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Change in pore structure and composition of hardened cement paste during the process of dissolution

Kazuko Haga[a,*], Masahito Shibata[a], Michihiko Hironaga[b], Satoru Tanaka[c], Shinya Nagasaki[d]

[a]*Taiheiyo Consultant Co. Ltd., 2-4-2, Osaku, Sakura City, Chiba 285-8655, Japan*
[b]*Central Research Institute of Electric Power Industry, 1646, Abiko City, Chiba 270-1194, Japan*
[c]*Department of Quantum Engineering and Systems Sciences, University of Tokyo, 7-3-1, Hongo, Bunkyo, Tokyo 113-8656, Japan*
[d]*Institute of Environmental Studies, Graduate School of Frontier Sciences, University of Tokyo, 7-3-1, Hongo, Bunkyo, Tokyo 113-8656, Japan*

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Abstract

An understanding about the dissolution phenomena of cement hydrates is important to assess changes in the long-term performance of radioactive waste disposal facilities. To investigate the alteration associated with dissolution, dissolution tests of ordinary Portland cement (OPC) hydrates were performed.

Through observation of the samples after leaching, it was confirmed that ettringite precipitation increased as the dissolution of the portlandite and the C-S-H gel progressed. EPMA performed on cross-sections of the solid phase showed a clear difference between the altered and unaltered parts. The boundary between the two parts was termed the *portlandite (CH) dissolution front*. As the leaching period became longer, the CH dissolution front shifted toward the inner part of the sample. A linear relationship was derived by plotting the distance moved by the CH dissolution front against the square root of the leaching time. This indicated Ca ion movement by diffusion.

Keywords: Dissolution; Alteration; Cement paste; Pore size distribution; Leaching

1. Introduction

Cementitious materials have been used as structural or filling materials in radioactive waste disposal facilities and there are plans to continue to use these materials for such purposes. However, the long-term alteration of cement, in terms of its mechanical strength and chemical properties, is far from being completely understood, leaving uncertainty in the predictions of the long-term safety performance of the disposal facilities. In disposal facilities to be constructed underground, cementitious materials would be dissolved and altered by contact with groundwater. This dissolution-induced alteration is considered to be one of the major factors that alters the physical properties of cement. It is anticipated that dissolution of cement hydrates will result in changes in the pore structure. It is also reported that an increase in the pore volume may have significant effects on physical characteristics, such as strength and permeability, as well as the ion diffusion coefficient [1–3]. Therefore, the pore structure should be considered as one of the important factors determining the barrier properties of a cement-based structure. It is also an indispensable factor in terms of examination of the duration of the barrier properties, in view of the fact that changes in the pore structure of hardened cement paste could change the alteration rate of the hardened cement itself.

Chemical properties of porewater, such as pH, Eh, and element concentration, which are dependent on the dissolution of cement hydrates, are deemed to affect radionuclide transport and the surrounding environment. In this respect, it is considered essential to clarify hardened cement dissolution phenomena, and many studies have been carried out on this topic. Among these, Atkinson et al. [4,5], Atkinson and Guppy [6], and Berner [7] made predictions of the long-term development of changes in the composition of aqueous phases by modeling the cement dissolution phenomena. Also, Faucon et al. [8,9] studied the dissolution-induced alteration of cement hydrates, to find that, as dissolution proceeds, the hydrate phase and structure of hydrates would be altered. Nevertheless, only a few studies have focused on the pore structure changes caused by dissolution of hardened cement. In recognition of the fact that it is very important to

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* Corresponding author. Tel.: +81-43-498-3858; fax: +81-43-498-3859.
E-mail address: Kazuko_Haga@grp.taiheiyo-cement.co.jp (K. Haga).

