K：水泥材料特性

K.1：Paper－Effects of Hydrogencarbonate and Chloride in Groundwater on Leaching of Cementitious Materials

Contents

EFFECTS OF HYDROGENCARBONATE AND CHLORIDE IN GROUNDWATER ON LEACHING OF CEMENTITIOUS MATERIALS

INFLUENCE DE L'ACIDE CARBONIQUE ET DES CHLORURES CONTENUS DANS LE SOL SUR LA LIXIVIATION DES MATERIAUX CIMENTAIRES

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ABSTRACT - This paper presents the results of an experimental study on the effects of hydrogencarbonate and chloride in immersion solution on leaching of cementitious materials. Hydrogencarbonate reacted with calcium leached from specimen to form a calcite layer on the surface of specimen, which inhibited leaching of cementitious materials. The higher the concentrations of sodium hydrogencarbonate, the less cementitious materials were leached. On the other hand, the leaching was found to be accelerated by elevating the concentration of sodium chloride compared with pure water leaching. Furthermore, in case of immersion solution containing both hydrogencarbonate and chloride were investigated to understand the behavior of leaching by practical groundwater.

Na
HCO$_3$

RÉSUMÉ - L'article présente les résultats d'une étude expérimentale sur l'influence de l'acide carbonique et des chlorures en solution sur la lixiviation des matériaux cimentaires. L'acide carbonique qui réagit avec le calcium lixivié forme une couche de calcite à la surface de l'échantillon, qui inhibe la lixiviation ultérieure du matériau cimentaire. Plus la concentration en acide carbonique est élevée, moins il y a de matériau cimentaire lixivié. Au contraire, la lixiviation s'est avérée accélérée par la teneur en chlorures, en comparaison avec la lixiviation par l'eau pure. De plus, on a considéré le cas d'immersion dans une solution contenant à la fois des chlorures et de l'acide carbonique pour comprendre le mécanisme de la lixiviation observé en pratique dans les sols.

1. Introduction

Upgrading techniques for evaluating long-term durability of cementitious materials, especially of leaching resistance against groundwater attack, with a view to construction of a radioactive waste repository under the ground, is urgently demanded in Japan. Previously, leaching resistance has been investigated using pure water (Atkinson et al., 1988; Berner, 1988; Adenot, 1992; Faucon, 1998; Rahman, 1999; Mainguy, 2000; Yasuda, 2002; Yokozeki, 2003; Haga, 2005; Sugiyama, 2006); however, various constituents of groundwater may affect leaching phenomena.

The goal of this study is to examine experimentally how the practical groundwater around the planned site for a low-level radioactive waste repository at Rokkasho in Japan affects the leaching of cementitious materials. This paper focuses on the effects of hydrogencarbonate commonly contained in groundwater and chloride possibly contained in deep groundwater on leaching phenomena. The results of leaching tests with a variety of immersion solutions show that rich hydrogencarbonate inhibits leaching due to calcite precipitation; in contrast, rich chloride accelerates it due to the increased solubility of calcium hydroxide. The interaction between hydrogencarbonate and chloride is also discussed. OH

Ca

2. Experimental procedures

2.1. Specimens

Figure 1. Specimen condition

We conducted leach tests into various solutions using the specimens illustrated in Figure 1. Their mix proportions are shown in Table I where the mixes with low-heat Portland cement and fly ash were simulated for use in a radioactive waste repository in Japan. These specimens were cured in water of 50°C for 91 days for the purpose of accelerating the reaction of cement and fly ash.

Table I. Mix proportions

	Cement type	Ad.	W/B	S/B	Abbr.
Cement paste	Ordinary Portland cement	-	0.35	-	O
	Low-heat Portland cement	Fly ash			LF
Mortar			0.50	2.0	LFm

Ad.: Mineral admixture, W/B: Water binder mass ratio, S/B: Sand binder mass ratio

2.2. Series of leach tests

This experiment was composed of four series of leach tests shown in Table II; series G for an exploratory experiment using groundwater simulant solutions (*3.1*); series C for examining the effect of sodium hydrocarbonate concentration (*3.2*); series S for examining the effect of sodium chloride concentration (*3.3*), and series CS for examining the effect of the balance of hydrogencarbonate vs. chloride (*3.4*). Solution for leach test was periodically replaced with new solution, of which the ratio to surface area of specimen was 100cm^3/cm^2. All of the leach tests were carried out in N_2 gas-filled grove boxes (approx.20°C) to keep solutions from carbonating.

↖ CO_2 from air?

2.3. Measurement techniques

Table II. Variety of solutions subject to series of leach tests

Solution type	Concentration (mg/L, approx.)							Initial pH	Test series	Abbr.
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-			
Pure water	0	0	0	0	0	0	0	7.0	Control	P
Fresh-groundwater simulant solution	185	5	5	5	70	15	400	8.4	G	Fg
Saline-groundwater simulant solution	9500	160	1100	320	17000	600	400	7.4	G	Sg
Sodium hydrogencarbonate solution	150	0	0	0	0	0	400	8.8	C	Ch
	15	0	0	0	0	0	40	8.0	C	Cm
	1.5	0	0	0	0	0	4	7.0	C	Cl
Sodium chloride solution	11024	0	0	0	17000	0	0	5.7	S	Sh
	1102	0	0	0	1700	0	0	5.9	S	Sm
Hydrogencarbonate and chloride mixed solution	26	0	0	0	17	0	40	8.1	CS	CmSl
	1117	0	0	0	1700	0	40	8.6	CS	CmSm
	11039	0	0	0	17000	0	40	8.4	CS	CmSh
	11174	0	0	0	17000	0	400	8.6	CS	ChSh

The pH and Ca^{2+} concentration of leachate solutions were measured by the glass electrode method and inductive-coupled plasma atomic emission spectrometry, respectively. In this paper, the leaching phenomena from specimens are discussed with OH^- leaching amounts converted from pH rises of solutions and Ca^{2+} leaching amounts per unit exposure area. The solid-phase degradation of specimens was also examined by electron probe X-ray microanalysis (EPMA), X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

3. Results and discussion

3.1. Leach test results with pure water and groundwater-simulant solutions

3.1.1. pH rise and calcium leaching

Figure 2 shows a comparison of measured pH rises of pure water, and groundwater-simulant solutions Fg and Sg. The pH of pure water, in which cementitious materials were immersed, rises in the familiar manner. In the case of immersion in groundwater-simulant solutions, the rises of pH, by contrast, were much less and the pH rise in Sg was than that of Fg. As shown in Figure 3, the similar results of leach tests with each specimen are obvious. The amount of leaching OH^- in solutions Fg and Sg was approximately 1/100 and 1/10000 of that pure water, respectively. On the other hand, Ca^{2+} leaching from specimens immersed in groundwater-simulant solution Fg was also inhibited (Figure 4).

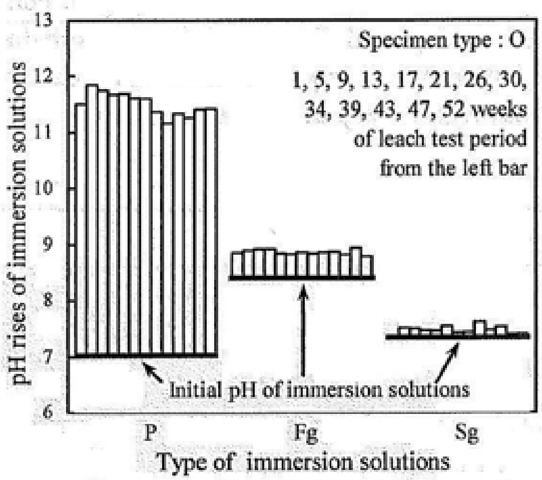


Figure 2. Comparative pH rises of immersion solutions (series G)

less

in

3.1.2. Changes of solid phase in specimens

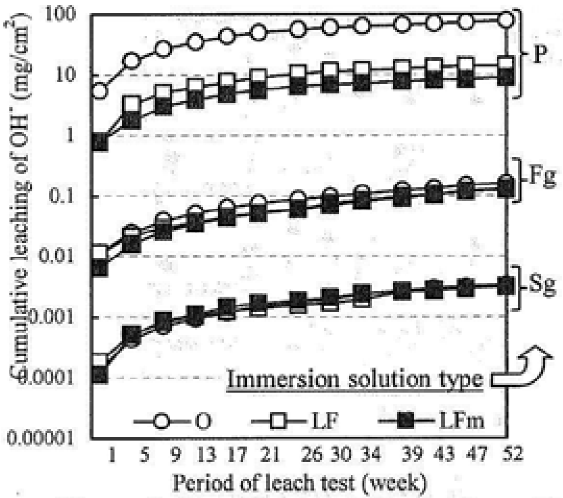


Figure 3. Comparative OH^- leaching from specimens (series G)

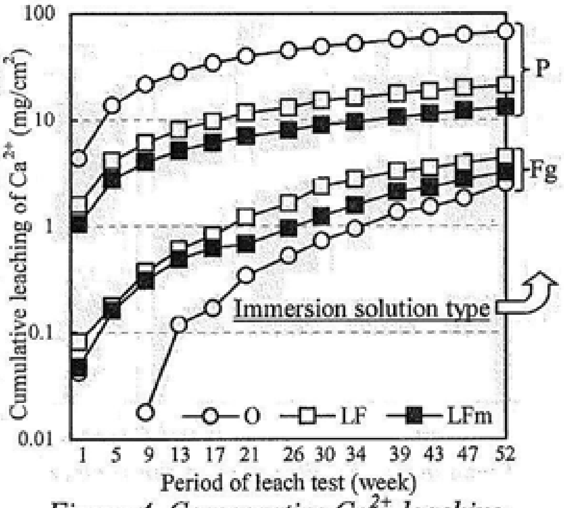


Figure 4. Comparative Ca^{2+} leaching from specimens (series G)

The solid phase changes of specimens were analyzed to confirm the above leaching-inhibition phenomena. The calcium distributions in specimens immersed in various solutions measured by EPMA are displayed in Figure 5. In the case of immersion in pure water, specimen O was degraded deeper than LF. It is believed that specimen O contained more calcium hydroxide, which dissolves well in pure water; therefore, the increase in porosity, connected to the increase in leachability, was larger when calcium hydroxide was leached completely. In cases of immersion in Fg and Sg solutions, the calcium distributions changed little, as shown in Figure 5.

These results obtained from the above analyses suggest a precipitation reaction on the surface of specimens as a leaching inhibitor. Figure 6 shows the distributions of Si, Ca and C at the surface-minute-region 100x500μm of specimens immersed in Fg and Sg. It may be clearly observed that Ca and C were concentrated on the surface of the specimen immersed in Sg. The mineralogical composition of precipitation was identified as calcite ($CaCO_3$) as shown in Figure 7. The figure also indicates that the precipitation identified on the surface of specimen immersed in solution Fg was similarly calcite. The reason concentrated Ca and C layers were not observed is supposed to be that the thickness of the layers was below the EPMA detection limit. The surface appearance of specimens seemed to vary by immersion solution type as SEM images show in Figure 8. The surface of specimen immersed in pure water appears porous because of leaching of cement hydrates. On the other hand, in cases of immersion in Fg and Sg, precipitation substances, which were identified as calcite by energy dispersive X-ray spectroscopy, can be observed although the crystal growth configurations are very different.

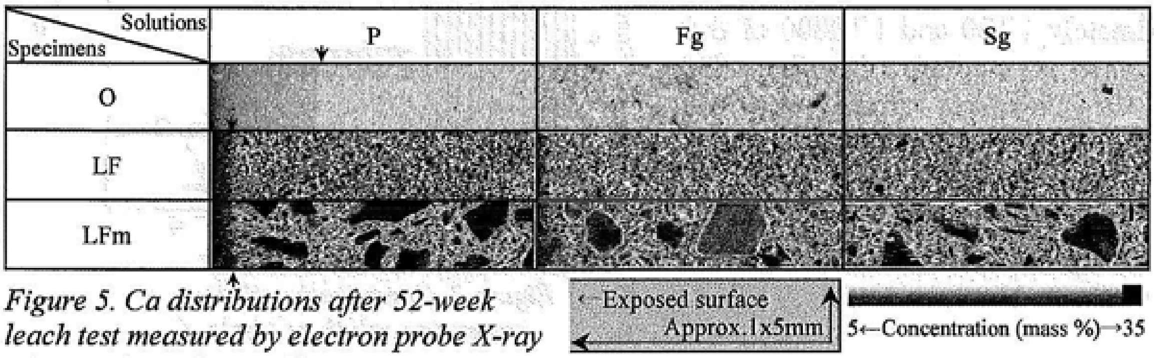


Figure 5. Ca distributions after 52-week leach test measured by electron probe X-ray microanalyzer (series G)

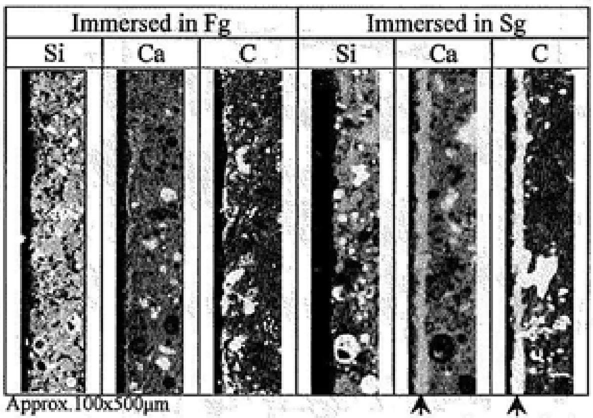


Figure 6. Elementary distributions at the surface of specimens after 52-week leach test measured by electron probe X-ray microanalyzer

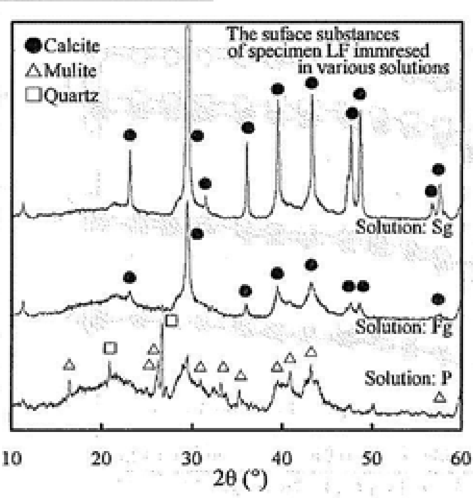
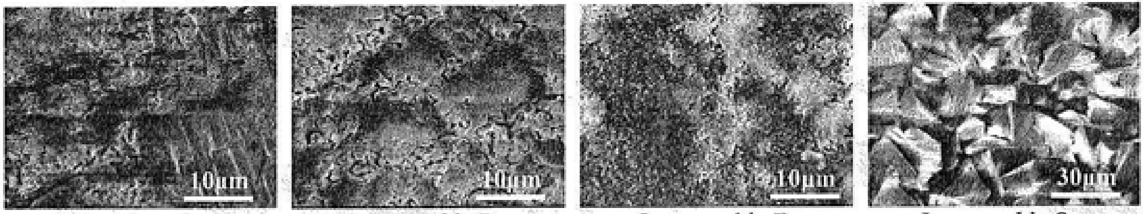


Figure 7. Results of XRD analyses of precipitations at the surface of specimens



Sound portion Immersed in P Immersed in Fg Immersed in Sg

Figure 8. SEM images of the surfaces of specimen type O after 52-week leach test

3.1.3. Mechanism of leaching inhibition subjected to hydrogencarbonate action

Calcite precipitation was identified by EPMA, XRD and SEM on the surface of specimens immersed in solution Fg and Sg containing rich hydrogencarbonate of 400 mg/l. The calcite precipitation was formed by a reaction of hydrogencarbonate with calcium leached from cementitious materials. At this point, the higher the pH condition, the more easily the calcite precipitated. It is believed that the calcite-precipitated layer on the surface worked as an inhibitor of leaching from cementitious materials. The reason the leaching in solution Sg was less than that in Fg (cf. Figure 3 and 4) may be the thicker calcite-precipitated layer (cf. Figure 6) resulting from the additional contribution of rich calcium ion in solution Sg to the precipitation reaction as illustrated in Figure 9.

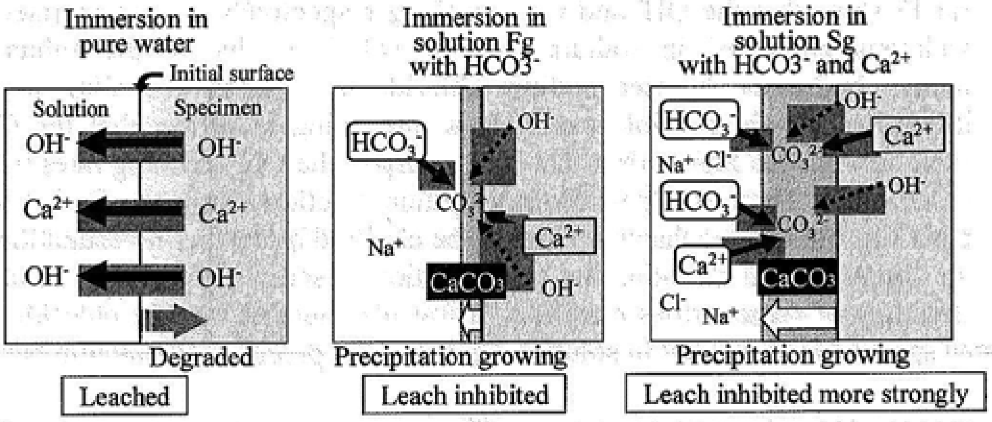
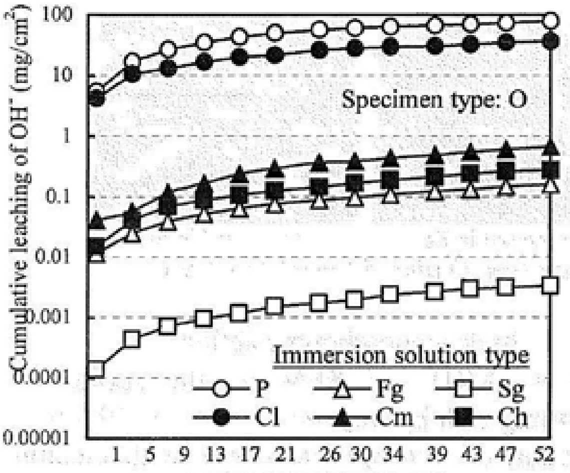


Figure 9. Simplified mechanism of leaching inhibition of cementitious materials immersed in solutions containing hydrogencarbonate

3.2. Effect of sodium hydrogencarbonate concentration on leaching inhibition

In the preceding section it was mentioned that rich hydrogencarbonate in solutions can inhibit leaching from cementitious materials. This section discusses the effect of concentration of hydrogencarbonate on leaching inhibition. Figure 10 shows the cumulative OH^- leaching from specimen O immersed in sodium hydrogencarbonate solutions of various concentrations: Cl, Cm and Ch, as well as pure water, and groundwater simulant solutions Fg and Sg. It is apparent from the figure that the higher the hydrogencarbonate concentration the less OH^- is leached. Elevating concentration of hydrogencarbonate similarly inhibited the calcium leaching, as shown in Figure 11. It was clarified that the further growth of a calcite-precipitated layer by elevating concentration of hydrogencarbonate can enhance the leaching inhibition effectiveness.



