of the slow mass transport across the interface and slow dissolution and precipitation kinetics of clay minerals.

Several techniques have been employed to accelerate the slow transport and mineral transformations in liquid-saturated compact or solid samples, including experiments at elevated temperatures (Nakayama et al. 2004; Balmer et al. 2017), application of electrical gra-
and, for the first time, a consistent interpretation of all experimental data. The calcite precipitation at cement–clay interfaces without an electric potential was discussed in the first paper (Nakarai et al. 2021).

2. Material and methods

We produced composite specimens of cement paste and (hydrogen) carbonate–bentonite–sand mixtures to investigate cement–bentonite interactions. The electromigration experiments using the composite specimens are described in detail in our publication (Nakarai et al. 2010), but as the description is not available in English, the procedure is also summarized here. For all experiments, we used the same type of cement paste using ordinary Portland cement (OPC). The cement was in contact with bentonite–sand mixtures (dry density of 1600 kg/m³ and sand ratio of 30 wt%) and various amounts of sodium hydrogen carbonate (NHC samples) or sodium carbonate (N2C samples) (Table 1). Reference samples without carbonates (BLC samples) were also prepared. The evolution of the samples was investigated after using electrochemical migration for different periods (Table 2). These experiments allowed us to systematically investigate the influence of bentonite/sand/carbonate mixing proportions and the elec-
trocological migration period.

2.1 Composites of bentonite–sand mixtures and cement paste

(1) Preparation of bentonite–sand mixtures

Six composite mixtures of bentonite, sand, and carbonate (BLC, NHC1, NHC4, N2C1, N2C4, and N2C12) were prepared as shown in Table 1. Sample BLC corresponds to the current Japanese buffer material composition (JAEA and FEPC 2007), which is based on an Na-type bentonite (70 wt%) (Kunigel V-1) mixed with sand (30 wt%). In these experiments, only the fraction with grain size of 1.2–5 mm from schalstein sand was used.

The bentonite–sand mixture was similar to the material used for an earlier study (Sugiyama et al. 2005). The target dry density of the mixture was 1.6 × 10³ kg/m³, which resulted in a residual water content of 41 % after saturation with water. To achieve this density, the water content of the bentonite–sand mixture was adjusted to 26 % for efficient compaction. A low dry density and high water content facilitate a relatively high effective mobility for the dissolved species, which in turn reduces the execution times required for migration experiments.

Two types of carbonate, sodium hydrogen carbonate (NaHCO₃) and sodium carbonate (Na₂CO₃), were added to the sand–bentonite mixture. Sodium compounds were selected because they do not transform Na-type bentonite into other bentonite forms (e.g., Ca-type bentonite) and thus preserve the chemical and mechanical properties of the bentonite. The carbonate was added at 1 %, 4 %, and 12 %, relative weight to dried bentonite, to produce the desired carbonate/bentonite mixtures. The mixtures were designed such that the bentonite and sand contents were constant for all specimens and the added carbonate was assumed to be dissolved in the pore water of bentonite mixtures. Porosity changes caused by swelling of the bentonite were not considered in this study.

The 12 % addition was only used with sodium carbonate. Maximum carbonate additions were limited by the solubility, i.e., the 12 % addition affords a carbonate/water ratio equal to 32.3 g carbonate/100 g water, which is almost similar to the solubility limit for sodium carbonate (30.7 g/100 g water at 25 °C). For sodium hydrogen carbonate, the 4 % addition corresponds to 10.8 g carbonate/100 g water, which is similar to its solubility limit of 9.6 g/100 g water at 20 °C. When the water bound in interlayers of montmorillonite is excluded from chemical equilibrium calculations (Pusch et al. 1990; Van Loon et al. 2007), the added carbonates become much higher than the solubility limits. This leads us to believe that not all carbonate was dissolved and that even for low carbonate additions the carbonate concentrations in the bentonite pore water were in equilibrium with the (hydrogen) carbonate.

The bentonite and sand were mixed with an Omni-mixer. After the first round of mixing for 30 s, the target water content of 26 wt% for compaction was achieved by spraying a defined amount of water during the second mixing for 60 s. While carbonate was dissolved in the sprayed water in advance for the specimens with 1 % carbonate (NHC1 and N2C1), powdered chemicals were additionally mixed with the spraying distilled water for higher carbonate content samples (NHC4, N2C4 and N2C12). After mixing, the moisture content of the samples was homogenized by storage in a polyethylene bag for 24 h. The achieved water content was also checked by oven-drying the samples at 105 °C for 24 h.

(2) Preparation of cement paste

Cement paste samples were produced with the same recipe as for ordinary Portland cement (OPC). Table 3 shows the average chemical compositions based on two representative samples. Firstly, fresh OPC paste was cast in a cylindrical mold with a diameter of 100 mm and height of 200 mm with a water-to-cement ratio of 0.45. The specimens were cured under sealed conditions for one day and then cured in water for 28 days at 20 °C. To reduce the effect of segregation, the first 10 mm from both the top and the bottom of each specimen were removed. For electrochemical migration tests, disks with a thickness of 25 mm were prepared from the remaining material. Before preparing a composite specimen with compacted bentonite–sand mixtures, the cement paste was fully saturated with calcium hydroxide solution by vacuum saturation.

(3) Preparation of composite specimens

For the electromigration tests (see Fig. 1 and Appendix A), the bentonite–sand mixture was compacted on the hardened cement paste in an acrylic resin-based migration cell, which was originally designed for concrete chloride migration tests (Japan Society of Civil Engineers Standard JSCE-G571:2003). The bentonite–sand mixture was compacted 11 times per layer by dropping a 2.5 kg rammer from a height of 300 mm. A wire mesh electrode was placed 65 mm from the interface and covered with a 10-mm layer of bentonite–sand–carbonate mixture. The total length of the composite specimen was 100 mm.

2.2 Migration tests

All tests were conducted at 20 °C and under atmospheric pressure. As a reference, a test without electrochemical acceleration was conducted using sample BLC0. All
other samples were accelerated by applying a constant DC voltage difference of 5 V across the interface. To apply the electrical potential gradient, stainless steel electrodes (4 mm aperture, $70 \times 70 \text{mm}^2$ wire mesh) were used. While the cathode was embedded in the bentonite–sand mixture, the anode was immersed in a saturated calcium hydroxide solution in contact with the surface of the cement paste specimen, as shown in Fig. 1 and Appendix A. The electrical gradient was applied for three different time periods: short (S: 110 h), medium (M: 260 or 310 h), and long (L: 720 h). The accumulated amount of charge during these periods is shown in Table 2.

