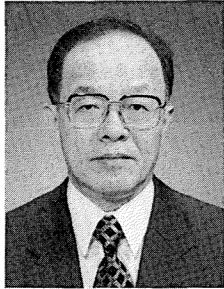
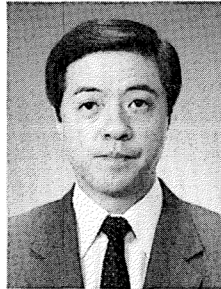


ASR GEL COMPOSITION, SECONDARY ETTRINGITE FORMATION, AND EXPANSION OF
MORTARS IMMERSSED IN NaCl SOLUTION

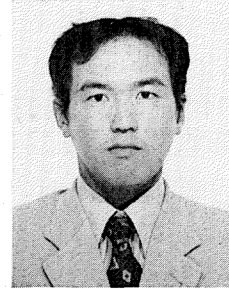
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In this study, we pursue the changes in microstructural features and characteristics of ASR gel composition in mortars containing reactive aggregate after immersion in NaCl solution. These characteristics are compared with their expansion behavior. Mortars immersed in NaCl solution undergo greater expansion than those in NaOH solution, and this may be a result of the formation of ASR gel with a relatively low alkali content. However the coexistence of ettringite with ASR gel is indicated by EDS analyses, so it is not possible at this stage to infer whether the formation of secondary ettringite increases mortar expansion or not.

Keywords: ASR, NaCl, de-icing salt, ASR gels, ettringite, SEM, EDS-BSE analysis

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1. INTRODUCTION

The effect of NaCl contributed by deicing salt or seawater on ASR damage to concrete is an important issue in the field of concrete structure maintenance. A recent survey of the effects of deicing salt on ASR-induced expansion reported that mortar containing a reactive aggregate may exhibit greater or lesser expansion when immersed in NaCl solution than in water, depending on the reactivity of the aggregate [1]. Another field investigation, this time on ASR-affected concrete piles in a partially submerged marine environment, has revealed that ASR causes significant damage to the submerged portions of even relatively new marine structures, but not to the above-water portions [2]. Thus, if reliable repair of ASR-affected structures in saline environments is to be achieved, a better understanding of the mechanisms by which NaCl influences ASR is crucial [3]. The mechanism by which NaCl influences the expansion of hardened concrete containing reactive aggregate has been studied by a number of groups. At least part of the expansion in mortar containing reactive aggregate is certainly due to a rise in the OH⁻ ion concentration in the pore solution, which is brought about by intrusion of NaCl, and Cl⁻ ions themselves accelerate ASR in concrete [4,5]. However, recent reports [6,7] have suggested that C₃A and gypsum as well as alkalis in the cement play an important role in the expansion of mortar containing a reactive aggregate. In fact, SEM examinations of opal-containing mortars immersed in 1M NaCl solution for longer than a year showed that large amounts of chloride-bearing ettringite had formed in the mortars [8]. However, ambiguity remains as regards the mechanism by which the formation of secondary ettringite is related to mortar expansion in an NaCl solution.

The aim of this study is to pursue the changes in microstructural features indicated by BSE-EDS analysis and the characteristics of ASR gel composition in reactive aggregate-containing mortars when immersed in NaCl solution, and to relate them to the expansion behavior of the mortars.

2. EXPERIMENTAL OUTLINE

2.1 Materials

Calced flint with a size fraction of 2.5 mm to 0.6 mm was used as the reactive aggregate. Its dissolved silica (Sc) and alkalinity reduction (Rc) in the ASTM chemical test (C 289) were 1063 and 70 mmol/l, respectively. Japanese Toyoura standard sand was used as a non-reactive aggregate. The C₃A content of the ordinary and sulfate-resisting Portland cements used was 9.2% and 3.1%, respectively; the Na₂O equivalent of the two was 0.67% and 0.59%, respectively. The chemical and mineral compositions of these cements, as calculated by the Bogue method, are given in Table 1.

Table 1 Chemical Composition of Ordinary and Sulfate-Resisting Portland Cement (%)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Ordinary	22.0	5.2	2.7	63.6	1.5	1.9	0.40	0.41	47	27	9.2	8.2
Sulfate-resisting	22.2	4.2	4.6	64.1	0.4	2.2	0.34	0.38	51	25	3.4	14.0

2.2 Mortar Specimens for Expansion Testing

Mortar was prepared with a total aggregate to cement ratio of 2.0 and a water-cement ratio of 0.5. Reactive aggregate replaced 30% by mass of the non-reactive aggregate. Mortar bars measuring 25.3 by 25.3 by 285.5 mm, were cured in a sealed state for 28 days, then immersed in 1M NaCl solution at 38 °C. For expansion tests in 0.6M NaOH solution, a further series of mortars was prepared with an aggregate-cement ratio of 2.25 and a water-cement ratio of 0.6, with 10% by mass of aggregate replaced by reactive aggregate. The same cements were used [9].