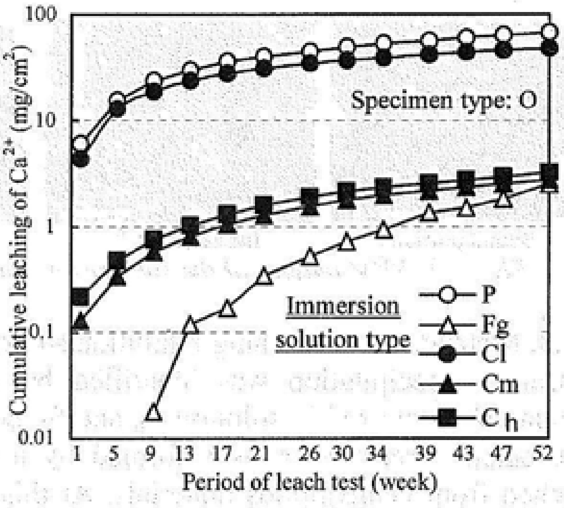
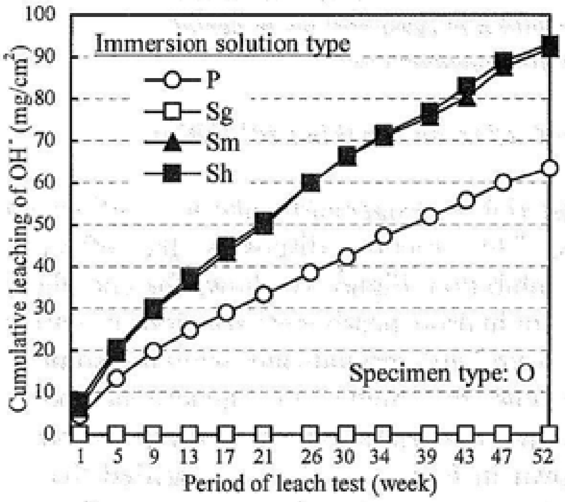


Figure 10. Effects of HCO_3^- conc. on OH^- leaching from specimens (series C)

Figure 11. Effects of HCO_3^- conc. on Ca^{2+} leaching from specimens (series C)

3.3. Effect of sodium chloride concentration on leaching acceleration

Figures 12 and 13 show that the OH^- and Ca^{2+} leaching respectively was accelerated in the case of specimens immersed in sodium chloride solutions, due to the enhanced solubility of calcium hydroxide by rich sodium chloride in solution according to the chemical equilibrium as a main possible cause. It is interesting to reflect that the Ca^{2+} leaching rate in solution Sh was higher than that in Sm despite the OH^- leaching rates being nearly equal to each other. There is a possible substitution reaction where the Ca ion was displaced by the Na ion, but this mechanism needs to be clarified by further investigation. It was confirmed in Figure 14 that elevating the concentration of sodium chloride in solution accelerated the leaching of cementitious materials. It was also notable that the chloride ion barely penetrated specimens immersed in solution Sg due to the precipitated-calcium barrier.



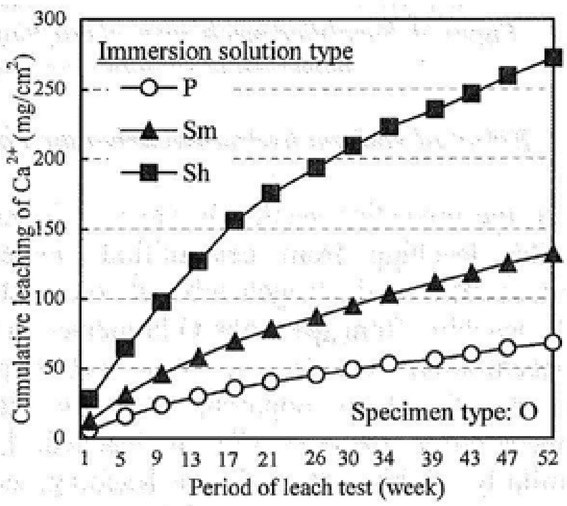


Figure 12. Effects of Cl^- conc. on OH^- leaching from specimens (series S)

Figure 13. Effects of Cl^- conc. on Ca^{2+} leaching from specimens (series S)

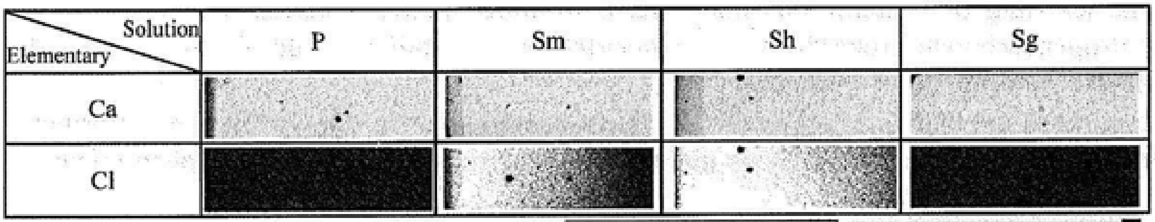


Figure 14. Ca and Cl distributions of specimen O immersed in NaCl solutions for 52-week

3.4. Leach tests with solutions containing both hydrogencarbonate and chloride

Figure 15 shows the change in the OH^- leaching amount from the specimens immersed in solutions containing both hydrogencarbonate and chloride. In the case of immersion in ChSh containing rich hydrogencarbonate of 400 mg/l vs. even rich chloride of 17000 mg/l, the leaching was inhibited from the early test stages due to precipitation of calcite. On the other hand, even in the case of immersion in solutions of CmSl, CmSm and CmSh, which contain hydrogencarbonate of 40 mg/l, the leaching rate gradually decreased although OH^- leached at about the same rate as immersion in pure water at first week.

The above results indicate that the leaching of cementitious materials is inhibited above a certain concentration of hydrogencarbonate (40 mg/l indicated in this study, it may well be able to inhibit at lower concentration based on the precipitation equilibrium of calcite) regardless of concentration of chloride, which simply affects the inhibition progress.

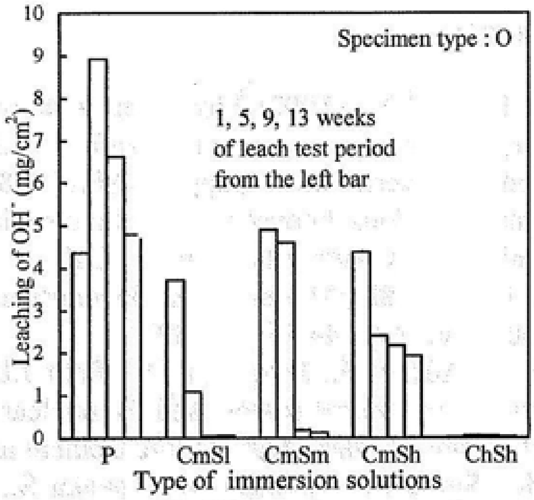


Figure 15. Effects of concentration balance of HCO_3^- vs. Cl^- on OH^- leaching

4. Conclusions

Based on the findings obtained from the foregoing investigations, the following main conclusions were drawn:

(1) Rich hydrogencarbonate in solution can react with calcium leached from cementitious materials to form a calcite layer on the surface of the specimen. The precipitated-calcite layer inhibits the leaching of cementitious materials.

(2) The higher the concentration of hydrogencarbonate, the less cementitious materials are leached.

(3) On the other hand, the leaching is accelerated by elevating the concentration of sodium chloride compared with pure water leaching.

(4) The leaching of cementitious materials is inhibited above a certain concentration of hydrogencarbonate regardless of concentration of sodium chloride which simply affects the progress of inhibition

Future tasks are explaining the reaction phenomena based on the chemical equilibriums, development of a numerical analysis method and experimental proof of the phenomena in situ.

5. Acknowledgements

The authors thank Professor Y. Tsuji of Gunma University, Professor M. Shoya of the Hachinohe Institute of Technology, Associate Professor E. Sakai of the Tokyo Institute of Technology, Associate Professor M. Hisada of Tohoku University, and Associate Professor T. Ishida of Tokyo University for their valuable advice.

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Contents

K.2：Slides－Effects of Hydrogencarbonate and Chloride in Groundwater on Leaching of Cementitious Materials

CONSEC '07 Fifth International Conference on Concrete under Severe Conditions Environment and Loading Tours, France June 4-6, 2007

Effects of Hydrogencarbonate and Chloride in Groundwater on Leaching of Cementitious Materials

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Point:

Retardation and acceleration of leaching rate due to the action of groundwater components

Keywords:
Radioactive waste disposal, Long-term durability, Leaching, Groundwater components, Dissolution-precipitation reaction

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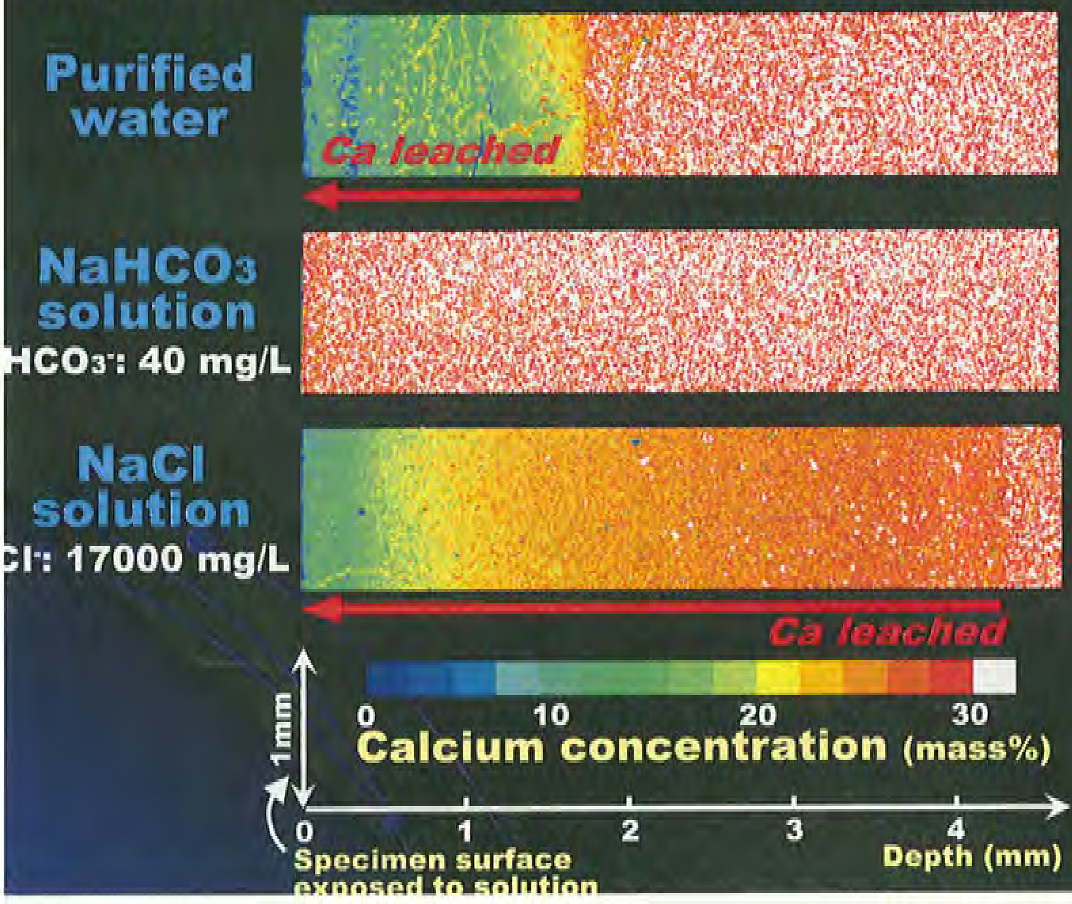
◆ Representative experimental results

***Calcium distribution** in specimens immersed for one year*



Why retarded?

Why accelerated?

How much leaching occurs in mixed solutions of HCO_3^- & Cl^- ?

Background of this research

The current state of *radioactive waste disposal* in Japan

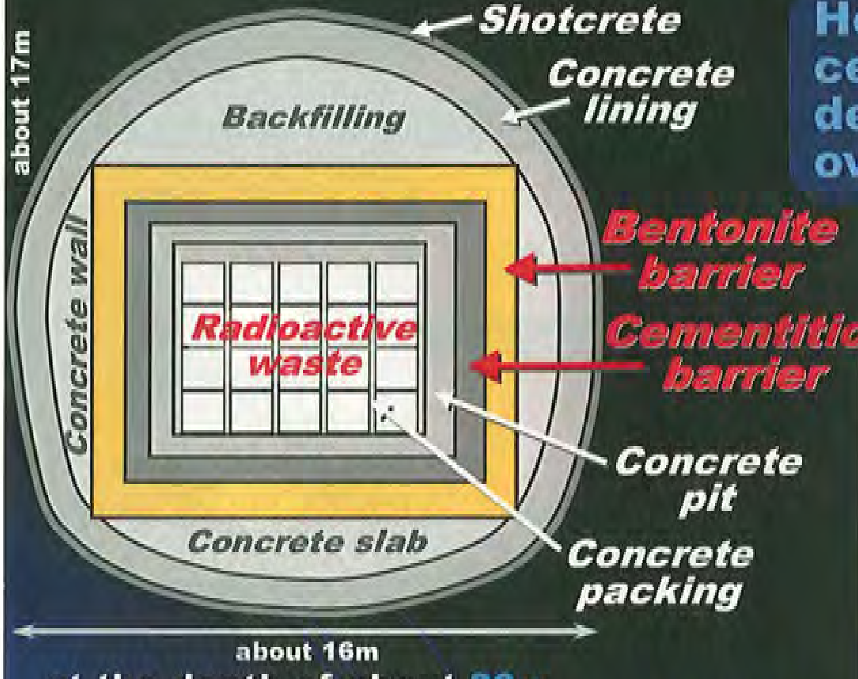
- **Near-surface disposal** (about 10m deep)
  at the Rokkasho disposal site for relatively lower-levels of low-level radioactive waste *Now in operation*

- **Sub-surface disposal** (about 50-100m deep)
  at the Rokkasho disposal site for relatively higher-levels of LLW
  Now in the design and assessment phase
  ↳ **A type of cementitious member is required to perform as an engineered barrier**
  :radionuclide-diffusion resistant and -sorption capable

- **Deep geological disposal** (deeper than 300-500m)
  for high-level radioactive waste
  Now in the planning and scouting candidate-site phase

Sketch of current design for *sub-surface disposal facility*

for low-level radioactive waste at the Rokkasho disposal site in Japan



at the depth of about 80m

How cementitious materials deteriorate over a prolonged time?

→ ***Leaching*** is focused on in this research

Test tunnel at the Rokkasho disposal site →

◆ Objectives of this research

Leaching mechanism of cementitious materials immersed in *purified water* is mostly understood.

Experimental term

☑ *To clarify experimentally the effects of groundwater components*

Effects of HCO_3^- and Cl^- introduced in this presentatio

HCO_3^-: common component in groundwater of any depth
Cl^-: found in high concentration in deep or coastal groundwater with seawater or ancient seawater origin

Modeling and calculating term (in progress)

☐ *To build a prediction method for leaching based on groundwater components*

◆ Experimental methods

Specimen parameters

- *Cement paste specimen, W/C=0.35*

Immersion method

- *Solution volume / surface area = 100 cm^3/cm^2*
- *Solutions periodically replaced about every four weeks for one year*

Leaching analyses

☑ *pH Changes of solutions measured using pH electrode*
☑ *Ca leached from specimens analyzed using ICP-AES*
☑ *Ca distribution in specimens analyzed using EPMA*

Variety of immersion solutions

- *The groundwater at 80m at the Rokkasho disposal site contains HCO_3^- of about 40mg/L*
- *Seawater contains Cl^- of about 17000mg/L*

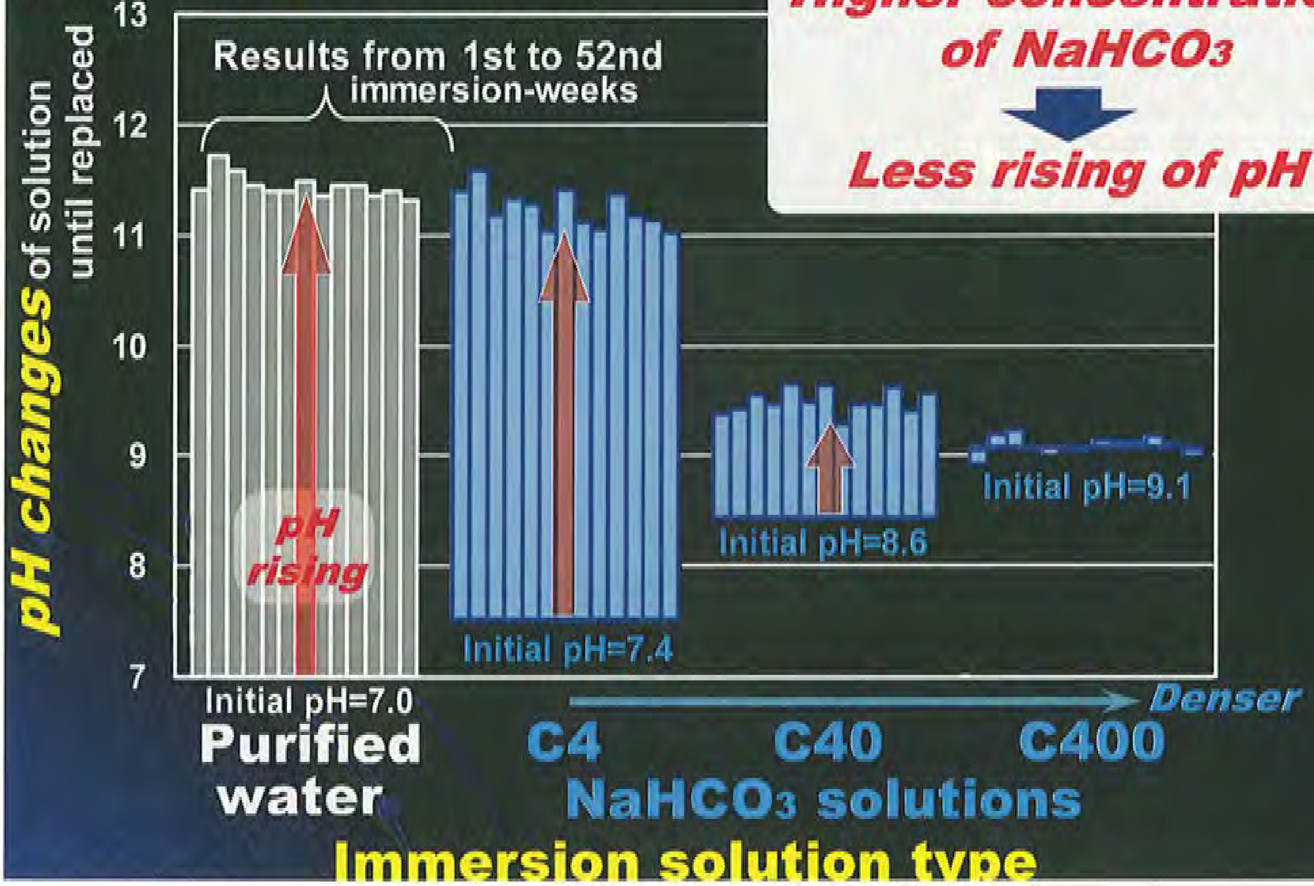
Solution type	Targeted conc. mg/L			Measured pH value	Code name
	Na^+	HCO_3^-	Cl^-		
Purified water	0	0	0	7.0 theoretical	P
$NaHCO_3$ solution	1.5	4	0	7.4	C4
	15	40	0	8.6	C40
	150	400	0	9.1	C400
NaCl solution	1102	0	1700	5.9	S1700
	11024	0	17000	6.0	S17000
$NaHCO_3$ + NaCl solution	26	40	17	8.0	C40S17
	1117	40	1700	8.0	C40S1700
	11039	40	17000	8.2	C40S17000
	11174	400	17000	8.5	C400S17000