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Table 1
Experimental condition and analytical items

Samples for leaching	OPC hydrate 2.5 × 10 × 10 mm (w/c = 0.7, under sealed condition for 1 year at 20 °C) Decarbonated ion-exchanged water (purged by N_2 gas for 24 h)
Liquid/solid ratio for leaching	1000 (w/w)
Leaching period	1, 5, 8, 14, 26, and 56 weeks
Condition of dissolution test	In the glovebox filled with nitrogen gas
Analytical item	Porosity, bulk density (mercury injection porosimeter) Element distribution in solid phase (EPMA) Form of hydrates (SEM) Identify of crystal phase(XRD) Quantitative analyses of hydrates (DTA/TG)

investigate hardened cement alteration due to dissolution when estimating physical and chemical durability and in the modeling of cement alteration, cement hydrate dissolution tests have been conducted to assess the changes in the hydrates and the pore structures [10,11]. We have reported that the silicate anion chains of C-S-H gel were elongated in the samples after leaching, and that the structure of hydrates would change as a result of dissolution [12]. In addition, based on results obtained by dissolution tests of alite hydrate (a primary component in Portland cement clinker), we showed that the change in the pore structure is related to the type of dissolving hydrate, and that dissolution of the primary hydrate, i.e., portlandite, increases the pore volume with size approximately 1 μm [13].

In this study, hardened ordinary Portland cement (OPC) slabs were leached in ion-exchanged water and the solid samples were then subjected to detailed analyses, with the aim of obtaining an insight the relationship between the change in hydrate phases associated with dissolution and the structural change in the pores. We selected experimental conditions that were far from those of radioactive waste disposal facilities, such as the use of the OPC paste with a high water-to-cement ratio of 0.7 and dissolution under the condition of a liquid to sample ratio of 1000, because we wished to observe the alteration of hardened cement with dissolution over a relatively short period. It is assumed that the alteration in real facilities would proceed much more slowly than the alteration in this experiment, but we believed that the phenomena involved in the former would be similar to those in the latter.

2. Experiments

The experimental conditions are summarized in Table 1.

2.1. Test samples

OPC was mixed with ion-exchanged water at a water-to-cement weight ratio of 0.7. It was then hydrated in a sealed container at 20 °C for 1 year to produce hardened cement. The test samples were prepared by cutting the hardened cement into slabs of 2.5 × 10 × 10 mm with a diamond cutter. The chemical composition of the OPC used in the preparation of test samples is shown in Table 2.

2.2. Dissolution tests

The cement hydrates were sealed in polyethylene containers with ion-exchanged water at weight ratio of 1000 and left to react in a thermostatic chamber at 20 °C for a predetermined period. The leaching water was not exchanged. After a specified period, they were separated into solid and liquid phases by decantation. The solid samples were dried in a vacuum dryer. The entire process, from the leaching of samples through the vacuum drying, was conducted in a controlled atmosphere in a glove box where air was replaced with N_2 gas.

2.3. Analysis method

After being vacuum-dried, the solid phase samples were subjected to measurements of pore size distribution, bulk density, etc., using mercury intrusion porosimetry (MIP, Auto Pore II 9220, Micrometrics). Some sample pieces were embedded in resin, cut through the center, and polished for element concentration analyses using electron probe microanalysis (EPMA, JEOL JXA-8621). To observe the hydrates in the cross-section, a scanning electron microscope (SEM, JEOL JSM6100) was used. The other sample pieces were prepared for X-ray diffraction analyses (XRD, RINT2050, Rigaku) to identify crystal phases and for differential thermal analysis and thermogravimetry (DTA/TG, SSC5000, Seiko Instruments).

3. Results and discussions

3.1. Changes in the hydrate phase

Crystal phases identified by XRD are shown in Table 3. In the initial samples, hydrate phases of portlandite, C-S-H gel, and AFm phase ($3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}12H_2O$ or $7CaO{\cdot}2Al_2O_3{\cdot}CaCO_3{\cdot}24H_2O$) were observed. The diffraction peaks strength of the portlandite became smaller as the samples were leached for longer periods and, finally, no peak was observed in the samples leached for 56 weeks. The results of the quantitative determination of portlandite and calcite using DTA/TG are shown in Table 4. The amount of

Table 2
Chemical composition of OPC used in the experiments

Chemical composition (wt.%)									
SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	LOI	Total
21.2	63.8	5.6	2.9	1.5	2.1	0.23	0.38	0.68	98.39

Table 3
The crystal phase in the solid phase of leached specimen identified by XRD

Crystal phase	Initial sample	Leaching period (weeks)					
		1	5	8	14	26	56
Portlandite $Ca(OH)_2$	◎	○	○	△	△	△	—
C-S-H	△	△	△	△	△	△	△
Ettringite[a]	—	—	—	△	—	△	△
AFm phase[b]	△	△	△	△	△	△	△
Calcite $CaCO_3$	—	—	△	△	△	△	—

XRD Intensity: ◎: Strong, ○: Medium, △: Weak, —: ND.

