The Effect of Calcium Leaching on the Chloride Diffusivity of Hydrated Tricalcium Silicate Pastes

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Abstract. Calcium leaching of cement-based materials induces detrimental effects on diffusion properties related to long-term durability. This paper investigates the effect of calcium leaching on the chloride diffusivity of hydrated tricalcium silicate (C\textsubscript{3}S) pastes. Different concentrations of ammonium nitrate solutions were used to accelerate the calcium leaching of C\textsubscript{3}S pastes. The degree of alternation of C\textsubscript{3}S pastes was characterized by Ca/Si. The chloride diffusivity of the leached C\textsubscript{3}S pastes was obtained by the steady-state electro-migration test. Results show that the chloride diffusivity of the leached C\textsubscript{3}S pastes increases with the increasing degree of alteration. Compared with the sound C\textsubscript{3}S pastes, the diffusivity of the leached C\textsubscript{3}S pastes is increased 1.8-3.6 times depending on the degree of alteration.

1. Introduction

Long-termly in the cold regions or environmental water like seawater, concrete structures (dams, bridges, water tanks) are easily subjected to the actions of calcium leaching, freeze-thaw cycles, drying shrinkage and chloride attack, which result in the durability deterioration and lifetime reduction of concrete structures [1-7]. Calcium leaching impacts the internal chemical environment and microstructures of cement-based materials, which mainly decides the chloride diffusion behavior in cement-based materials [8]. It’s important to investigate the effect of calcium leaching on the chloride diffusivity of cement-based materials.

Many studies about the effect of calcium leaching on the diffusivity of cement-based materials have been carried out. Marchand et al. [9] have investigated the influence of calcium hydroxide dissolution on the transport properties of hydrated cement pastes (HCP) by the NIST CEMHYD3D model. Choi et al. [10] have studied the effect of calcium leaching on the pore structures, strength, and chloride penetration resistance in concrete. Phung et al. [1] have studied the evolution of microstructures and transport properties of HCP under the condition of accelerated leaching by the one-dimensional model for Ca-leaching in ammonium nitrate (NH\textsubscript{4}NO\textsubscript{3}) solution. They also have investigated experimentally the changes about microstructures and transport properties of leached HCP accounting for mix composition [2]. Tang et al. [3], Song et al. [8] and Kurumisawa et al. [11] have investigated the influence of calcium leaching on chloride diffusion properties of HCP. Those literature can provide us a fundamental insight about the effect of calcium leaching on the microstructures and diffusion properties of cement-based materials.

Compared with deionized water, the accelerated leaching rate of 6 mol/L NH\textsubscript{4}NO\textsubscript{3} solution for HCP is increased 130 times [12]. NH\textsubscript{4}NO\textsubscript{3} solution is usually employed as an aggressive solution to accelerate the calcium leaching of cement-based materials. The test methods of diffusion coefficient reviewed by Patel et al. [13] include through-diffusion, in-diffusion, electro-migration (including
steady-state electro-migration and non-steady-state electro-migration) and electrical resistivity. Among those methods, the through-diffusion is a time-consuming conventional method. Under an applied voltage, the electro-migration test could reduce the test time and obtain effective results.

In this paper, the influence of calcium leaching on the chloride diffusivity of tricalcium silicate (C₃S) pastes will be studied. Firstly, the NH₄NO₃ solution was used to accelerate the calcium leaching of the C₃S pastes. The degree of alternation of the leached C₃S pastes was controlled by changing the concentration of the NH₄NO₃ solution and characterized by Ca/Si. Subsequently, the chloride diffusivity of the leached C₃S pastes was determined by the steady-state electro-migration test. Finally, the effect of calcium leaching on the chloride diffusivity of C₃S pastes was discussed.

2. Experimental program

2.1. Materials and specimen preparation

C₃S pastes were prepared at a water-to-cement ratio (w/c ratio) of 0.45. The block C₃S was crushed and passed through a sieve whose mesh number was 300 mesh (the maximum size of sieved particles was about 48 μm). The C₃S powders and deionized water were fully mixed and cast in cylindrical vials (φ26×50) in a glove box filled with N₂. The specimens were cured at 20 ℃ for 6 months until the desired age of testing. The test specimens (φ26×3) were obtained by cutting the cylindrical specimens. The test specimens were divided into control group (CSP0) and experimental group (CSP). The control group was placed in vacuum desiccators at 25 ℃, whose relative humidity (RH) was maintained at 98% using the saturated K₂SO₄ solution. The experimental group further undergoes the process of calcium leaching using the different concentrations of NH₄NO₃ solutions.

