Effect of Calcium Leaching on Diffusivity of Blended Cement Paste and Mortar

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Abstract
Cement-based materials used at radioactive waste disposal sites are required to possess long-term stability. However, when these materials come in contact with groundwater, calcium leaching from the solid occurs, and the material becomes porous. The use of mineral admixtures is recommended to minimize porosity. However, few studies have focused on the diffusion performance of cement-based materials blended with mineral admixtures after leaching. Therefore, in this study, the diffusion performance of such materials using blended cement after leaching was evaluated. It was found that the diffusion coefficient of the blended cement increased with leaching, and when leaching progressed considerably, the diffusion coefficient of the blended cement was close to that of ordinary Portland cement. Furthermore, the diffusion coefficient after leaching demonstrated good correlation with the pore volume when the pore diameter was 50 nm or larger.

1. Introduction
Cement-based materials are used in radioactive waste facilities. Because radioactive waste facilities are required to have structural stability for tens of thousands of years depending on the type of nuclide, the cement-based materials used in radioactive waste facilities are also required to exhibit long-term stability. Concrete comprises an aggregate and a cement matrix, and typically, the aggregate is relatively stable. Therefore, it is necessary to evaluate the performance of the cement matrix, which constitutes calcium silicate hydrate (C-S-H) and calcium hydroxide produced during the reaction of cement with water (Mainguy et al. 2000; Wan et al. 2013; Gaitero et al. 2014). It has been reported that calcium is easily leached from these products when cement-based materials come in contact with groundwater for an extended period. Therefore, the use of cementitious materials with high leaching resistance is recommended. As a material with high resistance to leaching, blended cement has been produced using mineral admixtures such as fly ash (FA), silica fume (SF), and blast furnace slag (BFS) (Perlot et al. 2006; Gaitero et al. 2008; Kamali et al. 2008; Jain and Neithalath 2009; Cheng et al. 2013). These materials contain less calcium hydroxide than ordinary Portland cement (OPC) and, therefore, have high leaching resistance. Moreover, it has been reported that a dense-cured product is created, and the leaching resistance is high because the formed pore structures are different. Blended cement is known to have a high resistance to leaching; however, its performance after leaching has not been investigated extensively. Although the authors have developed a leaching model of OPC paste and estimated the diffusion coefficient after leaching (Kurumisawa et al. 2017), related studies on blended cement have not been conducted. In addition, studies on the decrease in mortar strength have been conducted (Bernard et al. 2008; Kamali-Bernard et al. 2009; Bary et al. 2014; Jebli et al. 2016, 2018). Although some studies have investigated the diffusion performance of cementitious materials using OPC after leaching, few studies have focused on the diffusion performance of concrete with mineral admixtures after leaching (Ahmed 2012; Pichler et al. 2012; Phung et al. 2016). Therefore, the purpose of this study was to evaluate the degree of leaching resistance of cement pastes and mortars produced using blended cement. Samples with different leaching degrees were prepared, and the effect of leaching on the diffusion coefficient were analyzed.

2. Experimental
2.1 Sample preparation
Hardened cement paste was prepared using OPC (density of 3.16 g/cm³), water, FA (density of 2.34 g/cm³), BFS (density of 2.89 g/cm³), and SF (density of 2.1 g/cm³). The water–binder ratio (W/B) was 0.6 for all mix proportions, the FA replacement ratios were 0.15 and 0.3, the BFS replacement ratios were 0.5 and 0.7, and the SF replacement ratio was 0.1 (RWMC 2015). The W/C was set to 0.6 to accelerate the leaching process and evaluate its effect. The paste sample was mixed every hour until the bleeding water disappeared. Table 1 lists the chemical compositions of the materials used, and Table 2 lists the mix proportions of the cement pastes.
Mortar samples were prepared to investigate the effects of the interfacial transition zone (ITZ). Several samples of hardened cement paste were used in the mortar. Curing was performed in water at 50°C for three months to accelerate the cement reaction. After curing, approximately 5–10 mm of the upper and lower ends of the casting and the side surface were removed and used for the tests. Unlike the paste sample, the mortar sample was not subjected to bleeding treatment. The density of the sand was 2.59 g/cm³, and the water absorption ratio was 1.5% (RWMC 2017).