◆ *Results* $NaHCO_3$ solutions

pH changes of solutions

Higher concentration of $NaHCO_3$

Less rising of pH

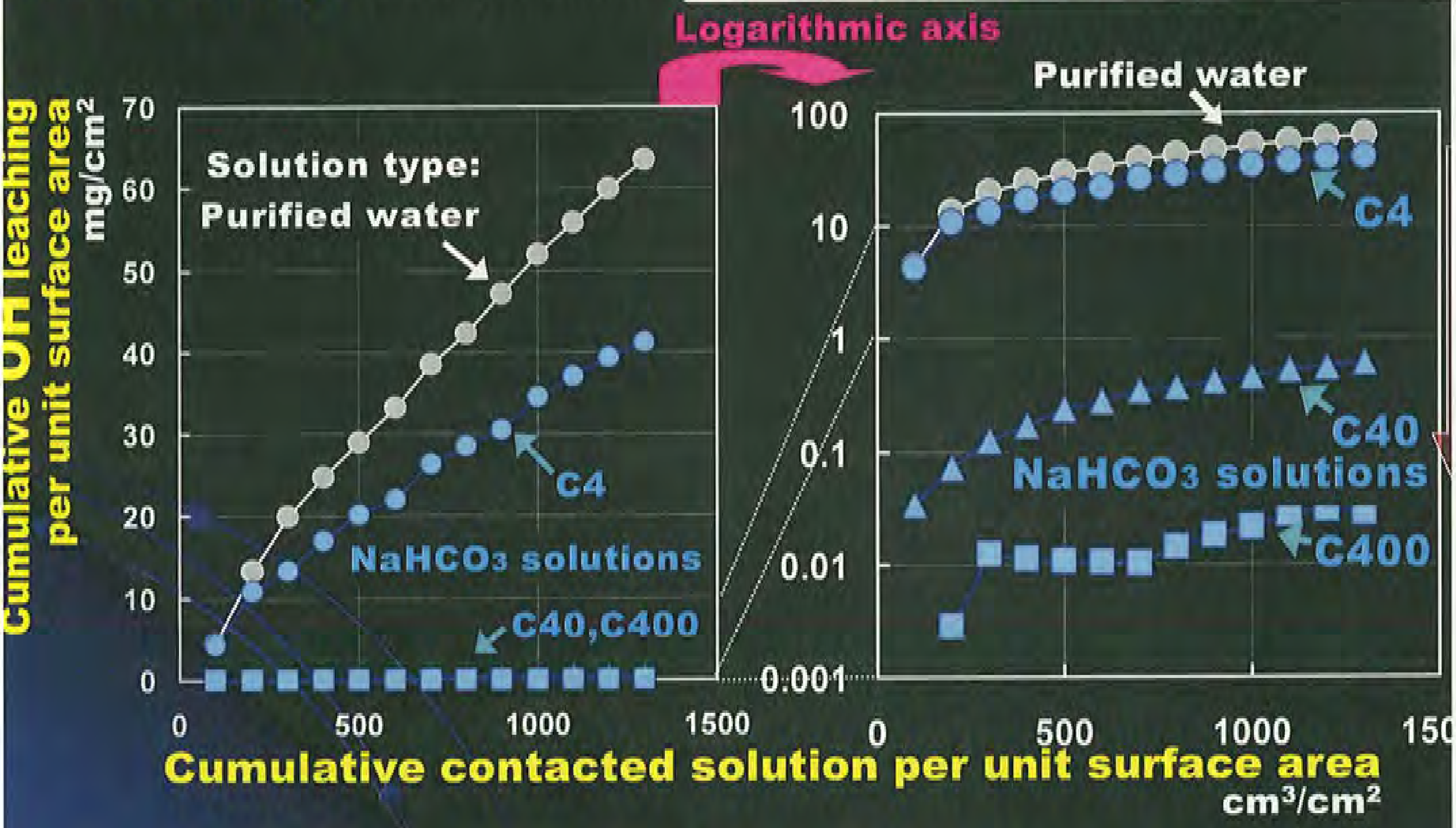


NaHCO$_3$ solutions

OH leaching from specimens

Higher concentration of NaHCO$_3$

Less OH leached

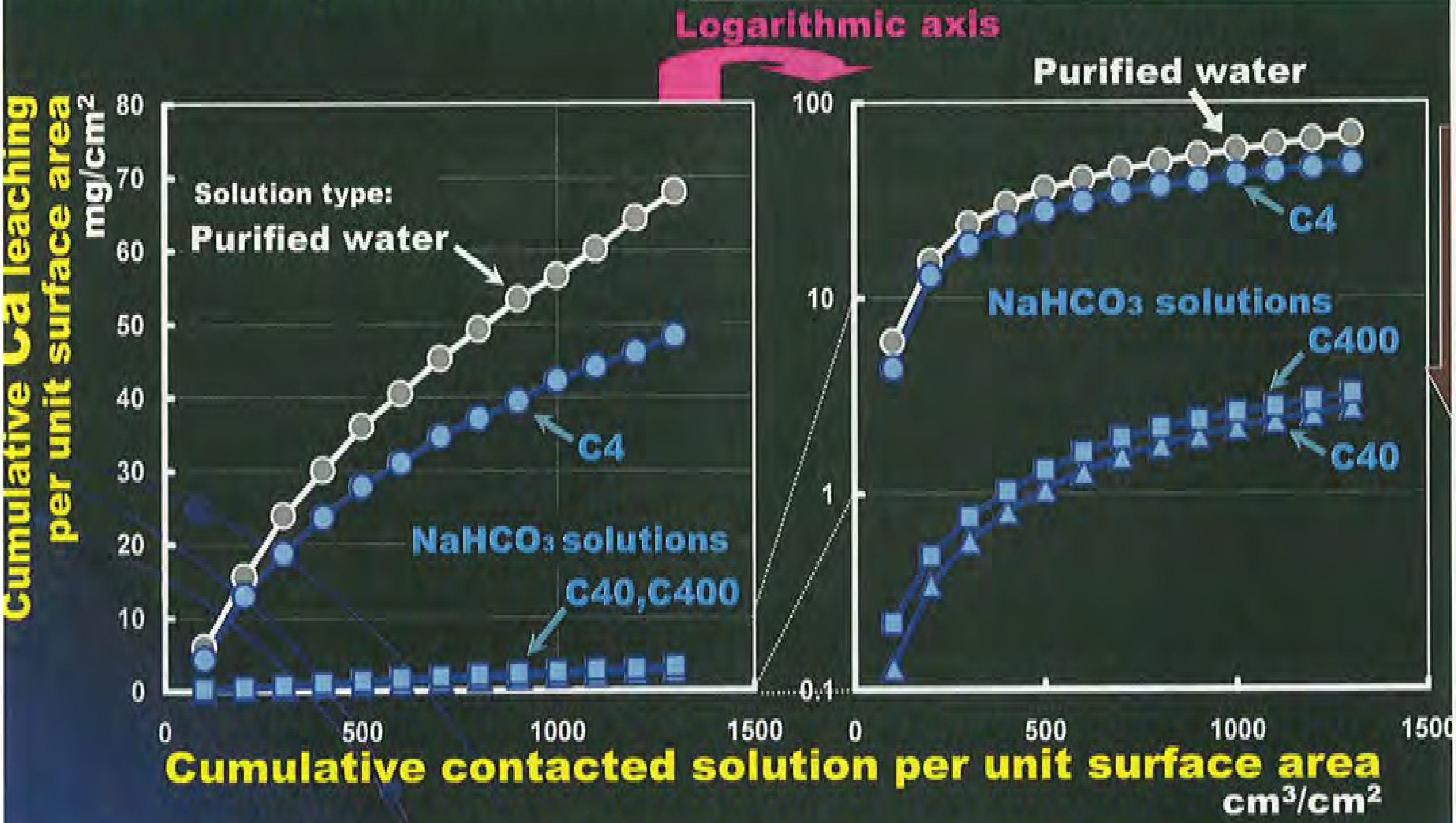


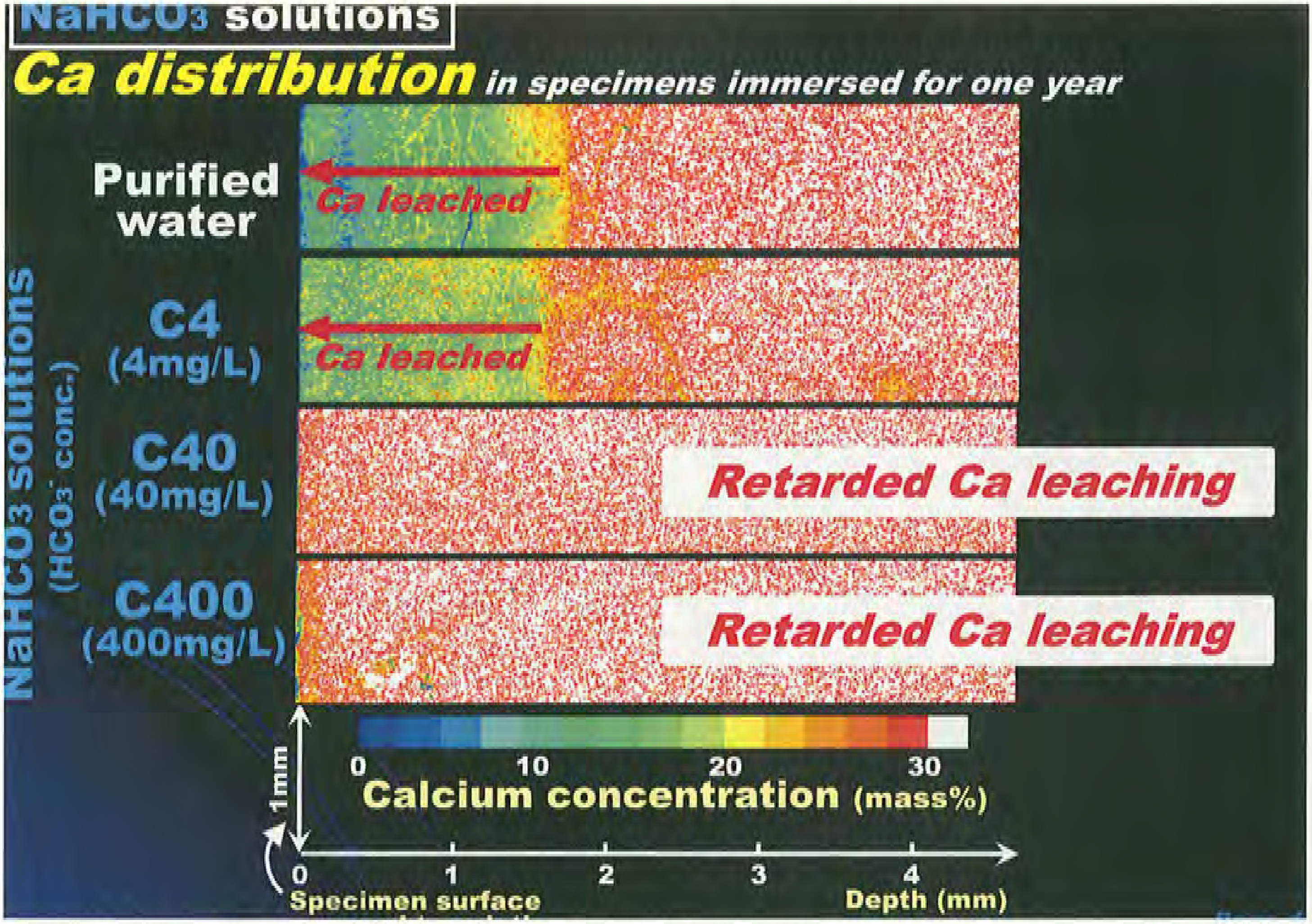
NaHCO$_3$ solutions

Ca leaching from specimens

High concentration of NaHCO$_3$

Less Ca leached



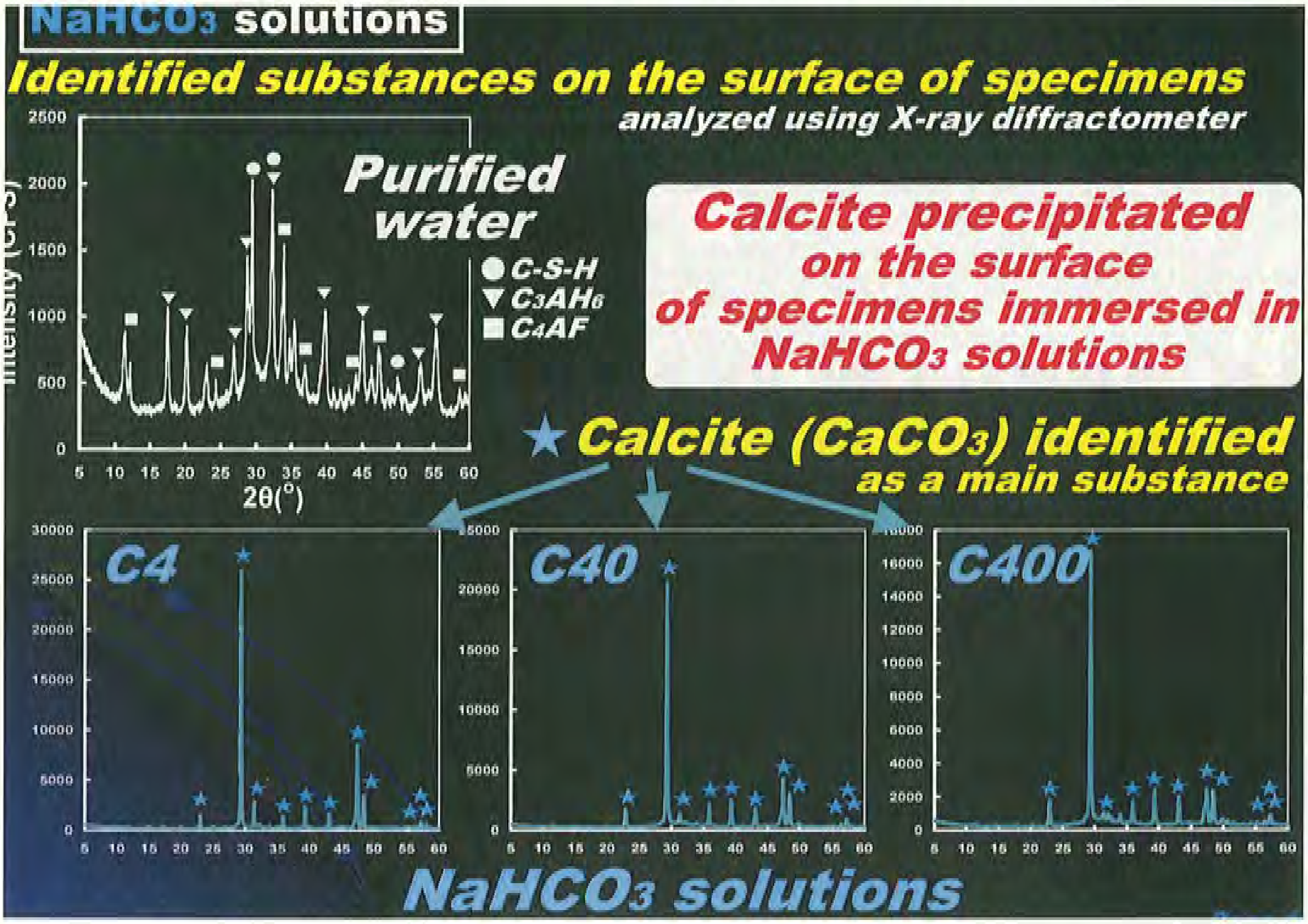


$NaHCO_3$ solutions

Ca distribution in specimens immersed for one year

Retarded Ca leaching

Retarded Ca leaching



$NaHCO_3$ solutions

Identified substances on the surface of specimens

analyzed using X-ray diffractometer

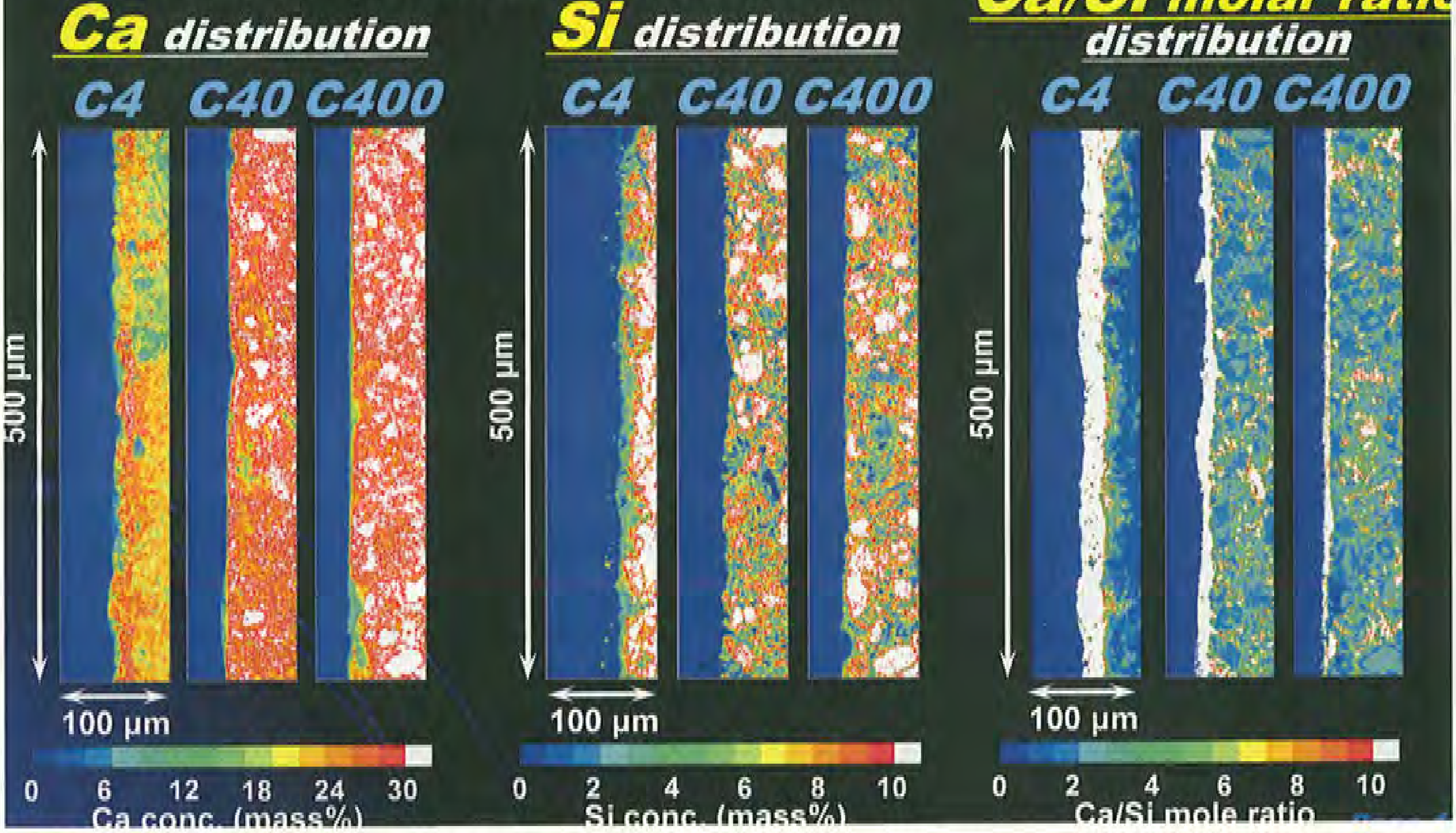
Calcite precipitated on the surface of specimens immersed in $NaHCO_3$ solutions

★ **Calcite ($CaCO_3$) identified as a main substance**

$NaHCO_3$ solutions

$NaHCO_3$ solutions

Calcite-precipitated layer
on the surface of specimens analyzed using EPMA



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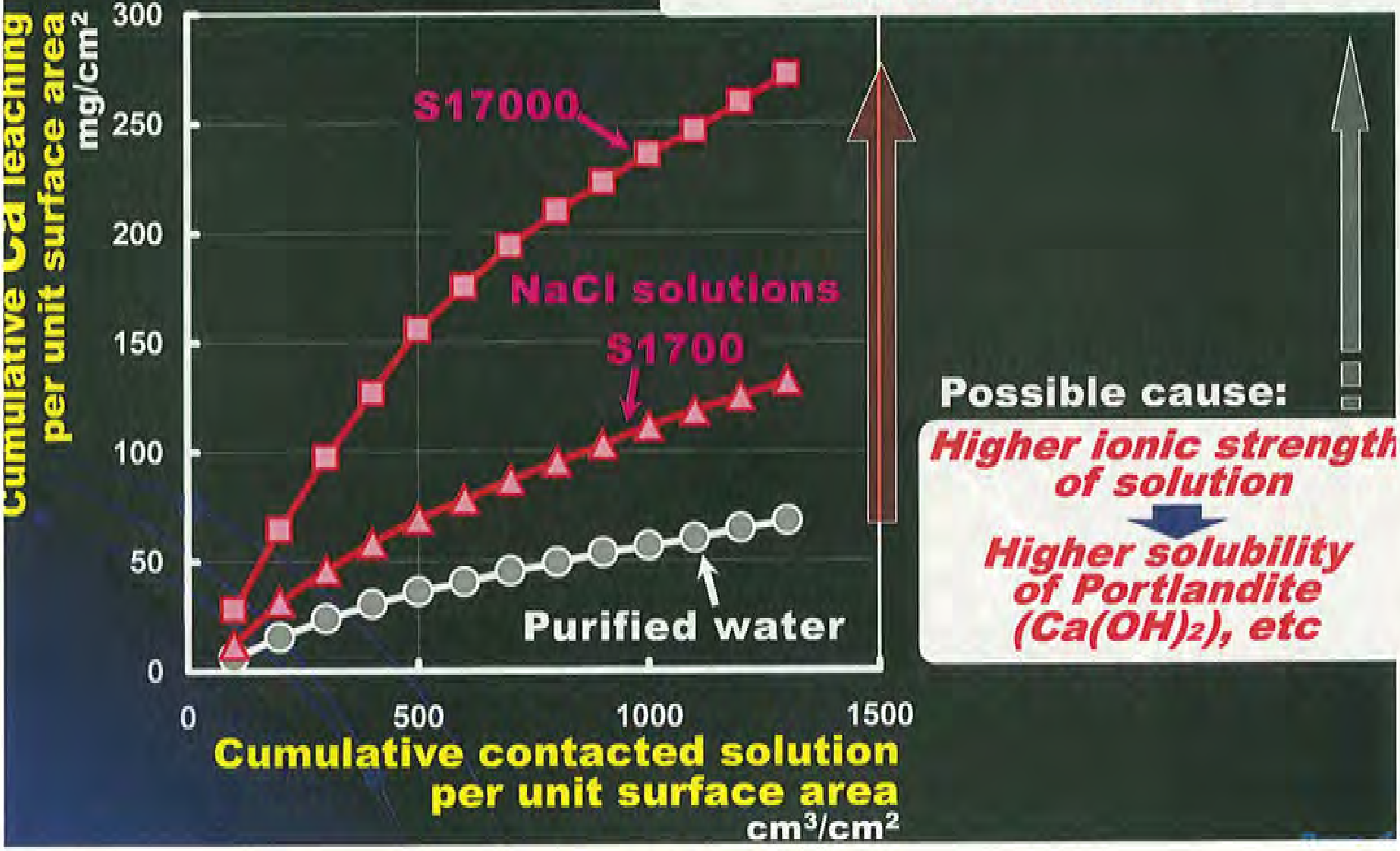
NaCl solutions