### 2.3 Post-mortem analysis

Following the electrochemical migration tests, each test cell was dismantled and the experimental specimen was removed. As illustrated in Fig. 2, each specimen was cut into smaller samples using a low-speed precision diamond cutter with a thin blade (blade thickness: 0.3 mm) and characterized using the following experimental methods. Because difference in carbonate type showed minor impact on the obtained results of electrical charge (Table 2), this paper focused its main discussion on the comparison among BLC, NHC4, and N2C12.

![Fig. 1 Schematic diagram of electrochemical migration test setup for composite specimens.](image1)

![Fig. 2 Schematic diagram of samples for measurements after electrochemical migration testing.](image2)

(1) Characterization of cement paste sub-samples

The cement paste specimens were divided into several layers, two of which were collected for subsequent analysis. The layers of interest included the cement paste layer within 2 mm from bentonite interface (surface) for investigating the reactions at the interface, and the layer located between 10 and 15 mm from the interface (inner) for confirming the stability of the inner part. The exact thickness of the interface layer is not known, as it was technically not feasible to cut the specimen thinner than 5 mm. Since degradation of the inner cement paste layer (10–15 mm from the interface) was not detected, only the results obtained for the surface layer are presented in this work.

Each layer of cement paste was entirely crushed and sieved through a 90-μm-pore filter to obtain particles with size $<90 \mu m$ for thermogravimetry and differential thermal analyses (TG-DTA). The weight change was measured from room temperature (~20 °C) to 800 °C at a rate of 20 °C/min. The temperature range between 400 and 500 °C was used to determine the amount of portlandite (Ca(OH)$_2$) and the range between 600 and 750 °C was used to calculate the amount of calcium carbonate (CaCO$_3$). The mass of cement in the sample measured at 800 °C was used to determine the relative mineral contents.

The mineral contents in the surface layer of the samples subjected to the long-term electrochemical migration tests (BLC-L, NHC4-L, and N2C12-L) and the reference sample (BLC-0) were qualitatively analyzed by X-ray diffraction (XRD). Powder samples were used after vacuum drying for 24 h. We used a system with a Cu-K$_\alpha$ X-ray source, tube voltage of 32 kV, tube current of 20 mA, scanning range of $\theta = 5°$ to $55°$, step width of 0.02°, and step measurement time of 2 s.

For BLC-0, BLC-S/L, NHC4-L, and N2C12-S/M/L, cement paste specimens were longitudinally cut to conduct electron probe micro-analysis (EPMA) on their cross-sections. The analyzed plane surface area was 40 mm wide and 65 mm long. After careful polishing by silicon carbide powder with kerosene, followed by vacuum drying, the plane surface was coated with a carbon or gold conductive layer. The accelerating voltage was set to 15 kV and the pixel size was 50 μm. The counting interval was 40 ms. The target elements in the cross-section were calcium and carbon for the quantitative analysis wollastonite and calcite, and were used as reference materials.

The pore size distributions of the cement paste were estimated by mercury intrusion porosimetry (MIP) for several representative specimens (BLC-0, BLC-L, NHC4-L, and N2C12-M). Because of the limitation of experimental capacities, N2C12-L was not measured so that the later discussion includes limitations caused by the difference in the test periods. In addition, although the use of MIP for investigating the pore structure of cement-based materials has been criticized (Diamond 2000), it was applied here to discuss general trends in...
porosity changes. The samples were crushed and selected pieces with size in the 2–5 mm range were dried in a vacuum desiccator for 24 h before the measurements.

(2) Experimental investigation of bentonite–sand–carbonate sub-samples
The bentonite–sand mixture specimens were divided into seven layers (numbered from 1 to 7, in the direction from the interface), all with a thickness of 10 mm, except for the one closest to the cement paste interface, which only had a thickness of 5 mm. Each layer was crushed to obtain particles with a size below 150 μm in order to measure cation concentrations and swelling capacities. The concentrations of calcium and sodium ions in bentonite mixtures before and after migration tests were measured as exchangeable ions using the ammonium acetate method (Lavkulich 1981). The cations were extracted from the bentonite–sand mixture using a 1.0 M ammonium acetate solution and then their concentrations were measured by atomic absorption spectroscopy (AAS).

To observe the swelling capacities of the bentonite mixtures before and after the migration tests, the swell index was measured as an increase in the free volume according to the Japan Bentonite Manufacturers Association Standard JBAS104:77. We mixed 2.0 g of the bentonite–sand mixture powder with 100 mL of distilled water and the volumetric increase (with a unit of mL/2 g based on the standard) was visually measured after 24 h. Similar procedure can be found in ASTM D 5890.

2.4 Geochemical thermodynamic modeling
To assist with the interpretation of the experimental results, we created a geochemical model for the cement paste and bentonite–sand–carbonate mixtures with the geochemical modeling software GEMS 3.3 (Wagner et al. 2012; Kulik et al. 2013). The thermodynamic setup was based on the PSI/Nagra chemical thermodynamic database in combination with the CEMDATA 14.01 database (Lothenbach 2014) for thermodynamic modeling of OPC paste. We used an extended Debye-Hückel activity model (Truesdell Jones equation), which is believed to be applicable up to molar ionic strength (Wagner et al. 2012).

The chemical composition of the cement paste was calculated based on the experimentally derived composition shown in Table 1. NaOH and KOH were not considered in this model as they were leached from the samples during experimental sample preparation. The resulting phase compositions are shown in Appendix B. One should remark that mineral phases present with zero amounts are included as possible secondary phases in the setup, but these phases are not stable initially.

Table 4 shows the calculated equilibrium concentrations of major ions and chemical species in pore solutions of cement paste and bentonite–sand mixtures. The equilibrated composition in the cement paste showed portlandite and C–S–H as the main phases, as well as smaller amounts of hydrogarnet, ettringite, hydrotalcite, monosulfate, and traces of hemicarbonate. The hydrogarnet phase was not experimentally observed, but it is included in the setup as it is believed to be the major Fe-containing phase in aged cement (Dilnesa et al. 2014; Vespa et al. 2015).