An ammonium nitrate solution was used to accelerate the alternation of the hardened cement paste and mortar, and the degree of alternation of the paste was simulated by varying the concentration of the ammonium nitrate solution (Carde et al. 1996; Kamali et al. 2008). A sample with the diameter of 30 mm and height of 5 mm was used for uniform leaching. In the paste sample, the concentration of the ammonium nitrate solution was 1.0 mol/L; the liquid–solid ratios (mass%) were 5 (low), 7.5 (medium), and 12.5 (high); and the resulting degree of leaching changed, with an immersion period of 20 weeks. Mortar leaching was performed for three months under the conditions listed in Table 3. The leaching degree was based on the chemical composition of the matrix, determined using an electron probe microanalyzer (JEOL JXA-8100, acceleration voltage of 15 kV, irradiation current of 5 × 10⁻⁸ A, and beam diameter of 10 µm) and the amount of CaO reduction in the control sample. Here, because the concentration of Al₂O₃ in the specimen did not change after leaching, as compared to that before leaching, the leaching degree of calcium (mass%) was determined using the ratio of the concentration of Al₂O₃.

### 2.2 Experimental method

1. **Pore-size distribution measured via mercury intrusion porosimetry**

   The pore-size distribution was determined using mercury intrusion porosimetry (MIP). The sample had dimensions of 5 mm × 5 mm × 5 mm and was freeze-dried (ultimate vacuum degree was approximately 30–40 Pa). The measurement range of the pore diameter was 0.003–300 µm (applied pressure: 0.5–60000 psia).

2. **Diffusion coefficients**

   A diffusion cell was used to measure the chloride ion diffusion coefficient. A 0.4 M NaCl solution was placed on the primary side, and ultrapure water was used on the secondary side. The conversion factor was calculated by measuring the change in the concentration of chloride ions that diffused through the sample and moved to the secondary cell. Under these test conditions, the cell solution volume (V) was 500 cm³, and the solution concentration was 0.4. The thickness of each sample was 5 mm. The diffusion coefficient D was calculated using the

### Table 1: Compositions of constituent materials (mass%).

| OPC | FA | BFS | SF |
|-----|----|-----|----|
| Na₂O | 0.28 | - | - | - |
| MgO | 1.45 | 0.98 | 5.3 | 0.7 |
| Al₂O₃ | 5.22 | 23.74 | 12.78 | 0.79 |
| SiO₂ | 21.52 | 60.77 | 32.9 | 93.86 |
| P₂O₅ | 0.23 | 0.31 | - | 0.12 |
| SO₃ | 2.04 | 0.4 | 3.96 | 0.53 |
| Cl | 0.011 | - | - | 0.074 |
| K₂O | 0.47 | 1.26 | 0.36 | 1.12 |
| CaO | 64.56 | 2.3 | 43.37 | 0.26 |
| TiO₂ | 0.28 | 1.39 | 0.55 | - |
| Fe₂O₃ | 2.65 | 4.85 | 0.3 | 0.36 |
| LOI | 1.13 | 2.69 | 1.31 | 2.13 |

### Table 2: Conditions of cement paste.

| Binder type | W/B | OPC | FA | BFS | SF |
|-------------|-----|-----|----|-----|----|
| OPC | 0.6 |
| FAC15 | 85 | 15 | - | - |
| FAC30 | 70 | 30 | - | - |
| BFC50 | 50 | - | 50 | - |
| BFC70 | 30 | - | 70 | - |
| SC10 | 90 | - | - | 10 |

