Release of Superplasticizers and Other Organic Additives from Altered Cement

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EXECUTIVE SUMMARY

The behavior of superplasticizers and other organic additives in cementitious materials is an issue for the long-term safety of high-level radioactive waste disposal. These organic substances may be leached into groundwater in contact with cementitious material and possibly affect radionuclide migration behavior in the surrounding rock. To evaluate the impact of these organics on radionuclide migration, the release properties of organics and leaching alteration properties of cementitious hydrated phases were studied in this project. The experimental data suggested that the components of superplasticizers (SP) will hardly be released from cementitious hydrated phases, even in the case of leaching degradation. Raw materials of cement powder contained low molecular weight organics and cement grinding aids and these organics were released from the cementitious hydrated phases during the leaching alteration process. The cementitious hydrated phases altered with enlarged hydraulic pores for the C-S-H phase in specimens examined after immersion experiments. However, the progression rate of the alteration front was decreased by using low-pH cement in any leachant solution. SPs possibly decompose into relatively small molecular weight polymers over the long term. Accelerated experiments were therefore conducted and decomposition phenomena were detected using several molecular analysis methods.

CONTENTS

1   INTRODUCTION

Cementitious materials are used widely without any problems in conventional tunnel construction and excavation. However, if such materials are introduced into radioactive waste disposal facilities as, for example, concrete liner, grouting material and mechanical plugs, the impact of the chemical stability of cementitious materials on post-closure safety has to be considered. Over the last few decades, this issue has been the subject of frequent study. The major topics are

(1) The chemical impact of leaching alkali and alkaline earth ions (Na, K or Ca) on the bentonite buffer.
(2) The impact of hyperalkaline solutions following the degradation of ordinary Portland cement on the bentonite buffer and surrounding rock .

The use of low-pH cement is considered to be an effective measure for reducing the negative impact of the degradation of cementitious materials on the stability of the host rock and the bentonite buffer. Low-pH cement is used as a substitute for OPC (ordinary Portland cement), the leachate of which may reach a pH of 12-13. The target pH for the development of low-pH cement is therefore set at around 11(NUMO, 2004). The material properties of three representative low-pH cement materials (HFSC, LAC and SAC) have been studied in the laboratory and it has been concluded that the fundamental mechanical properties of the low-pH mortar are as good as those of OPC mortar (NUMO, 2008).

An effective general method for obtaining low-pH cement is to add fine-grained pozzolanic material, i.e. silica fume, to OPC. On the other hand, incidental problems such as loss of workability will be caused by using large amounts of silica fume. In this situation, superplasticizers (SP) are needed to maintain workability without adding water. Superplasticizers are effective organic additives for reducing the viscosity of cement containing fresh mortar, concrete and grout. Although SPs have the advantage of increasing workability, their long-term behavior and chemical impact on nuclide migration from the viewpoint of long-term safety need to be investigated.

Since 2005, Nagra, SKB, Posiva and NUMO have been conducting a joint project to develop a fundamental methodology for evaluating the chemical properties of organic compounds contained in cementitious materials, such as superplasticizers used in cementitious grouting material. Firstly, as in the last SKB-Posiva-NUMO project on low-pH (pH$\leq$ 11) injection grout for deep repositories (Bodén & Sievänen, 2005), the aim in the fabrication of the grouting materials was to exclude organic additives. The main physical requirement for the grouting materials is fluidity, i.e. an ability to penetrate, and workability. Although these mechanical properties could be achieved in the laboratory, there was a significant loss of fluidity during Posiva's field injection test. The main reason was thought to be lack of dispersion in the grouting slurry and Posiva therefore decided to use superplasticizers to achieve sufficient fluidity of the slurry. There are a few major types of superplasticizer and it is necessary to select those with less inhibiting effects on Kd values and high efficiency options for achieving sufficient fluidity of the grouting slurry. NUMO's task in the joint project was to determine the molecular type of organic compounds released from the hardened cement matrix during immersion tests. The immersion tests were based on the accelerated leaching alteration method to obtain information about the relationship between release and adsorption of organic compounds from altered hydrates in the cementitious material.

2 EXPERIMENTAL PROCEDURE

2.1 Materials and specimens

Two cementitious grout systems, a low-pH system and a normal pH system as reference, were used in the experiments. The low-pH system has 3 specimen types, one with no SP and two with added SP. The ordinary pH system has 2 types, one without and one with SP. The chemical compositions of the cementitious materials and the mixing proportions for each specimen are shown in Table 2.1-1 and Table 2.1-2, respectively.

Table 2.1-1: **Chemical compositions of cement (UF16) and silica fume (Grout Aid) in dry weight (%).**

	C	SiO$_2$	Al$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	P$_2$O$_5$	Fe$_2$O$_3$	TiO$_2$	MnO	SO$_3$	Sr
UF16	0.14	22.8	3.65	65.3	0.79	0.08	0.43	0.11	4.39	0.25	0.23	1.76	0.0033
Grout Aid	0.31	96.2	1.16	0.48	0.53	<0.03	0.79	0.05	0.28	0.01	0.04	0.09	0.0022

Table 2.1-2: **Mixing proportions for low-pH and normal pH systems (g/g).**

| Specimen		Water /DM	UF16 /DM	Grout Aid /DM	SP/DM	Type of superplasticizer
Normal System	XREF52	1.21	0.930	0.070	-	-
	REF52	1.21	0.930	0.070	0.01	SP40
Low-pH System	XP308B	1.40	0.592	0.408	-	-
	P308B	1.40	0.592	0.408	0.04	Mighty 150
	P379G	1.20	0.592	0.408	0.015	Glenium 51

*DM : weight of binder in dry material base, SP40: less water reducing effect than other SPs, used in REF52 to keep the same level of water/DM ratio as in other case**s.**

The component materials of the grouts were as follows:

- Ultrafine 16 (UF16): Sulfate-resistant Portland cement
- Grout Aid (GA): Silica fume slurry (solid content: 50 mass%)
- SP40: Poly melamine sulfonate (PMS)-based superplasticizer
- Mighty 150: Poly naphthalene sulfonate (PNS)-based superplasticizer
- Glenium 51: Polycarboxylate (PC)-based superplasticizer

All initial hardened specimens and raw materials were provide to CRIEPI by Posiva. Grout specimens were mixed and cast in a plastic tube around 1.5 m long and 50 mm in diameter. Both tube ends were sealed and cured at room temperature (12°C) for four weeks until delivery to CRIEPI. The hardened specimens were processed into several different shapes as discussed below after two additional months of curing at room temperature (20°C). The hardened pastes were thus cured at room temperature for a total of three months. One type of hardened paste, i.e. XP308B, was mixed without using SP and showed numerous voids and

microcracks as seen in Figure 2.1-1. This initial defect caused difficulties for the minute cutting needed for shaping the immersion specimens, so XP308B was recast using a 4x4x16 cm mold to allow vibrating compaction. This hardened paste was cured under 20°C humid air conditions for three months before processing into the shapes used for testing.
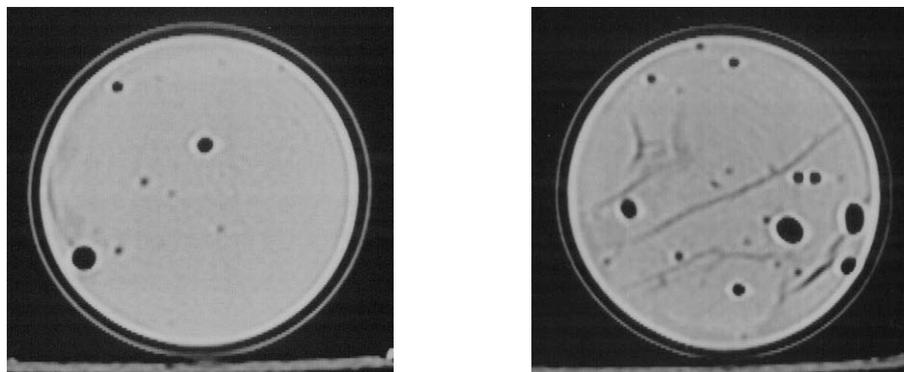
a) P308B   b) XP308B

Figure 2.1-1: **Tomographic images of delivered specimens: a) P308B, b) XP308B. Images were photographed using X-ray computer tomography. Several cracks are apparent in the XP308B hardened paste, compared with P308B.**

2.2   Leaching test methods

Leaching tests were conducted for both uncured fresh grouts and cured hardened grouts. The fresh grouts were placed directly in leachants, while the cured hardened grout specimens were immersed in leachants in the form of powders, thin-plates and block-shapes. In all the experiments, three types of leachant, namely synthetic fresh groundwater (ALL-MR), synthetic saline groundwater (OL-SR) and deionized water, were used. Table 2.2-1 shows the ion concentrations in the leachants ALL-MR and OL-SR. ALL-MR and OL-SR were prepared by mixing suitable reagents into deionized water. The leachants were prepared by mixing chemical reagents in an N_2-filled glove box following the method outlined by Vuorinen et al. (2004).

Table 2.2-1: **Ion concentrations of ALL-MR and OL-SR (mg·dm^{-3}).**

	Na	Ca	K	Mg	HCO$_3^-$	SO$_4^{2-}$	B	F	Br	Sr	Cl	Si
ALL-MR	55.2	5.14	3.91	0.71	65.0	4.20	-	-	-	-	48.9	2.39
OL-SR	4800	4000	21.0	54.6	-	9.60	0.92	1.19	105	35.0	14726	-

2.2.1   Fresh leaching test

Fresh grouts were mixed at a temperature of 20°C in accordance with the mixing proportions shown in Table 2.1-2 and were cast into polypropylene vessels immediately after mixing. The leachants were poured slowly into the grout-embedded vessels one hour after the beginning of mixing. The leachant/grout volume ratio was fixed at 4.0. The cross-section of the vessel was 33.1 cm^2. After pouring in the leachant, the vessels were sealed and kept in N_2 gas-filled glove boxes at 20°C. The fresh leaching test is a batch-type test and the specimens were set for each sampling period. The sampling periods were set at 1, 3, 7, 28 and 56 days.

2.2.2   Powder leaching tests

Hardened grouts were ground into a powder with a grain size less than 100 μm and the ground powder specimens were dried for 24 hours using an aspirator. The particle size distribution of all the powdered samples was confirmed to be almost the same. After drying, the powder specimens were immersed in each leachant at 20°C. The leachant/powder ratios were fixed as 10, 50, 100 and 1000 $cm^3 \cdot g^{-1}$. The powder leaching test is a batch-type test aimed at obtaining quantitative data on the liquid and solid phases under ionic equilibrium conditions between the solid and liquid phases for various leachant/powder ratios. All leaching procedures except grinding and drying were performed in N_2 gas-filled glove boxes to avoid carbonation. The sealed vessels were mixed well at the start of the immersion test; afterwards the specimens were maintained under static conditions for a total of 38 weeks. The solid phase in each vessel was confirmed not to be in a concretion condition at the end of the immersion test.

2.2.3   Thin-plate leaching tests

These tests were performed to determine the physical and chemical properties of uniformly altered mass specimens and the plates therefore had to be as thin as possible. The thickness of the specimens was determined to be 0.5 mm with 20 mm sides based on the required stiffness during handling. Thin-plate specimens were cut from blocks of hardened paste as mentioned above using a fine cutting machine. During the slicing procedure, ethanol was used as a cooling agent for the blade. The ethanol was dried and removed from the specimens using an aspirator for 24 hours after slicing. The prepared thin-plate specimens were immersed in each leachant at 20°C, with 16 pieces of specimen being placed in one vessel containing 2 liters of leachant. The liquid to solid ratio for leachant volume to contacted surface area of the specimen is 14.9 $cm^3 \cdot cm^{-2}$. The leachants were exchanged every 6 weeks to accelerate leaching by maintaining a high ionic concentration gradient between the leachant and the porewater in the solid phase. The leachants were thus exchanged 4 times during the 30-week immersion period. All experimental procedures except for specimen preparation were carried out in N_2 gas-filled glove boxes to prevent carbonation.

2.2.4   Block leaching tests

Block leaching tests were performed to evaluate the progression rate of the leaching alteration front in each cement system. The hardened paste was cut into 20 mm cubic blocks. During the cutting procedure, deionized water was used as a cooling agent for the blade. The block-shaped specimens were dried using an aspirator for 24 hours after slicing. The prepared specimens were immersed in vessels filled with 2 liters of leachant at 20°C and the liquid to solid ratio for leachant volume to contacted surface area of specimen was 83.3 $cm^3 \cdot cm^{-2}$. The leachant was exchanged every 4 weeks during the immersion period, from 1 to 53 weeks, to accelerate leaching alteration by maintaining a high ionic concentration gradient between the leachant and the porewater in the solid phases. All leaching procedures except for specimen preparation were done in N_2 gas-filled glove boxes to prevent carbonation.

2.3   Analytical methods

Liquid phase analyses for both the organic and inorganic cases were carried out for all experiments. In the case of the solid phase analyses, element concentration mapping analyses were performed only for the block-shaped specimens with the aim of estimating the relative

differences in progression rates of the leaching alteration front. Structural analysis of the Si ion in Si-containing compounds was performed only for powder specimens that were sufficiently homogeneously altered to estimate the state of C-S-H during the immersion period. Pore size distribution analysis was applied to the thin-plate specimens and 5 mm thickness of surface area for the block-shaped specimens. Observational shape analysis of hydrates and other compounds was carried out on thin-plate and block-shaped specimens, particularly focusing on the surface of the altered phases and immediately beneath the altered phases to estimate the difference in shape of hydrates and pore size. The other solid phase analyses, i.e. qualitative and quantitative analyses of crystal components and hydrates, were applied to all specimens. The aims of detection for each analytical method are as follows:

2.3.1   Liquid phase organic analyses

Total organic carbon (TOC) was measured using a TOC analyzer. The molecular weight of dissolved organics was determined by gel permeation chromatography (GPC).

2.3.2   Liquid phase inorganic analyses

The pH of the leachate was measured using a pH meter and the concentration of the main elements was analyzed using Inductively Coupled Plasma –Atomic Emission Spectrometry (ICP-AES).