The concentrations of NH₄NO₃ solutions (the weight ratio of the specimen and NH₄NO₃ solution was 1:30) used in this paper were 0.24, 0.40, 0.60 and 1.00 mol/L, and the immersion time was 7 days without renewal of the solution. After the immersion, the test specimens were cleaned in an ultrasonic tank filled with deionized water for 3 min and weighed by a high-precision balance to calculate their mass losses. The contents of Ca in NH₄NO₃ solutions were measured by the EDTA titration to calculate the corresponding Ca/Si of the specimens. The specimens were placed in the vacuum desiccators (98% RH) for more than 14 days until their internal RH and external RH were in equilibrium. And then the specimens were immersed in epoxy resin to maintain their internal RH and external RH were in equilibrium. The specimens were ground and polished on both top and bottom surface using the SiC paper (grid sizes 320, 800, 1000, 1500, 2000, 3000, 5000). The lateral surface of the specimens was covered with the resin to ensure a unidirectional diffusion. Finally, the specimens were placed in the vacuum desiccators (98% RH) for more than 14 days before testing.

2.2. The steady-state electro-migration test

The steady-state electro-migration test was used to determine the chloride diffusion coefficient of C₃S pastes. A schematic diagram of the experimental setup is illustrated in Figure 1 (a). The setup was composed of the anodic compartment and the cathodic compartment, which were connected with the anode and cathode of a 12-V DC power, respectively. The test specimen was placed between the two compartments. The anodic compartment was filled with the NaOH solution (0.3 mol/L), and the cathodic compartment was filled with NaCl solution (1.0 mol/L) and NaOH solution (0.3 mol/L). The volume of solutions in both compartments was 280 ml. Two copper electrodes were placed in the two compartments in such a way that the electrical field was applied across the test specimen. In the test, the solution in anodic compartment was taken out periodically and the chloride concentration was titrated with AgNO₃ solution (0.0102 mol/L).

3. Result and discussion

3.1. Ca/Si

C₃S pastes can be regarded as composite materials which are composed of capillary pores, unhydrated
cement core (UCC), calcium silicate hydrate (CSH), and calcium hydroxide (CH). The contents of Ca and Si in the compositions (i.e., UCC, CSH, and CH) of C₃S pastes are given in Table 1 [14].

Table 1. The contents of Ca and Si in the compositions of C₃S pastes [14]

| Compositions | UCC (mol) | CSH (mol) | CH (mol) |
|--------------|-----------|-----------|----------|
| Ca           | m(1 − α)ω₉₅₆ Ca / M₉₅₆ | 1.7mα / M₉₅₆ | 1.3mα / M₉₅₆ |
| Si           | m(1 − α)ω₉₅₆ Si / M₉₅₆ | mα / M₉₅₆ | 0 |

Note: m is the mass of C₃S powders; α is the degree of hydration; ω₉₅₆ and ω₉₅₆ are the mass percent of Ca and Si in C₃S powders, respectively (ω₉₅₆ = 3M₉₅₆ / M; ω₉₅₆ = M₉₅₆ / M); M, M₉₅₆ and M₉₅₆ are the molar mass of C₃S, Ca and Si, respectively.

The calcium leaching of C₃S pastes can be divided into two stages including the relatively faster stage of the CH dissolution and the relatively slower stage of the CSH dissolution [14]. At the initial stage of calcium leaching, the CH were dissolved first, and then the CSH were dissolved to supplement the local chemical equilibrium when the CH were almost dissolved [15]. When the CH were completely dissolved, the critical mass loss (Ω₉₅₆) of C₃S pastes calculated by Eq. (1) was 13.9% [14]. It can be considered as the stage of the CH dissolution when the mass loss of C₃S pastes is smaller than 13.9%. It can be considered as the stage of the CSH dissolution when the mass loss of C₃S pastes is larger than 13.9%.

\[ \Omega_{th} = \frac{1.3m\alpha}{M} \left( \frac{M_{CH} - M_{CH} \times \rho}{m(1 + w/c)} \right) \]  \hspace{1cm} (1)

where, M₉₅₆ and M₉₅₆ are the molar mass and the molar volume of CH, respectively; ρ is the density of NH₄NO₃ solution.