2.3 BSE-EDS Analysis Procedure

At 14, 56, 119, and 406 days after immersion in NaCl solution, mortar slices were cut from the center of the mortar bars for BSE-EDS analysis. These were dried by ethanol replacement, followed by overnight

vacuum drying at room temperature. The dried slices were impregnated under vacuum with ultra-low viscosity epoxy resin. The polished surfaces were sputter coated with a 30 nm layer of gold-palladium alloy. The samples were then examined using a Hitachi S-2250N SEM equipped with a back scatter detector and a Horiba EMAX-5770W energy-dispersive X-ray analyzer.

3. RESULTS

3.1 Expansion Characteristics of Mortars in NaCl and NaOH Solutions

The expansion curves for mortars made with both the ordinary and sulfate-resisting Portland cements and immersed in 1M NaCl and 0.6M NaOH solutions are presented in Fig.1. The mortars are found to expand rapidly immediately upon immersion in both solutions. The rapid progress of expansion in NaCl solution was maintained up to about 120 days, reaching a maximum value of about 1.5% in the case of ordinary cement. In the later stages, the mortars continued to expand at a lower rate. Even at an early age, however, expansion rates in NaOH solution were lower than those in NaCl solution. The expansion rate for mortars in NaOH solution rapidly decreased after about 100 days of immersion, reaching an ultimate expansion of about 1.0%. As Fig.1 demonstrates, the expansion of sulfate-resisting cement mortars was less than two thirds that of ordinary Portland cement mortars.

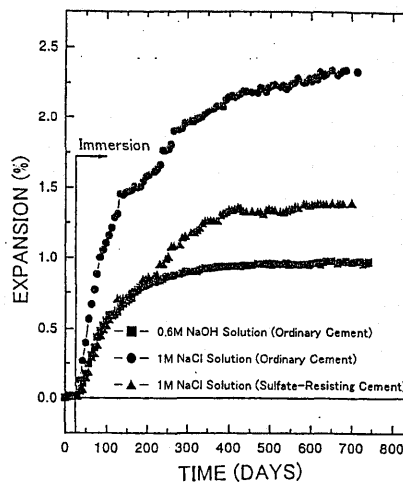
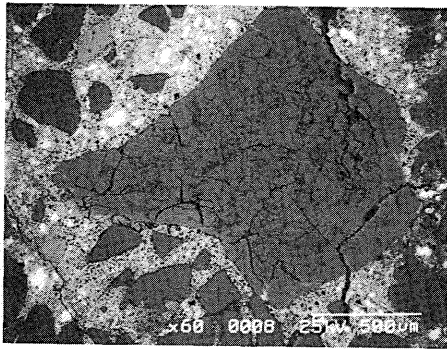


Fig.1 Expansion curves for mortars in NaCl and NaOH solution

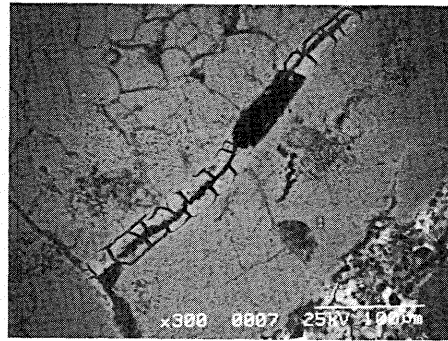
3.2 ASR Gel Composition in Immersed Mortars

Careful SEM examinations over the whole of the polished face of mortar samples cured for 28 days in a sealed state at 38 °C showed that the cement paste developed the normal microstructural features and that large amounts of ASR gel were present within relatively wide cracks in reactive aggregate particles. Low- and high-magnification BSE micrographs of a reactive aggregate particle found in the polished section of a mortar sample immersed in NaCl solution for 56 days are presented in Photograph 1. Here, there are many cracks within the reactive aggregate particles and some cracks are filled with large amounts of ASR gel. The average mole percentages of SiO₂, CaO, and (Na₂O+K₂O) obtained by BSE-EDS analysis at about 10 spots in ASR gel areas in five different reactive aggregate particles are plotted in the ternary phase diagram in Fig. 2. These particles were selected from mortars pre-cured for 28 days in a sealed state. Figure 2 also shows that little change occurred in the mole percentages of (Na₂O+K₂O) in the gels during immersion in NaCl solution. However, it is found from the plots of K₂O/Na₂O content ratios at various immersion times (Fig.3) that potassium in the ASR gels produced in mortars during the pre-curing period was replaced by sodium during the relatively early stages of immersion in NaCl solution. Additional alkalis were not incorporated in the gels; only Na⁺ and K⁺ ions were exchanged. The replacement of potassium by sodium may have no effect on the expansion of ASR gels [10].