2.3.3   Solid phase analyses (powder, thin-plate and block specimens)

The physico-chemical properties of the solid phases altered by leaching were analyzed by:

a; XRD (qualitative analysis of crystal components, X-Ray Diffraction) .
b; TG-DTA and DSC (quantitative and qualitative estimation of hydrates, Thermo-Gravimetry with Differential Thermal Analysis and Differential Scanning Calorimetry).
c; EPMA (element concentration mapping, Electron Probe Micro Analyzer).
d; SEM (observational shape analysis of hydrates and other compounds, Scanning Electron Microscope).
e; MIP (pore size distribution analysis, Mercury Intrusion Porosimetry).
f; 29Si-NMR (structural analysis of Si ion in Si-containing compounds, especially C-S-H phases, Nuclear Magnetic Resonance).

3 RESULTS AND DISCUSSION

3.1 *Release of organics and pH*

3.1.1 Fresh leaching tests

Figure 3.1-1 shows the amount of organic carbon elution (TOC) from fresh grout leachates. The elution of organic substances was identified for both XREF52 and XP308B, both of which are SP-free compositions. The sample XREF52 showed higher TOC than XP308B. As the amount of cement (UF16) in the cementitious material in dry weight ratio is 93.0 % for XREF52 and 59.2 % for XP308B (Table 2.1-2), the difference in the amount of TOC is considered to be dependent on the amount of cement. Based on the above result, TOC elution of solution leached with XP308B and XREF52 is understood to be caused by the grinding aid (CGA) contained in the cement.

Addition of SP increased the amount of TOC in both the normal and low-pH systems and the influence of SP on elution was clearly recognizable. TOC amounts eluted from the low-pH cement system were confirmed to be smaller compared with the normal pH system. In addition, when P308B (with Mighty 150 added) was immersed in the synthetic saline groundwater system (OL-SR), the amount of TOC elution was higher than in the cases where it was immersed in other leachates.

To interpret the influence of SP on TOC values, the initial content of TOC was calculated numerically for each grout material to estimate the amount of grout remaining after the immersion period. Table 3.1-1 shows the density and TOC for each raw material. TOC for each grout was calculated using the following equation (3-1)
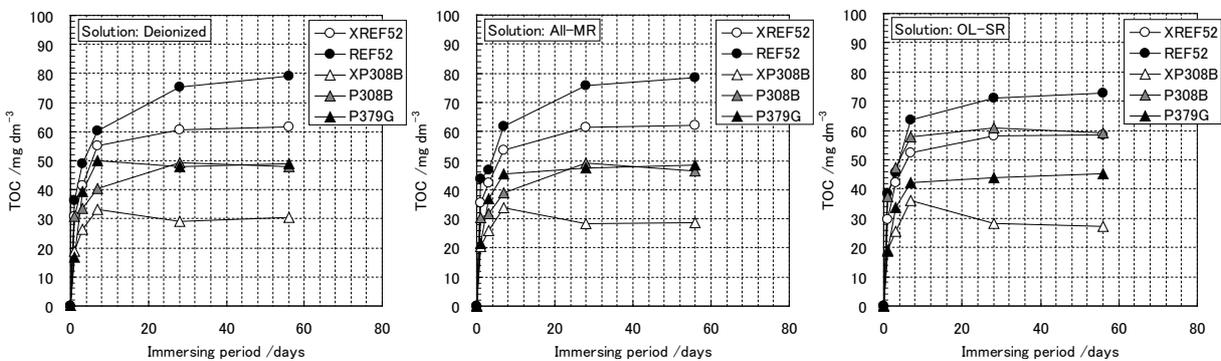

Figure 3.1-1: Change with time in TOC in the leachate (fresh leaching test).

$$TOC_{ini} = \frac{C \times TOC_C + S \times TOC_S + SP \times TOC_{SP}}{C + S + SP + W} \qquad (3\text{-}1)$$

Where TOC_{ini}: initial TOC of grout (weight %)
               TOC_C, TOC_S, TOC_{SP} : TOC of cement, Grout Aid, SP (weight %)
               C: mixing proportion of cement (weight %)
               S: mixing proportion of Grout Aid (weight %)
               SP: mixing proportion of superplasticizer (weight %)
               W: mixing proportion of water without water from Grout Aid (weight %)

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The TOC values for weight per unit volume were calculated by multiplying TOC (weight ratio) by the density of the grout. The calculated results are shown in Table 3.1-2. The TOC values for the low-pH system are higher than for the normal pH system, mainly because of the high TOC in Grout Aid. However, the amount of TOC released in the case of the low-pH system was lower than that for the normal pH system. Therefore, organic compounds were thought to be hard to elute, with most of them remaining in the hardened grout as shown in Figure 3.1-2.

**Table 3.1-1:   Density and TOC of raw materials.**

Material		Density /kg m^{-3}	TOC* /weight%
Cement	Ultrafine 16	3150	0.14
Silica	Grout Aid	1390	0.31
Superplasticizer	SP40	-	7.98
	Mighty 150	-	22.4
	Glenium 51	-	24.4

*TOC values were measured by TOC-SSM (Solid Sample Combustion Unit).

Table 3.1-2:   Calculated initial TOC for each grout paste.

	Density* /g dm^{-3}	Calculated TOC							
		Mass Unit /weight%				Volume Unit /g dm^{-3}			
		Total	Items			Total	Items		
			UF16	GA	SP		UF16	GA	SP
XREF52	1439	0.0801	0.0607	0.0195	0.0000	1.153	0.873	0.280	0.000
REF52	1439	0.1162	0.0607	0.0195	0.0361	1.672	0.873	0.280	0.519
XP308B	1358	0.1404	0.0355	0.1049	0.0000	1.907	0.483	1.424	0.000
P308B	1358	0.5471	0.0355	0.1049	0.4068	7.431	0.483	1.424	5.525
P379G	1404	0.3058	0.0388	0.1144	0.1526	4.293	0.544	1.606	2.143

*Density was calculated using the densities of component materials and mixing proportions.
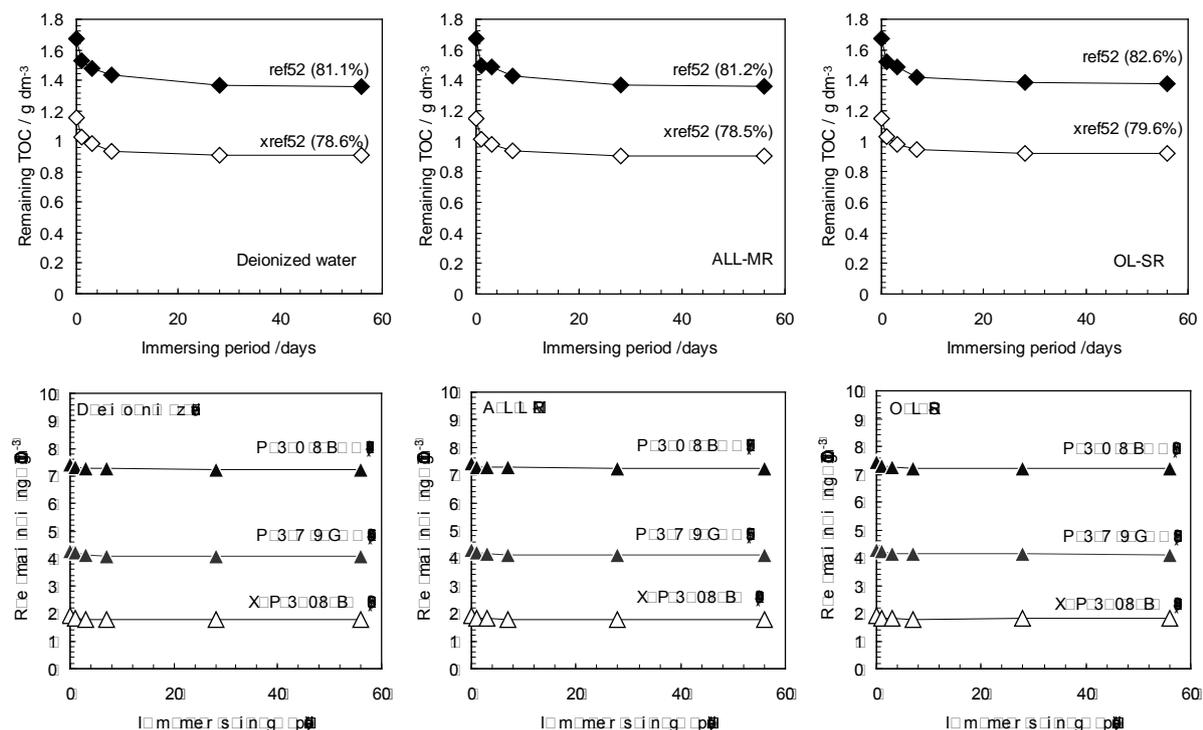
*The values adjacent to the specimen name indicate the TOC remaining at 56 days. It is noted that the range of the vertical axis in the low-pH system (bottom figures) is about 5 times greater than for the normal pH system (upper figures).

Figure 3.1-2:   Remaining TOC in hardened grouts for the immersion period.

Based on the TOC results, most of the eluted organic substances were attributed to the cement grinding aid. In order to examine the increase in the amount of TOC due to addition of SP, gel permeation chromatography (GPC) analyses were carried out on leachates at 56 days. Figure 3.1-3 shows examples of GPC analysis profiles and their interpretation. Figure 3.1-3-A shows the profile for Mighty 150 and Figure 3.1-3-B shows the result for leachate in the P308B fresh leaching test. The main component in Mighty 150 constituted by ten naphthalene skeletons corresponding to the peak at 19 – 23 minutes was detected as shown Figure 3.1-3-A; there was also an occurrence of raw material with naphthalene dimer corresponding to the 24 minute peak in the figure. On the other hand, there was no appearance of large molecular weight organics in the leachate as shown in Figure 3.1-3-B, but the occurrence of low molecular weight organics that would be derived from cement grinding aid (CGA) was detected in the figure. GPC analyses of fresh leaching test results are shown in Table 3.1-3. It was confirmed that cement grinding aid is present in all the solutions. While melamine was not found in REF52 (SP40) with added SP40, MS transmutation substances such as methylol amine or a homologue of methylol amine (H_2N-CH_2-OH), which is a homologue of its dimer, were recognized. A homologue of methylol amine is a constituent of melamine and was considered to represent decomposed melamine substances or melamine foreign substances. In P308B with added Mighty150, the NS dimer of naphthalene sulfonate acid (NS) was recognized using a KS type column in GPC. For P379G with added Glenium51, when leached in deionized water and the synthetic fresh groundwater system (ALL-MR), the methacrylic acid M-PEG monomer (MAA-M-PEG) was recognized and this is considered to be an unreacted monomer of Glenium 51. Similarly, it was understood that, when immersed in the saline groundwater system (OL-SR), the unreacted monomer MAA-M-PEG was also eluted.

When SP was added, in each case no high molecular weight polymers, which are the major ingredients of SP, were recognized. It was clear that the elution of organic components is limited to low molecular weight substances such as monomers and dimers.
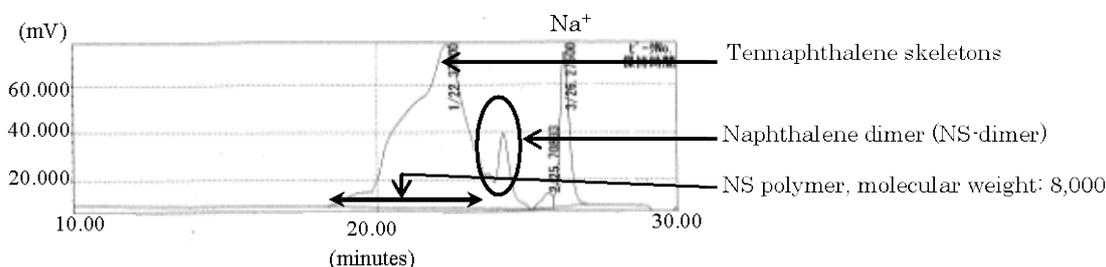
[A] GPC profile for Mighty 150 (using column KS)
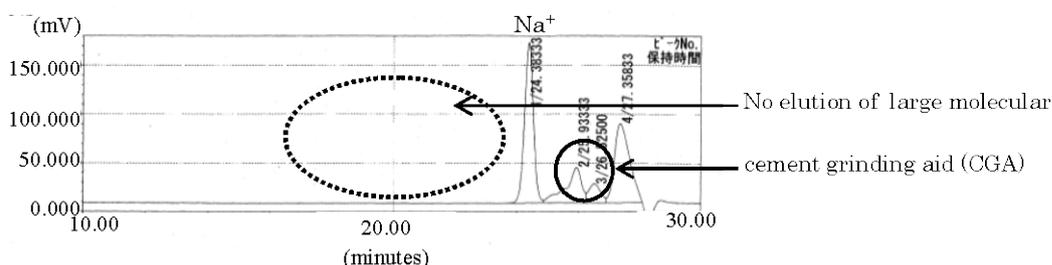
[B] GPC profile for P308B leachate in fresh leaching test (using column SB)

Figure 3.1-3:   Results of GPC analysis and interpretation.

Table 3.1-3:   Results of GPC analysis (fresh leaching test).

