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Deteriorated hardened cement paste structure analyzed by XPS and ^{29}Si NMR techniques

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ABSTRACT

In this report, X-ray photoelectron spectroscopy (XPS) and ^{29}Si-MAS-NMR was used for the evaluation of deteriorated hardened cement pastes. The deterioration by ammonium nitrate solution was accompanied by changes in the pore structure as well as by structural changes in the C–S–H in the hardened cement paste. The CaO/SiO_2 ratio of the C–S–H decreased with the progress of deterioration, there was also polymerization of the silicate in the C–S–H. It was confirmed that the degree of polymerization of silicate of the C–S–H in hardened cement paste can be determined by XPS. It was also shown that the polymerization depends on the structure of the C–S–H.

1. Introduction

When concrete structures are exposed to actual environments for long periods of time, the concrete deteriorates, and the mechanical characteristic of the concrete changes. For example, the storage of radioactive waste is necessary for tens of thousands of years, and the performance of the concrete structures holding it must be maintained during this length of period. It is possible to know the early performance of concrete structures, but it is difficult to know the long-term performance. Therefore, it is very important to know and able to predict the long-term behavior of concrete, and it is important to clarify the mechanisms affecting the behavior. The calcium ion concentration in the pore solution of concrete decreases during long periods, and this leads to a dissolution of the calcium bound in the skeleton of the portlandite crystals $Ca(OH)_2$ and calcium–silica–hydrates (C–S–H). Calcium leaching leads to significant changes in the concrete microstructure, especially, there is a large increase in porosity. Much study focusing on the pore structure has been reported, but there are not many investigations focusing on the calcium silicate hydrate (C–S–H) structure in hardened cement paste, the matrix of the concrete [1–7]. The C–S–H is the main component comprising 60% or more by volume of hardened cement paste, and it controls the properties of hardened cement paste such as the diffusivity and strength [8–10]. The porosity of concrete changes when concrete is exposed to the elements, and it may be expected that the chemical structure of the C–S–H changes.

Solid-state Nuclear Magnetic Resonance (NMR) and TMS methods have been used for the characterization of silicate anion structures in cement chemistry [11–18]. The NMR measurements are used for bulk measurements. The CaO/SiO_2 ratio and bonding state of the Si in C–S–H are determined by X-ray Photoelectron Spectroscopy (XPS) [19–28]. The differences in polymerization of silica were determined by the binding energy shifts [29–31], and highly polymerized silica has higher binding energies. Further, with XPS it is possible to obtain details of the hardened cement paste such as the distribution of Si.

There are some studies of the dissolution of metal from leached cement paste [32,33], but there is no study of the bonding state of silicate in leached cement paste by XPS as far as we know. Therefore this study focuses on changes in the chemical structure of the C–S–H. The purpose of the study is to clarify the effect of leaching on the bonding state of the silicate of C–S–H in hardened cement paste by XPS and NMR.

2. Experimental

2.1. Sample preparation

Ordinary Portland cement (OPC) produced in Japan was used. The density of OPC is 3170 kg/m^3 and the Blaine surface area of OPC is 3340 cm^2/g. The chemical composition and the mineral composition calculated by the Bogue equation of OPC are shown in Table 1. The water/cement ratio for the hardened cement pastes (HCP) was 0.6

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Table 1
The chemical composition and mineral composition of cement.

Chemical composition (wt.%)	
CaO	64.56
SiO_2	21.52
Al_2O_3	5.22
Fe_2O_3	2.65
MgO	1.45
SO_3	2.04
Na_2O	0.28
K_2O	0.47
TiO_2	0.28
P_2O_5	0.23
MnO	0.09
Cl	0.011
ig.loss	1.13
Mineral composition of the cement by Bogue, calculated (%)	
C_3S	62.1
C_2S	14.9
C_3A	9.4
C_4AF	8.1

[34], to avoid the effect of unhydrated cement on the experimental results, and produce the lower CaO/SiO_2 ratio specimen. After mixing, the specimens were demolded after 24 h, and cured at 50 °C in saturated calcium hydroxide solution for 91 days to accelerate the hydration of the cement. Ammonium nitrate solution was used to accelerate the deterioration of the hardened cement paste, and the degree of deterioration of the hardened cement paste was simulated by changing the concentration of the ammonium nitrate solution [35,36]. It was possible to produce hardened cement pastes with different CaO/SiO_2 ratios by varying the concentrations of the ammonium nitrate solutions. In this study, the concentrations of the ammonium nitrate solutions (specimen weight: NH_4NO_3 solution weight = 1:30) were 0.25, 0.4, and 0.6 M and the immersion time was 7 days without renewal of solution. The specimens were cut from the center of bulk samples (30 mm in diameter and 100 mm in height) and the shape of specimens for the immersion was 3 mm high and 30 mm in diameter to produce homogeneous deterioration of the specimens. After immersion, we measured the CaO/SiO_2 ratios of the cross-sections of specimens by EPMA, and confirmed that the samples were homogeneous.