Ca leaching from specimens

Higher concentration of NaCl

More Ca leached



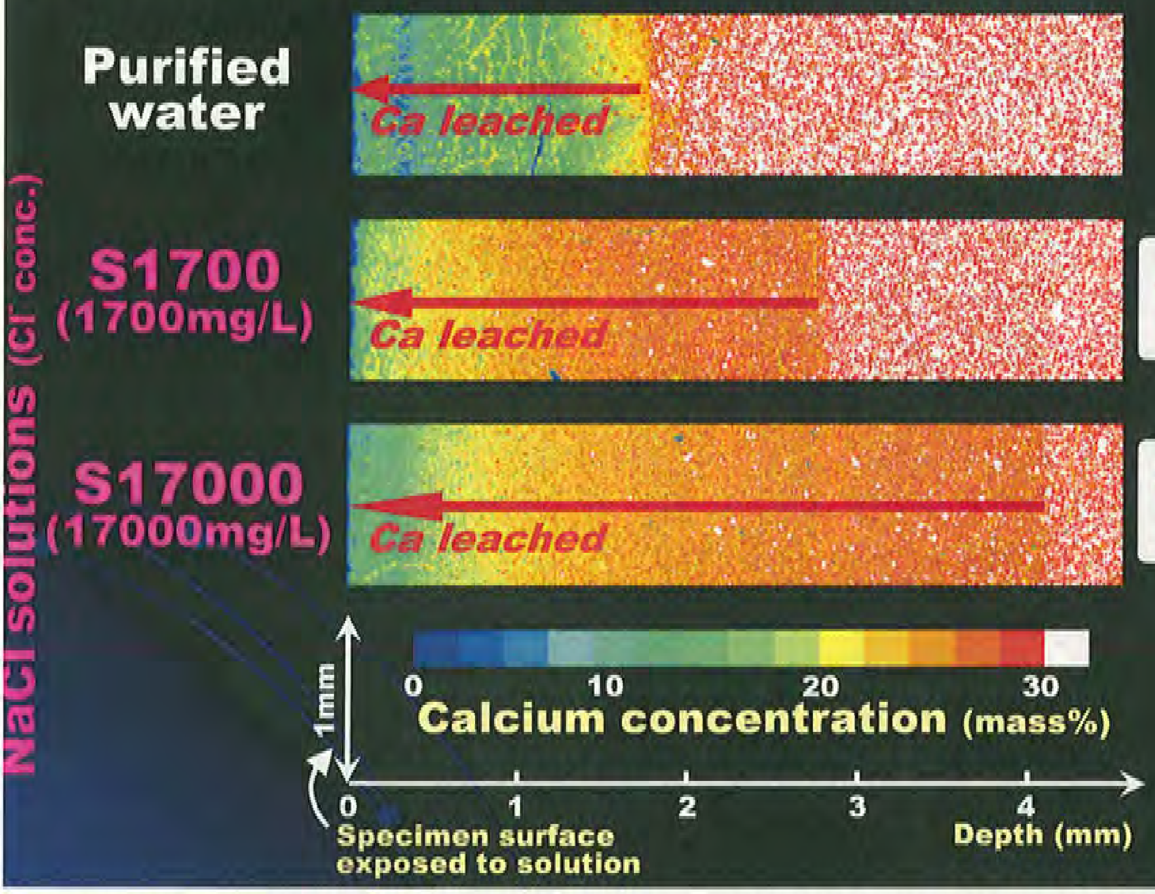
Possible cause:

Higher ionic strength of solution

Higher solubility of Portlandite ($Ca(OH)_2$), etc

NaCl solutions

Ca distribution in specimens immersed for one year



Accelerated Ca leaching

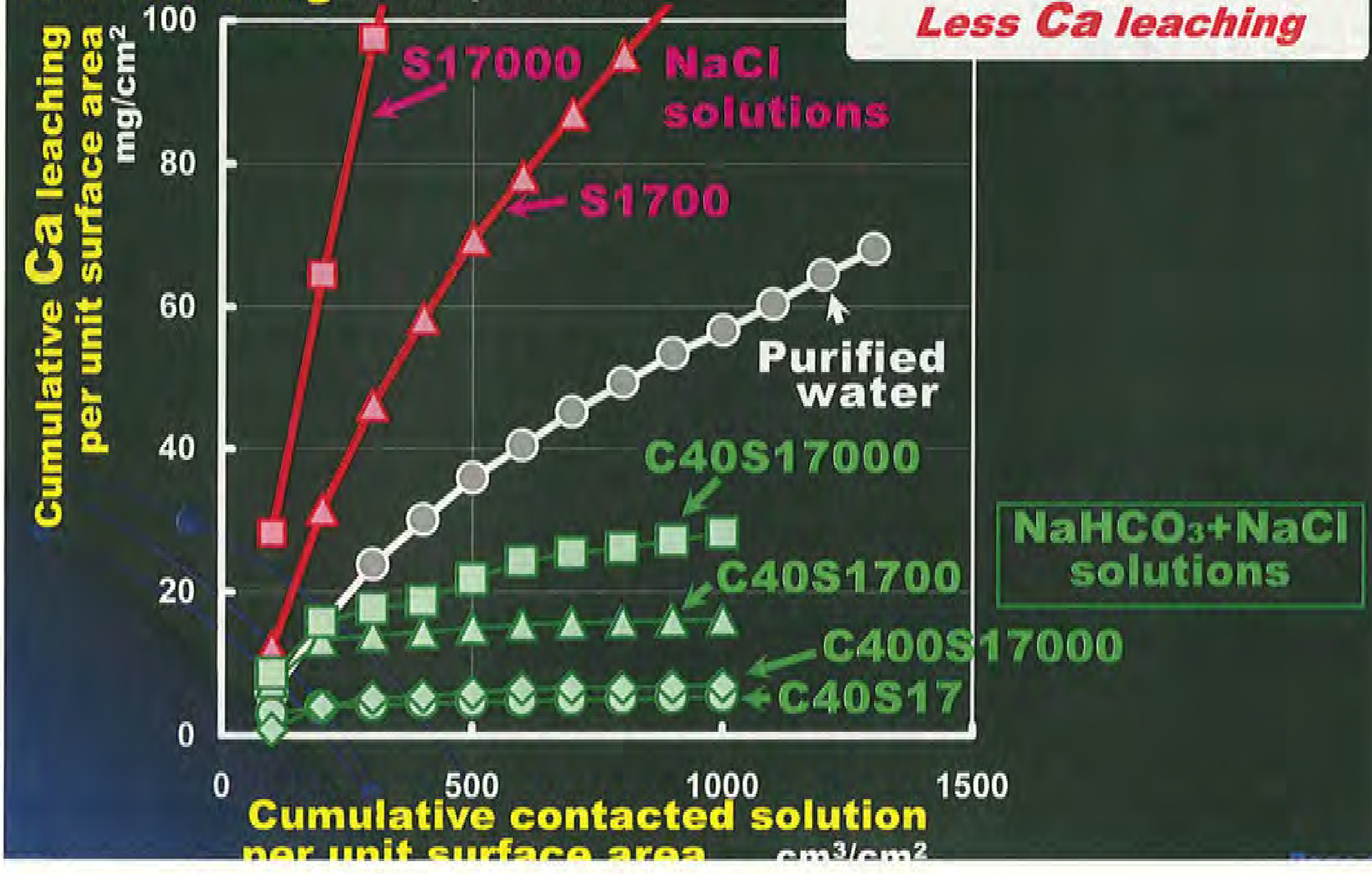
Accelerated Ca leaching

NaHCO$_3$ + NaCl solutions

Ca leaching from specimens

Higher conc. of HCO$_3^-$

Less Ca leaching



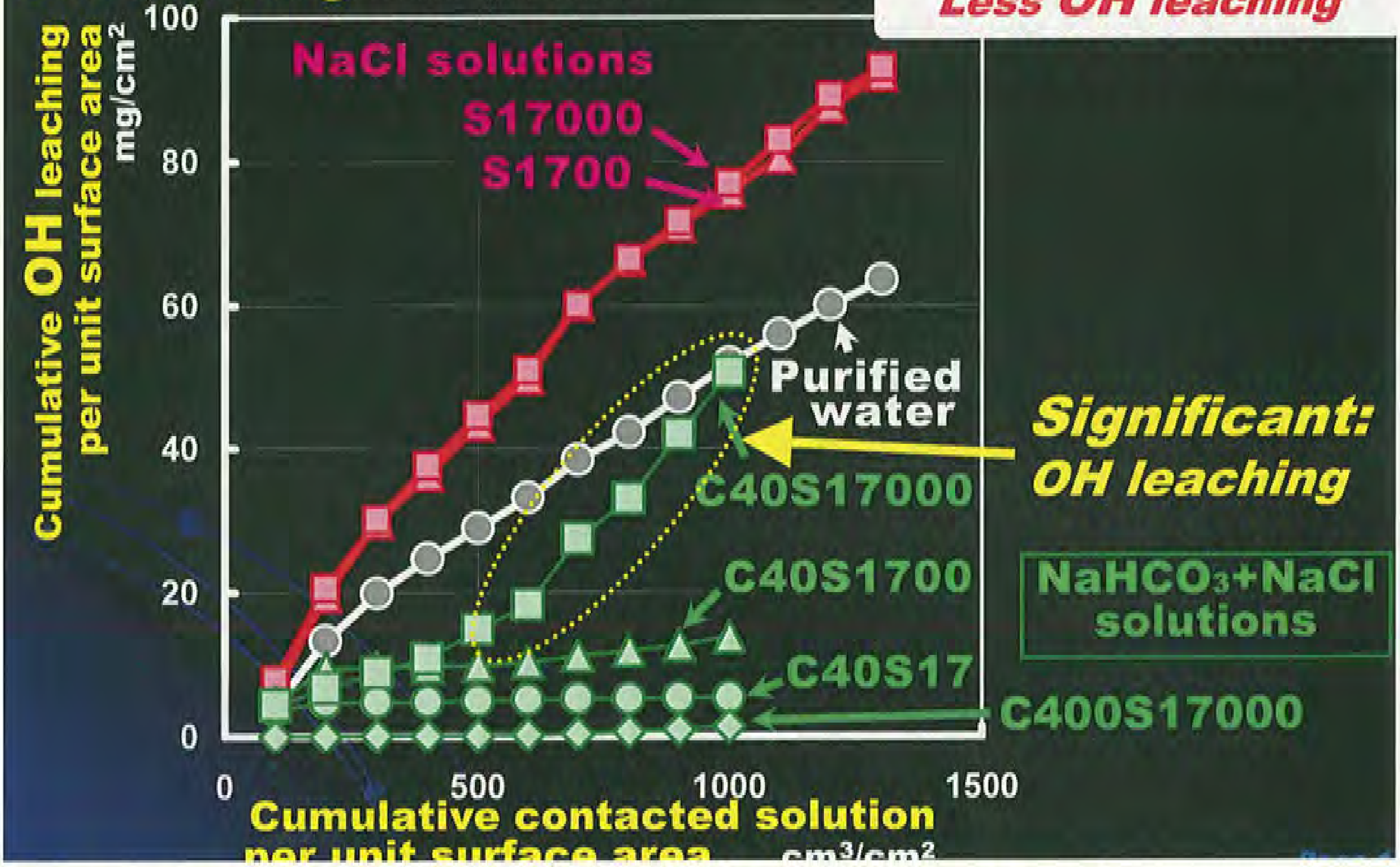
C75

NaHCO3 + NaCl solutions

***OH leaching** from specimens*

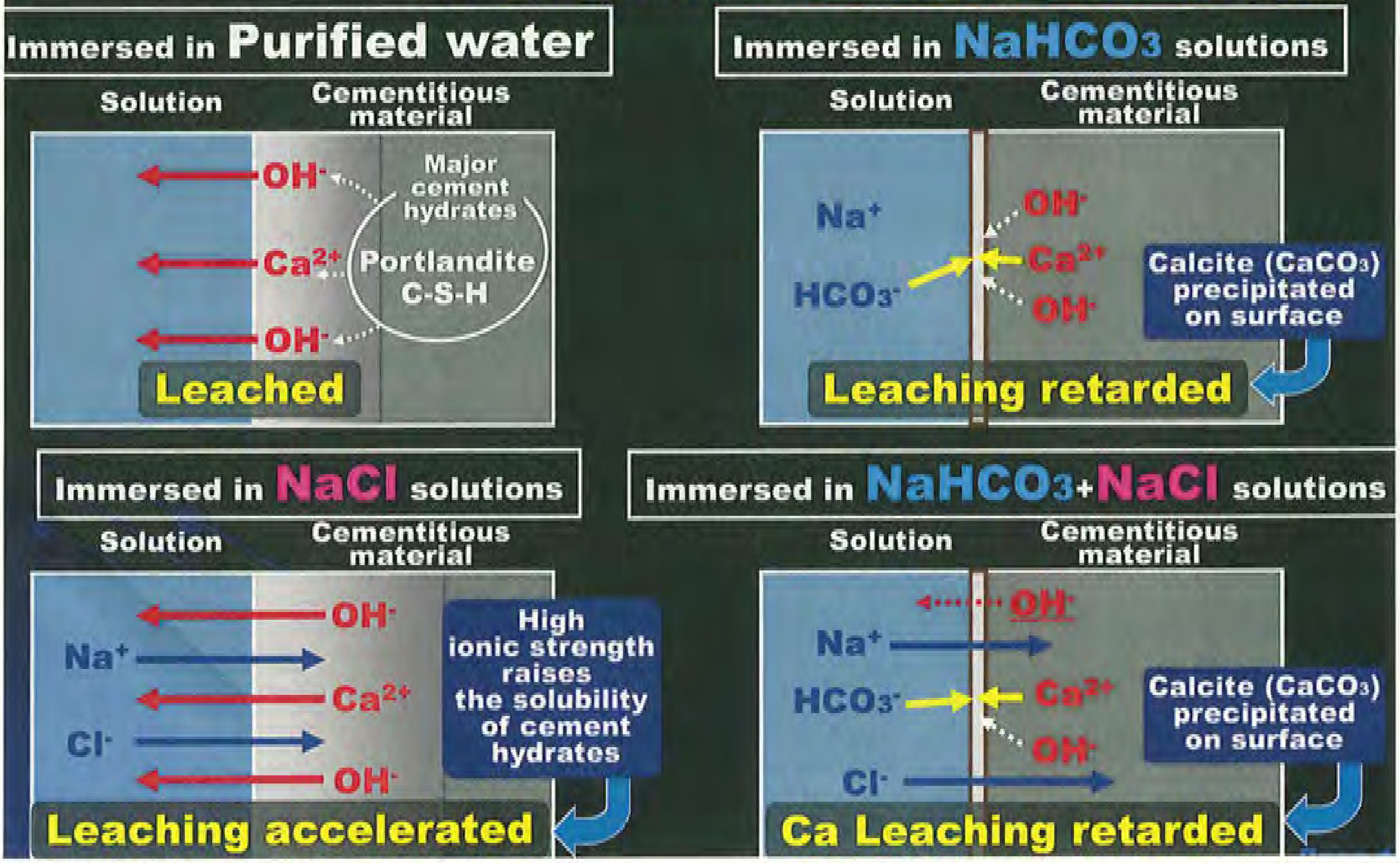
Higher conc. of HCO_3^-

Less OH leaching



Significant: OH leaching

◆ *Conceptual leaching mechanism in solutions with HCO_3^- or/and Cl^-*



Immersed in Purified water

Leached

Immersed in NaHCO3 solutions

Calcite ($CaCO_3$) precipitated on surface

Leaching retarded

Immersed in NaCl solutions

High ionic strength raises the solubility of cement hydrates

Leaching accelerated

Immersed in NaHCO3+NaCl solutions

Calcite ($CaCO_3$) precipitated on surface

Ca Leaching retarded

Conclusions

☑ The denser HCO_3^- (4-400mg/L),
the more retarded the leaching
because of calcite precipitated
on the surface of specimens
by reaction of Ca^{2+} with HCO_3^-.

☑ The denser NaCl (Cl^-:1700-17000mg/L),
the more accelerated the leaching
because of raised solubility of cement hydrates
by higher ionic strength of solution.

☑ Ca leaching of specimens immersed in mixed solution
of HCO_3^- (40-400mg/L) and Cl^- (17-17000mg/L) was retarded.
However, the dense Cl caused
OH leaching increasingly.

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Associate Professor **M. Hisada**
of Tohoku University,
Associate Professor **T. Ishida**
of the University of Tokyo

Thank you.

Merci.

ありがとうございました。

K.3：Paper－Changes of Pore Structure and Ionic Diffusivity of Hardened Cement Paste Exposed to Conditions at Several Levels of Temperature and Humidity

1st International Conference on Microstructure Related Durability of Cementitious Composites
13-15 October 2008, Nanjing, China

CHANGES OF PORE STRUCTURE AND IONIC DIFFUSIVITY OF HARDENED CEMENT PASTE EXPOSED TO CONDITIONS AT SEVERAL LEVELS OF TEMPERATURE AND HUMIDITY

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Abstract

Exposure tests of hardened ordinary Portland cement paste specimens to elevated temperature levels such as 60 or 80°C under humidity conditions at 40, 90%RH, or water immersion were conducted to gain a better understanding of the influence of radioactive decay heat generated in wastes on the performance of a cementitious barrier system for low-level radioactive waste disposal in Japan. The pore structure of cement paste specimens, which were exposed to high temperature conditions, was determined by mercury intrusion porosimetry in order to compare to the change of their ionic diffusivity.

According to the results, it was confirmed that the exposure to low humidity conditions under 60 and 80°C can rough pore structure and increase total pore volume. On the other, it was observed that the high temperature exposure of specimens of W/C=0.35 to higher humidity conditions such as 90%RH or water immersion changes the pore size smaller due to the hydration of unreacted cement but increased the total pore volume. The higher the temperature, the more total pore volume increased. The ionic diffusivity of specimen of W/C=0.35 increased according to the total pore volume.

1. INTRODUCTION

A wide variety of low level radioactive wastes is generated by operation, inspection and decommission of facilities in nuclear power stations and nuclear fuel cycle facilities. For relatively low level wastes, concrete pit disposal has been in full operation [1,10]. Sub-surface disposal for relatively high level wastes is now in designing and assessment phase [11]. For the sub-surface disposal facility, cementitious material is packed in spaces between disposed wastes placed within the concrete pit, and artificial barriers composed of low diffusivity layer (cementitious material) and low water-penetration layer (bentonite material) are located at outside in tunnel at a depth of approx. 50-100m, as shown in Fig.1. The cementitious barrier is expected to absorb nuclides and have low ionic diffusivity to control the transfer of radioactive nuclides. Studies are ongoing on application of binding materials, such as low-heat Portland cement-fly ash based binders and optimal composition of low water-powder ratio [2]. One of most significant tasks on the artificial barrier is to forecast long-term (more than several thousand years) change in their performances. For example, leaching of cement hydrates into the underground water has been pointed out [3,5,6] and its influence on the ionic diffusivity are currently investigated by linked with the porosity change [7,8].