Leachant	Specimen	GPC column[1]	Detected organics[2]	Odor
Deionized water	XREF52	SB	CGA	Odorless
	REF52	SB	CGA, MS transmutation	Amic
	XP308B	SB	CGA	Odorless
	P308B	SB, KS	CGA, NS dimer	NS
	P379G	SB	CGA, M-PEG monomer	Odorless
ALL-MR (freshwater)	XREF52	SB	CGA	Odorless
	REF52	SB	CGA, MS transmutation	Amic
	XP308B	SB	CGA	Odorless
	P308B	SB, KS	CGA, NS dimer	NS
	P379G	SB	CGA, M-PEG monomer	Odorless
OL-SR (saline water)	XREF52	SB	CGA	Odorless
	REF52	SB	CGA, MS transmutation	Amic
	XP308B	SB	CGA	Odorless
	P308B	SB, KS	CGA, NS dimer	NS
	P379G	SB	CGA, M-PEG monomer	Odorless

[1] SB: Shodex OHpak SB804x2, KS: Shodex KS804x2
[2] CGA: Cement Grinding Aid

Figure 3.1-4 shows the pH changes in the leachate. When immersed in deionized water, in XREF52 and REF52 (SP40) (normal pH systems), pH will increase with the progression of the immersion period, suggesting elution of e.g. Ca^{2+}, Na^+, K^+ and OH^-. On the other hand, in XP308B, P308B and P379G (low-pH cement systems) independent of the type of SP, pH increased up to 7 days and decreased thereafter (Figure 3.1-5, Figure 3.1-6). It was considered that ions such as Ca^{2+}, Na^+, K^+ and OH^- in the liquid phase were released from hydrates up to

7 days but that, in accordance with the progression of the pozzolanic reaction, these ions were consumed and/or adsorbed on the produced C-S-H phase.
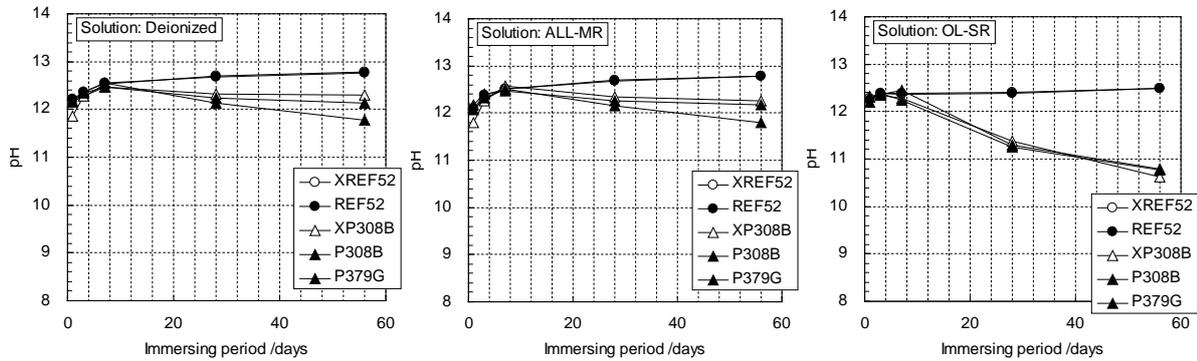

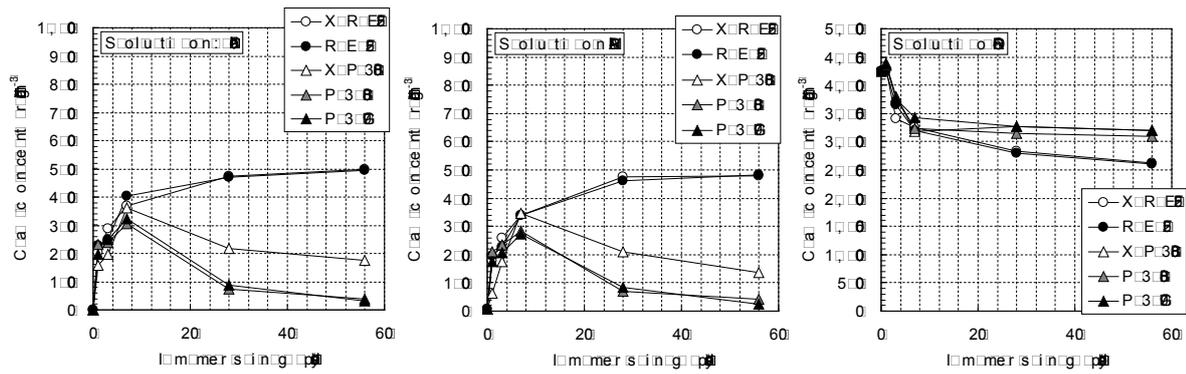**Figure 3.1-4:** Change with time of pH in leachates (fresh leaching test) .

Figure 3.1-5: Change with time of Ca concentration in leachates (fresh leaching test).
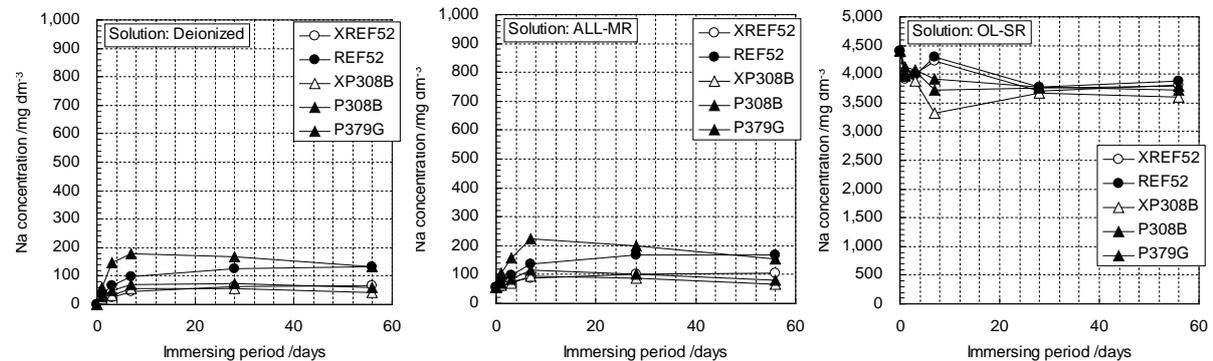

Figure 3.1-6: Change with time of Na concentration in leachates (fresh leaching test).

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3.1.2   Powder leaching tests

Figure 3.1-7 shows the amount of total organic carbon elution (TOC) in powder leaching tests. TOC was eluted from both XREF52 and XP308B (no SP added). For all solutions (with a leachate to powder ratio of 10), TOC after 38 weeks in XREF52 was around 30 mg/dm^3, indicating TOC around 1.5 times higher than that of XP308B. As the amounts of cement in XREF52 and XP308B are equivalent to 93.0 % and 59.2 % of dry weight ratio respectively, the amounts of TOC are considered to be dependent on the amount of cement. Accordingly, TOC elution of XP308B and XREF52 is understood to be caused by the grinding aid contained in the cement. SP addition caused an increase in TOC, suggesting elution of SP ingredients. When P308B (Mighty150 added) was immersed in any leachant, the amount of TOC elution was larger than that of P379G (Glenium 51 added). The difference can be explained by the different dosage of each SP. PC-based SPs, i.e. Glenium 51, have the advantage of a high water-reducing effect with low dosage compared to PNS-based SPs, i.e. Mighty150.
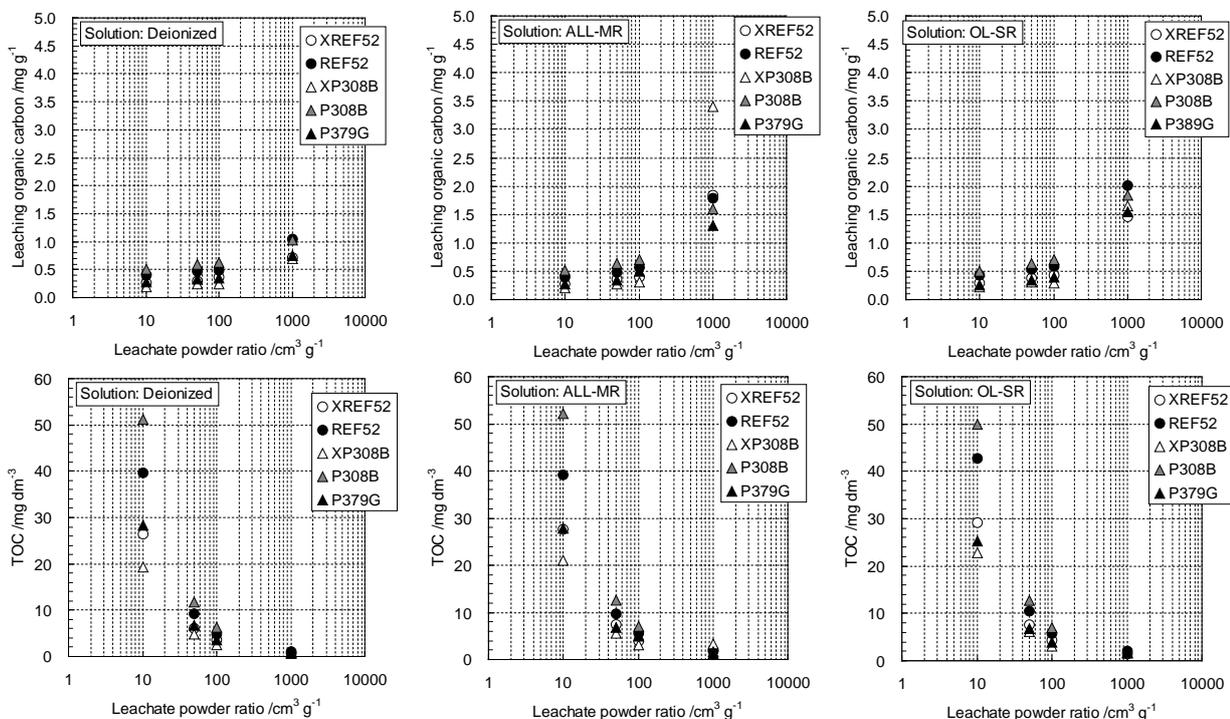
*Upper figures: in unit volume of leachate, lower figures: in unit mass of immersed powder

Figure 3.1-7:   TOC concentrations in leachate (powder leaching test).

Table 3.1-4 to Table 3.1-6 show identification results for eluted organic substances analyzed by GPC. Similarly to the results for fresh grout leaching tests, cement grinding aid (CGA) was eluted from the hardened hydrated phase and low molecular weight organic substances contained in SP together with CGA were eluted from the hardened hydrated phase with addition of SP. With a high liquid to solid ratio, the eluted TOC concentration was very small and it was hard to obtain sufficient TOC for detection by GPC despite concentrating the amount obtained.

Table 3.1-4: **Results for GPC analysis (powder in deionized water).**

Specimen	L/S ratio	Detected Organics	Odor
XREF52	10	CGA	Odorless
	50	CGA	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
REF52	10	CGA, MS transmutation	Amic
	50	CGA, MS transmutation	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
XP308B	10	CGA	Odorless
	50	CGA	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
P308B	10	CGA, NS dimer	Faint
	50	CGA, NS dimer	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
P379G	10	CGA, M-PEG monomer	Odorless
	50	CGA	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless

Table 3.1-5: **Results for GPC analysis (powder in ALL-MR).**

Specimen	L/S ratio	Detected Organics	Odor
XREF52	10	CGA	Odorless
	50	CGA	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
REF52	10	CGA, MS transmutation	Amic
	50	CGA, MS transmutation	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
XP308B	10	CGA	Odorless
	50	CGA	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
P308B	10	CGA, NS dimer	Faint
	50	CGA, NS dimer	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
P379G	10	CGA, M-PEG monomer	Odorless
	50	CGA, M-PEG monomer	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless

Table 3.1-6:   Results for GPC analysis (powder in OL-SR).

Specimen	L/S ratio	Detected Organics	Odor
XREF52	10	CGA	Odorless
	50	CGA	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
REF52	10	CGA, MS transmutation	Odorless
	50	CGA, MS transmutation	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
XP308B	10	CGA	Odorless
	50	CGA	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
P308B	10	CGA, NS dimer	Odorless
	50	CGA, NS dimer	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless
P379G	10	CGA, M-PEG monomer	Odorless
	50	CGA	Odorless
	100	CGA	Odorless
	1000	CGA	Odorless

Figure 3.1-8 shows pH changes during powder leaching tests. For all leachate/solid weight ratios, the resulting pH was always lowest in the saline water system and there was not much difference between the deionized and ALL-MR waters. In the case of the normal pH grouts (XREF52 and REF52(SP40)) immersed in deionized water, in the range 10 $cm^3 \cdot g^{-1}$ to 100 $cm^3 \cdot g^{-1}$ for the liquid-solid ratio, the decrease in pH along with the increase in liquid-solid ratio was relatively small, with around 12.7 in both cases. However, when the liquid-solid ratio increased from 100 $cm^3 \cdot g^{-1}$ to 1000 $cm^3 \cdot g^{-1}$, the pH decreased by about 1.0. It was considered that, with a liquid-solid ratio of 1000 $cm^3 \cdot g^{-1}$, all the CH (portlandite) that acts as a pH buffer dissolves with dilution of the solution and pH becomes lower. On the other hand, in the low-pH cement systems (XP308B, P308B, and P379G), the pH was around 10.9 for all liquid-solid ratios. This difference can be explained by the different hydrates in each type of cementitious material. The low-pH cement system containing no CH does not have a pH buffering effect such as REF52 and there is only leaching degradation of the C-S-H phase. However, in such a case, C-S-H with a low Ca/Si ratio in the low-pH cement systems may have a strong absorption effect on Na^+ and K^+. Also, when immersed in the freshwater system (ALL-MR), the same level of pH was indicated in both the case of the low-pH and the normal pH cement systems. However, when immersed in the saline water system (OL-SR), the pH of the leachate of all grout types was lower compared to immersion in deionized water and the freshwater system (ALL-MR). Due to an excess of electrolytic ingredients, the OH^- concentration leached from the hardened hydrated cement was relatively lower.
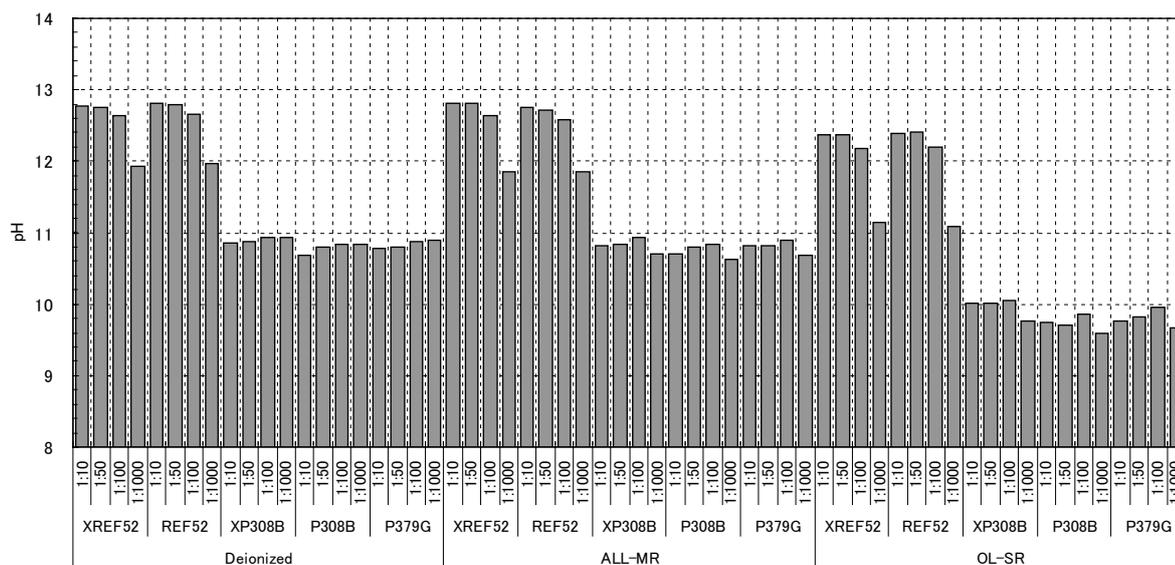
*pH was measured after 38 weeks of immersion and monitored in a glove box.

