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Effects of calcium leaching on diffusion properties of hardened and altered cement pastes

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ABSTRACT

It is very important to predict alterations in the concrete used for fabricating disposal containers for radioactive waste. Therefore, it is necessary to understand the alteration of cementitious materials caused by calcium leaching when they are in contact with ground water in the long term. To evaluate the long-term transport characteristics of cementitious materials, the microstructural behavior of these materials should be considered. However, many predictive models of transport characteristics focus on the pore structure, while only few such models consider both, the spatial distribution of calcium silicate hydrate (C-S-H), portlandite, and the pore spaces. This study focused on the spatial distribution of these cement phases. The auto-correlation function of each phase of cementitious materials was calculated from two-dimensional backscattered electron imaging, and the three-dimensional spatial image of the cementitious material was produced using these auto-correlation functions. An attempt was made to estimate the diffusion coefficient of chloride from the three-dimensional spatial image. The estimated diffusion coefficient of the altered sample from the three-dimensional spatial image was found to be comparable to the measured value. This demonstrated that it is possible to predict the diffusion coefficient of the altered cement paste by using the proposed model.

1. Introduction

In order to provide safe, environmentally sound solutions to managing radioactive waste, it is very important to predict alterations in cementitious materials, such as concrete used for fabricating disposal containers for radioactive waste. Therefore, it is necessary to understand the alteration of cementitious materials caused by calcium leaching when they are in contact with ground water in the long term, e.g., ten thousand years. Calcium leaching in this period leads to a change of macro properties and microstructure in cementitious materials. To evaluate the long-term transport properties of cementitious materials, the microstructural behavior of these materials, such as alteration by calcium leaching, should be considered. However, many predictive models of transport characteristics focus only on the pore structure (Iqbal and Ishida, 2009; Bejaoui and Bary, 2007; Yokozeki et al., 2004), while only few such models consider the spatial distribution of calcium silicate hydrate (C-S-H), portlandite, and the pore spaces. Although X-ray CT has been proposed for measuring the spatial distribution of the phases, its resolution is insufficient for measuring the extent of calcium leaching (Burlion et al., 2006; Wan et al., 2012, 2013). Laser scanning confocal microscopy (LSCM) has been proposed to produce three-dimensional images of cementitious material; thus, this method would make it possible to detect particles in the submicron range (Yio et al., 2015). However, it is difficult to distinguish between hydrate products such as C-S-H and portlandite by LSCM (Head and Buenfeld, 2006). As previously mentioned, it is difficult to get real three-dimensional images of cementitious materials at the micro level; to overcome this difficulty, a statistical method was applied to reconstruct a three-dimensional image of cementitious materials from a previous study (Kurumisawa et al., 2012). The authors of a previous study investigated the diffusivity of a non-altered hardened cement paste using a three-dimensional spatial image model. This model was reconstructed with the auto-correlation function calculated based on a backscattered electron image of hardened cement paste, thus clarifying the effect of diffusivity of C-S-H on diffusivity of hardened cement paste. However, this method has not been applied to an altered hardened

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cement paste such as calcium leaching; the effect of calcium leaching on diffusivity of hardened cement paste is not clarified. This study focused on the spatial distribution of the cement phases in an altered cement paste with calcium leaching. The three-dimensional spatial image of these materials was produced by using these auto–correlation functions. Finally, we attempted to estimate the diffusivity of the altered cement paste by using a finite difference method in conjunction with the three-dimensional spatial image.

2. Experimental

2.1. Sample preparation

Ordinary Portland cement (OPC) produced in Japan was used in this study. The density of OPC is 3170 kg/m^3 and the Blaine surface area is 3340 cm^2/g. The chemical composition of OPC is listed in Table 1. The water-to-cement ratio for the hardened cement pastes (HCP) was maintained at 0.6 (RWMC, 2013) to prevent the effect of unhydrated cement on the experimental results and to produce a lower CaO/SiO$_2$ ratio specimen by leaching. After mixing, the specimens were poured into a mold where they cured for 24 h. After 24 h, the specimens were demolded and cured at 50 °C in a saturated calcium hydroxide solution for 91 days to accelerate the hydration of the cement. An ammonium nitrate solution was used to accelerate the alternation of the hardened cement paste, and the degree of alternation of the paste was simulated by changing the concentration of the ammonium nitrate solution (Carde and François, 1997; Moranville et al., 2004). As a result, this produced hardened cement pastes having different CaO/SiO$_2$ ratios. In this study, the concentrations of the ammonium nitrate solution (specimen weight: NH_4NO_3 solution weight = 1:30) used were 0.25, 0.4, and 0.6 M, respectively, as listed in Table 2, and the immersion time was 7 days without renewal of the solution. The specimens were cut from the center of bulk samples (30 mm in diameter and 100 mm in height) and the specimens used for immersion were 3 mm thick and 30 mm in diameter to produce a homogeneous alternation of the specimens. After immersion, we measured the CaO/SiO$_2$ ratios (non-altered, 0.25, 0.4, and 0.6 M were 3.2, 1.8, 1.3, and 1.0, respectively) at the cross-sections of the specimens by using an electron probe micro analyzer (EPMA), as shown in Fig. 1, and confirmed that the samples were homogeneous. The concentration of elements in specimens was determined by standard material (Wollastonite) and the degree of CaO leaching was calculated from the CaO concentration as measured by the EPMA.