[a] $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$.

[b] $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 12H_2O$ or $7CaO \cdot 2Al_2O_3 \cdot CaCO_3 \cdot 24H_2O$.

portlandite decreased as the leaching period increased and it became undetectable in the samples leached for 56 weeks. This result was consistent with the results obtained using XRD. The portlandite in the samples was considered to have dissolved completely during the 56 weeks of the test.

Ettringite was observed in the samples after leaching. Faucon et al. [9] also reported in their study that ettringite was generated in the surface layer of the samples after leaching and was considered to be a secondary mineral formed as a result of dissolution. The ettringite observed in our experiments was also considered to be a secondary mineral formed in the process of hydrate dissolution. The AFm phase, which was observed in the initial samples, was still found unchanged in the samples after leaching. Calcite was observed in some samples, and it is assumed that this was formed by the reaction of atmospheric carbon dioxide and portlandite. The cause of formation could be attributed to the fact that the test samples were prepared in air, although the dissolution tests themselves were conducted in an atmosphere-controlled glove box.

3.2. Changes in the pore structure

3.2.1. Changes in the bulk density

The relationship between leaching period and bulk density is shown in Fig. 1. The bulk density became smaller with increasing leaching period. This indicates that the dissolution progressed gradually. The decrease in the bulk density was relatively rapid until the 14th week. However, it remained almost unchanged after this, meaning that the weight reduction due to dissolution was mostly completed by the 14th week.

3.2.2. Changes in the pore structure

The change in the pore volume with increasing leaching period is shown in Fig. 2. The change in pore volume becomes larger with longer leaching periods. After the 14th week, the pore volume increase rate became moderate.

Table 4
Quantity of $Ca(OH)_2$ and $CaCO_3$ in the solid phase of leached specimen determined by DTA/TG (wt.%)

	Initial sample	Leaching period (weeks)			
		1	5	14	56
Portlandite $Ca(OH)_2$	22.73	15.29	9.95	5.34	ND
Calcite $CaCO_3$	ND	ND	3.84	2.48	ND

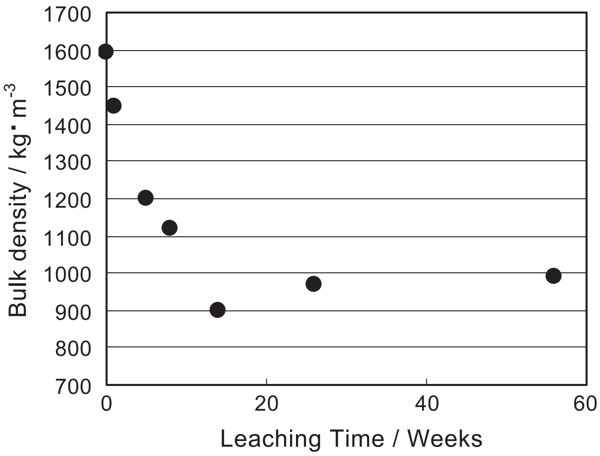

Fig. 1. Relationship between leaching time and bulk density of solid phase of leached specimen.

The distributions of pore sizes in the initial samples and those after leaching for 56 weeks are shown in Fig. 3. A comparison of these samples showed an increase in the pore volume in the pore size range between 0.05 and 0.5 μm after leaching. The totals pore volume of the sample after leaching was also larger. Each of the various hydrate phases that constitute hardened cement has a different shape. In Portland cement, the primary hydrate phases are C-S-H gel and portlandite. Daimon et al. [14] considered that the C-S-H gel consisted of gel particles with an internal structure, together with pores with equivalent diameters of 3.2–200 nm. These pores were termed *intergel particle pores*. The smaller pores within the gel particles, termed *intercrystallite pores*, had diameters of 1.2–3.2 nm. Pores smaller than both these types were termed *intracrystallite pores*. The idea is not that the pores are classified into gel pores and capillary pores, but that the pores derived from C-S-H gel are identified in detail. Based on this information, pores below 0.2 μm were