2.2. X-ray diffraction (XRD) measurements

Samples for the measurements were powder that was crushed by ball mill, dried under Argon gas, and mixed with 10 wt.% of corundum (Al_2O_3) as an internal standard. The conditions of the XRD measurements were 40 kV, 40 mA, and with a CuKα X-ray monochromater. A 0.02 2θ step and 2-second count time from 5 to 60° was used. The Rietveld method was used for the quantitative analysis of the composition of the hydrated cement (showing C_3S, C_2S, C_3A, C_4AF, AFm (monosulfate:$C_3A \cdot CaSO_4 \cdot 12H_2O$), Aft (ettringite), CH, katoite, gypsum, and calcite) with the Siroquant software [37].

2.3. Backscattered electron image (BEI) measurements

A 3 mm cube was cut from freeze dried samples of the hardened cement pastes and used for the BEI observations. These dried specimens were immersed in epoxy resin in vacuum; after the hardening of the epoxy resin, a specimen surface was polished using SiC paper, and finally smoothed by 0.25 μm diamond paste, and a carbon coat was applied to provide electric conductivity on the specimen surface. The electron microscopy imaging (Shimadzu, SSX550) was conducted under the following conditions: an acceleration voltage of 15 keV, a working distance of 17 mm, a field size of 200 × 150 μm, and a pixel size of 0.32 μm. The resulting resolution in this study is 0.32 μm, and it was not possible to distinguish pores narrower than 0.32 μm in diameter. Observations were carried out on 16 fields in each specimen. Unhydrated cement (UH), calcium hydroxide (CH), C–S–H (including fine pores and other hydrates), and pores larger

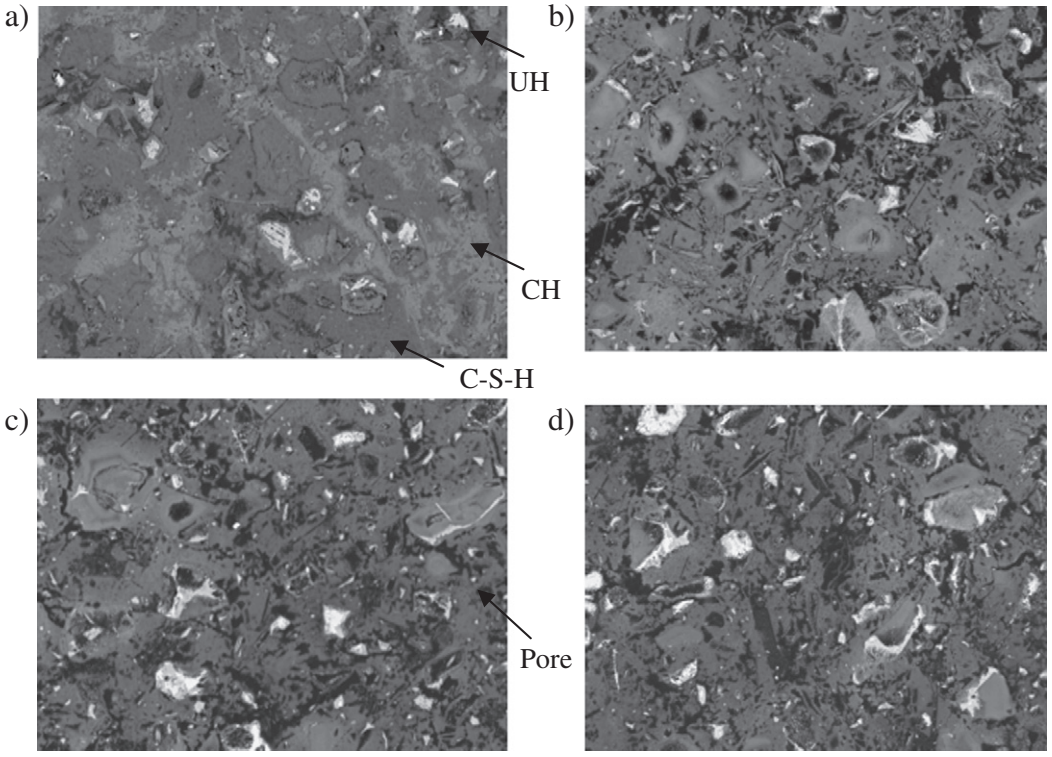

Fig. 1. Backscattered electron image of specimens (size: 200 * 150 μm, a: Non-deteriorated, b: 0.25 M NH_4NO_3, c: 0.4 M NH_4NO_3, d: 0.6 M NH_4NO_3).