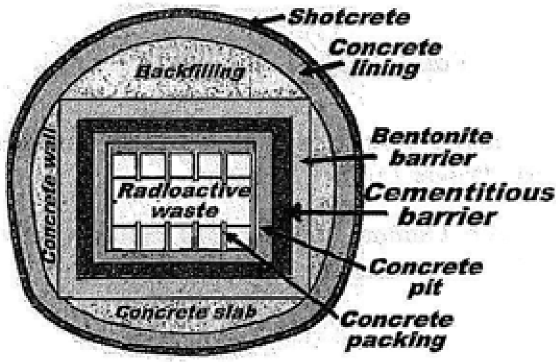


Figure 1: Sketch of current design for sub-surface disposal facility

Considerably large amounts of radioactive nuclides with short life can be contained in wastes to be disposed after now, one of examples being ^{60}Co, which has the half-life of approx. 5.3 years. Wastes might be heated by decay heat from these radioactive elements in certain cases. Accordingly, from the perspective of rationalizing facility design and improving accuracy in safety evaluation, it is necessary to quantitatively analyze the effect of heat from wastes upon the performance of barrier. Although we can find several studies on the effect of temperature conditions on the strength characteristics and on the high temperature loads at several hundred degrees in the fire, no papers discuss on the change of pore structure in the temperature atmosphere of 40-80°C assumed at disposal facilities, and its effect upon the diffusion behavior. Then, the present paper shows experimental findings and analysis concerning change of pore structure of ordinary Portland cement paste specimens when they were exposed to a variety of temperature and humidity conditions and, for a part of specimens, the effect upon the ionic diffusivity.

2. EXPERIMENTAL OUTLINE

2.1 Specimens

Using ordinary Portland cement, we prepared cement paste specimens according to the mix proportions shown in Table 1. Dimensions of specimens are 2x2x8cm for analysis of pore structure and 4x4x4cm for measurement of diffusion coefficient. Specimens were removed from molds 24 hrs. after setting and cured in the 20°C humid air condition (98%RH or higher) up to one year.

Table 1: Mix proportions of cement paste

Cement type	W/C	Code
Ordinary Portland cement	0.35	O35
	0.55	O55

2.2 Conditions of exposure tests

TRU disposal
vs. HLW ? ?

Two-level temperature and three-level humidity condition were set as shown in Table 2. Specimens were exposed to a total of six combinations of abovementioned temperature and humidity conditions for 3, 6 and 12 months. The temperature conditions were selected taking reference from the temperature limit (80°C) on concrete, which were under consideration for TRU waste disposal in Japan, and the temperature limit (65°C) established on the concrete for reactor containment vessels in Japan. We assumed underwater or high humidity environments by underground water and low humidity atmosphere in consideration of the effect of ventilation in tunnel. Temperature changes at the start and termination of exposure tests were taken as 10°C/hr and tests were conducted in globe-boxes in which control of N_2 atmosphere is possible for the purpose to exclude the effect of CO_2 in the atmosphere.

Table 2: Conditions of exposure tests

Parameter	Condition
Temperature	60, 80 °C
Humidity	40, 90%RH, water
Exposure period	3, 6, 12 months

2.3 Analytical tests of specimens

A mercury intrusion porosimeter was employed in the analysis to understand the effect of exposure to a variety of temperature-humidity combination upon pore structure. Samples for the analysis were collected by D-dry pre-treatment for 48 hours of crushed material of about 5mm taken from central part of specimens. The pore size distribution was calculated for a cylindrical model on conditions that the surface tension of mercury was 0.484N/m and the contact angle of the mercury and specimens was 130° in the range of diameter between 3.3nm and 360μm. They were evaluated using the average of two measurements. The pore volume per bulk mass was converted to the volume of pores per bulk volume (cm^3/cm^3) using the bulk density of D-dried specimens.

Thermogravimetric analysis was also conducted to investigate the progress of hydration. The content of Portlandite (g/g-after heating at 950°C) was determined using weight reduction at about 400-500°C.

2.4 Measuring method of diffusion coefficient

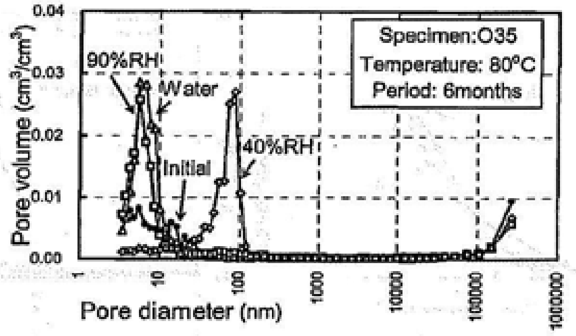
Investigation was conducted concerning the effect of change of pore structure caused by the exposure to high temperature atmosphere upon the diffusion resistance characteristics of hardened cement. The radiocarbon ^{14}C was assumed, which was mentioned as one of governing nuclides for safety evaluation of the radioactive nuclide leakage. As it was widely taken that most of the nuclide is in organic structure, the effective diffusion coefficient of acetate ions (CH_3COO^-) was measured by the steady-state penetration type diffusion test. According to the fact that the most part of sodium acetate is dissociated to CH_3COO^- in the alkaline region, the effective diffusion coefficient was determined by filling the high concentration cell with sodium acetate in hardened cement equilibrium solution, which was adjusted so that the acetate ion concentration was maintained at approx. 2000ppm, and measuring time-dependent change of organic carbon concentration in the low concentration cell (equilibrium solution of hardened cement). Measurements were conducted three times (in 20°C environment) on specimens O35 and O55 (shaped to 30x30x5t mm), which were exposed to the atmosphere of the humidity 90%RH under the high temperature condition of 60°C and 80°C. Its relationship with pore volume was established by using the average of the above-mentioned measurements.

3. RESULTS AND DISCUSSION

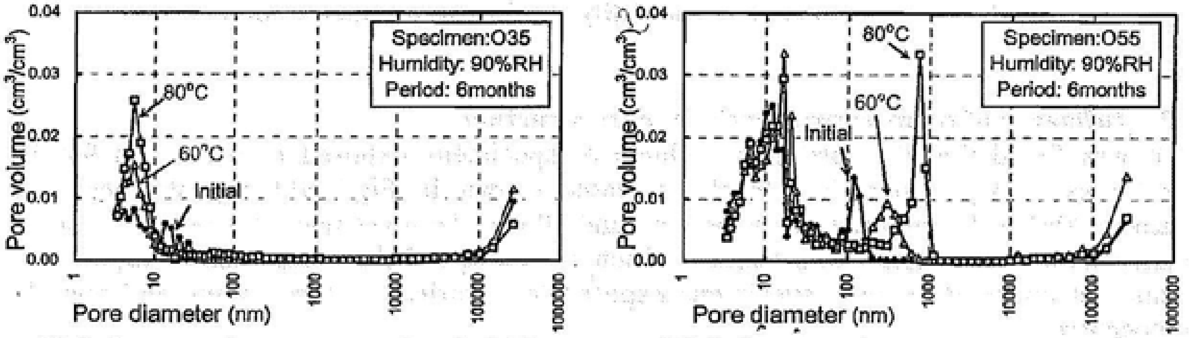
3.1 Evaluation method of pore structure

Fig.2 show typical analytical results on effects of temperature and humidity conditions and W/C on the pore size distribution. It was found that the pore size distribution was significantly varied depending upon exposure conditions and a certain tendency was observed, such as increase and decrease of pore volume in a range of diameter and shift of peak diameters. However, the direct analysis using pore size distribution is rather difficult when more than one peak diameters exist, as the problem of ink bottle effect was pointed out. Evaluation techniques of the pore continuity and independence were recently investigated in certain cases [4], and a finding was drawn that the threshold pore size and the total pore volume might adequately be applied for understanding pore structure since they were associated with pore connectivity [9].

In the present paper, the relationship between the pore diameter and the cumulative pore volume is shown. Change of pore structure are also analyzed with the attention placed upon the threshold pore diameter and the total pore volume. The threshold pore diameter used in the paper means an approximate diameter from which the volume of pores rapidly rises, although it is a qualitative judgment. It is shown in Fig.2 that a small volume of pores are observed for diameters greater than approx. 100μm in all specimens but no distinctive characteristics is found in the quantitative scale. As this is apparently affected by tiny air voids and irregularity on the surface of analytical specimens, it was decided to exclude them from evaluation. Then, the cumulative pore volume is determined and evaluated for the range of pore diameters 3.3nm-33μm. The cumulative pore volume was shown in the range of 3.3-1000nm for the cement paste specimens used in the present study because pores with 1000nm-33μm are not found in significant quantity.



(i) Influence of humidity condition, O35

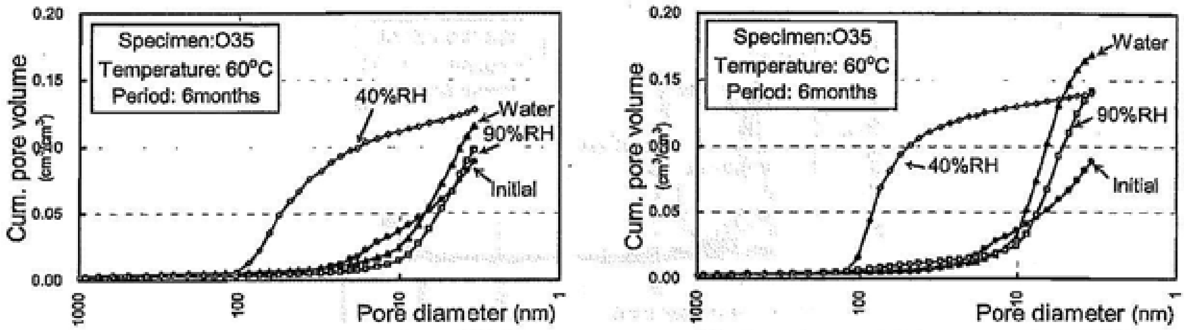


(ii) Influence of temperature level, O35 (iii) Influence of temperature level, O55

Figure 2: Typical analytical results on pore size distribution of specimens exposed to various high temperature conditions

3.2 Influence of humidity conditions on pore structure

Fig.3-(i) shows change of the pore structure of O35 specimens exposed to a variety of humidity conditions at the temperature condition of 60°C for 6 months. When they were compared with initial specimens before exposure test, the threshold pore diameter tended to get smaller in water and 90%RH conditions, whereas the threshold pore diameter shifted to greater side and the total pore volume also increased by exposure to 40%RH atmosphere. Furthermore, the tendency appeared more remarkably by exposure to the atmosphere in 80°C temperature condition as shown in Fig. 3-(ii). When it is assumed that the ink bottle effect is negligible in the gel pores with the diameter less than 3.3 nm, it can be recognized that capillary pores around 10 nm is widely decreased by exposure to the 40%RH atmosphere as shown in Fig.2-(i). Since this change of pore structure was presumably caused by removal of the hydration water from calcium silicate hydrates, if low humidity condition to disposal facilities is envisioned it is necessary to reflect the time-spatial behavior of water removal to the evaluation of the pore structure change when assessing the barrier performance.



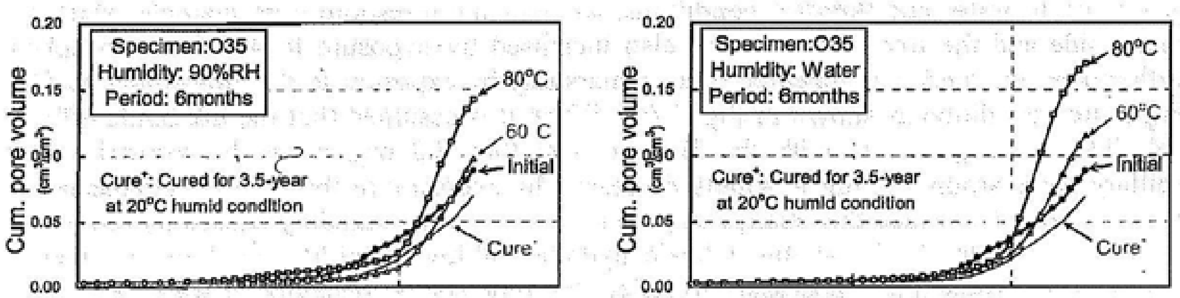
(i) Specimen O35 exposed to 60°C (ii) Specimen O35 exposed to 80°C

Figure 3: Influence of humidity conditions on pore structure

3.3 Influence of temperature levels on pore structure

It was found that the total pore volume of specimens exposed to water and 90%RH conditions in any temperature levels increased shown in Fig.3 although the peak pore diameter shifted to smaller size, namely around 10 nm. To investigate this phenomenon, we analyzed the pore structure of specimen, which was cured in 20°C humidified air for up to 3.5 years and compared it with specimens exposed to a variety of temperature and humidity atmosphere.

Fig.4-(i) compares it with specimens exposed to the humidity 90%RH conditions. The threshold pore diameter and total pore volume of specimen cured for a long period are smaller than those of specimen cured in 20°C humid condition for one year. On the contrary, the total pore volume of specimens exposed to high temperature atmosphere of 60 and 80°C under the condition of humidity 90%RH for six months increased as described above. The tendency was similar in the case of exposure to water, which presented superior water supply condition and the tendency was more remarkable (Fig.4-(ii)).



(i) Specimen O35 exposed to 90%RH (ii) Specimen O35 immersed in water

Figure 4: Influence of temperature levels on pore structure

Furthermore, Fig.5 shows the effect of exposure period on the change of pore structure when the specimen O35 was exposed to 80°C-90%RH condition. The increasing tendency of total pore volume is shown in Fig.5 when the exposure period is elongated. Concerning to phenomena of increased total pore volume in the condition that the water is supplied with ease as shown above, it is conceivable that unreacted cement hydrates to form different pore structure and change of structural form is caused by some cement hydrates, including C-S-H, under the influence of high temperature loads, dissimilar to the transition to coarse pore structure led by the removal of hydration water under low humidity.

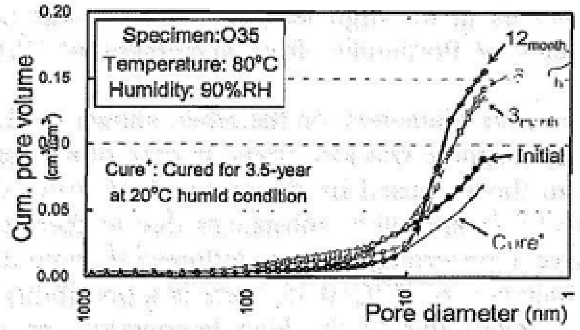


Figure 5: Influence of exposure periods on change of pore structure

Then, contents of Portlandite measured for the purpose to find the degree of hydration were compared in Fig.6. Increased contents of Portlandite were shown by specimens cured in a long period and specimens exposed to any temperature-humidity atmosphere. As a result of comparison of the effect of exposure period on specimens exposed to 80°C-90%RH condition, we cleared that Portlandite contents was increased along the progress of exposure. It is suggested from theses findings that the compositional structure of cement hydrates formed under the high temperature (60°C or 80°C) and high humidity (90%RH or submerged), such as C-S-H is different from that of products formed in 20°C humid condition and it is conceivable that one of causes is increased capillary pores smaller than approximately 10 nm by formation of organizational structure that contains smaller pores.

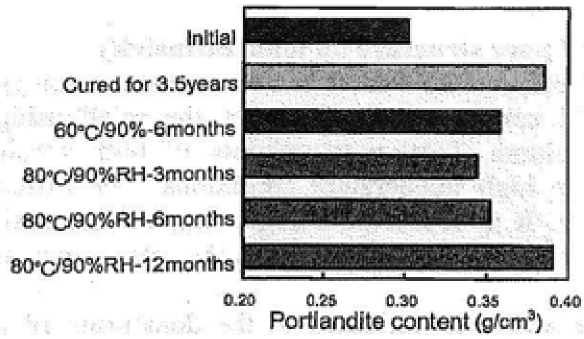


Figure 6: Change of Portlandite content of Specimen O35

Fig.7 shows change of pore structure of W/C=0.55 specimens exposed to a variety of temperature and humidity conditions. As compared with results of W/C=0.35 shown in Fig.4-(i), it is characteristic that the threshold pore diameter was shifted to larger diameters when the exposure temperature was raised. Little remarkable change was found in capillary pores of 10 nm or smaller under the condition of W/C=0.55 from also the pore size distribution shown in Fig.2-(iii), provided that the ink bottle effect in the gel pores was neglected. The hydration was sufficiently advanced on W/C=0.55 specimens during the 20°C humid atmospheric curing for one year with little amount of cement left as unreacted. It is conceivable that, therefore, volume increase of pores with diameters smaller than 10 nm caused by formation of C-S-H and similar substances in the high temperature load was not remarkably observed. Actually, increased contents of Portlandite from specimens of W/C=0.55 after curing was comparatively small.

The increased threshold pore diameters, on the other, shown by the specimen O55 exposed to the humidity 90%RH atmosphere was also found in case of submerging exposure, showing different phenomena from those caused by the removal of water described in Section 3.2. Similarly, denaturing of C-S-H and other substances due to thermal loads is pointed out as one of causes for the above. Concerning changes of threshold pore diameter in different order from that of denaturing behavior of W/C=0.35, there is a possibility that varied hydrates and pore structure from W/C levels due to the high temperature exposure based on different mechanisms.

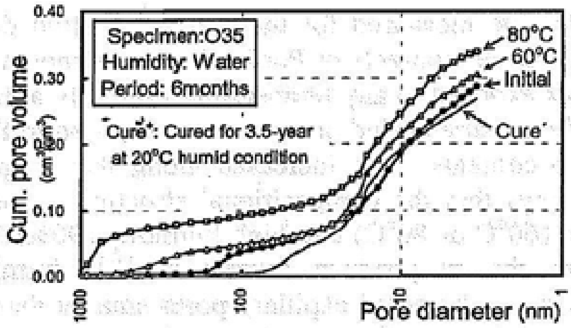


Figure7: Change of pore structure of specimen O55

3.4 Influence of changes of pore structure on ionic diffusivity

The effective diffusion coefficient of acetate ion was measured on specimens exposed to 60 and 80°C under 90%RH conditions. Fig.8 shows the relationship between diffusion coefficient and total pore volume. Total pore volumes of both specimens O35 and O55 increased by the exposure to high temperature conditions. The diffusion coefficient also showed tendency of increase. It is found from Fig.8 that the increasing rate of diffusion coefficient by the high temperature load is greater than the rate of increase by the increase of water to cement ratio.

It is conceivable that the above is attributed to the denaturing of C-S-H, which forms hardened cement matrix by the high temperature loads, as shown by the remarkable volume increase of pores with diameter less than approx. 10 nm in the pore structure analysis (Fig.4-(i)). Namely, this is affected by the fact that the pore structure with small tortuosity and relatively high connectivity characteristics was formed by increased porosity of matrix itself.

On the other, it would be comparable with the dependency of increase of diffusion coefficient by increase water to cement ratio upon the increase of more coarse capillary pores and its tortuosity characteristics. Additionally, it is not deniable that fine cracks of the order of nm may be formed by the high temperature loads. Authors view that the more detailed analysis is required for understanding of the effect of high temperature loads on the diffusion behavior of ions.

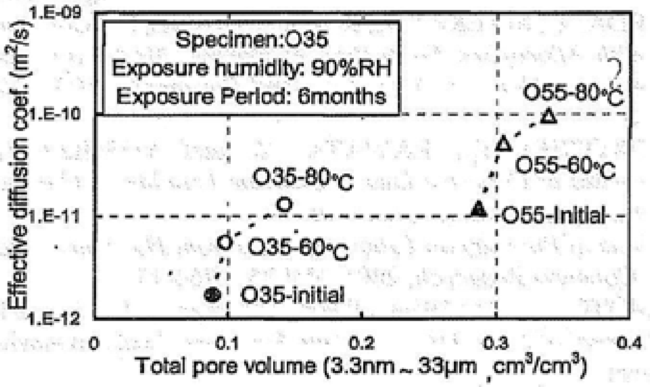


Figure 8: Relationship between total pore volume and effective diffusion coefficient

4. CONCLUSIONS

The followings are found within the range of the present experimental condition by exposure of W/C=0.35 ordinary Portland cement paste specimens to a variety of temperature and humidity conditions, analysis of pore structure using the mercury intrusion porosimeter and steady-state penetration type diffusion tests on acetate ions:

(1) The threshold pore diameter of W/C=0.35 and 0.55 specimens shifted to larger size and the total pore volume were increased by exposure of them to the high temperature (60 and 80°C) and low humidity (40%RH) condition.

(2) In case of W/C=0.35, the capillary pores of approx. 10 nm or smaller and the total pore volume were increased along the period of exposure to the high temperature humid atmosphere (60 and 80°C at 90%RH) even when the water was sufficiently supplied to specimens (in water). This change of pore structure suggested possible formation of hydrates with different structure by hydration of unreacted cement under the high temperature, in addition to denaturing of cement hydrates such as C-S-H. This is taken as a possible cause.