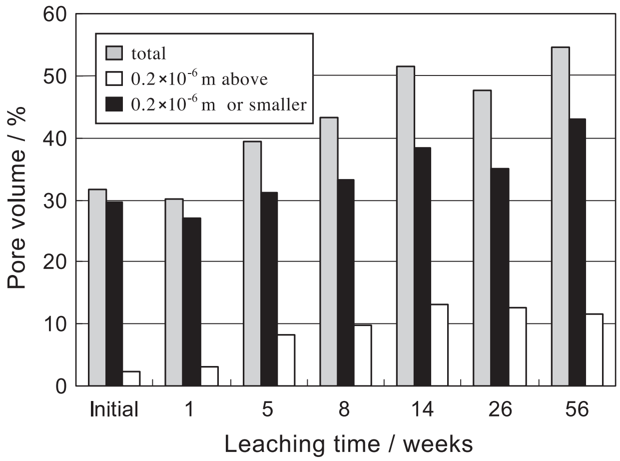

Fig. 2. Leaching time dependency of pore volume.

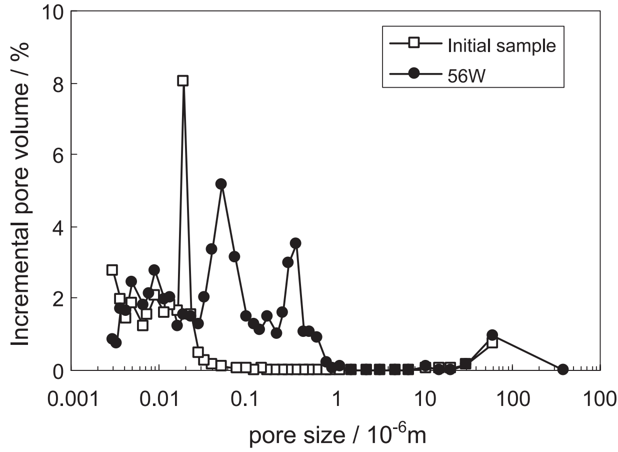

Fig. 3. Pore size distribution of sample initially and after leaching for the weeks 56th.

considered to be related to the C-S-H gel. On the other hand, in hardened cements, portlandite is often observed in the form of crystals larger than a few microns. It was determined that, in dissolution tests of alite hydrate, pores with a size of around 1 μm increased along with the progress of dissolution of the portlandite [11]. It was thus assumed that pores of 0.2 μm or smaller were attributable mainly to the C-S-H gel, while those larger than 0.2 μm were attributable mainly to the portlandite.

It was recognized that pore size distribution measurement by MIP presents some problems. For example, it is reported that pore diameters obtained from MIP measurements are smaller than those observed by SEM. This is thought to depend on a factor known as the "inkbottle problem." However, portlandite in hardened cement is a large crystal and the C-S-H gel is a very small crystal in comparison. Therefore, it was believed that the change in pore size distribution caused by the dissolution of portlandite and C-S-H gel was distinguishable, it is recognized as being questionable whether it is appropriate to classify the pore volume using a pore diameter cut-off at 0.2 μm. However, it has been confirmed that there is a good correlation between the dissolution of portlandite and the increase in the volume of pores larger than 0.2 μm in leaching examinations of alite hydrate [13].

Having recognized the above-mentioned limitation, we would like to consider the changes in pore volume assuming that pores of 0.2 μm or smaller were attributable mainly to the C-S-H gel, while pores larger than 0.2 μm were attributable mainly to the portlandite. Therefore, in Figs. 2 and 4, the pore volume of samples is shown separately for a size of 0.2 μm or smaller and for larger than 0.2 μm.

As shown in Fig. 2, after 14 weeks, the alteration of pores larger than 0.2 μm is small. Quantitative analyses of hydrates using DTA/TG showed that nearly 80% of the portlandite present in the initial samples was leached out by the 14th week. This means that there is a correlation between the dissolution of portlandite and the increase in the volume of pores larger than 0.2 μm. It was thought that the alteration of the C-S-H gel continued because an increase in the pore volume below 0.2 μm continued.