The Ca/Si of C₃S pastes is 3.0 without the action of calcium leaching, and the Ca/Si of the major hydration productions CSH is 1.7. When the CH were completely dissolved, the Ca/Si of the leached C₃S pastes is 1.858. The Ca/Si of C₃S pastes in other cases can be estimated by the mass loss or the content of Ca in the NH₄NO₃ solution by EDTA titration. When the mass loss of the leached C₃S pastes is Ω, the content of Ca in the NH₄NO₃ solution can be calculated by [14],

\[ m_{Ca} = \begin{cases} 
\frac{1000\Omega m(1 + w/c)}{(M_{CH} - M_{CH} \times \rho)} & (\Omega \leq \Omega_{th}) \\
\frac{1300m\alpha + 1700m(\Omega - \Omega_{th})(1 + w/c)}{M + M_{CSH} - M_{SiO₂} - \rho_0(M_{CSH} - M_{SiO₂} / \rho_{SiO₂})} & (\Omega > \Omega_{th}) 
\end{cases} \]  \hspace{1cm} (2)

where, m₉₅₆ the content of Ca in the NH₄NO₃ solution [mmol]; Ω is the mass loss of C₃S pastes [%]; M₉₅₆ and M₉₅₆ are the molar mass and the molar volume of CSH, respectively; ρ₀ is the density of water; M₉₅₆ and ρ₉₅₆ are the molar mass and density of SiO₂.

According to the above analysis, the mass loss of CSP, the content of Ca in the NH₄NO₃ solution and the Ca/Si in CSP are given in Table 2. Under the action of 7-days calcium leaching, the mass loss and the content of Ca in the NH₄NO₃ solution increases with the increasing concentration, and the Ca/Si in CSP decreases with the increasing concentration. There is not much difference between the theoretical values calculated by the mass loss and the experimental values calculated by the EDTA titration. When the concentration of NH₄NO₃ solution is 0.24 mol/L, the Ca/Si of CSP0.10 is larger than 1.858, which demonstrates that the loss of Ca comes from the phase of CH in CSP. When the concentration of NH₄NO₃ solution is equal to (or larger than) 0.4 mol/L, the Ca/Si of CSP is smaller than 1.858, which demonstrates that the loss of Ca comes from the phases of CH and CSH in CSP.

Table 2 The mass loss, the content of Ca and the Ca/Si

| Specimens | CSP0 | CSP0.24 | CSP0.40 | CSP0.60 | CSP1.00 |
|-----------|------|---------|---------|---------|---------|
| NH₄NO₃ (mol/L) | -    | -       | 0.24    | 0.40    | 0.60    | 1.00    |
| Ω (%)      | 0    | 10.76   | 16.07   | 19.98   | 25.85   |
3.2. The migration coefficient of chloride ions

In the electro-migration test, chloride ions are transported in C₃S pastes under an applied voltage. When the chloride flux through the C₃S pastes reaches a steady state, the Nernst-Planck equation describing the chloride ions migration in the solution can be given as [16],

\[
J = -D \frac{\partial C(x)}{\partial x} \left( \frac{ZE}{RT} \frac{\partial E}{\partial x} - \frac{C_u(x)}{\partial x} \right)
\]

(3)

where, \( J \) is the unidirectional flux of chloride ions [mol m⁻² s⁻¹]; \( D \) is the diffusion coefficient [m² s⁻¹]; \( \partial C/\partial x \) is the variation of concentration [mol m⁻³]; \( \partial x \) is the variation of distance [m]; \( \partial E \) is the variation of potential [V]; \( C \) is the chloride concentration of cathodic solution [mol m⁻³]; \( \partial C_u(x)/\partial x \) is the chloride migration in the cathodic solution; \( u \) is the forced velocity of solute [m s⁻¹]; \( Z \) is the electrical charge of chloride ions; \( F \) is the Faraday number [96500 C mol⁻¹]; \( R \) is the gas constant [8.314 J mol⁻¹K⁻¹]; \( T \) is the absolute temperature [K].

The three terms of Eq. (3) are the contributions due to diffusion, migration, and convection, respectively. Under the effect of the applied voltage, the contributions of diffusion and convection in C₃S pastes are small and can be neglected. The chloride flux (steady state) can be measured by the variation of chloride-ion concentration with time in the anodic compartment, see Figure 1 (b). The migration coefficient of chloride ions can be given as [17],

\[
D = \frac{RTLV_1}{ZF\Delta C_1/A} \frac{\Delta C_1}{\Delta t}
\]

(4)

where, \( V_1 \) is the volume of anodic solution [m³]; \( A \) is the disc area of specimen [m²]; \( L \) is the thickness of specimen [m]; \( \Delta C_1/\Delta t \) is the chloride-ion migration rates [mol L⁻¹ s⁻¹].