### Table 3: Conditions of mortar leaching.

| Binder type | W/(C+B) (by weight) | NH₄NO₃ (mol/L) | Liquid/Solid (by weight) | NH₄NO₃/Paste (by weight) |
|-------------|---------------------|----------------|--------------------------|--------------------------|
| O-1 | 1.0 | 0.05 | 100 | 0.4 |
| O-1-N0.4 | 0.95 | 150 | 0.6 |
| O-1-N0.6 | 0.95 | 250 | 1.0 |
| O-1-N1.0 | 1.0 | 0.05 | 100 | 0.4 |
| O-1-N1.4 | 1.0 | 150 | 0.6 |
| O-1-N1.0 | 1.0 | 250 | 1.0 |
| O-1.4-N0.4 | 1.4 | 0.05 | 100 | 0.4 |
| O-1.4-N0.6 | 1.4 | 150 | 0.6 |
| O-1.4-N1.0 | 1.4 | 250 | 1.0 |
| F-1 | 1.0 | 0.05 | 100 | 0.4 |
| F-1-N0.4 | 1.0 | 150 | 0.6 |
| F-1-N0.6 | 1.0 | 250 | 1.0 |
| F-1-N1.0 | 1.0 | - | - |
| B-1 | 1.0 | 0.05 | 100 | 0.4 |
| B-1-N0.4 | 1.0 | 150 | 0.6 |
| B-1-N0.6 | 1.0 | 250 | 1.0 |
| B-1-N1.0 | 1.0 | - | - |
following equation:

\[ D = \frac{L}{C_n} \times \frac{dc}{dt} \times \frac{V}{A} \]

where \( L \) is the thickness of the test piece (cm), \( C_n \) is the chloride ion concentration of the primary cell (mol/L), \( A \) is the cross-sectional area of the test piece (cm²), \( V \) is the cell solution volume (L), and \( \frac{dc}{dt} \) is the concentration gradient of chloride ions (mol/L/s). Finally, the diffusion coefficient in the steady state was obtained.

(3) Composition of hydrates measured by scanning electron microscopy with energy-dispersive X-ray analysis

The freeze-dried sample was embedded in epoxy resin, and the surface was polished with SiC abrasive papers and diamond pastes. The polished surface was observed using scanning electron microscopy (SEM), and elemental analysis was performed using energy-dispersive X-ray analysis (EDX). Using SEM-EDX, both the CaO/SiO\(_2\) molar ratio (C/S) and the Al\(_2\)O\(_3\)/SiO\(_2\) molar ratio (A/S) of C-S-H were determined from measurements conducted at 10 points or more. Meanwhile, C-S-H was determined using the difference in brightness of the backscattered electron image.

3. Results and discussion

3.1 Hardened cement paste

(1) EDX analysis

Figure 1 shows the relationship between the leaching degree of calcium and the C/S of C-S-H. C/S decreased linearly with leaching, regardless of the type of cement used. Calcium leaching from cement-based materials elutes from calcium hydroxide, followed by calcium from C-S-H. When the leaching degree is 20% or more, most of the calcium hydroxide is leached out, and it is considered that the leaching of C-S-H continues.

Figure 2 shows the relationship between leaching and the A/S of C-S-H. The A/S increased with leaching in some specimens, but there was no significant change as leaching progressed. Therefore, the calcium contained in C-S-H was reduced through Ca leaching; however, aluminum was not leached and remained in the structure because Si and Al were not supplied from outside.

(2) Pore structure

Figure 3 shows the results for porosity measured using MIP. It was observed that the porosity increased as leaching progressed. The initial porosity values for all samples were similar; however, porosity increased significantly only in the OPC sample after leaching. This behavior was attributed to the calcium hydroxide present in the OPC sample, which mainly dissolved and formed pores. Meanwhile, because the amount of CH in the paste with mineral admixtures is small, the leaching of C-S-H progresses to form pores. This pore formation caused an increase in the pore volume when the pore diameter was 50 nm or larger.