The chemical composition of bentonite was obtained from literature reports (Ito et al. 1993; Ochs et al. 2004; JAEA and FEPC 2007). For simplicity, we used only Na-montmorillonite as the montmorillonite phase (data from Berner et al. 2013) and calculated calcite, dolomite, magnetite, pyrite and natron as further stable mineral phases present in minor amounts. Other minor minerals were lumped in an inert phase in order to simplify the system. The system included a cation exchange phase for bentonite, and the selectivity coefficients were obtained from (Bradbury and Baeyens 2005). The pH calculated in the bentonite–sand mixtures showed 9.04, which agrees with calculations of Ochs et al. (2004). Upon addition of large amounts of Na2CO3 to the bentonite, pH rises to 11.1, which is slightly lower than the pH (~11.5) in the saturated solution with Na2CO3 because a partial dissolution of montmorillonite gives pH buffering effect.

3. Results and discussion
3.1 Initial compositions calculated from the geochemical model
First indications of solute fluxes and expected precipitates can be extracted from Table 4. Comparison of the values of modeled pore water compositions on both sides of the interface indicates the expected direction of solute fluxes. For the reference sample, without electrical acceleration, hydroxide and calcium ions diffuse from the cement layer toward the bentonite, while silica, sodium, and carbonate species diffuse in the opposite direction. Near the interface, solute fluxes from opposing directions meet and result in the formation of carbonates and C–S–H. The migration of hydroxide will increase the pH of the bentonite if it is not buffered by mineral reactions. As precipitation of carbonate is favored at elevated pH, the carbonation front could move into the bentonite.

For the samples subjected to electric acceleration, diffusion along concentration gradients was accompanied by migration of ions and charged species in the electric field. The solute flux under concentration and electric potential gradients can be described by the so-called Nernst–Planck equations (Samson et al. 1999). Negatively charged species are driven by electrochemical migration toward the anode (cement compartment) and positively charged species are driven toward the cathode (in the bentonite). The movement of calcium and carbonate ions/species was accelerated, as both electrochemical migration and concentration gradients were operating in the same direction. Although calcium and carbonate ions/species migrate in the oncoming directions, they are not necessarily in contact for the entire duration of the experiment in the same region.
Table 4 Calculated equilibrium concentrations (mol/kgw) in pore solution and direction of solute flux between cement paste and bentonite mixtures.

| Species or total elemental concentration in pore solution (mol/kg) | OH⁻ (Main charged species) | Ca (Main charged species) | Si (Main charged species) | C (Main charged species) | Na (Main charged species) | H⁺ | pH | Ionic strength |
|---------------------------------------------------------------|-----------------------------|---------------------------|---------------------------|--------------------------|---------------------------|----|----|----------------|
| Cement paste (unaltered)                                      | 3.8×10⁻²                     | 2.1×10⁻² (Ca²⁺: 1.6×10⁻⁴) | 1.3×10⁻⁵ (HSiO₃⁻: 3.2×10⁻⁷) | 3.2×10⁻⁸ (CO₃²⁻: 5.6×10⁻⁹) | Not included              | 2.7×10⁻¹³ | 12.7 | 0.055 |
| Bentonite/sand (in the case of BLC)                          | 8.8×10⁻⁶                     | 2.9×10⁻⁴ (Ca²⁺: 1.8×10⁻⁶) | 1.8×10⁻⁴ (HSiO₃⁻: 2.5×10⁻⁶) | 1.9×10⁻³ (HCO₃⁻: 9.7×10⁻⁴) | 2.2×10⁻² (Na⁺: 2.2×10⁻⁵) | 1.1×10⁻⁹ | 9.0 | 0.034 |
| Bentonite/sand/carbonate (in the case of N₂C₄)               | 1.3×10⁻³                     | 5.3×10⁻⁶ (Ca²⁺: 9.9×10⁻⁷) | 7.4×10⁻³ (HSiO₃⁻: 3.7×10⁻⁶) | 1.1 (CO₃²⁻: 2.4×10⁻¹, Na(CO₃)⁻: 8.3×10⁻¹) | 2.4 (Na⁺: 1.3, Na(CO₃)⁻: 8.3×10⁻¹) | 1.0×10⁻¹¹ | 11.1 | 1.59 |
| Bentonite/sand/carbonate (in the case of N₂C₄)               | 4.4×10⁻⁶                     | 1.1×10⁻⁵ (Ca²⁺: 2.9×10⁻⁶) | 1.4×10⁻⁴ (HSiO₃⁻: 1.3×10⁻⁵) | 1.1 (HCO₃⁻: 6.8×10⁻¹, Na(CO₃)⁻: 2.0×10⁻¹) | 1.3 (Na⁺: 9.9×10⁻¹, Na(CO₃)⁻: 2.0×10⁻¹) | 3.2×10⁻⁹ | 8.7 | 1.08 |
| Bentonite/sand/carbonate (in the case of N₂C₁₂)              | 8.6×10⁻⁴                     | 3.7×10⁻⁶ (Ca²⁺: 7.8×10⁻⁷) | 1.3×10⁻² (HSiO₃⁻: 2.5×10⁻⁶) | 3.8 (CO₃²⁻: 3.3×10⁻¹, Na(CO₃)⁻: 3.4) | 7.5 (Na⁺: 4.1, Na(CO₃)⁻: 3.4) | 7.8×10⁻¹² | 11.1 | 4.48 |
| Main direction of solute flux due to concentration gradient (Cement ⇔ Bentonite) | C ⇒ B                       | C ⇒ B                     | C ⇐ B                     | C ⇐ B                   | C ⇐ B                   | C ⇐ B               |
| Main direction of solute flux due to electric potential gradient (Cement ⇔ Bentonite) | C ⇐ B (Opposite to conc. grad.) | C ⇒ B (Same as conc. grad.) | C ⇐ B (Same as conc. grad.) | C ⇐ B (Same as conc. grad.) | C ⇒ B (Opposite to conc. grad.) | C ⇒ B (Opposite to conc. grad.) |
For hydroxyl and sodium and silicate ions, electromigration and concentration gradients form in different directions. These gradients will change substantially the precipitation/dissolution behavior near the interface. If we assume that electromigration is the dominant transport process, hydroxyl will move toward the anode. Therefore, first portlandite and later C–S–H will be dissolved and the pH of the cement will decrease once portlandite is completely consumed. The pH change, accompanied by the influx of carbonate from the bentonite will move the carbonate precipitation front from the interface to the cement layer. Dissolved silica, presents mainly as anionic complexes, will be accelerated from the bentonite towards the cement and could cause the formation of C–S–H at the interface. One should note that total dissolved Si concentrations are orders of magnitude lower in bentonite than the dissolved carbonate concentrations. Total silica concentration could be increased in bentonite due to in-diffusion of OH which would increase pH and strongly accelerated dissolution of SiO2 and montmorillonite. However, as diffusion of OH is hindered by the direction of electric potential, the formation of high pH conditions in the bentonite causing significant release of silica into the pore water is suppressed. Therefore, C–S–H precipitation will be negligible compared to calcite formation.