Figure 3.1-8   Difference in pH for different leachate/solid weight ratios and leachate types (powder leaching test) REF52 (SP40).

3.2   Leaching alteration of the solid phase

3.2.1   Change in Ca/Si ratio in block leaching tests

EPMA analysis was carried out for the normal pH cement system (REF52 (SP40)) and the low-pH cement system (P308B) immersed in all leachant solutions for 52 weeks. Figure 3.2-1 shows the distribution of the Ca/Si molar ratio for a polished surface created by cutting across the center of altered block specimens immersed in all leachant solutions for 52 weeks. For the normal pH cement system (REF52(SP40)) immersed in deionized water, the Ca/Si ratio decreased from 1.9 to 1.0 within 6.0 mm of the contacting water surface. When the Ca/Si ratio decreases to around 1.5 to 1.6, this would suggest the disappearance of calcium hydroxide (CH). When the Ca/Si ratio near the contacting water surface was around 0.8 to 1.5, leaching alteration of C-S-H had also occurred following the disappearance of CH. On the other hand, when the low-pH cement (P308B) was immersed in deionized water, it was verified that the Ca/Si ratio decreased in a range around 1.5 mm from the surface and leaching alteration of C-S-H occurred near the contacting water surface. In the normal pH cement system immersed in the freshwater system (ALL-MR), no lowering of the Ca/Si ratio was observed. The results of the liquid phase analysis also showed almost no release of Ca^{2+} (Figure 3.2-2). In the low-pH cement system immersed in ALL-MR, the Ca/Si ratio was lowered around 0.5 mm from the contacting water surface. When immersed in ALL-MR, the inhibiting effect on the progression of the leaching alteration front was remarkable for the normal pH cement system. The reason was assumed to be a rapid release of Ca^{2+} due to disappearance of CH, resulting in the production of calcite as a secondary mineral on the contacting water surface when encountering HCO_3^-. In the normal pH cement system immersed in the saline water system (OL-SR), it was noted that the Ca/Si ratio was lowered to 1.2 to 1.3 over the entire cross-section and leaching of calcium hydroxide reached the central part of the specimen. On the other hand, in the low-pH cement system immersed in OL-SR, the Ca/Si ratio was lowered to

around 0.5 only at the surface and the decrease is believed to be due to the leaching alteration of C-S-H releasing much more Ca^{2+} than Si.
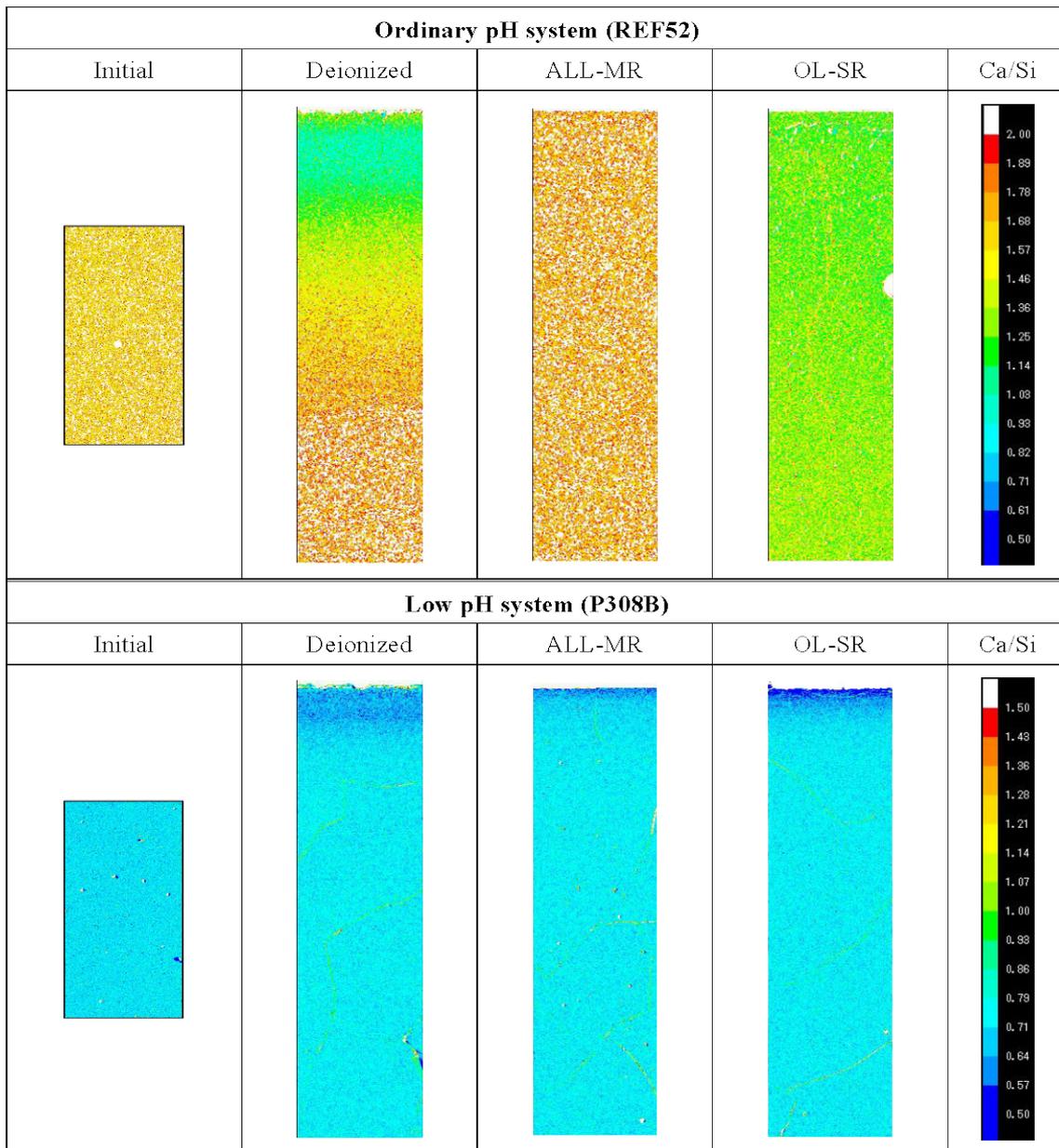
*analyzed area: 2.5 x 10 mm for immersed specimens and 2.5 x 5 mm for initial specimens
*upper row: contacting surface, lower row: inside block specimen

Figure 3.2-1:   Distribution of Ca/Si molar ratio in REF52(SP40) and P308B block specimens.

3.2.2   Amount of Ca²⁺ leached in block leaching tests

Figure 3.2-2 shows the amount of Ca^{2+} accumulated in leachates measured at the time of solution replacement. When immersed in deionized water, low-pH systems showed a small amount of leached Ca^{2+} while the normal pH system showed a trend for increasing leaching of Ca^{2+}. On the other hand, when immersed in the freshwater system (ALL-MR), for the normal pH cement system Ca^{2+} leaching was not observed; this is different from the test results in the

other leachants. When immersed in the saline water system (OL-SR), there was significant leaching of Ca^{2+}, with no notable difference being observed between the normal and low-pH cement systems.
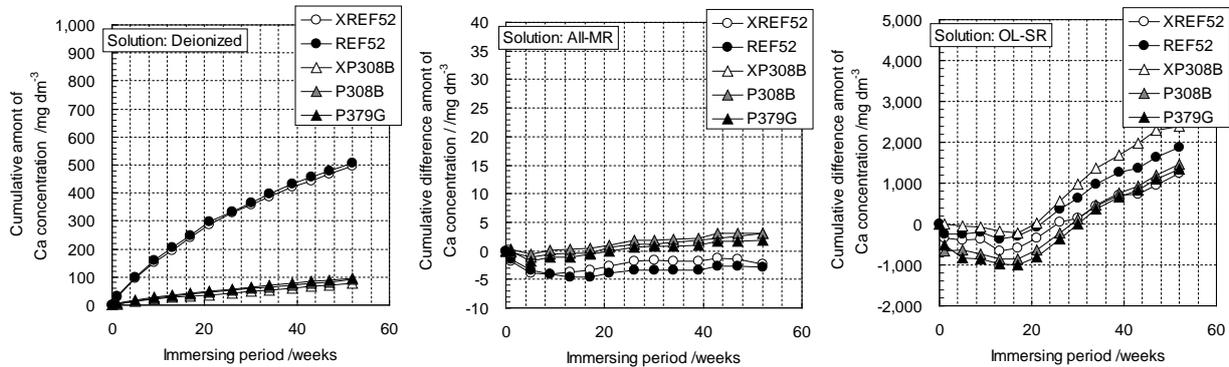
*The scale of the y-axis is in a suitable range for each immersion system

Figure 3.2-2: Change in Ca^{2+} concentration in leachant with time (block leaching test).

3.2.3 Amount of Ca^{2+} and Si leached in thin-plate leaching tests

Figure 3.2-3 shows the cumulative amount of Ca^{2+} in the leachate for each time of solution replacement. When the normal pH cement system was immersed in deionized water and the freshwater system (ALL-MR), the amount of leached Ca^{2+} increased at the time of initial solution replacement (6th week); after this the leaching rate stabilized. On the other hand, when the low-pH cement system was immersed in deionized water and ALL-MR, almost no leaching of Ca^{2+} was observed. It was assumed that secondary minerals such as calcite were formed. When immersed in the saline water system (OL-SR), there was the same tendency as in the block leaching test, i.e. leaching of a significant amount of Ca^{2+} without any clear difference between the normal and low-pH cement systems.

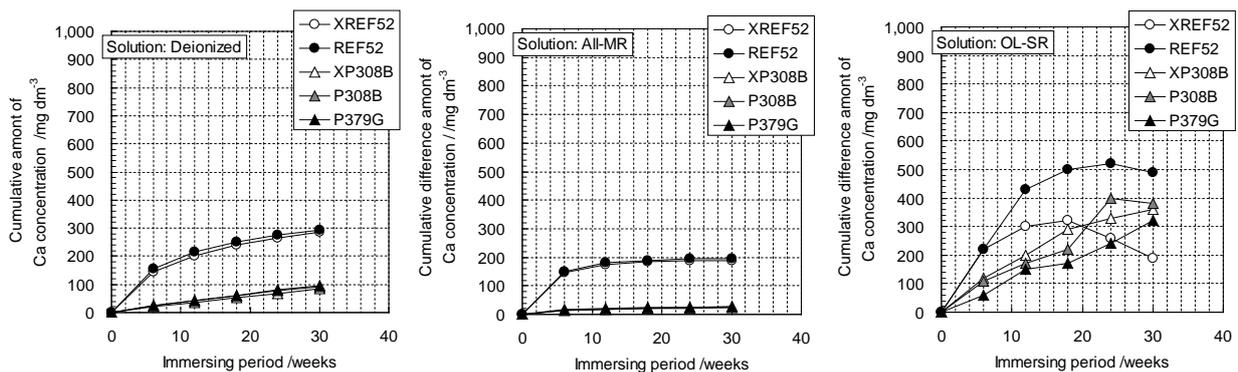**Figure 3.2-3:** Change in Ca^{2+} concentration in leachant with time (thin-plate leaching test).