Fig. 4 shows the increase in the pore volume associated with dissolution, both values being calculated based on the measured quantity of portlandite. The increase in the pore volume (V_p) resulting from the dissolution of portlandite was calculated using the following formula:

$$V_p(\%) = [(D_I P_I/m) - (D_L P_L/m)]M \times 100.$$

where D_I is the bulk density (g/cm^3) of the initial samples, P_I is the portlandite content by weight in the initial samples, D_L is the bulk density (g/cm^3) of the samples after leaching, P_L is the portlandite content by weight in the samples after leaching, m is the molecular weight of the portlandite (74 g/mol), and M is the molecular volume (33.0 cm^3/mol, calculated from the density of portlandite of 2.24 g/cm^3, as shown in Ref. [15]). The bulk density of each sample was determined by MIP, while the portlandite content by weight was determined by quantitative analysis with DTA/TG.

The calculated increase in the pore volume due to the dissolution of portlandite was always larger than the increase in the pore volume larger than 0.2 μm measured in experiments. This may indicate that some of the pores generated by the dissolution of the portlandite were filled with other precipitated minerals. The results of XRD analyses showed the presence of ettringite that had not been observed in the initial samples; hence, ettringite should be considered to be formed during the leaching period. It is also conceivable that the C-S-H gel precipitated to establish equilibrium between the porewater and the solid phase when leached Ca diffused from the inside of the sample to the surface. Fig. 5 shows the cross-sections of the initial samples

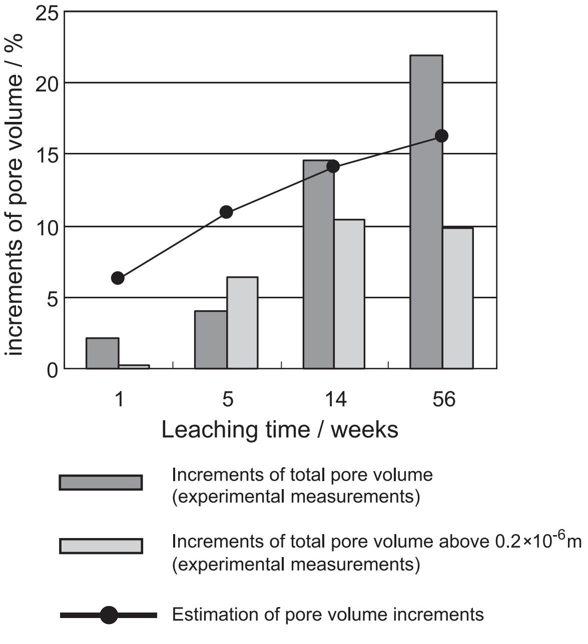

Fig. 4. Increments of pore volume associated with dissolution.