3.2 Resistivity changes during electrochemical migration

The accumulated amounts of charge and electrical resistivities during the electrochemical migration tests for three representative composite specimens are shown in Figs. 3 and 4. The slope of the accumulated charge in Fig. 3 is proportional to the resistivity of the composite specimen since the electric potential was kept constant. Electrical resistivity measurements of porous media are commonly used to calculate the formation factor (i.e., the resistivity of water-filled porous rock divided by the resistivity of water). Archie (1950) stated that the resistivity depends on the type of rock, its porosity and water saturation, as well as the salinity of water. For certain rock types, the formation factor can be used as a measure of pore geometry, leading to the so-called Archie’s law.

However, for rocks that contain conductive minerals, e.g., clays that exhibit a significant cation exchange capacity, this relationship does not apply (see Revil and Glover (1998) for an example).

Consequently, the electrical resistivities of the composite samples cannot be directly related to their porosities alone. Changes in pore water composition caused by dissolution/precipitation reactions and cation exchange in bentonite–sand mixtures may also have a significant impact on electrical resistivity. In the case of the composite samples, major differences in pore water composition can only be expected for the samples with and without the carbonate admixture. Addition of large amounts of carbonate will initially increase the ionic strength in the bentonite–sand area, but not in the cement side. Over the long term, pore water concentrations in the sample will be equilibrated by diffusion and electrochemical-migration. Therefore, after an initial equilibration phase, major resistivity changes are expected to be related predominantly to porosity changes caused by the precipitation/dissolution of minerals near the interface. In addition, cation exchange processes in bentonite (e.g., Ca2+ replacing Na+) will reduce swelling pressure and cause a redistribution of water between clay interlayers and free pores.

Figure 4 shows that the electrical resistivity increased over time for all samples. The highest increase in resistivity was observed for the sample with the highest amount of admixed carbonate (N2C12). This suggests a correlation between porosity changes and the carbonate content. Quickly after start of the experiment and up to 100 h, a significant resistivity increase was observed for sample N2C12. This indicated that the sample suffered from fast pore clogging. Furthermore, an additional increase in the resistivity was observed at the later stage after 600 h. This late increase might be related to the water redistributions rather than the pore clogging. The long-term resistivity increase was moderate for the sample without carbonate admixture (BLC) and small for the sample with small carbonate admixture (NHC4). No strong changes at early times were observed. The detailed behaviors are analyzed in the following sections.
3.3 Evolution of cement and bentonite without carbonate addition

Calcium profiles measured using EPMA (Figs. 5 and 6) show the formation of a calcium leaching front, which moves in direction from the interface to the inner part of the cement paste, with a gradual decrease in calcium content as it approaches the interface. This observation indicates some type of kinetic control of portlandite and C–S–H dissolution, as observed by Thiery et al. (2007).

The calcium leaching front can be characterized by a decrease in portlandite content and an increase in porosity. This was confirmed by TG-DTA and MIP tests of the cement-paste sub-samples in contact with the interface, as shown in Appendix C and Fig. 7, respectively, where the results were typical for degradation caused by calcium leaching in solution (Haga et al. 2005; Choi and Yang 2013). The observation of accelerated calcium leaching confirmed the successful application of the electrochemical migration technique for cement–bentonite interaction without carbonate addition. By contrast, degradation was not observed in the inner samples of the cement paste.

During electrical acceleration, the calcium leached from cement migrated into bentonite, where the influx of calcium caused changes in the cation occupancy, as shown in Fig. 8. Similar changes were reported previously in experiments using concrete and bentonite–sand mixtures by Sugiyama et al. (Sugiyama et al. 2005). As the calcium occupancy increased, sodium was expelled and its concentration in bentonite pore water increased markedly. The electric potential gradient toward the cathode caused an increase in the sodium flux toward the cathode. The increase in sodium with distance from the interface in Fig. 8 indicates that the applied electrical gradient determined the direction of sodium migration, rather than the sodium concentration gradient between bentonite and cement. Another indication of cation exchange is shown in Fig. 9; specifically, the measured swell indexes displayed a significant decrease at the...
surface layers of the bentonite mixture. This is a typical result when sodium is replaced with calcium (Pusch et al. 1990; Komine and Ogata 1996; Neretnieks 2014; Anh et al. 2017).

### 3.4 Evolution of cement and bentonite with carbonate addition

A strong dependence was observed between the electrical resistivity over time and the addition of carbonate admixture (as shown in Fig. 4). Hence, we carefully compared the changes in specimens with and without added carbonate over time to understand the effect of carbonate addition. Figs. 5 and 6 show the spatial profiles of calcium content in the cement paste for experiments performed without (sample BLC-L) and with carbonate admixture (samples NHC4-L and N2C12-L). The differences in the progress of the reaction fronts appear to be directly related to the differences in electrical resistivities of the composite samples; calcium leaching was enhanced in NHC4 (with lower electrical resistivity), whereas it was strongly reduced for N2C12 (with higher electrical resistivity).