Figure 3.2-4 shows the cumulative amount of Si in the leachate for each time of solution replacement. When the normal pH cement system was immersed in deionized water and the freshwater system (ALL-MR), the amount of leached Si increased continuously and it was verified that leaching alteration of C-S-H occurred at the first solution replacement time (6th week). Also, when the low-pH cement system was immersed in the leachates of these systems,

fairly high leaching of Si was observed at the time of initial solution replacement (6th week) and the amount of leaching increased for all immersion periods compared with the case of immersion of the normal pH cement system. This suggests that the leaching alteration of C-S-H is larger in the low-pH cement system under the same test conditions compared with the normal pH cement system. On the other hand, when any cement system was immersed in the saline water system (OL-SR), the amount of leached Si was less than for the cases of the other two types of immersing solutions. It was considered that secondary minerals such as smectite were being produced.
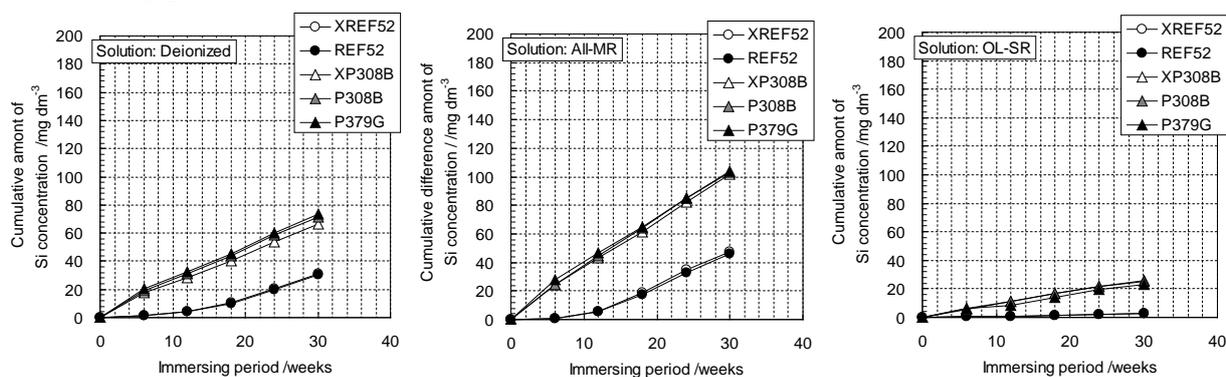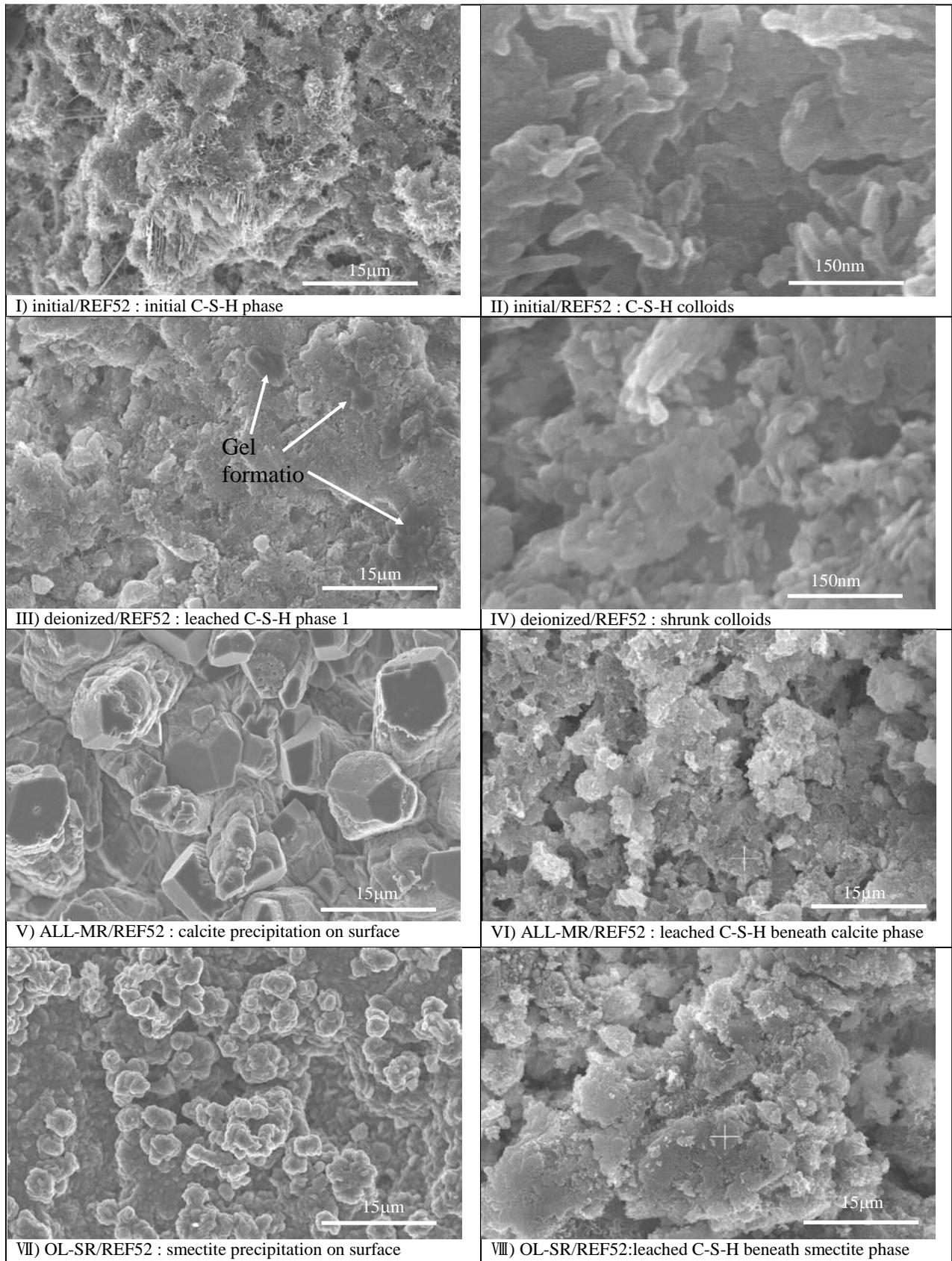

Figure 3.2-4: Change in Si concentration in leachant with time (thin-plate leaching test).

3.2.4 SEM observations of specimens in thin-plate leaching tests
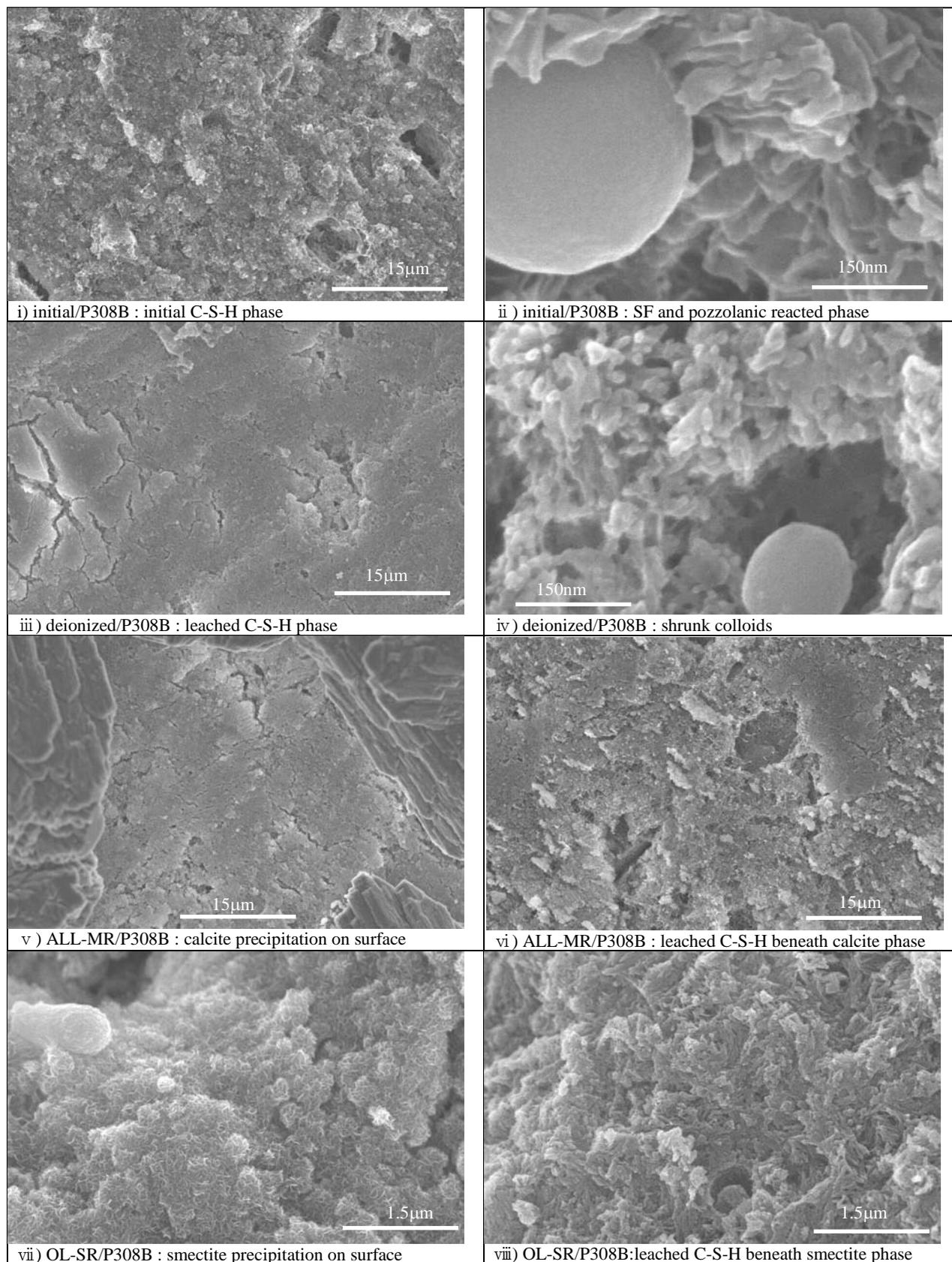
The initial states of hydration were observed on fractured sections of the specimens and the leaching alteration was observed on the surface of each thin-plate specimen. The initial states of hydration for REF52 (SP40) are shown in Figure 3.2-5-I and Figure 3.2-5-II. For the initial state of C-S-H colloids, there are numerous pores with sizes from several tens of nm to 10 µm. Almost the same trend was observed for the initial state of P308B (Figure 3.2-6-i and Figure 3.2-6-ii), but the small pores of the C-S-H colloids were observed to be much more compacted. In the case of immersion in deionized water, based on the leaching alteration at the surface, the volume of C-S-H colloids in REF52(SP40) was reduced slightly (Figure 3.2-5-IV), resulting in very rugged surface conditions and also some formation of gel products (Figure 3.2-5-III). The main components of the gel products were determined to be Ca and Si using EDX elemental analysis. On the other hand, in the deionized water P308B maintained fairly smooth surface conditions with generation of pores around 10 µm in diameter (Figure 3.2-6-iii); shrinkage of C-S-H colloids was also observed (Figure 3.2-6-iv).

In ALL-MR, significantly more polyhedral shaped crystals of calcite precipitated on the surface of REF52 (SP40) (Figure 3.2-5-V) compared to P308B (Figure 3.2-6-v). The reason was assumed to be the difference in the leaching ratio of Ca^{2+}; much more Ca^{2+} had leached from the surface of REF52 (SP40) that contains a lot of CH. In contact with HCO^{3-} in the leachant, this then leads to calcite precipitation on the surface of specimen. However, despite significant precipitation of calcite, the C-S-H phase just below the calcite layer was altered, with generation of numerous pores with diameters of several tens of nm to 10 µm (Figure 3.2-5-VI, Figure 3.2-6-vi). In OL-SR, many round crystals with small plates were precipitated on the surface of both types of specimen (Figure 3.2-5-VII, Figure 3.2-6-vii). The crystals were identified as a kind of smectite, because of the indication from EDX elemental analysis that the main components were Mg and Si with small amounts of Cl and Ca. The XRD results

discussed below also support this interpretation. However, despite its coating effect on the surface of the specimen, the C-S-H phase beneath the smectite layer had been altered with generation of different pore sizes, resulting in a very irregular C-S-H phase (Figure 3.2-5-VIII, Figure 3.2-6-viii).

I) initial/REF52 : initial C-S-H phase

II) initial/REF52 : C-S-H colloids

III) deionized/REF52 : leached C-S-H phase 1

Gel formatio

IV) deionized/REF52 : shrunk colloids

V) ALL-MR/REF52 : calcite precipitation on surface

VI) ALL-MR/REF52 : leached C-S-H beneath calcite phase

VII) OL-SR/REF52 : smectite precipitation on surface

VIII) OL-SR/REF52:leached C-S-H beneath smectite phase

Figure 3.2-5:   Morphogenic change in hydrates and pores (REF52 (SP40)).

i) initial/P308B : initial C-S-H phase

ⅱ) initial/P308B : SF and pozzolanic reacted phase

ⅲ) deionized/P308B : leached C-S-H phase

ⅳ) deionized/P308B : shrunk colloids

ⅴ) ALL-MR/P308B : calcite precipitation on surface

ⅵ) ALL-MR/P308B : leached C-S-H beneath calcite phase

ⅶ) OL-SR/P308B : smectite precipitation on surface

ⅷ) OL-SR/P308B:leached C-S-H beneath smectite phase

Figure 3.2-6:   Morphogenic changein hydrates and pores (P308B).