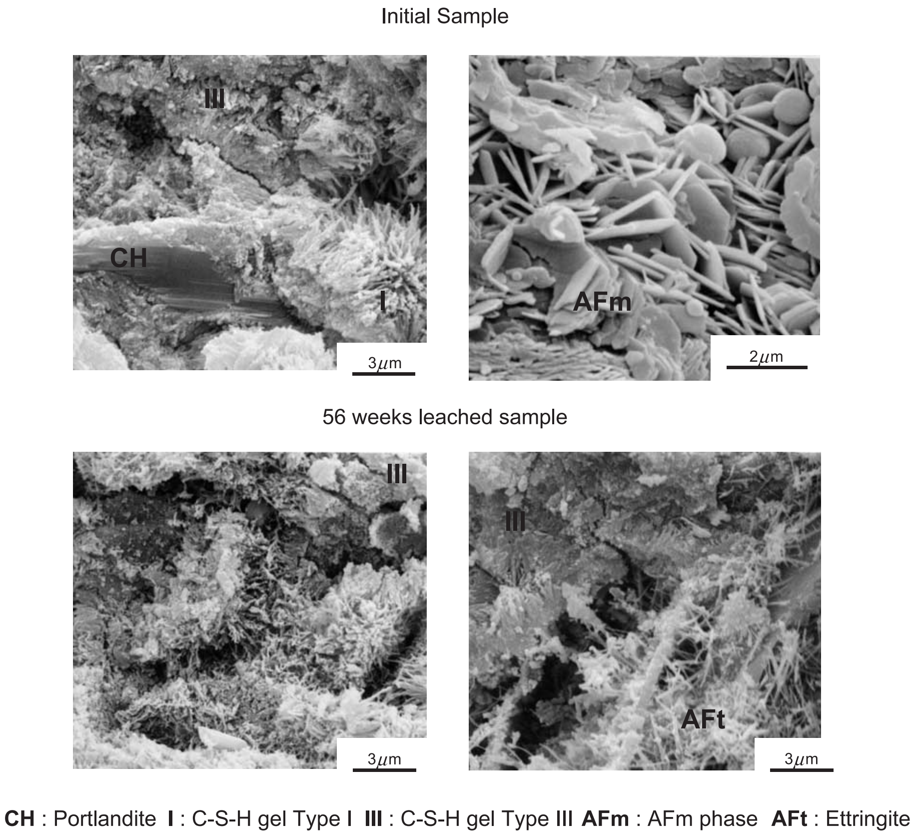

Fig. 5. Micrographs of secondary electron image of the sample initially and after leaching for 56 weeks.

and of the samples after leaching for 56 weeks, observed using SEM. The major hydrates observed in the initial samples were layered crystals that could be considered to be portlandite, as well as Type III C-S-H gel; others were Type I C-S-H gel and the AFm phase. C-S-H gel is categorized into Types I–IV, depending on its appearance [16]. Each type is denoted as follows: Type I, fibrous; Type II, reticulate; Type III, equant; Type IV, dense gel. Types III and IV are frequently observed in fully hydrated samples, while Types I and II are likely to be found in samples from relatively early stages. In the samples leached for 56 weeks, the large layered crystals, which were considered to be the portlandite,

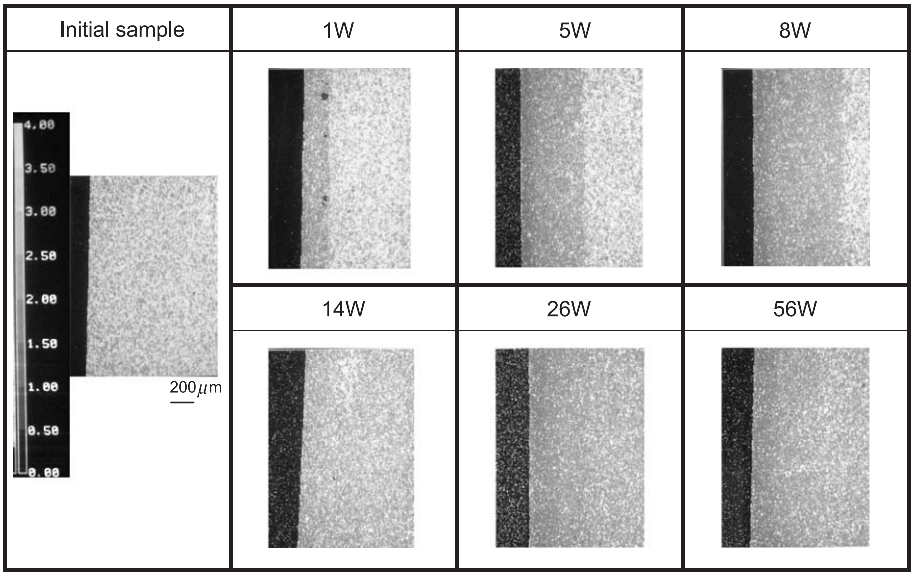

Fig. 6. CaO/SiO_2 mole ratios on the cross-section of the hardened cement paste leached for various time.

had disappeared. Instead, Type III C-S-H gel were observed, as well as the well-developed Type I C-S-H gel and needle-like crystals (probably ettringite) growing in large pores. These hydrates were assumed to have precipitated.

Since the pore sizes of intercrystals of Type I C-S-H gel and ettringite were observed to be 0.1 μm or less, it was determined that the generation of these minerals was the cause of the increase in the pore volume for sizes about 0.05 μm, which was identified in the measurement of pore size distribution of samples after leaching (Fig. 3). In addition, the increase in the pore size 0.2 μm or smaller remaining until the 14th week (shown in Fig. 2) was also assumed to have been caused by the precipitation of these minerals.