(3) As a result of the diffusion test, the total pore volume and the effective diffusion coefficient of OPC specimens exposed to the humidity 90%RH were increased due to the high temperature loads.

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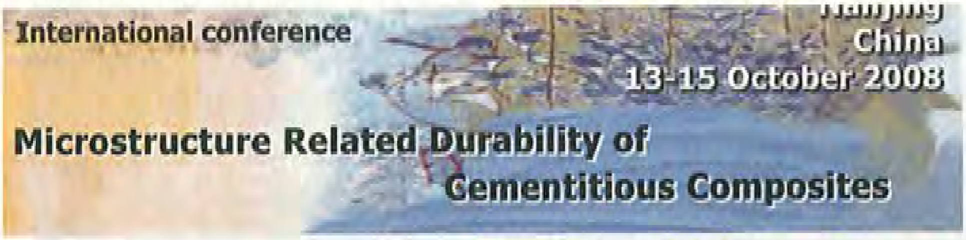
K.4：Slides－Changes of Pore Structure and Ionic Diffusivity of Hardened Cement Paste Exposed to Conditions at Several Levels of Temperature and Humidity



International conference

Nanjing
China
13-15 October 2008

Microstructure Related Durability of
Cementitious Composites

14:50-15:10, 14th October 2008
Parallel Session 15 -
Novel Experimental Techniques
(Chair: Yong Yuan)
Location: Violet Hall, Zijin Building

Changes of Pore Structure and Ionic Diffusivity of Hardened Cement Paste Exposed to Conditions at Several Levels of Temperature and Humidity

I.KURASHIGE, T.YOSHIDA, T.CHIDA and M.HIRONAGA
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CRIEPI Central Research Institute of Electric Power Industr

CRIEPI was established in 1951 as a Japanese nonprofit public benefi
corporation to undertake research and development activities relate
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broad range of topics, guided by its mission of achieving energy
security and addressing global environmental issues.

Presentation outline

Keywords: Radioactive waste disposal, Cementitious barrier, Barrier performance, Thermal alteration, Pore structure, Ionic diffusivity

1. **Overview of radioactive waste disposal in Japan**
   - ***1.1 Waste classification and disposal methods in Japan***
   - ***1.2 Current research tasks on cementitious barrier for the sub-surface disposal***
2. **Results of baseline experimental study on "Alteration of cementitious material due to thermal attack and change of barrier performance"**
   - ***2.1 Overview of Experimental methods and conditions***
   - ***2.2 Results of MIP measurement of pore structure and discussion about change mechanisms***
   - ***2.3 Results of ionic diffusivity measurement and discussion about relationship between pore structure and diffusivity***

Classification & disposal methods of radioactive waste in Japan

Waste class				*Waste example*	*Disposal method*
Waste from Fuel Nuclear Cycle Facilities	Waste from NPPs*	Waste below clearance level		Most waste from decommissioning NPPs	Recycling/disposal as non-radioactive materials
		LLW (Low-level radioactive waste)	Very low-level	Concrete, metal, etc.	Near-surface disposal without engineered barrier
			Relatively low-level	Solidified liquid waste, filter, spent equipment, consumables, etc.	Near-surface disposal with engineered barrier (bentonite)
			Relatively high-level	Solidified control rod, core-internals, liquid waste, spent equipments, etc.	***Sub-surface disposal*** with engineered barriers (bentonite & cementitious material)
			Waste including relatively much volume of long half-lifetime nuclides	Solidified fuel assembly parts, etc.	Geological disposal
		HLW (High-level radioactive waste)		Vitrified waste	

**NPP: Nuclear Power Plant*

Partly under discussion

What is the sub-surface disposal in Japan ?

⇒ Japanese-unique method

Near-surface disposal (about 10m deep)

at the *Rokkasho* disposal site for relatively lower-levels of LLW

Now in operation

★Sub-surface disposal (about 50-100m deep)

at the *Rokkasho* disposal site for relatively higher-levels of LLW

Now in the design and assessment phase

A type of cementitious member is required to perform as an engineered barrier for a long period

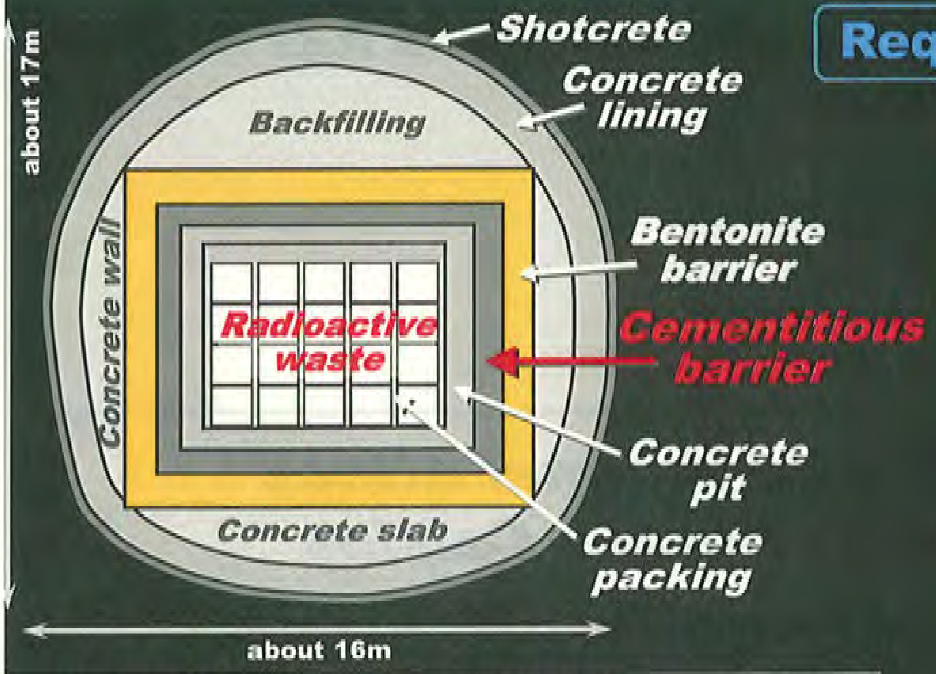
Deep geological disposal (deeper than 300m)

for HLW

Now in the planning and scouting candidate-site phase

Location of Rokkasho village in Japan

Required performance of cementitious materials for the sub-surface disposal in Japan



Sketch of current design for **sub-surface disposal facility** in tunnel at the depth of about 80m

Required performance

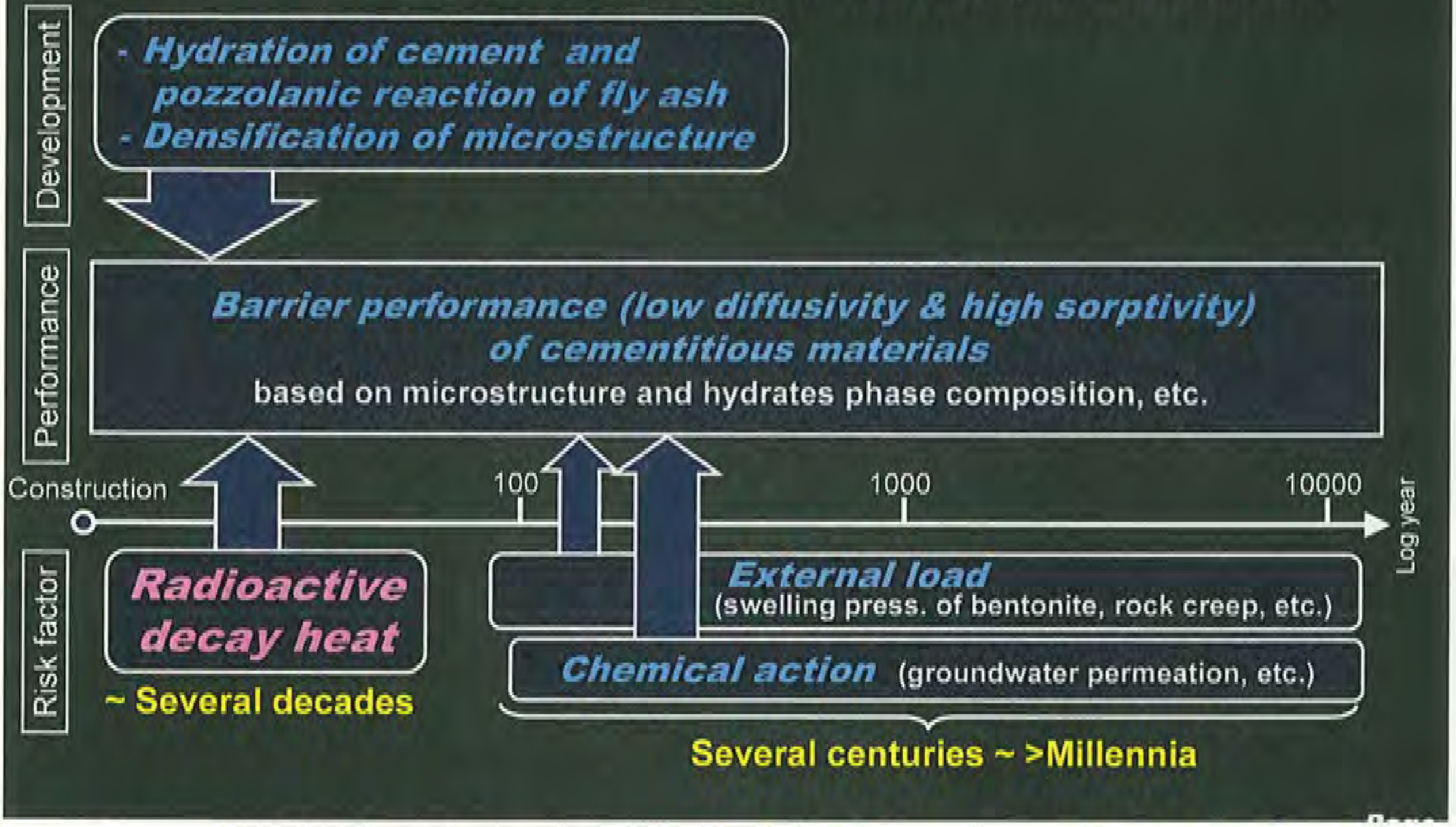
Radionuclide
-*diffusion resistant*
-*sorption capable*
and
Durable
for more than thousands year

Special mixture design

- *-Very low W/P ratio*
- *-Low-heat cement*
- *-Fly ash*
- *-Limestone powder*
- *-Expansive additive*
- *-Super plasticizer*

Current research tasks for the sub-surface disposa

Basic concept of development and deterioration Of cementitious barrier performance



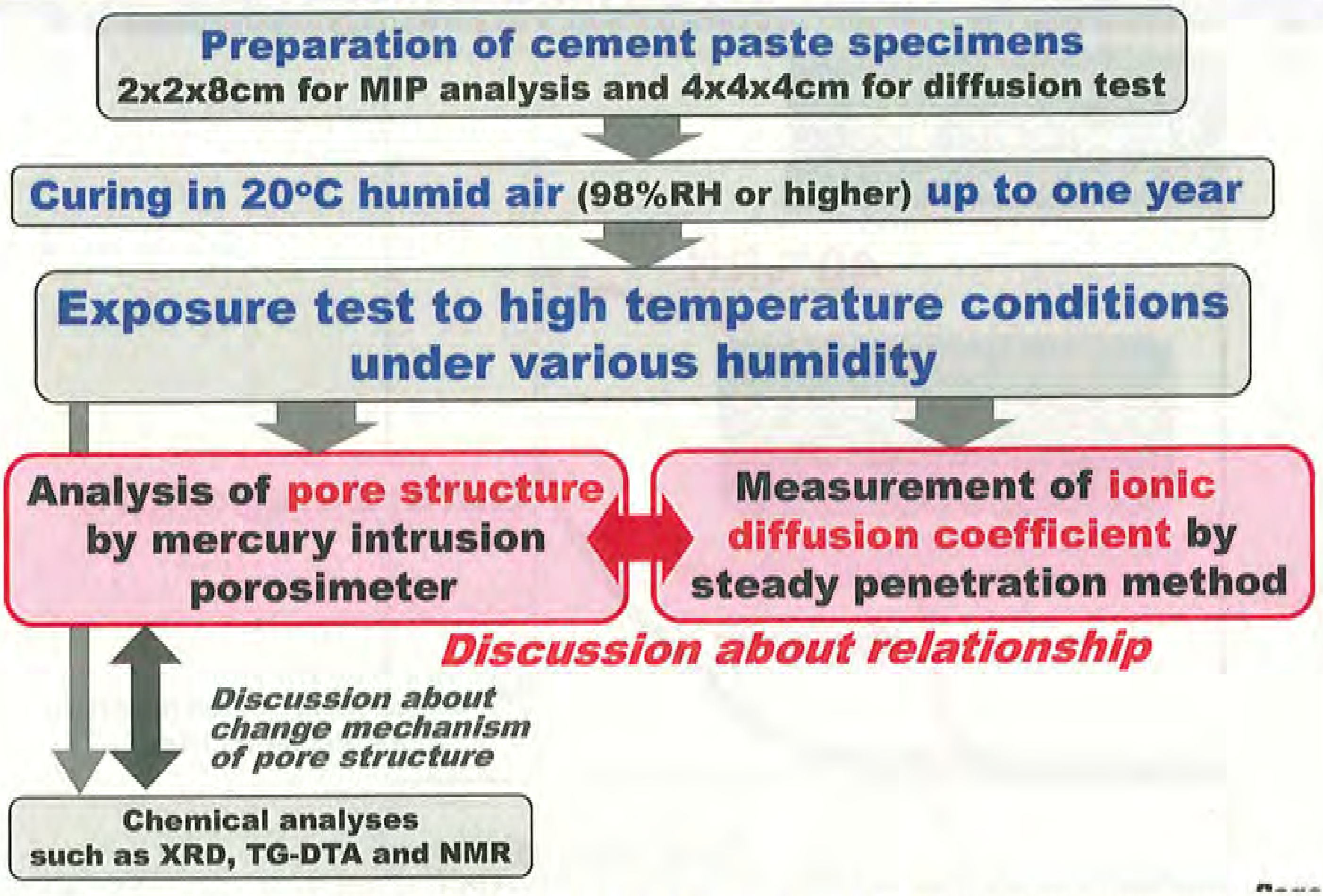
Motivation and viewpoint of the current study

◆ *It is believed that the mild thermal attack below approx. 100 degrees Celsius has **little or no detrimental effect on strength property.***

On the other hand,

◆ ***How** does the mild thermal attack below approx. 100 degrees Celsius **affect the mass transportation property such as ionic diffusivity based on pore structure of cementitious materials?***

Experimental procedure



Preparation of cement paste specimens
2x2x8cm for MIP analysis and 4x4x4cm for diffusion test

Curing in 20°C humid air (98%RH or higher) up to one year

Exposure test to high temperature conditions under various humidity

Analysis of pore structure by mercury intrusion porosimeter

Measurement of ionic diffusion coefficient by steady penetration method

Discussion about relationship

Discussion about change mechanism of pore structure

Chemical analyses such as XRD, TG-DTA and NMR

Experimental conditions

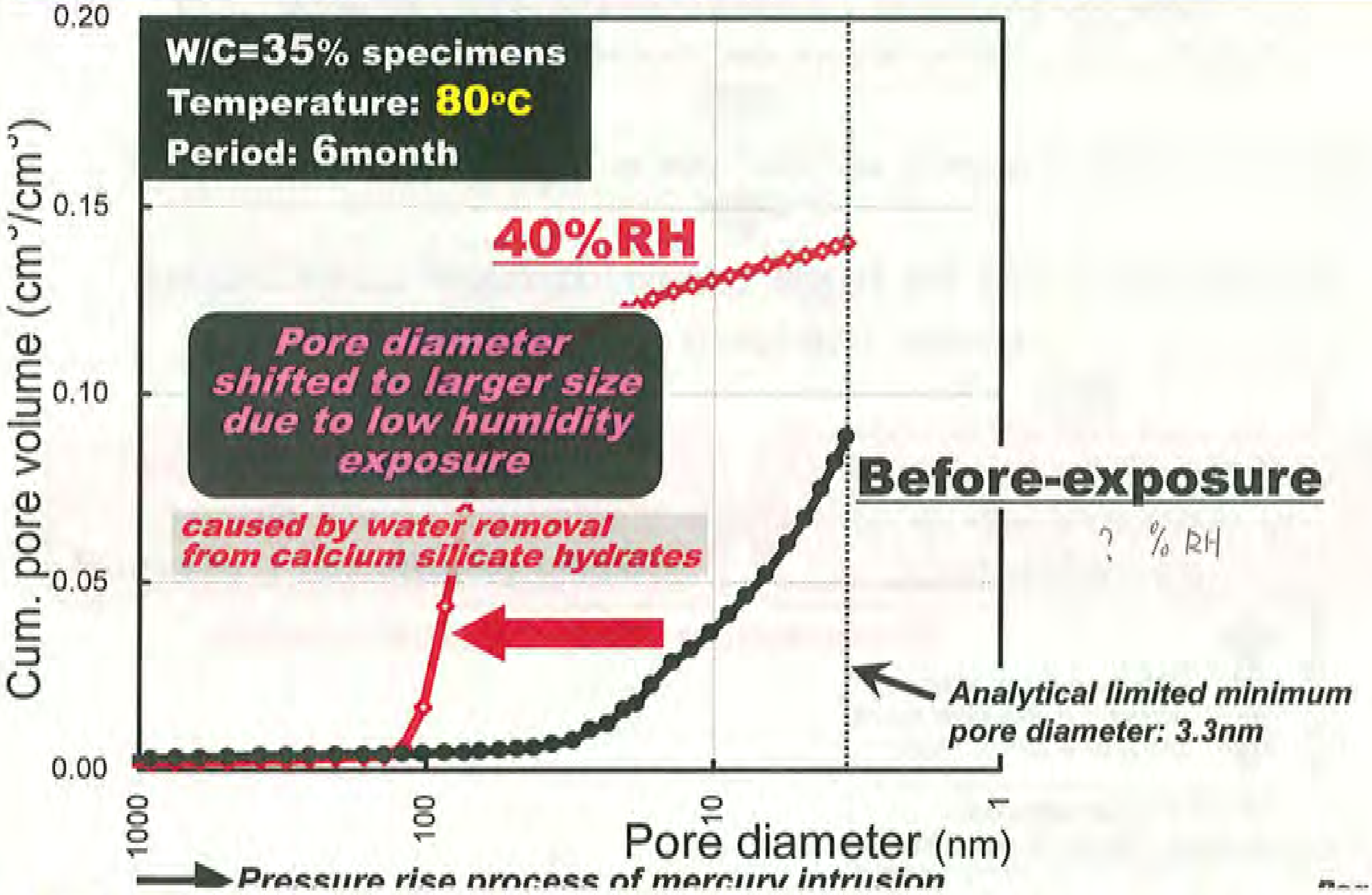
Parameter of cement paste specimens

Cement type	W/C
Ordinary Portland cement	*35 %*
	55 %

Conditions of high-temperature exposure test

Temperature	*60, 80 °C*
Humidity	*40, 90%RH, in water*
Exposure period	*3, 6, 12 months*

Effects of humidity conditions on pore structure change under high-temperature exposure in case of 80°C