The EPMA maps of calcium and carbon distributions for NHC4-L and N2C12-L samples (Figs. 5 and 6) further elucidate the cement leaching process. For NHC4-L, not all of the calcium was leached from the cement; instead, a significant amount remained bound in the carbonate. This result supports the hypothesis that the progress of the carbonation front is directly related to the flux of carbonate ions from the bentonite region. For N2C12-L, precipitation of calcite was restricted to the interfacial region and did not evolve. The strong localization of precipitation, in combination with the large increase in electrical resistivity at the initial stage sugTG-DTA (Fig. 10), XRD analysis (Appendix D), and porosity measurements (Fig. 7) for the cement specimens closest to the interfaces provided additional information on the cement leaching and calcite precipitation processes. For NHC4, all results indicated that alteration at the interface was promoted by carbonate addition. Portlandite was found to be completely dissolved and partially replaced by calcite. As a result of the partial replacement of hydrated cement phases with denser carbonate, the porosity increased (this is consistent with the relatively small increase in electrical resistivity; Fig. 4). The progress of the calcite precipitation front into the cement paste is related to both the movement of cations and anions in opposite directions and the pH dependency of calcite stability (Fredd and Scott Fogler 1998). Since hydroxide ions migrated towards the anode (see Appendix B), high pH (~12.5) could be maintained only in the presence of portlandite, while a low pH front moves into the cement region. At high pH, the stability of calcite is enhanced compared to neutral pH. Therefore, the calcite precipitation front followed the pH front. The thermal analysis results (Fig. 10) showed that the amount of precipitated calcite was larger by around 35% than that expected based on the amount of dissolved portlandite. This discrepancy indicates that additional calcium was leached from C–S–H causing a decrease in the Ca/Si ratio with partial dissolution of C–S–H. The changes in C–S–H might also explained the relative increase in pore size (Fig. 7) observed in studies utilizing blended cement (Ngala and Page 1997; Šavija and Luković 2016; Shi et al. 2016).

For the N2C12 sample, all results indicated a large reduction in the flux of reactive species across the interface when compared to all other studied samples. Portlandite dissolution, calcium leaching, calcite precipitation, and changes in porosity were all very minor for this sample (see Figs. 5–7, and 10, and Appendix C). The marked increase in electrical resistivity observed at the start of the electrochemical migration experiment (Fig. 4) is thought to be related to pore blocking by localized calcite precipitation at the cement–bentonite interface. It appears that mixing of highly concentrated carbonate–bentonite pore solution with the cement pore water produced sufficient calcite to clog the interface with a very thin precipitate layer. The experimental results that alterations were observed only within 100 hours suggested rapid pore clogging at the initial stage (before analyzing N2C12-M samples). This finding agrees with the experimental observation without elec-
trical gradient reported in the first paper (Nakarai et al. 2021). Furthermore, an additional increase in the electrical resistivity was observed at the end of the experiment. One of the possible reasons is water reduction in the bentonite mixtures around the cathodic anode caused by electrolysis of the stainless steel.

The experimentally observed changes in bentonite–sand–carbonate mixtures were in accordance with those observed for the cement phases. The measured changes in cation occupancy after the migration tests showed a significant influx of calcium ions from the cement region for the NHC4 sample (Fig. 11), whereas no significant changes were observed for N2C12 (Fig. 12). The changes in the swell index (Fig. 13) supported these observations, and the decrease in the swell index of NHC4 is linked directly to the higher calcium occupancy. It should be noted that the influx of calcium ions from the cement into bentonite for NHC4 indicated an excess of calcium leached from the cement phase when compared to the carbonate flux toward the cement area. For N2C12, the absence of calcium ingress was most likely related to the clogging of the interface rather than the consumption of calcium on the cement side.

We observed no significant differences in sample evolution for the two types of carbonate admixture, i.e., sodium carbonate or sodium hydrogen carbonate. The admixture of sodium carbonate resulted in a significantly higher pH (see Table 4) of the bentonite–sand pore water, compared to the admixture of sodium hydrogen carbonate. The higher pH changed the distribution of negatively charged carbon complexes from dominance of HCO$_3^-$ at neutral pH to dominance of CO$_3^{2-}$ at high pH. In addition, solubility of calcite is lowered at high pH. For both carbonate types, the total dissolved carbon in bentonite–sand pore water exceeded the total dissolved calcium concentration in cement pore water by orders of magnitude. At the interface between materials, where pH was elevated, dissolved calcium from the cement side and dissolved carbon from the bentonite–sand mixture side precipitated calcite. Excess carbon was driven by concentration gradients and electromigration into the cement compartment as CO$_3^{2-}$ at high pH and causes calcite precipitation in the cement paste. Residual calcium was transported into the bentonite compartment, but as concentrations were below solubility of calcite no formation of calcite could be expected.

For example, Fig. 14 shows the quantities of portlandite and calcium carbonate determined by thermal analysis in the surface layer of cement paste specimens after the electrochemical migration tests. The measured portlandite and calcium carbonate contents did not exhibit any significant differences for the different types of carbonate mixtures. This result suggests that changes at the cement–bentonite–carbonate interface depended on the carbonate concentration rather than the type of carbonate.
3.5 Evolution of cement in contact with bentonite

We found that the porosity and mineralogical evolution at the interface and at the adjacent materials depended strongly on the added amount of carbonate (Fig. 15). In the control sample lacking carbonate, the natural carbonate content of bentonite was not sufficient to precipitate significant amounts of calcite. Instead, the system evolution was controlled by calcium leaching from the cement. The calcium contents at the surface of the cement paste decreased with portlandite dissolution (Fig. 15(a)). Subsequently, the calcium ions leached from the portlandite in cement paste to bentonite; thus, the swelling capacity of bentonite decreased near the interface, as reported previously (Sugiyama and Tsuji 2008). There was no evidence of pore clogging in experiments with the control sample.

For the sample fabricated with carbonate at 4 %, we observed accelerated calcium leaching caused by an increase in porosity in the cement compartment (Fig. 15(b)). The electrochemical migration, which was used to accelerate the experiments, prevented the expansion of the high pH zone in the bentonite. In addition, the setup resulted in an excess of carbonate in bentonite–sand–carbonate pore water over calcium in cement pore water. As a result, a large portion of the hydrated cement phase was converted to calcite as a result of the enhanced influx of carbonate ions from the bentonite–sand–carbonate compartment. This, in turn, resulted in a zone with enhanced porosity and lower pH. The addition of a large amount of carbonate (12 %) into the bentonite strongly increased the concentration of calcium ions in the pore water. Shortly after the start of the migration experiments, mixing of the carbonate-rich bentonite pore water with calcium-rich cement pore water caused localized precipitation of calcite at the interface between both materials (Fig. 15(c)). The amount of precipitate was sufficient to result in localized clogging of pores, thus decreasing the electronic and mass fluxes between the compartments. Localized calcite precipitation at cement–clay interfaces was also previously reported (Gaboreau et al. 2012; Fernández et al. 2017; Mäder et al. 2017). It should be noted that these precipitates developed over extended periods and were related to the in-diffusion of dissolved carbon from the clay rock/materials (Maes et al. 1999; Tanaka 2018).