In Fig. 4, in the samples leached for 56 weeks, after which the portlandite was considered to have completely leached out, the measured pore volume was greater than that calculated from the result of the quantitative analysis of portlandite; this indicates that other types of hydrate were also dissolved. The dissolved hydrate is considered to be a part of the C-S-H gel that is amorphous and is not sensitive to XRD analysis, since there was virtually no change observed in the AFm phase in the identification of hydrate phases in XRD analyses.

3.3. Changes in element distribution in the solid phase

3.3.1. Change in the CaO/SiO$_2$ ratio along the cross-section of the solid phase

Fig. 6 shows the changes in the element concentration analyzed by EPMA along the cross-section of the samples. They are represented as a CaO/SiO$_2$ mole ratio (referred to hereafter as the C/S ratio).

After leaching, the C/S ratio in the samples had decreased dramatically in the surface layer, due to the leaching of Ca through the contact surface with the deionized water, while the composition of the initial samples was homogeneous. The inside of the samples after leaching had almost same composition as that of the initial samples. Therefore, the inside unaltered part and the altered part in the surface layer could be readily distinguished. As an area with a high C/S ratio indicating the presence of portlandite crystals was not observed in the altered part, it was thought that the portlandite had leached out completely. In this article, the boundary between the unaltered and the altered parts observed in this process is referred to as portlandite dissolution front (hereafter the *CH dissolution front*). The CH dissolution front gradually shifted inward with the increase in the leaching period. In the samples leached for 14 weeks, the CH dissolution front could not be observed, suggesting that the C/S ratio had decreased throughout the sample.

As a result of the analyses of the pore structure described above, the trend was found to be that the bulk density and pore volume changed fairly rapidly until the 14th week, but thereafter the change was slow to moderate. The period when the unaltered part could still be observed and the CH dissolution front was moving was consistent with that when the change in the pore structure was progressing rapidly. This fact suggests that the rapid change in the pore structure until the 14th week was due to the dissolution of portlandite.

Fig. 7 shows the result of the CaO concentration at the cross-section of a sample after 5 weeks analyzed using EPMA, as well as a diagram of a possible dissolution process. In cement hydrates, most of the Ca is supposed to occur as oxides. Consequently, in the EPMA analysis, oxide samples were used as standard materials and the element compositions in the samples were represented as oxides. The solid phase analyses showed that the CaO concentration was high in the unaltered part, decreased sharply beyond the CH dissolution front or in the altered part, and was reduced further toward the surface layer which was in contact with the leaching water. Based on these results, the process of alteration by dissolution was considered to proceed as follows: Firstly, at the CH dissolution front, the portlandite dissolves, then the dissolved component, i.e., Ca ions, is transported to the surface layer by diffusion. In the course of their transport through the altered part, Ca ions will change the composition of the porewater so that equilibrium can be reached between the porewater and the solid phase, allowing the precipitation of C-S-H gel

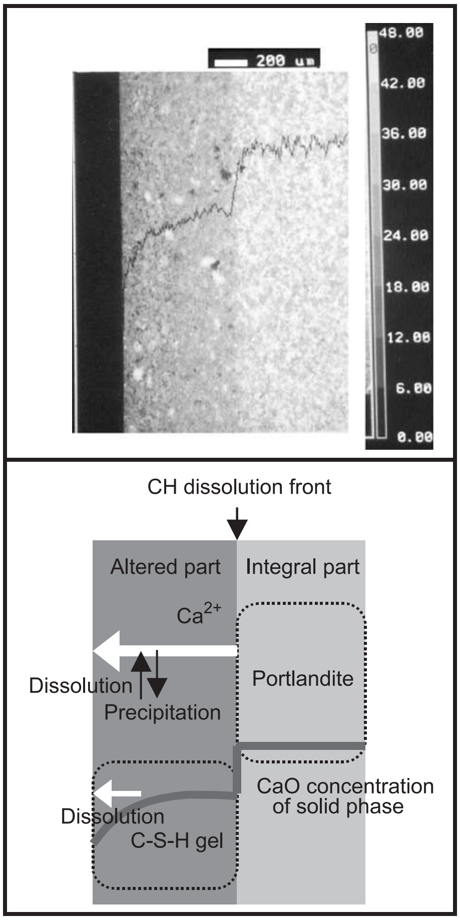

Fig. 7. CaO concentration on the cross-section of the 5 weeks leached sample and schematic reaction model of the dissolution.