W/C=35% specimens
Temperature: 80°C
Period: 6month

Pore diameter shifted to larger size due to low humidity exposure

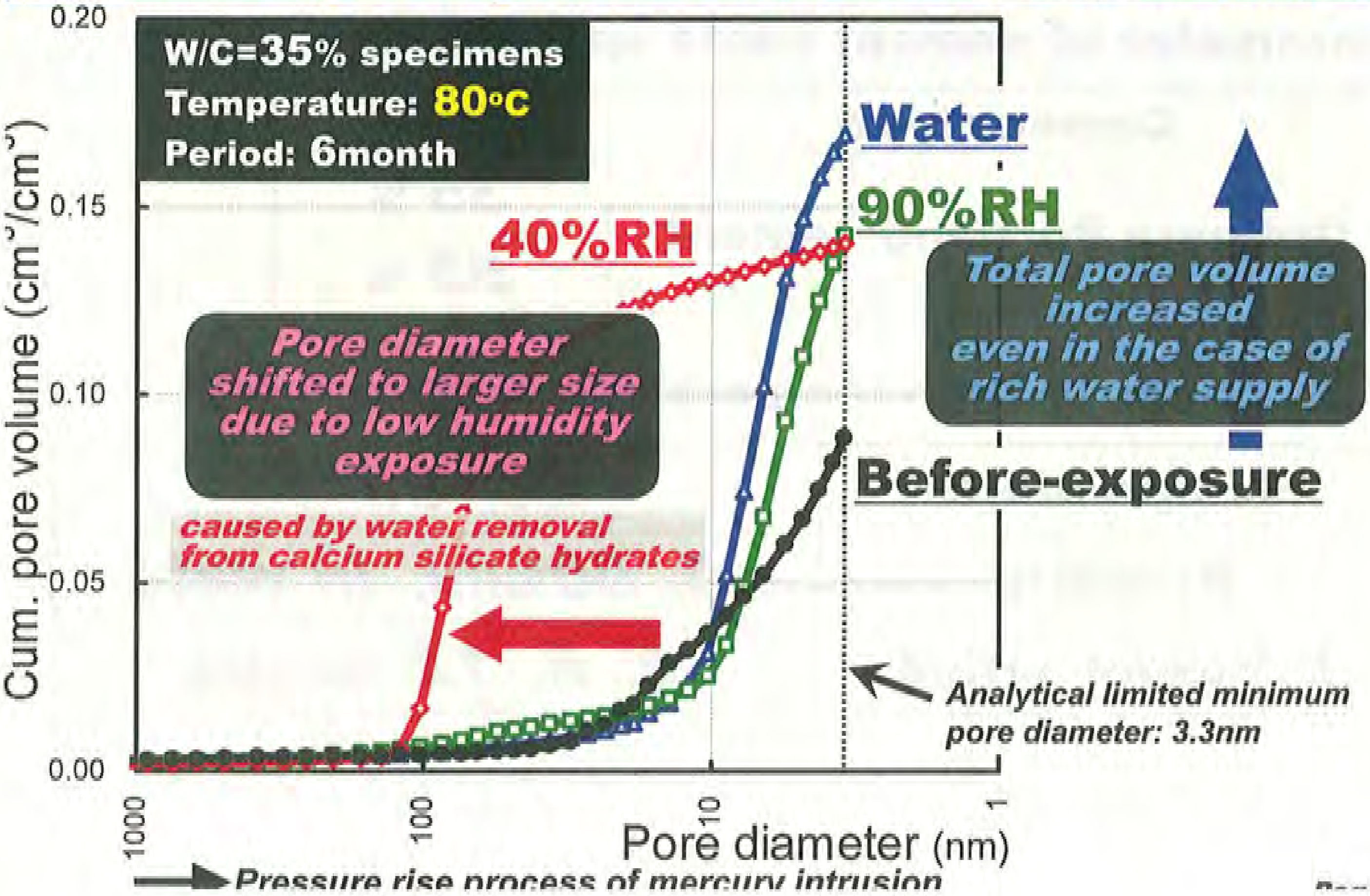
caused by water removal from calcium silicate hydrates

? % RH

Analytical limited minimum pore diameter: 3.3nm

→ *Pressure rise process of mercury intrusion*

Effects of humidity conditions on pore structure change under high-temperature exposure in case of 80°C



W/C=35% specimens
Temperature: 80°C
Period: 6month

Total pore volume increased even in the case of rich water supply

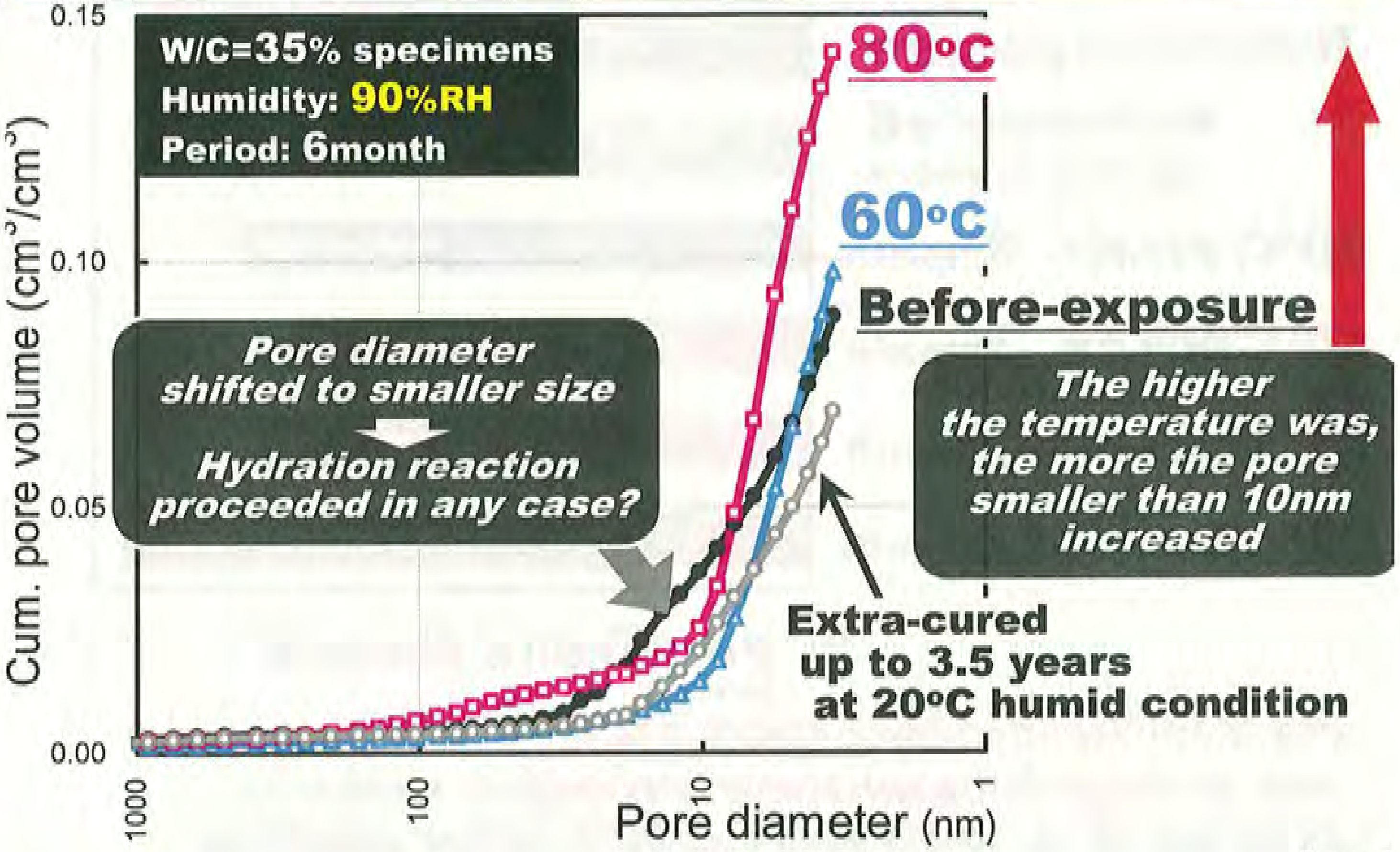
Pore diameter shifted to larger size due to low humidity exposure

caused by water removal from calcium silicate hydrates

Analytical limited minimum pore diameter: 3.3nm

→ *Pressure rise process of mercury intrusion*

Effects of temperature on pore structure change under exposure in case of 90%RH



W/C=35% specimens
Humidity: 90%RH
Period: 6month

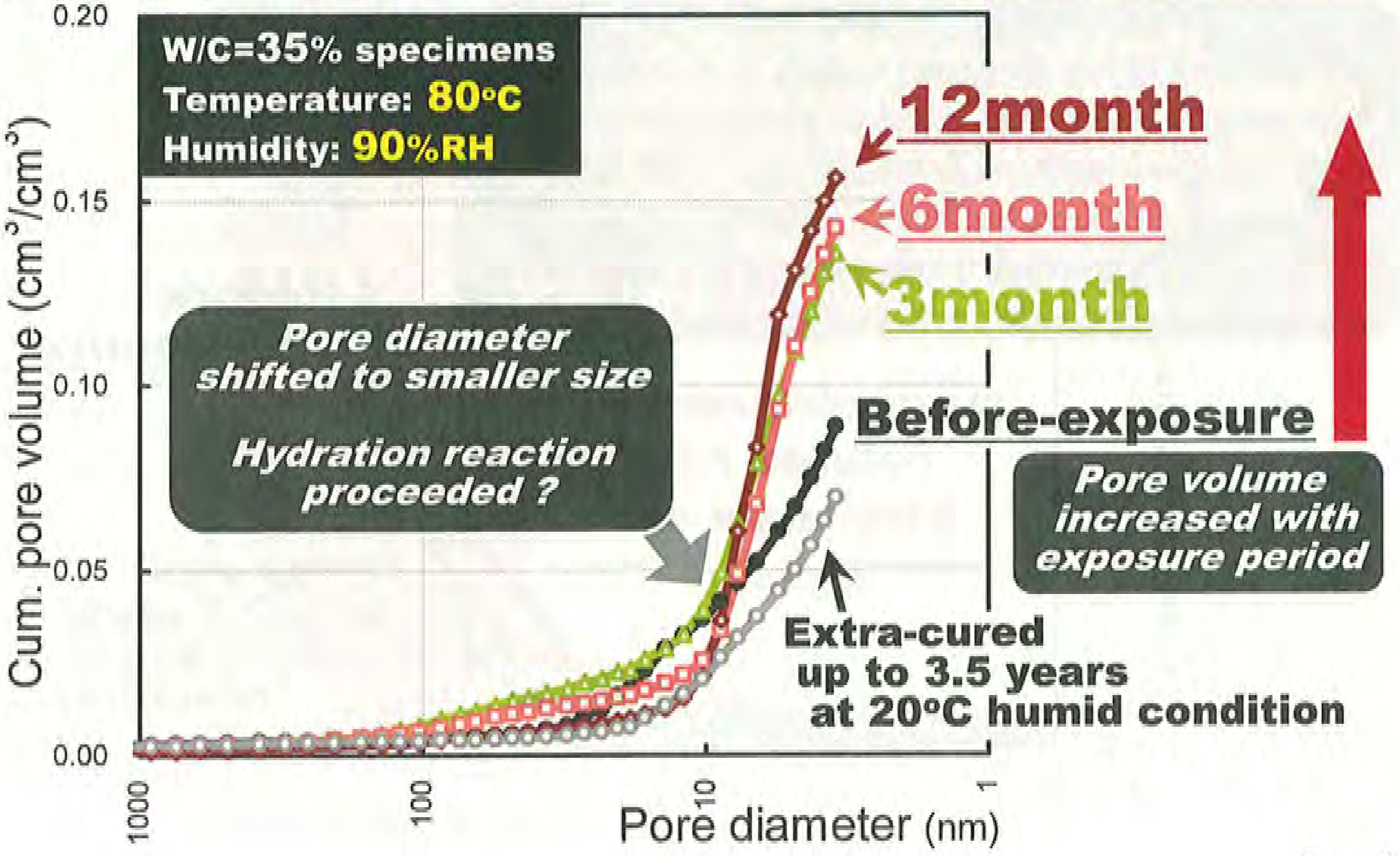
Pore diameter shifted to smaller size

Hydration reaction proceeded in any case?

The higher the temperature was, the more the pore smaller than 10nm increased

Extra-cured up to 3.5 years at 20°C humid condition

Effects of exposure periods on pore structure change under exposure at a 80°C/90%RH condition



W/C=35% specimens
Temperature: 80°C
Humidity: 90%RH

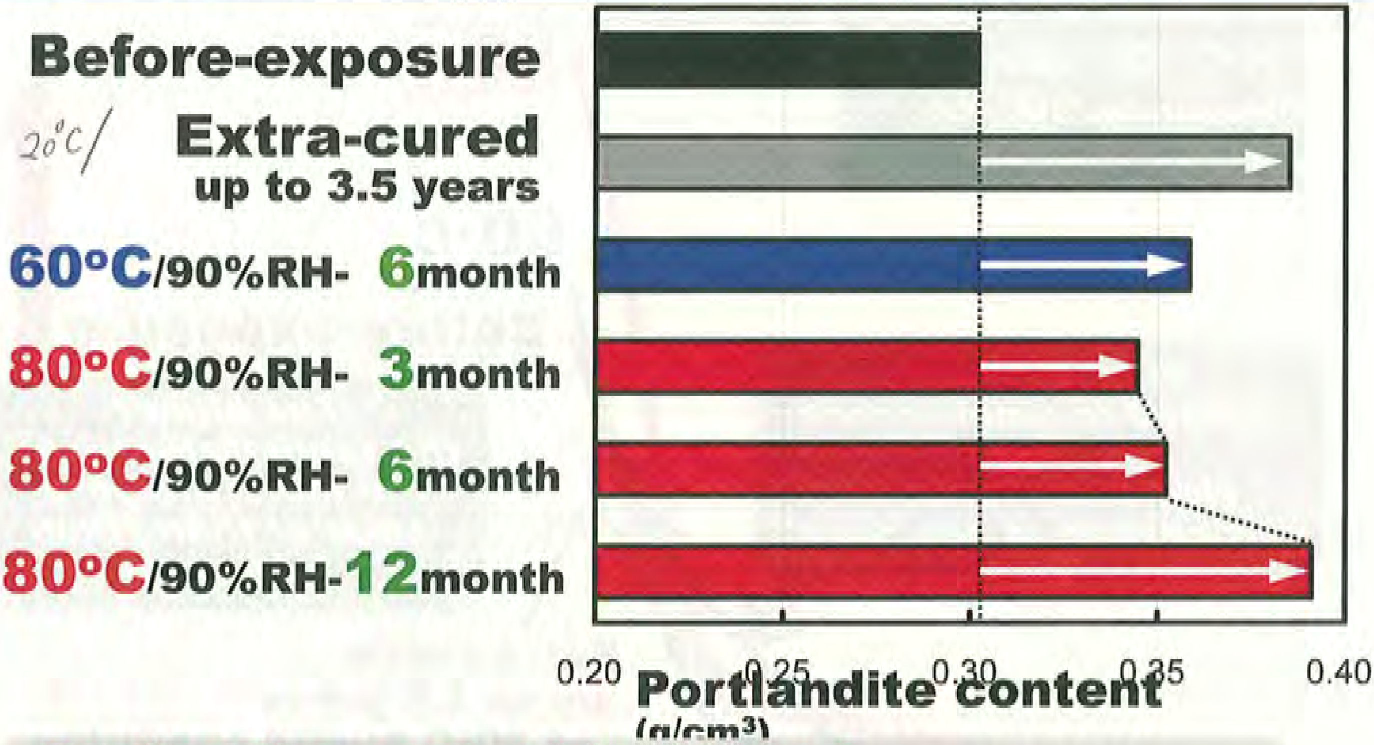
Pore diameter shifted to smaller size

Hydration reaction proceeded ?

Pore volume increased with exposure period

Extra-cured up to 3.5 years at 20°C humid condition

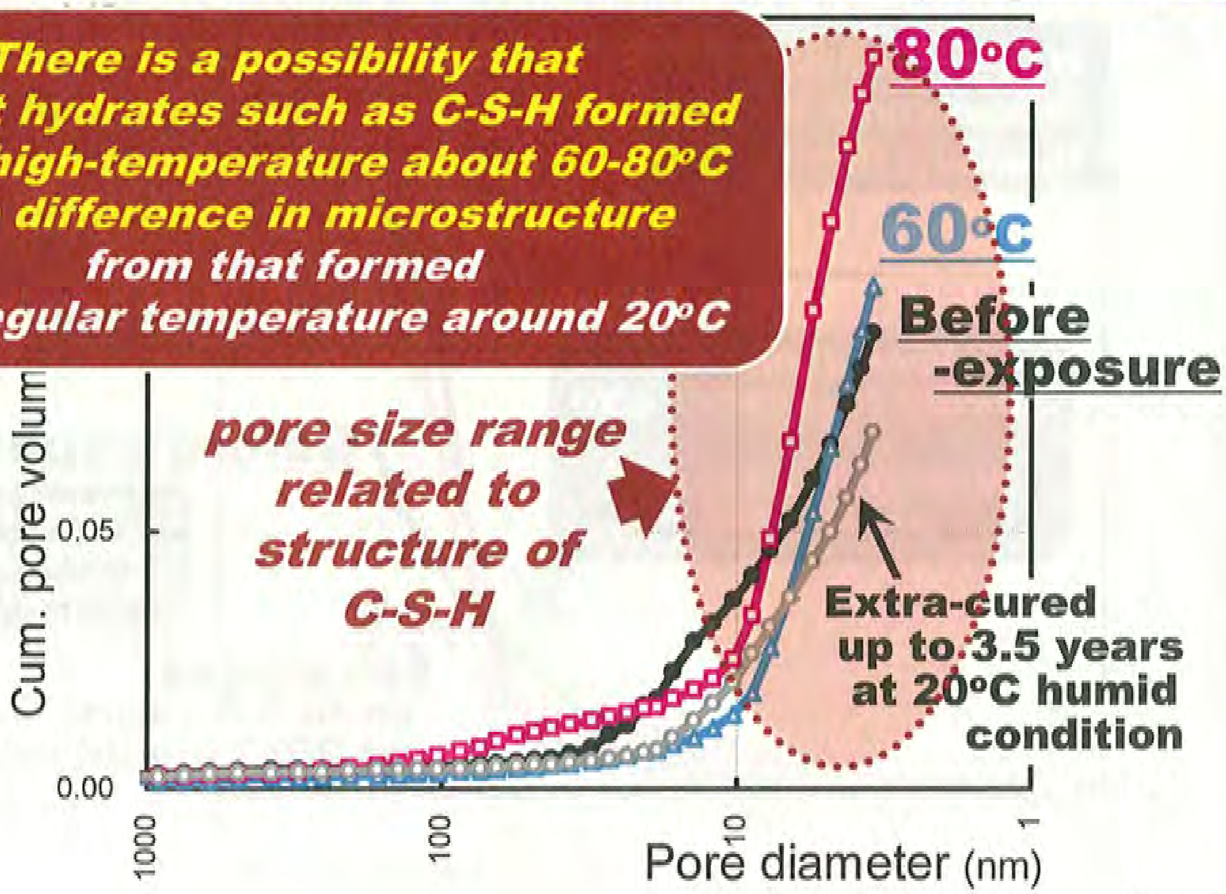
Changes of Portlandite $Ca(OH)_2$ content due to high-temperature exposure



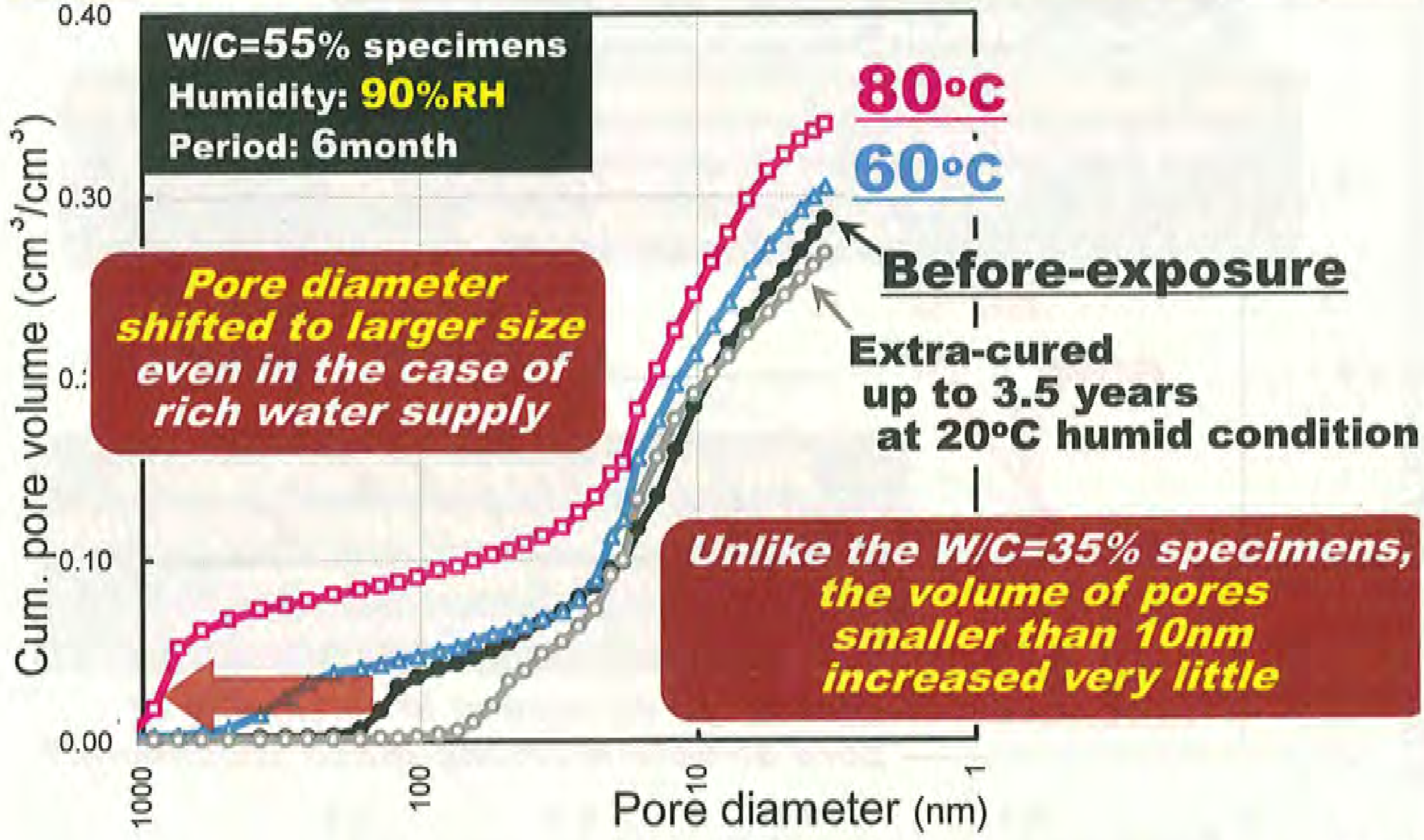
***Portlandite content increased due to high-temperature exposure** similar to extra-cured up to 3.5 years at 20°C humid condition*