(3) Diffusion coefficient

Figure 4 shows the relationship between the diffusion coefficient and Ca leaching. The diffusion coefficient increased as leaching progressed in all the samples without OPC. In the sample mixed with admixtures, the diffusion coefficient increased significantly with leaching and converged to approximately 10^{-10} m²/s. Figure 5 shows the relationship between the porosity measured via MIP and the diffusion coefficient. The controlled samples exhibited different diffusion coefficients, even for the same porosity. In the leached sample, a correlation between the porosity and diffusion coefficient was observed. Hence, in the leached sample, it was assumed that the pores generated through leaching dominated the diffusion process. Figure 6 shows the relationship between the porosity at 50 nm or larger and the diffusion coefficient. A correlation between these can be observed for all samples. Assuming that the relationship between porosity and the diffusion coefficient conforms with Archie’s relationship (Archie 1942), the correlation coefficients (R²) of the porosity and the porosity of 50 nm...
or larger were 0.68 and 0.73, respectively. Coarse pores were found to influence the diffusion process, as reported in a previous study (Li and Roy 1986). When this relationship is fitted using a power equation, the diffusion coefficient \( D (\text{m}^2/\text{s}) \) is expressed as \( D = 1.46 \times 10^{-9} \times \rho^{0.48} \), using a porosity value, \( \rho \), of 50 nm or larger. Therefore, the diffusion coefficient after leaching could be estimated when the porosity was 50 nm or larger, irrespective of the presence or absence of admixtures.

### 3.2 Mortar

Figure 7 shows the relationship between leaching and the diffusion coefficient of the mortar. For OPC, the increase in the diffusion coefficient with leaching occurred gradually, whereas the increase in blended cement was significant. This trend is similar to that of the paste sample, and it was found that an increase in porosity significantly increases the diffusion coefficient. Figure 8 shows the relationship between the porosity of pores of 50 nm or larger and the diffusion coefficient. Similar to the results for the paste sample, good correlation was observed, and the diffusion coefficient could be estimated when the pore volume of the mortar was known, regardless of leaching. Based on previous studies (Yang and Su 2002; Yang and Weng 2013), when the ITZ does not affect the diffusion coefficient, the diffusion coefficient of mortar \( D_m \) could be estimated using the diffusion coefficient of paste \( D_p \) and the volume fraction of aggregate \( V_s \), as expressed in Eq. (1).

\[
D_m = D_p \times (1 - V_s)^{1.5} \tag{1}
\]

For the dilution effect by aggregate, \( D_m \) can be expressed as Eq. (2) (Bentz et al. 1998).

\[
D_m = D_p \times (1 - V_s) \tag{2}
\]
Combining the tortuosity effect with the dilution effect, the diffusion coefficient of mortar can be expressed using the Bruggeman equation, as shown in Eq. (1) (McLachlan et al. 1990; Brugemann 1935). The Bruggeman equation is an effective medium approximation when inclusions with zero conductivity are embedded in the matrix.

Figure 9 shows a plot of the estimated and measured diffusion coefficient values. The estimated \( D_m \) was calculated using Eq. (1), using the diffusion coefficient of the paste obtained in the experiment, as discussed in Section 3.1. Because the predicted and measured values show good agreement, the diffusion coefficient of the mortar can be estimated if the diffusion coefficient of the paste and the quantity of aggregate are known. Therefore, the diffusion coefficient of the leached mortar was minimally affected by the ITZ. The authors have previously developed a method for estimating the diffusion coefficient of a leached paste (Kurumisawa et al. 2012, 2017), and this method can be applied to estimate the diffusion coefficient of mortar.

4. Conclusions

The main conclusions of this study are as follows:

The dissolution of calcium in C-S-H was followed by the leaching of calcium, but the dissolution of aluminum remained insignificant.

The diffusion coefficients of the leached cement paste and mortar, determined through MIP, showed good correlation with the pore volumes of 50 nm or larger. It was found that pore volumes of 50 nm or larger dominated the diffusion of ions in the paste and mortar samples after Ca leaching.

In this study, the diffusion coefficient of the leached mortar could be estimated based on the diffusion coefficient of the leached paste by using an equation in which the quantity of the aggregate is considered and the ITZ is neglected.

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