![Figure 1. Schematic diagrams of: (a) experimental device; (b) variation of chloride-ion concentration with time in the anodic compartment](image-url)
steady-state electro-migration, non-steady-state electro-migration or through-diffusion, the chloride diffusivities of HCP (whose curing ages range from 60 to 90 days) from the literature [18-21] are used to compare with the experimental results of this paper, as shown in Figure 3. In general, the experimental results of C₃S pastes are almost located in the diffusivity range of HCP from the literature. Therefore, the experimental results in this paper are reliable.

![Figure 2. The variations of Chloride-ion concentration with time in the anodic compartment for the test specimens](image1)

![Figure 3. Comparison between the data from the literature and our results (a the steady-state electro-migration; b non-steady-state electro-migration; c through-diffusion)](image2)

### Table 3 The results of the steady-state electro-migration test

| Specimens   | CSP0   | CSP0.24 | CSP0.40 | CSP0.60 | CSP1.00 |
|-------------|--------|---------|---------|---------|---------|
| ΔC₁/Δt (10⁻² mol L⁻¹ s⁻¹) | 3.92   | 7.14    | 9.09    | 14.96   |
| r²          | 0.9986 | 0.9919  | 0.9941  | 0.9932  |
| D (10⁻¹² m² s⁻¹)   | 1.38   | 2.36    | 2.91    | 4.67    |

3.3. The influence of calcium leaching on diffusion

In this section, the effect of calcium leaching on the diffusivity of C₃S pastes will be discussed. Figure 4 illustrates the dependencies of Ca/Si and the chloride diffusivity on the mass loss of C₃S pastes. It can be seen that the Ca/Si has a great influence on the diffusion of C₃S pastes. As shown in Figure 4, the Ca/Si decreases with the increasing mass loss, while the chloride diffusivity increases with the increasing mass loss. That is to say, the smaller the Ca/Si is, the larger the chloride diffusivity is. The degree of alteration of the leached C₃S pastes was characterized by Ca/Si. And the smaller the Ca/Si is, the larger the degree of alteration is. Therefore, the chloride diffusivity of the leached C₃S pastes increases with the increasing degree of alteration.

The mean value of chloride diffusivity for the control group (CSP0) is 1.305×10⁻¹² m²/s. After 7-days immersion in 0.24 mol/L NH₄NO₃ solution, the chloride diffusivity increased about 1.8 times, from 1.305×10⁻¹² m²/s to 2.36×10⁻¹² m²/s. Similarly, after the same period immersion in 1.00 mol/L NH₄NO₃ solution, the chloride diffusivity increased about 3.6 times, from 1.305×10⁻¹² m²/s to 4.67×10⁻¹² m²/s. The multiple of diffusivity for different degrees of alteration of C₃S pastes is different. Accordingly, compared with the C₃S pastes without the action of calcium leaching, the chloride diffusivity of the leached C₃S pastes is increased 1.8-3.6 times depending on the degree of alteration.

The effect of calcium leaching on the chloride diffusivity of C₃S pastes can be analyzed from the microstructures evolution caused by the calcium leaching. The calcium leaching causes significant degradation of microstructures in cement-based materials, which results in the increases of the specific surface area, total porosity, and pore size, and finally leads to a significant increase in the permeability of materials [2]. It leads to the dissolution of calcium hydroxide and the decalcification of C-S-H gel in the hydrated products and further brings about the increase of porosity in cement-based materials.
The increases of porosity and pore size caused by the action of calcium leaching induces the increase of diffusivity of C₃S pastes.

Figure 4. The dependency of Ca/Si and chloride diffusivity on the mass loss (a the theoretical values; b the experimental values)

4. Conclusions
This paper investigated the effect of calcium leaching on the chloride diffusivity of C₃S pastes. Different concentrations of NH₄NO₃ solutions were used to accelerate the calcium leaching of C₃S pastes and the steady-state electro-migration test was employed to obtain the chloride diffusivity of the leached C₃S pastes. The following conclusions were derived:

• In the process of calcium leaching, the Ca/Si of C₃S pastes decreases with the increasing mass loss, while the chloride diffusivity increases with the increasing mass loss.
• The chloride diffusivity of the leached C₃S pastes increases with the increasing degree of alteration.
• Compared with the sound C₃S pastes, the chloride diffusivity of the leached C₃S pastes is increased 1.8-3.6 times depending on the degree of alteration.

Acknowledgements
This study was funded by the National Natural Science Foundation of China (Grant No. 51678219), Fundamental Research Funds for the Central Universities (Grant No. 2018B14214).

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