Discussion about increase of total pore volume and fine pore volume smaller than 10nm due to high-temperature exposure

There is a possibility that cement hydrates such as C-S-H formed under high-temperature about 60-80°C have difference in microstructure from that formed under regular temperature around 20°C



Pore structure change due to high-temperature exposure: Case of W/C=55% specimens



W/C=55% specimens
Humidity: 90%RH
Period: 6month

80°C

60°C

Before-exposure

Extra-cured up to 3.5 years at 20°C humid condition

Pore diameter shifted to larger size even in the case of rich water supply

Unlike the W/C=35% specimens, the volume of pores smaller than 10nm increased very little

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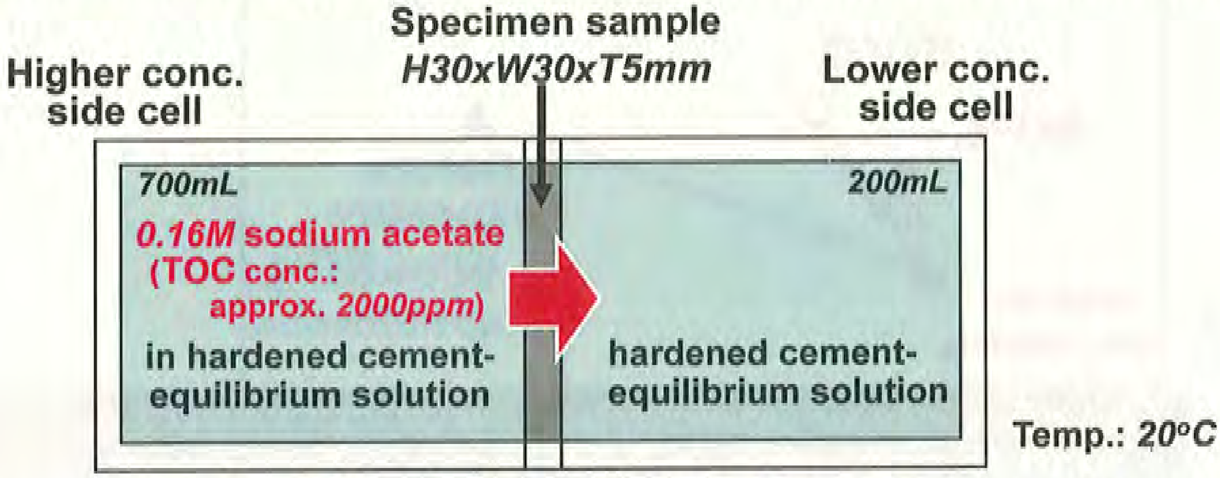
Measuring method of effective diffusion coefficient of organic carbon (acetate ion)

Q. Why acetate ion used?

How to perform

A. It is assumed that ^{14}C (half-life period: approx. 5730 years) is one of the dominant nuclides on leakage assessment and ^{14}C exists as organic in supposed underground environment.



Specimen sample
H30xW30xT5mm

Higher conc. side cell

700mL
0.16M sodium acetate
(TOC conc.:
approx. *2000ppm*)
in hardened cement-equilibrium solution

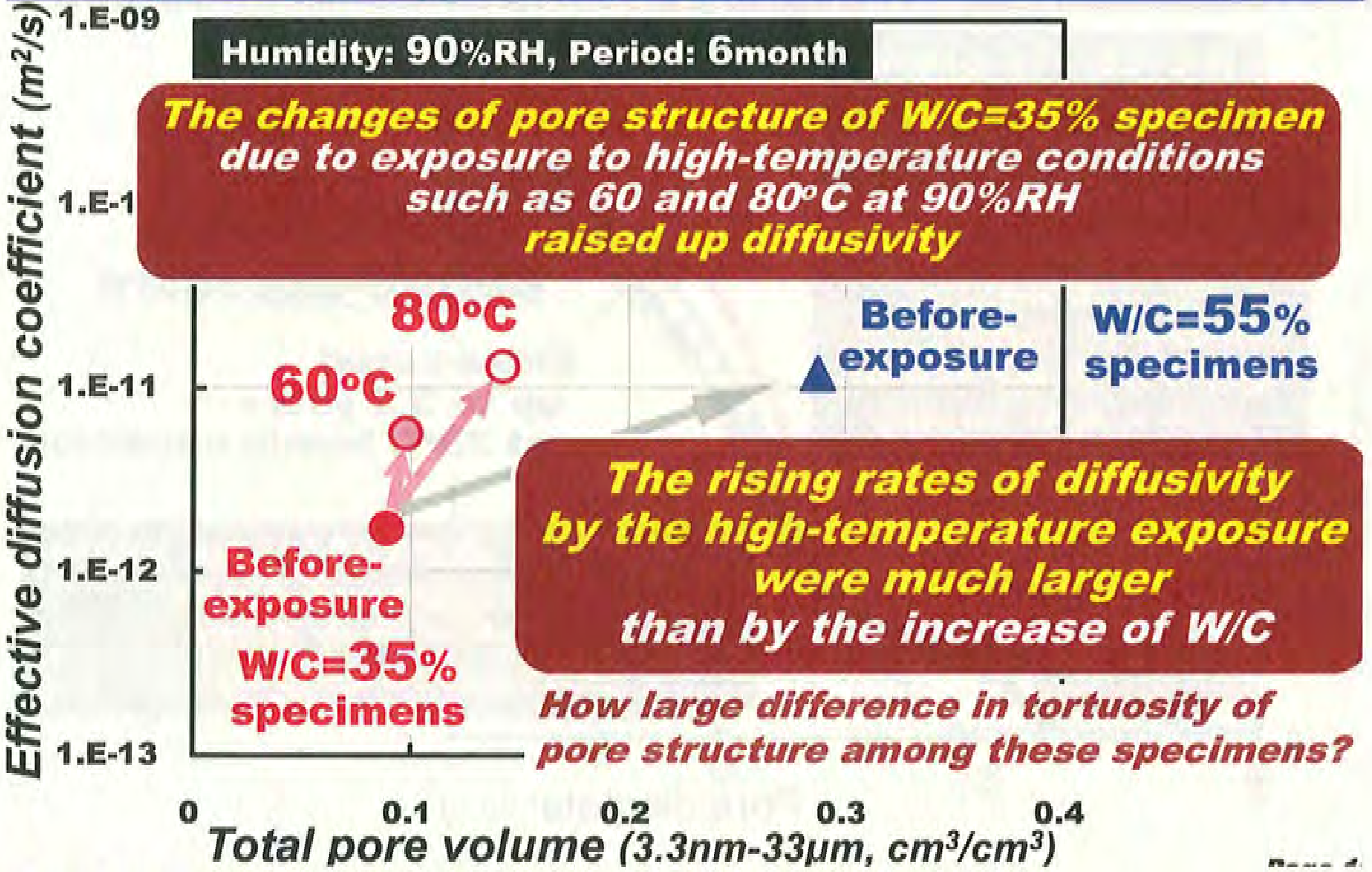
Lower conc. side cell

200mL
hardened cement-equilibrium solution

Temp.: 20°C

Effective diffusion coefficients were calculated with elevation of TOC concentration in the steady state.

Relationship between increase of total pore volume due to high-temperature exposure and rise of diffusion coefficient

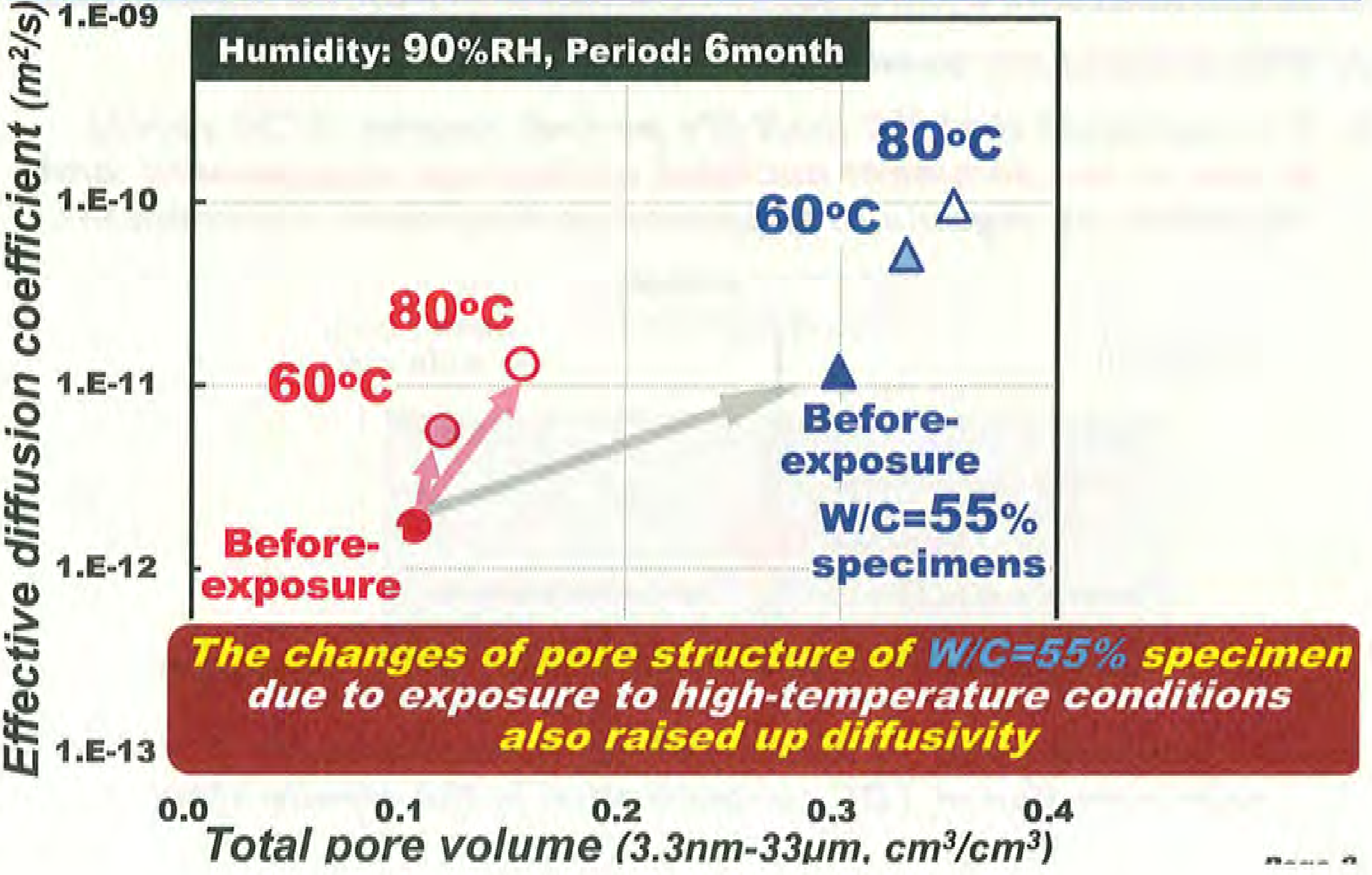


The changes of pore structure of W/C=35% specimen due to exposure to high-temperature conditions such as 60 and 80°C at 90%RH raised up diffusivity

The rising rates of diffusivity by the high-temperature exposure were much larger than by the increase of W/C

How large difference in tortuosity of pore structure among these specimens?

Relationship between increase of total pore volume due to high-temperature exposure and rise of diffusion coefficient



The changes of pore structure of W/C=55% specimen due to exposure to high-temperature conditions also raised up diffusivity

Conclusions

Motivation and viewpoint of this study

How does the condition below approx. 100 degrees Celsius affect the ionic diffusivity based on pore structure of cementitious materials?

1. ***Exposure to the high-temperature condition such as 60 and 80°C at 90%RH increases the total pore volume of ordinary Portland cement paste specimens of W/C=35 and 55%.***
2. ***The change of pore structure due to high-temperature exposure to the current experimental conditions causes the rise of ionic diffusivity.***
3. ***The rising rates of diffusivity by the high-temperature exposure were much larger than by the increase of W/C.***

Future tasks

- ***Effect of smaller pores than 3.3nm, which is analytical limited minimum size on MIP analysis, on ionic diffusivity***
- ***Behavior of mortar and concrete exposed to high temperature conditions (influence of aggregate; ITZ)***
- ***Behavior on wider temperature and humidity conditions***
- ***Effect of long-term water provision to thermal altered hardened cement paste***
- ***Chemical resistance to leaching and others of thermal altered hardened cement paste***

Thank you for your kind attention.


Great Wall, Sep. 2004

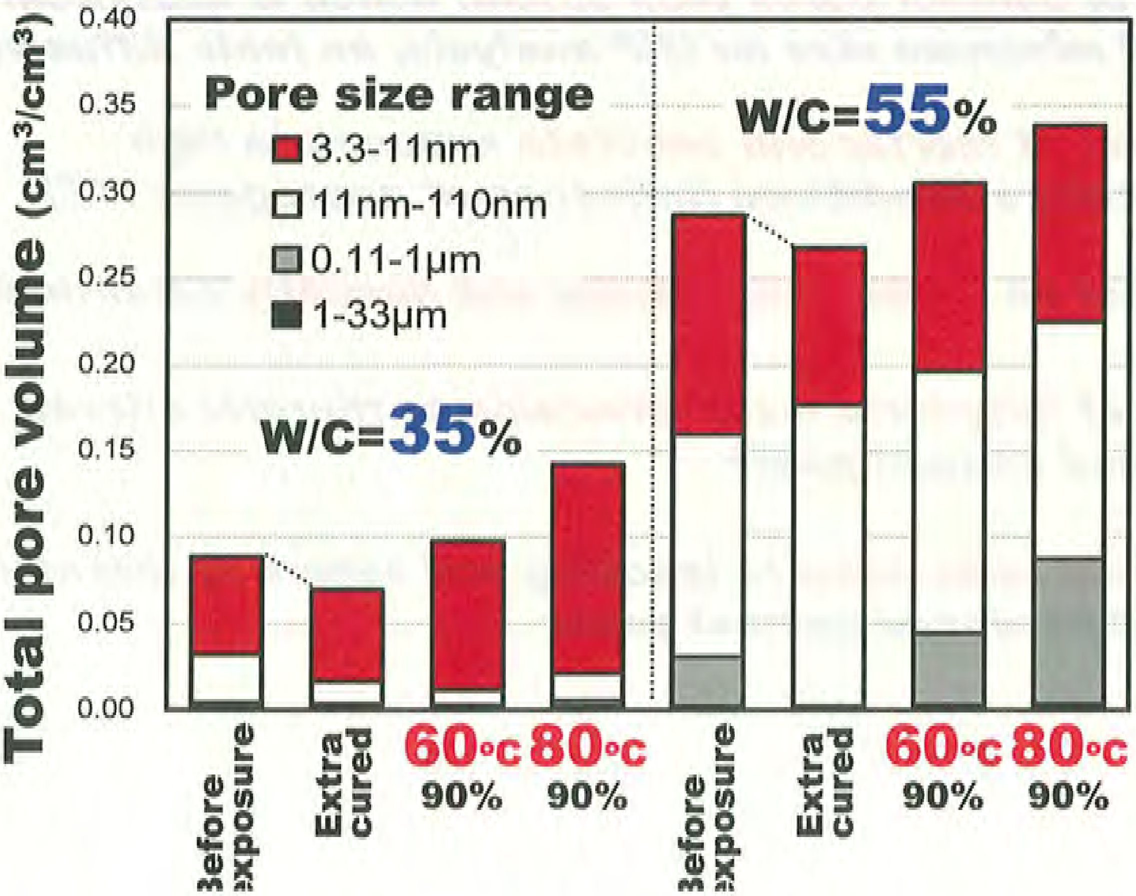

Three Gorges Dam, Mar. 2008

谢谢大家


Bird's Nest, Mar. 2008

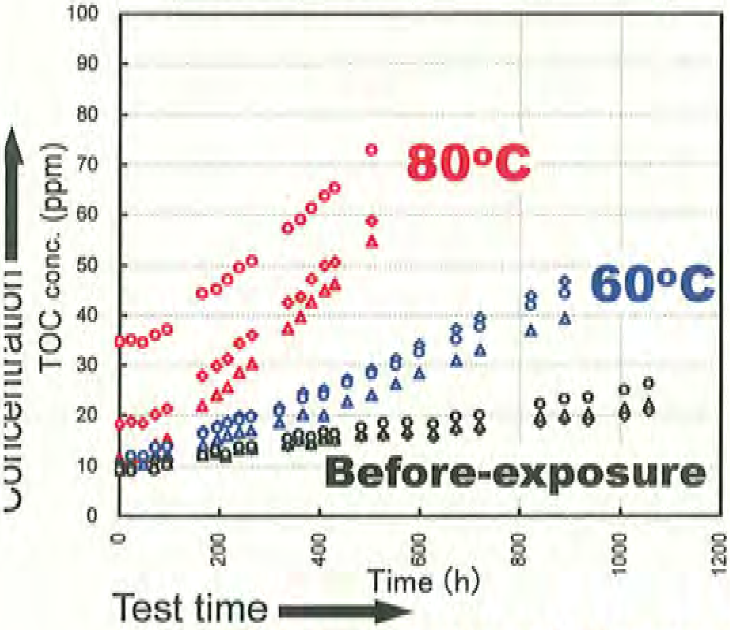

Beijing Gugong, Sep. 2004

Comparison of change of total pore volume due to high-temperature exposure

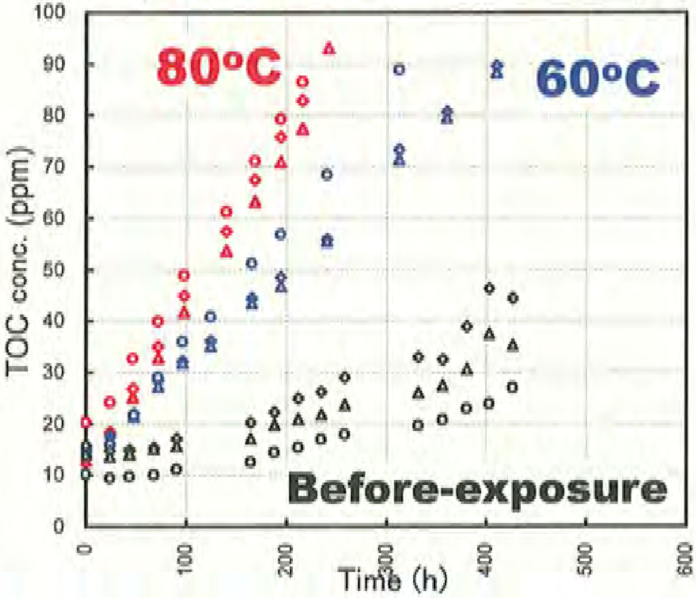


Measurement examples of elevation of TOC concentratio

W/C=35% specimens
Humidity: 90%RH
Period: 6month



W/C=55% specimens
Humidity: 90%RH
Period: 6month



Test results of three samples from an identical specimen were same level in each exposure condition

Dif Cf.

C^{14} v.s. TOC