The current study also reveals that experiments that utilize electromigration technique to accelerate transport across cement–clay interfaces are not representative for natural conditions. Under natural conditions, the diffusion of all species follows the concentration gradients, whereas the effect of additional electromigration might be opposed to the natural gradients. In the presented experiments, the accumulation of calcite at the clay–cement interface did not occur. Under natural conditions, calcite precipitates at the front of the pH plume that moves slowly into the clay compartment. In the accelerated experiments of this study a low pH plume is actually moving in the opposed direction, into the concrete compartment. This causes the carbonation front to move also in the opposed direction.

In these experiments, pore clogging occurred at very high carbonate addition in bentonite, in spite of electromigration. The very high carbonate content enabled rapid calcite precipitation, forming a very thin continuous layer at the clay–cement interface.

Pore clogging under natural conditions is often related to precipitation of C–S–H at the clay–cement interface. The high pH plume migrating into the clay compartment causes enhanced dissolution of SiO₂ and clay phases. This increases the amount of Si in the pore water. Silicon diffuses towards the interface where it reacts at elevated pH with calcium in cement–pore water and causes precipitation of C–S–H. This reaction is suppressed in the accelerated experiments as direction of electromigration prevents the pH increase in clay compartment and thus limits the amount of silicon released by dissolution reactions. A reversal of the direction of electromigration would increase the pH in the clay and thus promote dissolution, but as calcium ions and silica complexes are driven in opposing directions away from the interface, C–S–H formation is also effectively suppressed.

The present results suggest that it should be possible to control dissolution/precipitation processes at cement–bentonite interfaces by addition of carbonate to bentonite–sand mixtures. This addition enhances the availability of carbonate in the clay material and promotes therefore the precipitation of calcite near the interface. Such control is of particular importance to waste repository design concepts where pore clogging at the surface of cement materials is the target goal.
4. Summary

In this study, enhanced calcite precipitation at cement–bentonite interfaces was comprehensively investigated. The experiments were conducted with composite specimens of cement paste and bentonite–sand–carbonate mixtures. Transport across the interface was accelerated by application of an external electrical gradient. By observing the changes in electrical resistivity and undertaking extensive post-mortem analyses of specimens, we were able to understand the effect of carbonate admixture on calcite precipitation and interface evolution. We showed that calcite precipitation at the cement–bentonite interface was highly dependent on whether small or large amounts of carbonate were added, resulting in pore opening or clogging, respectively. Hence, if pore clogging at the surface of cement-based materials is the desired design goal, it is important to add a sufficient quantity of carbonate in relation to the interface porosity to ensure clogging. Although we focused on three conditions (samples without carbonate, with small sodium hydrogen carbonate, and with sodium carbonate) considering the minor impact of carbonate type on the measured electrical resistivity, carbonate could change pore water chemistry. More detailed analysis with various material compositions should be conducted in future studies. Furthermore, to discuss the practical applicability of added carbonate to engineered systems, studies investigating other impacts on material properties such as permeability, sorptivity, thermal conductivity, physical buffering and chemical buffering are required. In addition, experiments without electrical acceleration to confirm the results of this study under natural conditions were presented in a separate paper (Nakarai et al. 2021).

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References

Alexander, W. R., and McKinley, L., (2007). “Deep geological disposal of radioactive waste.” Elsevier.

Allan, M. L., (2000). “Materials characterization of superplasticized cement–sand grout.” Cement and Concrete Research, 30(6), 937-942.

Anh, H. N., Ahn, H., Jo, H. Y. and Kim, G.-Y., (2017). “Effect of alkaline solutions on bentonite properties.” Environmental Earth Sciences, 76(10), 374.

Archie, G. E. (1950). “Introduction to Petrophysics of Reservoir Rocks.” Aapg Bulletin-American Association of Petroleum Geologists, 34(5), 943-961.

Balmer, S., Kaufhold, S. and Dohrmann, R., (2017). “Cement-bentonite-iron interactions on small scale tests for testing performance of bentonites as a barrier in high-level radioactive waste repository concepts.” Applied Clay Science, 135, 427-436.

Berner, U., Kulik, D. A. and Kosakowski, G., (2013). “Geochemical impact of a low-pH cement liner on the near field of a repository for spent fuel and high-level radioactive waste.” Physics and Chemistry of the Earth, 64, 46-56.

Bradbury, M. H. and Baeyens, B., (2005). “Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: Linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides.” Geochimica Et Cosmochimica Acta, 69(4), 875-892.

Carde, C., Escadeillas, G. and François, A. H., (1997). “Use of ammonium nitrate solution to simulate and accelerate the leaching of cement pastes due to denitized water.” Magazine of Concrete Research, 49(181), 295-301.

Choi, Y. S. and Yang, E. I., (2013). “Effect of calcium leaching on the pore structure, strength, and chloride penetration resistance in concrete specimens.” Nuclear Engineering and Design, 259, 126-136.

Collier, N. C., Milestone, N. B. and Travis, K. P., (2019). “A review of potential cementing systems for sealing and support matrices in deep borehole disposal of radioactive waste.” Energies, 12(12).

Dauzeres, A., Le Bescop, P., Sardini, P. and Cau Dit Cournes, C., (2010). “Physico-chemical investigation of clayey/cement-based materials interaction in the context of geological waste disposal: Experimental approach and results.” Cement and Concrete Research, 40(8), 1327-1340.

Diamond, S., (2000). “Mercury porosimetry: An inappropriate method for the measurement of pore size distributions in cement-based materials.” Cement and Concrete Research, 30(10), 1517-1525.