2.2. Measurement of backscattered electron image (BEI)

After the NH_4NO_3 immersion, specimens were immersed in deionized water to remove the NH_4NO_3 solution for 1 day, and we immediately applied the freeze-dry method (liquid nitrogen for freezing and vacuumed in less than 10 Pa). A 3-mm cube was cut from freeze-dried samples of the hardened cement pastes and was used for BEI observations. The freeze-dried specimens were immersed in epoxy resin in a vacuum to maintain the microstructure of the specimen; once the resin hardened, the specimen surface was polished using SiC paper (grid sizes 800, 1000, 1500, 2000, 3000, and 5000). Finally, the surfaces of the specimens were smoothed by a 0.25-μm diamond paste (Scrivener et al., 2015), and a carbon coat was applied to provide electric conductivity to the specimen surfaces. Electron microscopy imaging was conducted under the following conditions: an acceleration voltage of 15 keV, a working distance of 17 mm, an area of 200 × 150 μm, and a pixel size of 0.32 μm. The resolution obtained in this study was 0.32 μm; it was not possible to distinguish between pores narrower than 0.32 μm in diameter. We adjusted the brightness of the image based on the brightness of the epoxy resin and unhydrated cement. Observations were carried out on 16 points on each specimen. Unhydrated cement (UH), unhydrated calcium hydroxide (CH), C-S-H (including fine pores and other hydrates), and pores larger than 0.32 μm were distinguished using image analysis software and by setting brightness thresholds. Each phase was separated by the threshold, which is the minimum value of brightness between the peaks of two phases. The average area fraction of each phase was considered the volume fraction (Igarashi et al., 2004), and the standard deviation of each phase in every sample was less than 0.06.

Table 1
Chemical composition of cement (wt%).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
21.31	5.39	2.75	64.57	1.76	2.05	0.17	0.4

Table 2
Conditions of hardened cement pastes.

Conditions	
Concentrations of ammonium nitrate (mol/L)	0.25, 0.40, 0.60
Liquid/Solid ratio (mass)	30
Leaching period	7 days
NH_4NO_3/Solid ratio (mass)	0.6, 1.0, 1.4

2.3. Measurement of the micro elastic modulus using a micro-indentation method

The specimens for indentation analysis were the same specimens as those used for the BEI. A Fischers scope (HC-100) was used for measuring the micro elastic modulus of the hydration products in the hardened cement paste. One hundred indents in a 10 × 10-μm grid were sampled in each specimen, consistent with the

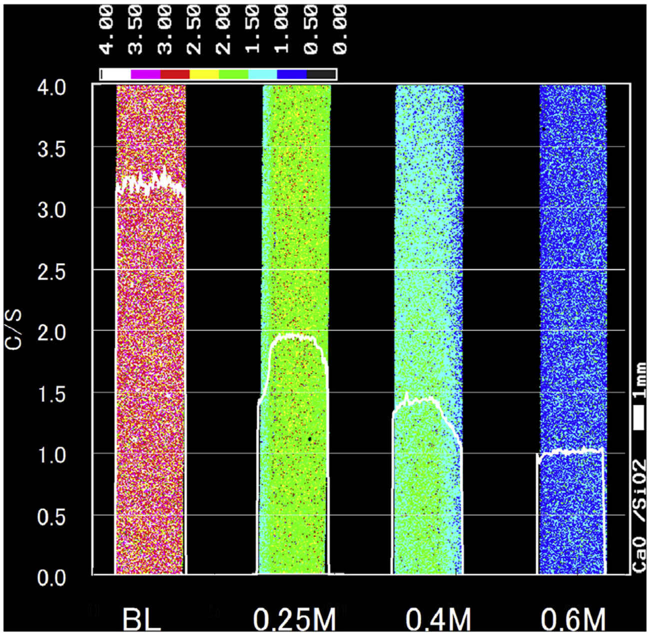

Fig. 1. CaO/SiO$_2$ distribution of specimens measured by EPMA. (Average CaO/SiO$_2$ is BL: 3.2, 0.25M:1.8, 0.4M:1.3, 0.6M:1.0.).