3.2.5 Change in hydrate composition in thin-plate leaching tests (XRD analysis)

In deionized water, loss of CH (portlandite) and ettringite was observed for the altered specimens of the normal pH cement system (XREF52 and REF52 (SP40)) (Figure 3.2-7). Ettringite also disappeared in the low-pH cement system (P308B, P308B and P379G). Disappearance of hydrates was also observed (Figure 3.2-8). In addition, broad peaks appeared in all cement systems at around $2\theta=40^o$ and 43° (Figure 3.2-7, Figure 3.2-8). These peaks may indicate generation of amorphous substances as a result of alteration of C-S-H as shown in Figure 3.2-5-III. There was no evidence suggesting peaks of talc and/or hydrotalcite.
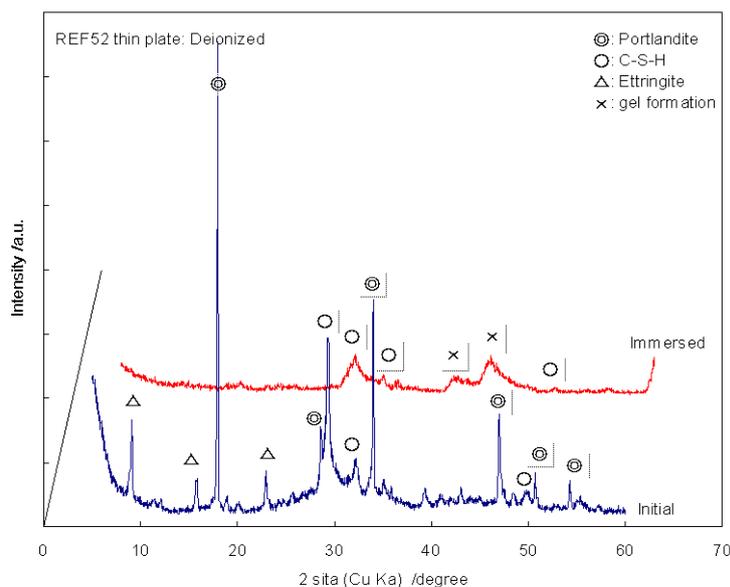
Figure 3.2-7: **Hydrate composition in REF52 thin-plate specimens in deionized water.**
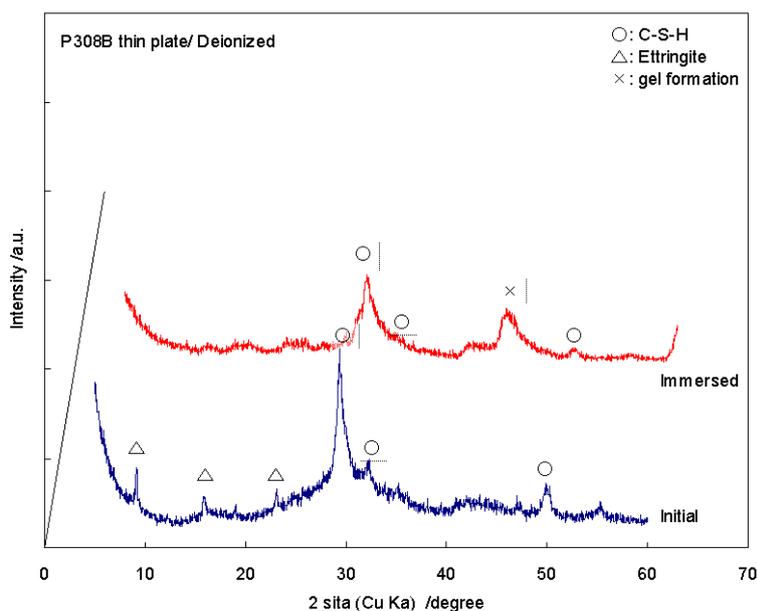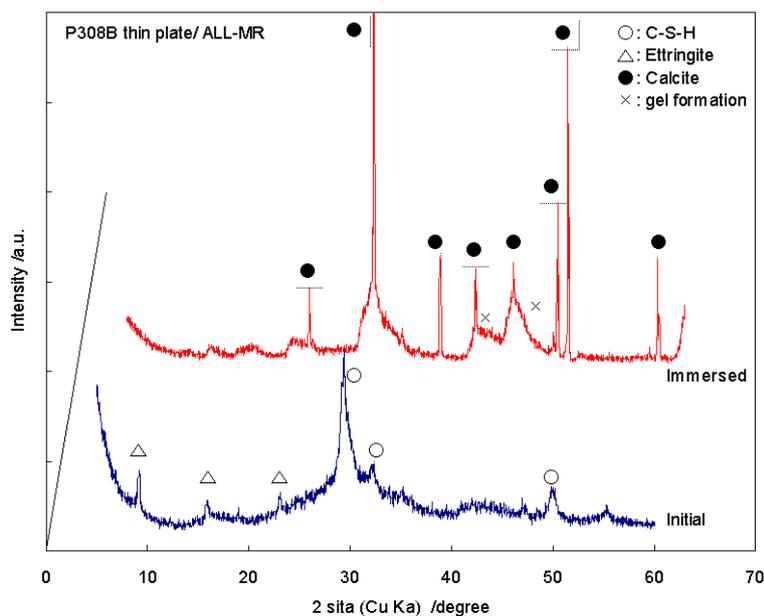

Figure 3.2-8: **Hydrate composition in P308B thin-plate specimens in deionized water.**

In leaching altered specimens of the normal pH cement system (XREF52 and REF52 (SP40)) in freshwater (ALL-MR), ettringite and CH disappeared and calcite was produced (Figure 3.2-9). Also, for the specimens of the low-pH cement system (XP308B, P308B, and P379G), it was verified that ettringite was lost and calcite was produced (Figure 3.2-10). In addition, in all the cement systems, as was the case when immersed in deionized water, broad peaks indicating amorphous substances were generated in the range $2\theta = 40°$ to 50°.
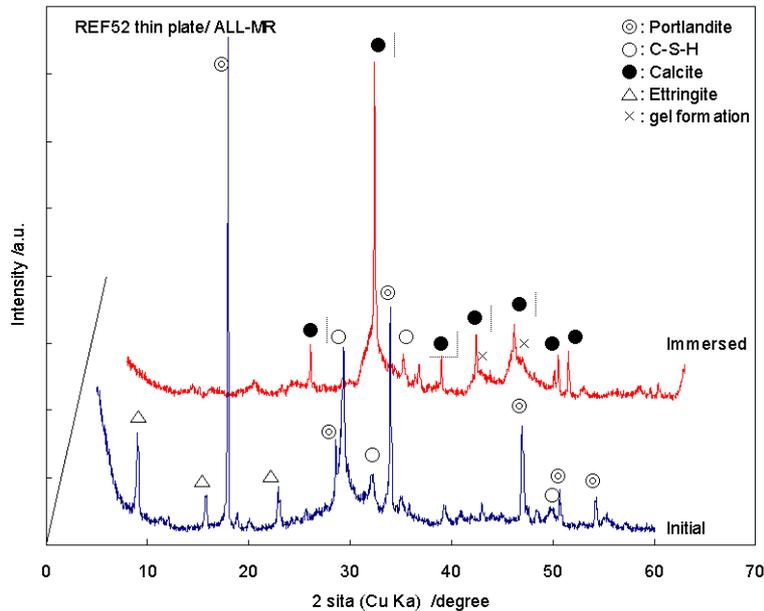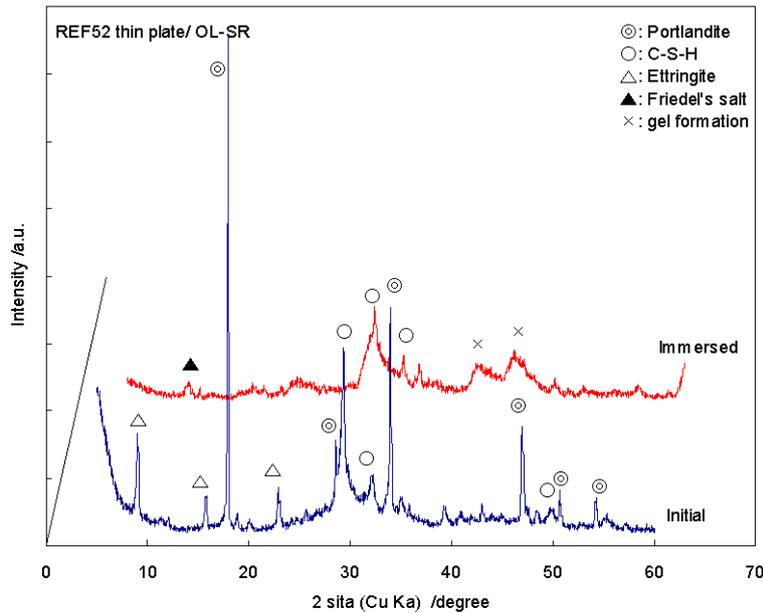

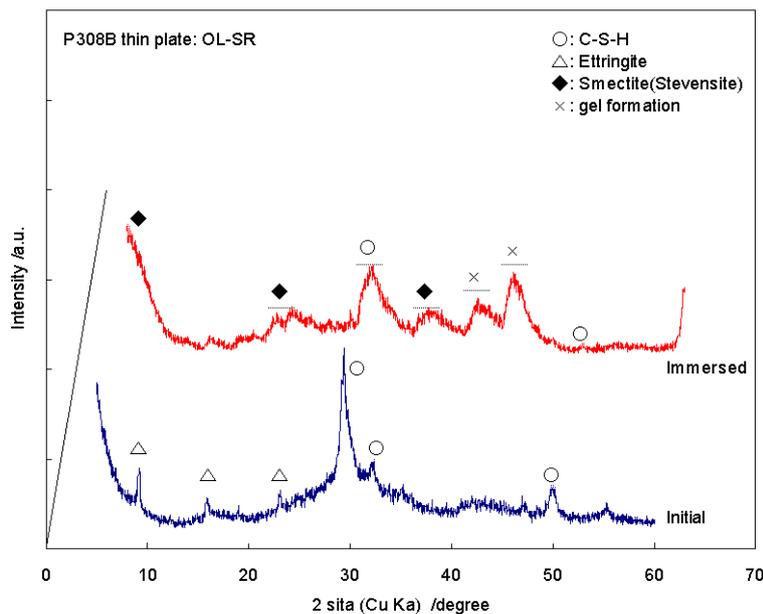**Figure 3.2-9:** **Hydrate composition in REF52 thin-plate specimens in ALL-MR.**

Figure 3.2-10: **Hydrate composition in P308B thin-plate specimens in ALL-MR.**

In the leaching altered specimens of the normal pH cement system in saline water (OL-SR), it was verified that calcium hydroxide (portlandite) and ettringite were lost, while Friedel salt ($Ca_2Al(OH)_6Cl_2H_2O$) was produced (Figure 3.2-11). In the leaching altered specimens of the low-pH cement system (XP308B, P308B and P379G), ettringite disappeared and a type of smectite such as stevensite was produced (Figure 3.2-12). In addition, in all the cement systems, broad peaks indicating amorphous substances were generated in the range $2\theta = 40°$ to 50°.

Figure 3.2-11:   Hydrate composition in REF52 thin-plate specimens in OL-SR.

Figure 3.2-12:   Hydrate composition in P308B thin-plate specimens in deionized water.
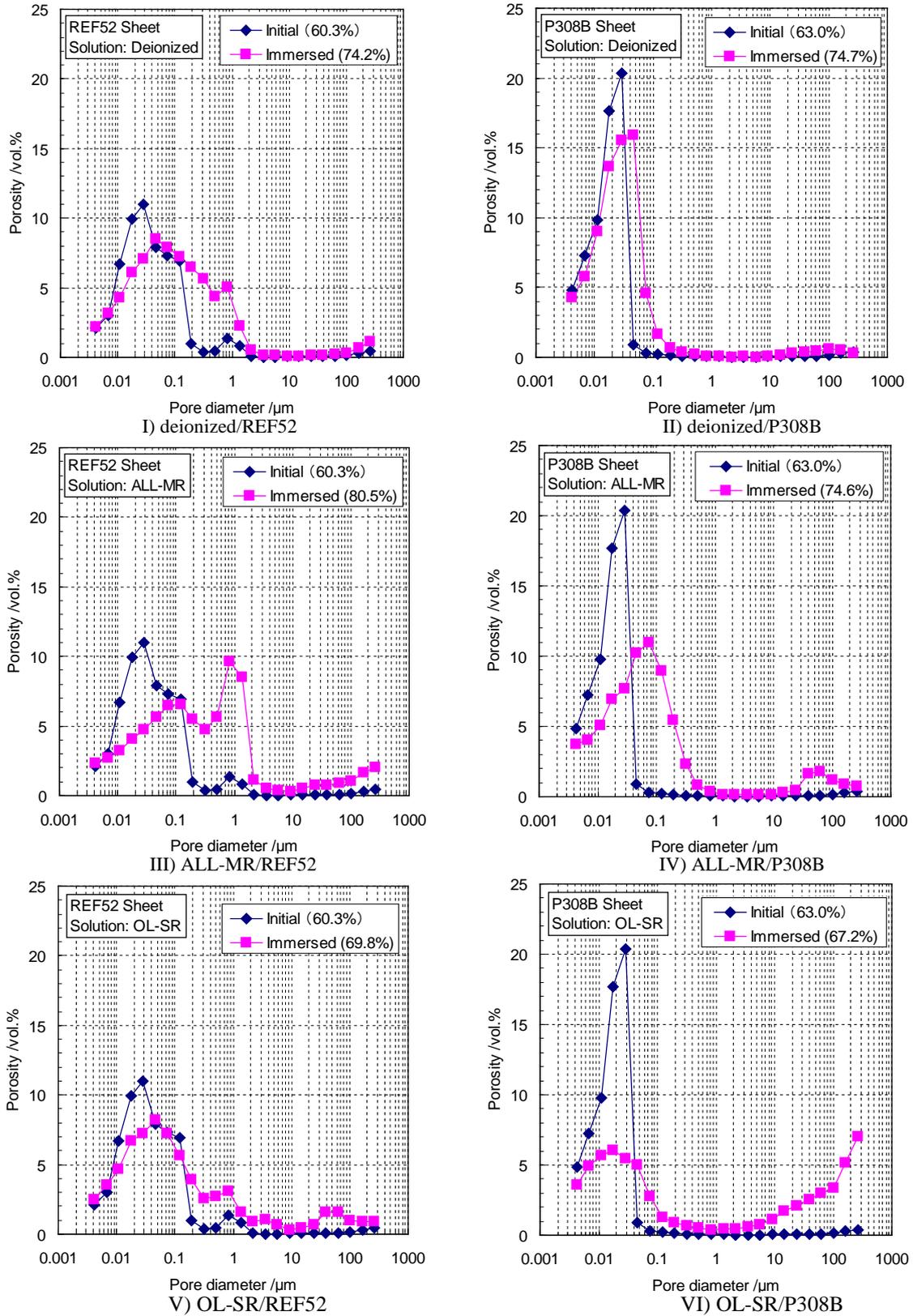
23

Figure 3.2-13: Change in pore size distribution (thin-plate leaching test).

Ettringite that was initially contained in all specimens disappeared during leaching tests irrespective of the type of solution, as shown in Figure 3.2-7 to Figure 3.2-12. From these results, it was concluded that all parts of every specimen were altered. When the normal pH cement system (XREF52 and REF52 (SP40)) was immersed in deionized water, a decrease in porosity for a pore diameter range of 0.01 to 0.04 µm and an increase in porosity for a pore diameter range of 0.1 to 2 µm were observed (Figure 3.2-13-I). In the low-pH cement system (XP308B, P308B and P379G), a decrease in porosity for a pore diameter range of 0.003 to 0.03 µm and an increase in porosity for a pore diameter range of 0.04 to 0.5 µm were observed (Figure 3.2-13-II). Porosity changes in the low-pH cement system in the pore size range of 0.03 µm or less were considered to be equivalent to voids among C-S-H colloids. The pore size of C-S-H colloids was confirmed by SEM images. The observed tendency for increasing porosity in the range 0.04 to 0.5 µm and the porosity decrease in the range 0.003 to 0.03 µm were attributed to expansion of the fine pores among C-S-H colloids due to shrinkage and/or a decrease in the number of C-S-H colloids along with leaching alteration. The increase in porosity of the normal pH cement system was larger than for the low-pH cement system and the increase in porosity around a pore diameter of 1µm was attributed to leaching of calcium hydroxide. When ALL-MR and OL-SR were used as leachants, the porosity for a pore diameter of greater than 10 µm increased much more than for the case of deionized water (Figure 3.2-13-III, -IV, -V and -VI). In addition, a notable decrease in porosity with a pore diameter of 0.03 µm or less and an increase in porosity for a pore diameter of 0.03 to 1 µm was observed in case of low-pH cement. Leaching alteration of the C-S-H phase for the thin-plate samples was more extensive in the case of ALL-MR and OL-SR than in the case of deionized water.