Dilnesa, B. Z., Lothenbach, B., Renaudin, G., Wichser, A. and Kulik, D., (2014). “Synthesis and characterization of hydrogarnet Ca_3(Al_{x}Fe_{1-x})_2(SiO_4)_3(OH)_{4-3y}.” Cement and Concrete Research, 59, 96-111.

Fernandez, R., Ruiz, I. and Cuevas, J., (2016). “Formation of CASH phases from the interaction between concrete or cement and bentonite.” Clay Minerals, 51(2), 223-235.

Fernandez, R., Torres, E., Ruiz, A. I., Cuevas, J., Alonso,
M. C., García Calvo, J. L., Rodríguez, E. and Turrero, M. J., (2017). “Interaction processes at the concrete-bentonite interface after 13 years of FEBEX-Plug operation. Part II: Bentonite contact.” *Physics and Chemistry of the Earth, Parts A/B/C*, 99, 49-63.

Fredd, C. N. and Scott Fogler, H., (1998). “The kinetics of calcite dissolution in acetic acid solutions.” *Chemical Engineering Science*, 53(22), 3863-3874.

Gaboreau, S., Lerouge, C., Dewonck, S., Linard, Y., Bourbon, X., Fialips, C., Mazurier, A., Prêt, D., Borschneck, D. and Montouillout, V., (2012). “In-situ interaction of cement paste and shotcrete with claystones in a deep disposal context.” *American Journal of Science*, 312(3), 314-356.

Gaucher, E. C. and Blanc, P., (2006). “Cement/clay interaction of cement paste and shotcrete with claystones in a deep disposal context.” *Bentonite Chemistry and Applications*, 71-83.

Haga, K., Shibata, M., Hironaga, M., Tanaka, S. and Nagasaki, S., (2005). “Change in pore structure and composition of hardened cement paste during the process of dissolution.” *Cement and Concrete Research*, 35(5), 943-950.

Ito, M., Okamoto, M., Shibata, M., Sasaki, Y., Danhara, T., Suzuki, K. and Watanabe, T., (1993). “Bentonite mineral composition analysis.” *Power Reactor and Nuclear Fuel Development Corporation. (in Japanese) JAEA and FEPC*, (2007). “Second progress report on research and development for TRU waste disposal in Japan.” *Japan Atomic Energy Agency (JAEA)*, The Federation of Electric Power Companies of Japan (FEPC).

Kang, H., (2014). “Support technologies for deep and complex roadways in underground coal mines: a review.” *International Journal of Coal Science & Technology*, 1(3), 261-277.

Komine, H. and Ogata, N., (1996). “Prediction for swelling characteristics of compacted bentonite.” *Canadian Geotechnical Journal*, 33(1), 11-22.

Kovári, K., (2003). “History of the sprayed concrete lining method—part II: milestones up to the 1960s.” *Tunnelling and Underground Space Technology*, 18(1), 71-83.

Kulik, D. A., Wagner, T., Dmytrieva, S. V., Kosakowski, G., Hingerl, F. F., Chudnenko, K. V. and Berner, U. R., (2013). “GEM-Selektor geochemical modeling package: revised algorithm and GEMS3K numerical kernel for coupled simulation codes.” *Computational Geosciences*, 17(1), 1-24.

Lavkulich, L., (1981). “Exchangeable cations and total exchange capacity by the ammonium acetate method at pH 7.0.” In: M. R. Carter, Ed., *Soil sampling and methods of analysis*, Ottawa: Canadian Society of Soil Science, 173-175.

Lothenbach, B., (2014). “CEMDATA: Thermodynamic data for hydrated solids in Portland cement system (CaO-Al2O3-SiO2-CaSO4-CaCO3-Fe2O3-MgO-H2O).” Available from: <https://www.empa.ch/web/s308/cemdata>.

Lupting, T. and Nilsson, L.-O., (1992). “Rapid determination of the chloride diffusivity in concrete by applying an electric field.” *Materials Journal*, 89(1), 49-53.

Mäder, U., Jenni, A., Lerouge, C., Gaboreau, S., Miyoshi, S., Kimura, Y., Cloet, V., Fukaya, M., Claré, F., Otake, T., Shibata, M. and Lothenbach, B., (2017). “5-year chemico-physical evolution of concrete–claystone interfaces, Mont Terri rock laboratory (Switzerland).” *Swiss Journal of Geosciences*, 1-21.

Maes, N., Moors, H., Dierckx, A., De Cannière, P. and Put, M., (1999). “The assessment of electromigration as a new technique to study diffusion of radionuclides in clayey soils.” *Journal of Contaminant Hydrology*, 36(3), 231-247.

Metcalfe, R. and Walker, C., (2004). “Proceedings of the International Workshop on Bentonite-Cement Interaction in Repository Environments, (NUMO-TR-04-05).” Tokyo: Nuclear Waste Management Organization of Japan (NUMO).

Nakarai, K., Shibata, M., Sakamoto, H., Owada, H. and Kosakowski, G., (2021). “Calcite precipitation at cement–bentonite interface. Part 1: Effect of carbonate admixture in bentonite.” *Journal of Advanced Concrete Technology*, 19(5), 433-446.

Nakarai, K., Watanabe, M., Ishii, H. and Koibuchi, K., (2010). “Effect of carbonate mixing into bentonite on calcium leaching of cementitious material.” *Proceedings of the Japan Concrete Institute*, 32(1), 713-718. (in Japanese)

Nakayama, S., Sakamoto, Y., Yamaguchi, T., Akai, M., Tanaka, T., Sato, T. and Iida, Y., (2004). “Dissolution of montmorillonite in compacted bentonite by highly alkaline aqueous solutions and diffusivity of hydroxide ions.” *Applied Clay Science*, 27(1), 53-65.

Neretnieks, I., (2014). “Development of a simple model for the simultaneous degradation of concrete and clay in contact.” *Applied Geochemistry*, 43(Supplement C), 101-113.

Ngala, V. T. and Page, C. L., (1997). “Effects of carbonation on pore structure and diffusional properties of hydrated cement pastes.” *Cement and Concrete Research*, 27(7), 995-1007.

Ochs, M., Lothenbach, B., Shibata, M. and Yui, M., (2004). “Thermodynamic modeling and sensitivity analysis of porewater chemistry in compacted bentonite.” *Physics and Chemistry of the Earth*, 29, 129-136.