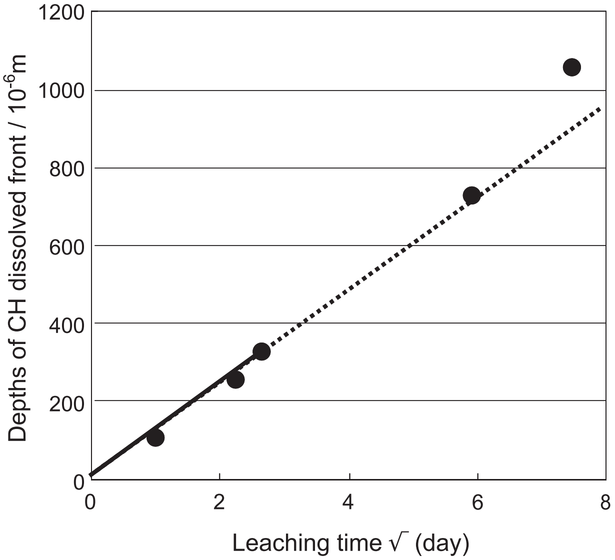

Fig. 8. Depths of the CH dissolved front as a function of the square root of time.

or ettringite. In addition, by referring to the CaO composition distribution of the solid phase, it was confirmed that C-S-H gel was also dissolved in the surface layer. This led to the conclusion that the dissolution/precipitation reactions occur so that the porewater and the solid phase reach equilibrium within a very small distance. Hence, it was considered that the causes of the changes in the volume of pores smaller than 0.2 μm were both the precipitation of ettringite and C-S-H gel and dissolution of C-S-H gel.

The results obtained from NMR analyses of the change in silicate anion structure of C-S-H gel have demonstrated that, in the presence of the portlandite, C-S-H gel does not dissolve [10,12]. In this study, the portlandite disappeared in the surface layer, although it remained in the inner part of the samples. In the surface layer, C-S-H gel was dissolved. Consequently, it was observed that, in general, portlandite and C-S-H gel dissolved simultaneously.

3.3.2. Movement of the dissolution front

Fig. 8 shows the relationship between the distance from the surface to the CH dissolution front observed in the samples up to 8 weeks and the square root of the leaching period. In the early stage of leaching, a linear relationship was derived by plotting the distance (surface to CH dissolution front) against the square root of the time. This suggests that the transport of Ca, the dissolved component of the portlandite, is by diffusion. Under the conditions set in this study, it can be expected that dissolution will raise the concentration of Ca in the leaching water and the concentration gradient in the porewater of the solid phase will decrease with the increase in the leaching period. In addition, in line with the increase in the leaching period, the pore volume also increased. The test results showed that the prolonged leaching period resulted in a change of the slope compared to that in the early stage. The reason for this is considered to be the influence of the change in composition of the leaching water and solid phases associated with the dissolution. If influenced by a decrease in the magnitude of the concentration gradient due to the increase in the concentration in the leaching water, the mass transport rate would probably be lowered. However, in this study, the slope in Fig. 8 leached for a longer period was steeper than that of the early stage, indicating that the Ca transport rate was becoming higher. This suggests the possibility of a strong effect due to the increase in the pore volume generated by the dissolution. In the future, priority should be given to quantitative evaluation of the relationship between the pore volume and the dissolution alteration rate to evaluate the long-term performance of cement-based structures.

4. Conclusions

(1) Portlandite dissolved with an increase in the sample leaching period; in the samples leached for a prolonged period, portlandite was not observed. Instead, ettringite was observed as a new phase generated in association with the dissolution.
(2) The changes in the pore volume were not only due to the portlandite dissolution; they were also affected by the precipitation and dissolution of ettringite and C-S-H gel.
(3) The CH dissolution front shifted toward the inner part of the sample with increasing sample leaching period. In the early stage of the dissolution tests, a linear relationship was observed between the distance moved by the CH dissolution front and the square root of time.

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