3.2.6   Alteration of C-S-H in powder leaching tests

Figure 3.2-14 and Figure 3.2-15 show the amount of leached Ca^{2+} and Si converted into unit mass of initial powder specimen, respectively. When the normal pH cement systems were immersed in deionized water and freshwater (ALL-MR), leaching of Ca^{2+} was clearly observed and the amount of leached Ca^{2+} increased with increasing liquid-solid ratio. For the $1000 \text{ cm}^3 \cdot \text{g}^{-1}$ case, Si leached only slightly due to alteration of C-S-H. On the other hand, when the low-pH cement systems were immersed in deionized and freshwater, in the range up to $100 \text{ cm}^3 \cdot \text{g}^{-1}$ for the liquid-solid ratio, the leached amount of Ca^{2+} was small. For the 1000 $\text{cm}^3 \cdot \text{g}^{-1}$ case, however, there was an indication of an excess amount of leached Ca^{2+} that had not precipitated as calcite. As in the case of thin-plate immersion, the low-pH cement systems showed much more leaching of Si than the normal pH system. When immersed in saline water (OL-SR), leaching of Ca^{2+} was clearly observed, but Si did not leach significantly as in other immersion cases. Particularly in the low-pH cement system, it was understood that C-S-H had altered into secondary minerals, e.g. smectite, as determined by XRD analysis, by exchanging Ca^{2+} and Mg^+ of the ionic layer in C-S-H.

Figure 3.2-16 shows ^{29}Si-NMR spectra of the initial and altered states of powder specimens (REF52(SP40) and P308B) for the case of a liquid-solid ratio of $1000 \text{cm}^3 \cdot \text{g}^{-1}$. The value on the horizontal axis in the figure indicates a chemical shift of the peak and the magnetic field increases towards the origin of the horizontal axis. In the initial state of the normal pH cement system, it was verified that the hydration of cement grains had progressed continuously. In the case containing unhydrated cement grains, the Q0 peak indicating the monomer state of the Si tetrahedron would be larger. The Q1 peak indicates one end of the dimer where another Si

tetrahedron bonded in one direction only; the Q2 peak indicates the center of the trimer where another Si tetrahedron bonded in 2 directions. As Q1 and Q2 show the end and mid-section of a chain respectively, the Si tetrahedron comprising C-S-H in the initial specimen of the normal pH cement system was verified as having a chain structure. In the normal pH cement systems, the Q2/Q1 ratio of the initial specimen was low, but in the leaching altered specimens immersed in any type of solution, the Q2/Q1 ratio increased as an indication of an expansion in the chain structure of the Si tetrahedron (connection made by leaching Ca^{2+} from the C-S-H phase, resulting in a low Ca/Si ratio of C-S-H). In all leaching altered specimens, the Q1 and Q2 peaks shifted to the right side of the horizontal axis (low magnetic field side), suggesting that Al was taken up in the altered C-S-H. In the initial specimens of the low pH cement system, the Q2/Q1 ratio is larger than the normal pH cement system and a weak Q3 peak is generated. This was understood to be due to the low Ca/Si ratio of the C-S-H structure. In the case of immersing low-pH cement in deionized water and freshwater (ALL-MR), the Q2/Q1 ratio and the peak positions were almost the same. This could be explained as almost no change having occurred in the chain structure of the Si tetrahedron comprising C-S-H during the leaching alteration of C-S-H. It was understood that Ca^{2+} and Si leached simultaneously, but the rather high rate of Ca^{2+} leaching from the C-S-H colloids of the low-pH cement system and the alteration of C-S-H would result in a decrease of C-S-H colloid volume with enlarging pore space among C-S-H colloids (Figure 3.2-13). When the low-pH cement system was immersed in saline water (OL-SR), it was concluded from the fact that the Q3 peak, which indicates the status of three-directional bonding of the Si tetrahedron with other Si, had generated.that alteration of C-S-H into smectite as shown in the results of XRD analysis had occurred.
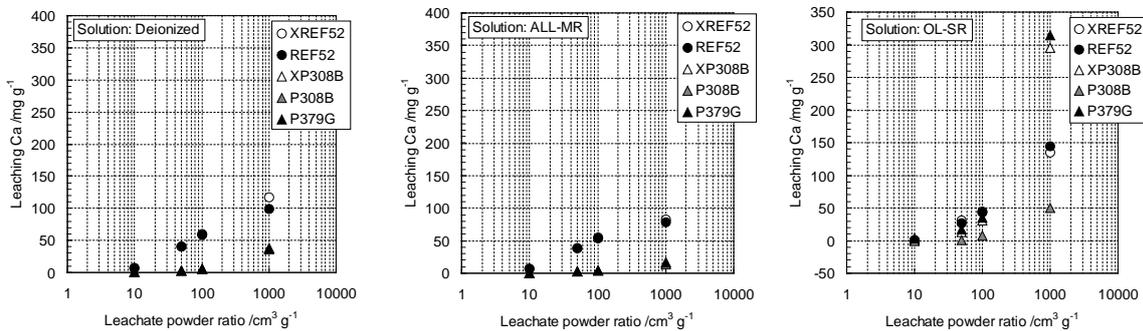

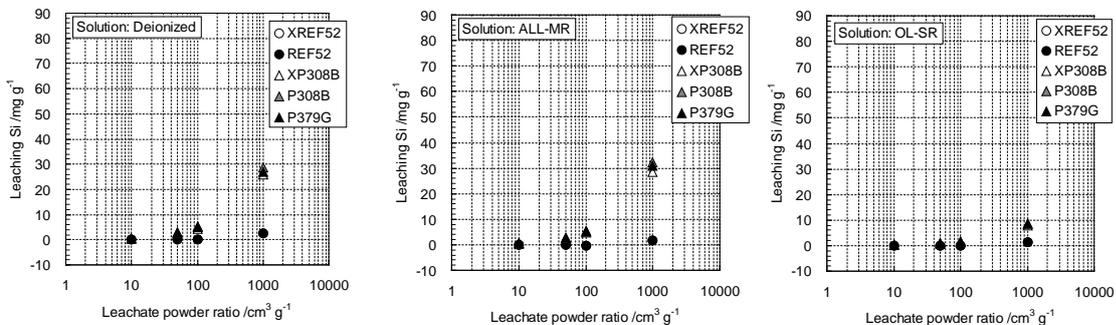Figure 3.2-14 : Ca^{2+} concentration for different leachate/solid mass ratios (powder leaching test).

Figure 3.2-15:   Si concentration for different leachate/solid mass ratios (powder leaching test).
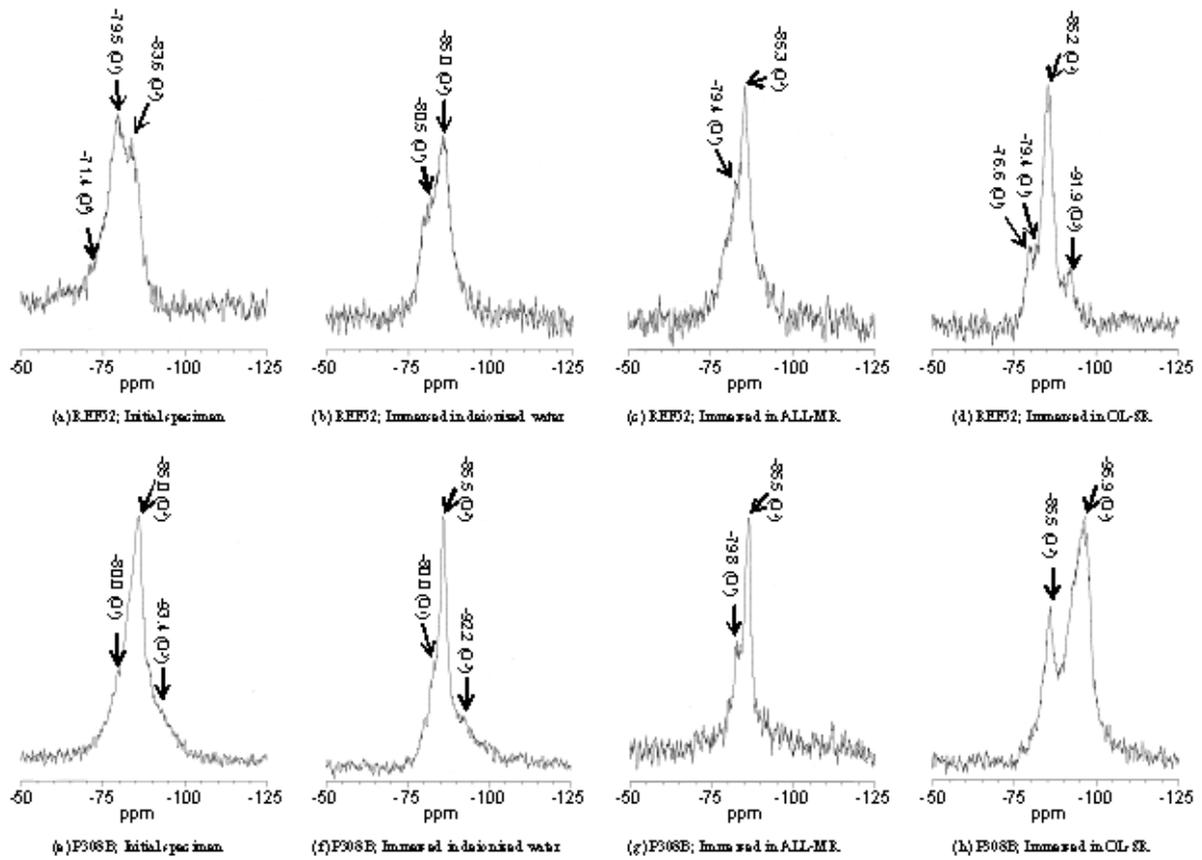
26

Figure 3.2-16: Comparison of ^{29}Si-NMR signals for REF52 (SP40) and P308B (powder leaching test).

4 ORGANIC COMPONENTS IN GROUNDWATER FROM ONKALO BOREHOLES

The following analyses were additionally conducted for three groundwater samples taken from the boreholes ONK-PVA1, ONK-KR4 and ONK-KR3 and supplied by POSIVA Oy. These liquid samples contain organics that leached in a low-pH cement grouting experiment. Organic components were analyzed using the methods listed below:

- TOC: after visual observation to check for floating material, a TOC analysis was carried out after filtration.
- GPC: samples were analyzed after vacuum concentration and filtration.
- Infrared spectroscopy (IR) and ^{1}H/^{13}C-NMR: analyses were carried out after vacuum concentration.

4.1 Results of TOC analysis

The TOC in each sample is shown in Table 4.1-1. KR4 showed a lower TOC content than PVA1 and KR3.

Table 4.1-1: TOC in ONKALO groundwater samples.

Sample	TOC (mg/L)
ONK-PVA1	14.4
ONK-KR3	14.4
ONK-KR4	10.8

4.2 Results of GPC analysis

 The GPC results are shown in Figure 4.2-1. No polymers indicating the main components of SP were present and only low molecular weight substances were detected. The main SP components would show a large peak around 20 minutes (Figure 3.1-3). This was thought to be due to humic substances in the groundwater and/or low molecular weight organics, i.e. cement grinding aid, from cements.
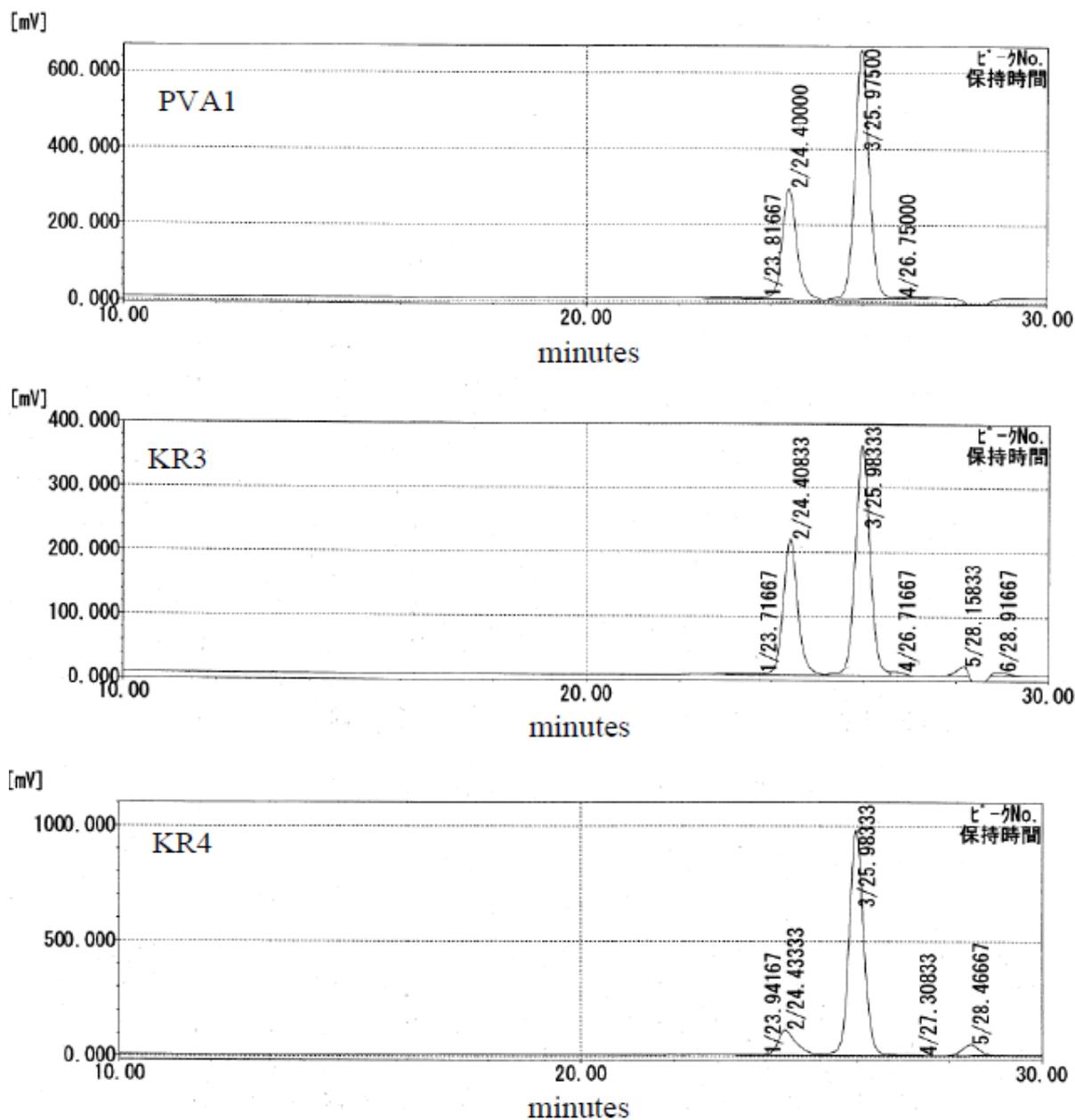
Figure 4.2-1: GPC profiles of samples ONK-PVA1, ONK-KR3 and ONK-KR4 (molecular weight distributions).