Ottosen, L. M., Christensen, I. V., Röig-Dalgård, I., Jensen, P. E. and Hansen, H. K., (2008). “Utilization of electromigration in civil and environmental engineering—Processes, transport rates and matrix changes.” *Journal of Environmental Science and...
Health, Part A, 43(8), 795-809.
Patel, R. A., Phung, Q. T., Seetharam, S. C., Perko, J., Jacques, D., Maes, N., De Schutter, G., Ye, G. and Van Breugel, K., (2016). “Diffusivity of saturated ordinary Portland cement-based materials: A critical review of experimental and analytical modelling approaches.” Cement and Concrete Research, 90, 52-72.
Pusch, R., (1992). “Use of bentonite for isolation of radioactive waste products.” Clay Minerals, 27(3), 353-361.
Pusch, R., Karnland, O., and Hökmark, H. (1990). “GMM-A general microstructural model for qualitative and quantitative studies of smectite clays,” (Technical Report 90-43). Stockholm: Swedish Nuclear Fuel and Waste Management Co.
Rachmadetin, J., Mizuto, M., Tanaka, S., Kozaki, T. and Watanabe, N., (2019). “Calcium carbonate precipitation in compacted bentonite using electromigration reaction method and its application to estimate the ion activity coefficient in the porewater.” Journal of Nuclear Science and Technology, 56(11), 959-970.
Read, D., Glasser, F. P., Ayora, C., Guardiola, M. T. and Sneyers, A., (2001). “Mineralogical and microstructural changes accompanying the interaction of Boom Clay with ordinary Portland cement.” Advances in Cement Research, 13(4), 175-183.
Revil, A. and Glover, P. W. J., (1998). “Nature of surface electrical conductivity in natural sands, sandstones, and clays.” Geophysical Research Letters, 25(5), 691-694.
Saito, H. and Nakane, S., (1999). “Comparison between diffusion test and electromechanical acceleration test for leaching degradation of cement hydration products.” Materials Journal, 96(2).
Saito, H., Nakane, S., Ikari, S. and Fujiwara, A., (1992). “Preliminary experimental study on the deterioration of cementitious materials by an acceleration method.” Nuclear Engineering and Design, 138(2), 151-155.
Samson, E., Marchand, J. and Beaudoin, J. J., (1999). “Describing ion diffusion mechanisms in cement-based materials using the homogenization technique.” Cement and Concrete Research, 29(8), 1341-1345.
Šavija, B. and Luković, M., (2016). “Carbonation of cement paste: Understanding, challenges, and opportunities.” Construction and Building Materials, 117, 285-301.
Shafizadeh, A., Gimmi, T., Van Loon, L., Kaestner, A., Lehmann, E., Maeder, U. and Churakov, S., (2015). “Quantification of water content across a cement-clay interface using high resolution neutron radiography.” Physics Procedia, 69, 516-523.
Shi, Z. G., Lothenbach, B., Geiker, M. R., Kaufmann, J., Leemann, A., Ferreiro, S. and Skibsted, J., (2016). “Experimental studies and thermodynamic modeling of the carbonation of Portland cement, metakaolin and limestone mortars.” Cement and Concrete Research, 88, 60-72.
Sugita, Y., Fujita, T., Takahashi, Y., Kawakami, S., Umeki, H., Yui, M., Uragami, M. and Kitayama, K., (2007). “The Japanese approach to developing clay-based repository concepts – An example of design studies for the assessment of sealing strategies.” Physics and Chemistry of the Earth, Parts A/B/C, 32(1–7), 32-41.
Sugiyma, T., Fukuoka, K. and Tsuji, Y., (2005). “Experimental investigation on alteration of the characteristics of bentonite sand mixtures at the interface with concrete by electrical migration method.” Journal of the Society of Materials Science, Japan, 54(8), 816-821.
Sugiyma, T. and Tsuji, Y., (2008). “Use of a migration technique to study alteration of compacted sand-bentonite mixture in contact with concrete.” Physics and Chemistry of the Earth, 33, S276-S284.
Tanaka, S., (2018). “Gypsum precipitation enhanced by electrokinetic method and porewater chemistry in compacted montmorillonite.” Applied Clay Science, 161, 482-493.
Tanaka, S., (2019). “Electrokinetic control of the growth of gypsum aggregates in compacted montmorillonite.” Applied Clay Science, 181, 105206.
Thiery, M., Villain, G., Dangla, P. and Platret, G., (2007). “Investigation of the carbonation front shape on cementitious materials: Effects of the chemical kinetics.” Cement and Concrete Research, 37(7), 1047-1058.
Thomas, A., (2008). “Sprayed concrete lined tunnels.” CRC Press.
Van Loon, L. R., Glaus, M. A. and Muller, W., (2007). “Anion exclusion effects in compacted bentonites: Towards a better understanding of anion diffusion.” Applied Geochemistry, 22(11), 2536-2552.
Vespa, M., Wieland, E., Dahn, R. and Lothenbach, B., (2015). “Identification of the thermodynamically stable Fe-containing phase in aged cement pastes.” Journal of the American Ceramic Society, 98(7), 2286-2294.
Wagner, T., Kulik, D. A., Hingerl, F. F. and Dmytrieva, S. V., (2012). “GEM-Selektor geochemical modeling package: TSolMod library and data interface for multicomponent phase models.” Canadian Mineralogist, 50(5), 1173-1195.
Watanabe, M. and Nakarai, K., (2008). “Effect of NaHCO$_3$ in bentonite on calcium leaching from cementitious material.” Proceedings of the Japan Concrete Institute, 30(1), 717-722. (in Japanese)
Whiting, D. and Mitchell, T. M., (1992). “History of the rapid chloride permeability test.” Transportation Research Record, 1335(1), 55-62.
Yamaguchi, T., Sawaguchi, T., Tsukada, M., Hoshino, S. and Tanaka, T., (2016). “Mineralogical changes and associated decrease in tritiated water diffusivity after alteration of cement-bentonite interfaces.” Clay Minerals, 51(2), 279-287.
Appendices

Appendix C. Changes in the amount of portlandite (CH) in the cement paste specimens closest to the interface over time.

Appendix D. XRD spectra of cement paste specimens before (BLC) and after (NHC4 and N2C12) electrochemical migration tests.