4.3   Results of IR analysis

The IR profiles are shown in Figure 4.3-1. The only chemical bonds detected were H_2O and/or CO_3^{2-}. The precipitates in each sample were composed mainly of inorganic salts, e.g. calcium chloride or calcium carbonate.
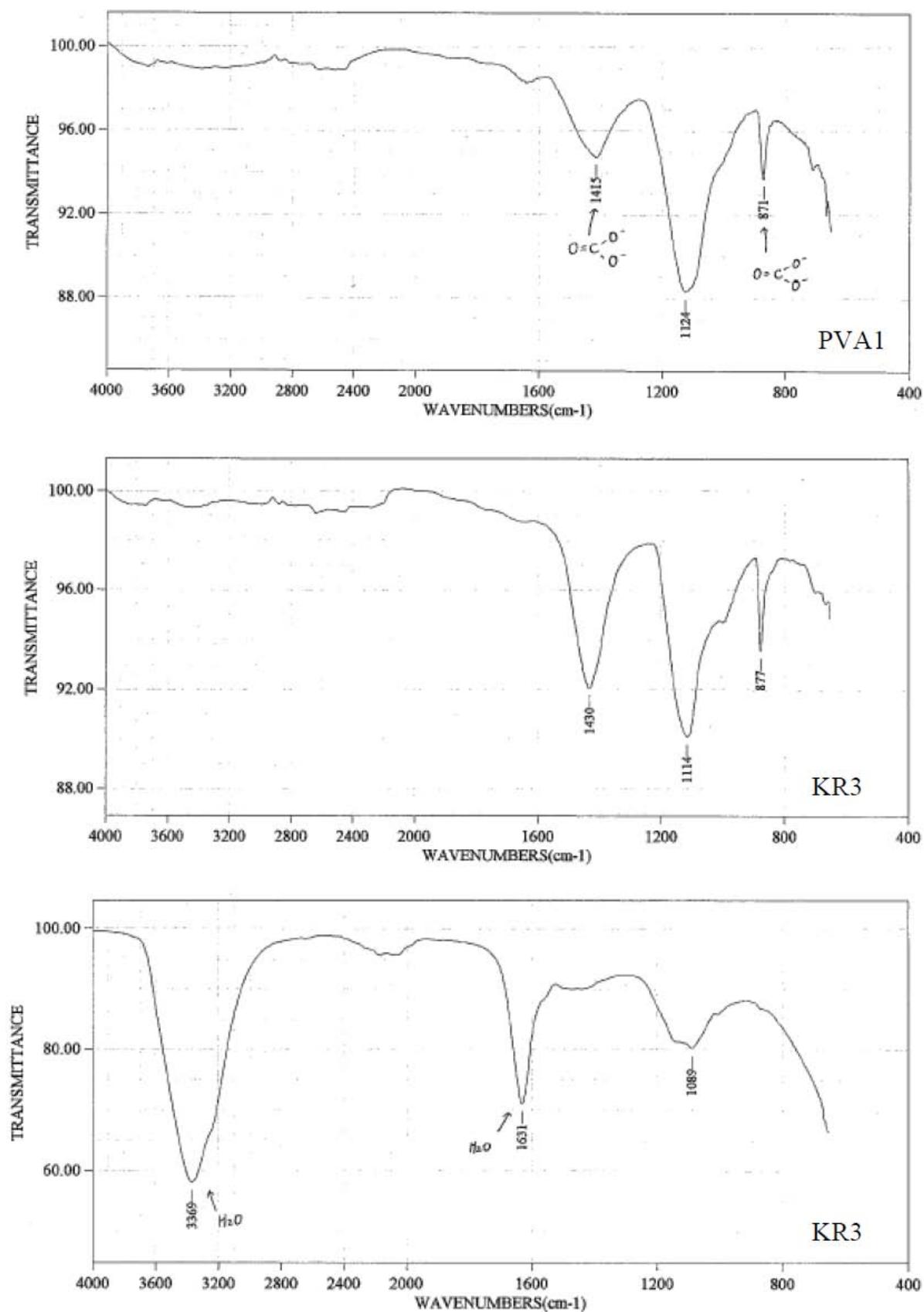
Figure 4.3-1: IR profiles of samples ONK-PVA1, ONK-KR3 and ONK-KR4 (chemical bonds).

4.4   Results of ^{1}H-NMR and ^{13}C-NMR analysis

The ^{1}H-NMR profiles are shown in Figure 4.4-1 and the analytical results of both detections are shown in Table 4.4-1. In each sample, ethoxy, hydroxy, acetyl, ethyl and methyl silene groups were detected, indicating the possible existence of some type of surface-active agent.

In KR4 (in addition to the possibility of a surface-active agent), it is also possible that some kind of chemical additive is released from the cementitious material, e.g. tri-ethanol-amine as a cement grinding aid, because of the detection of aromatic compounds, amino-methylene group and oxy-methylene group. It is also possible that eluted SP40 compounds are present, i.e. MS transmutation substances such as methylol amine or a group of methylol amine that is a homologue of its dimer.
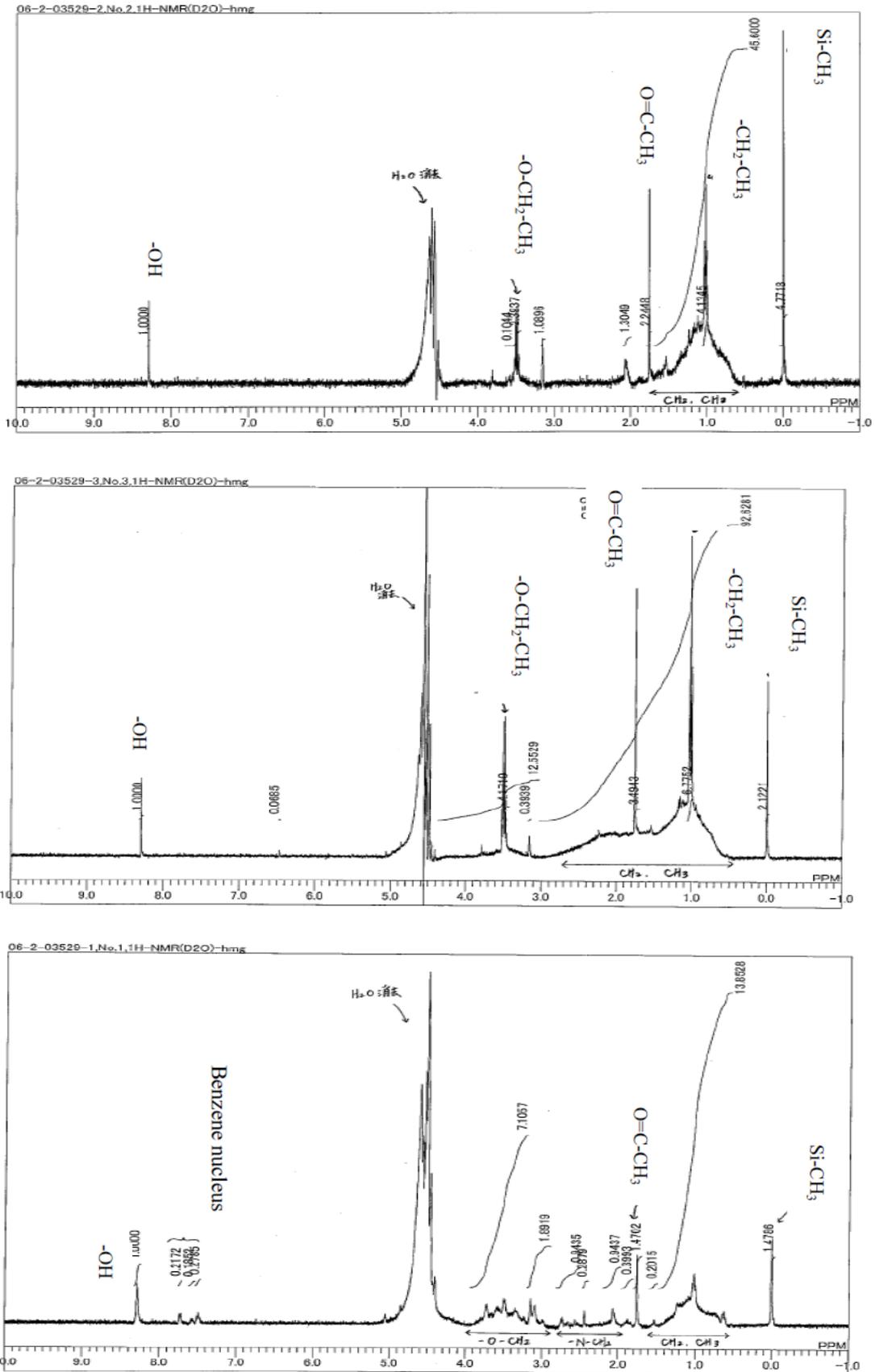
Figure 4.4-1: ¹H-NMR profiles (chemical bonds).

Table 4.4-1:   **Chemical bonding groups in ONKALO samples ONK-PVA1, ONK-KR3 and ONK-KR4, detected by NMR analysis.**

ONK-PVA1	^{1}H-NMR	ethoxy group, hydroxy group, acetyl group, ethyl group, methyl silene group
	^{13}C-NMR	n.d.
ONK-KR3	^{1}H-NMR	ethoxy group, hydroxy group, acetyl group, ethyl group, methyl silene group
	^{13}C-NMR	Carbonyl group
ONK-KR4	^{1}H-NMR	Aromatic compounds, amino-methylene group, oxy-methylene group, ethoxy group, hydroxy group, acetyl group, ethyl group, methyl silene group
	^{13}C-NMR	n.d.

5 CONCLUSIONS

The release of organics from hardened cementitious materials and the physico-chemical properties of cementitious materials altered by leaching were examined using powder, thin-plate and block-shaped specimens immersed in deionized, fresh and saline water. The main findings of this study can be summarized as follows:

- Cement grinding aid and some low molecular weight raw materials of superplasticizers, e.g. naphthalene dimer, melamines and M-PEG, were detected in the leachant from hardened cementitious grout materials. Elution of the main SP components was not detected in any leaching test.

- Low-pH cements are highly durable in terms of the progress rate of the leaching alteration front, but the degree of alteration of the C-S-H phase in a thin surface layer in contact with the leachant is strong and results in a layer of porous hydrates through extensive leaching of Si.

- To some extent, calcite and smectite will have a protective coating effect on the surface of cementitious materials in contact with freshwater and saline water, but beneath this layer there will be alteration damage due to gradual leaching of Ca^{2+} and Si from the C-S-H phase.

TOC, GPC, IR and NMR analyses were carried out on ONKALO groundwater samples to determine the possibility of SP elution from cementitious grouting materials. The main findings of this study can be summarized as follows:

- Each groundwater sample that had been in contact with the normal pH cement/ SP40 system and the low-pH cement/Mighty 150 system or that had not been in contact with any cementitious materials showed evidence of some surface-active agent, e.g. lubricating oil for the drill bit.

- In the normal pH cement/ SP40 system, there was possible elution of cement grinding aid and/or some SP40 compounds.

6 ACKNOWLEDGEMENTS

7 REFERENCES

Bodén, A., Sievänen, U. (2005): Low-pH injection grout for deep repositories, Summary report from a co-operation project between NUMO(Japan), Posiva(Finland) and SKB(Sweden), SKB Report R-05-40, Swedish Nuclear Fuel and Waste Management Co., Stockholm Sweden.

NUMO (2004): Proceedings of the international workshop on bentonite-cement interaction in repository environments, NUMO Technical Report NUMO-TR-04-05, Nuclear Waste Management Organization of Japan, Tokyo Japan.

NUMO (2008): Study on long term applicability of low alkaline cement for repository environments, NUMO Technical Report NUMO-TR-08-02, Nuclear Waste Management Organization of Japan, Tokyo Japan (in Japanese).

Vuorinen, U., Lehikoinen, J., Imoto, H., Yamamoto, T., Alonso, M.C. (2004): Injection Grout for Deep Repositories, Subproject 1: Low-pH Cementitious Grout for Larger Fractures, Leaching Testing of Grout Mixes and Evaluation of the Long –Term Safety, Posiva working report 2004-46, Posiva Oy, Helsinki Finland.