The results of SEM observations of mortars immersed in both NaCl and NaOH solutions show that more ASR gel is produced in mortars immersed in NaOH solution than in mortars immersed NaCl solution. However, although the initial content of reactive aggregate in mortars immersed in NaCl solution was three times that of mortars in NaOH solution (according to the mix proportions), the amount of reactive silica even in NaOH-immersed mortars may be high enough to maintain the progress of ASR. Unlimited amounts of OH⁻ ions would be supplied to mortars in NaOH solution and the OH⁻ ion concentration of the pore solution of these mortars is higher than that of mortars in NaCl solution. In NaOH-immersed mortars, the formation of ASR gel with low viscosity and higher fluidity, as a consequence of the higher alkali content associated with increased OH⁻ ion concentration, may lead to greater expansive stress relaxation.



(a)



(b)

Photograph 1 BSE micrographs for reactive aggregate particle (a) and ASR gel (b) in ordinary portland cement mortar immersed in NaCl solution for 56 days

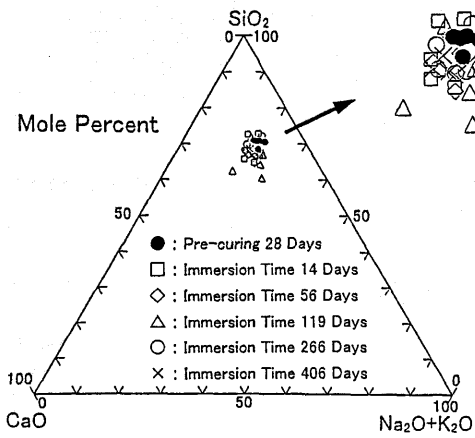


Fig.2 Ternary phase diagram for ASR gels in mortars

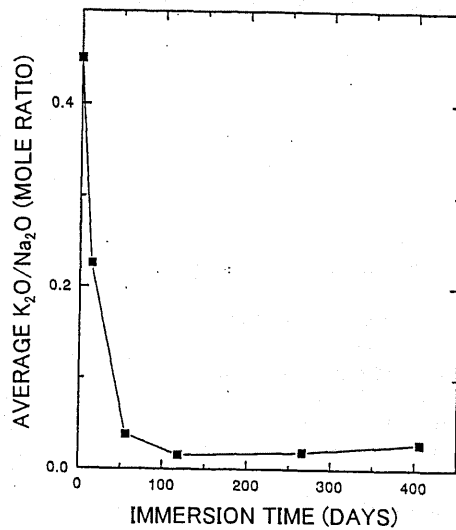


Fig.3 K_2O/Na_2O ratios of ASR gel in mortars immersed in NaCl solution

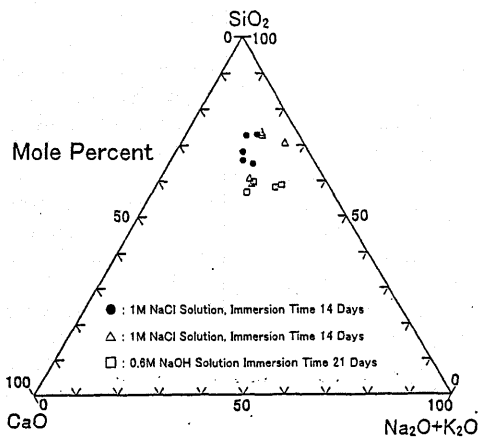
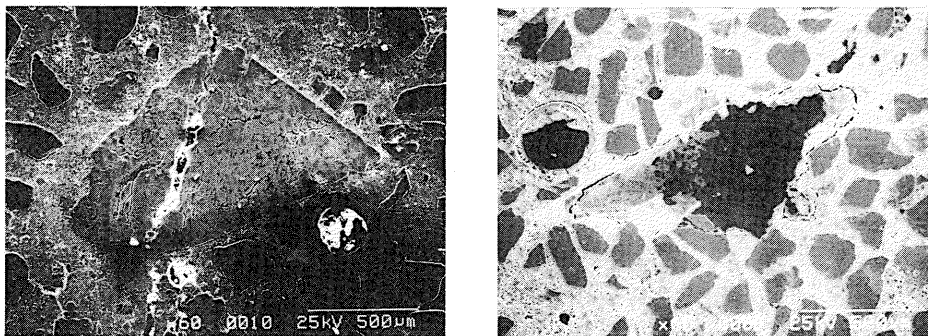


Fig.4 Ternary phase diagram for ASR gels in mortars

As shown in Photograph 2, gel remained inside reactive aggregate grains even in mortar immersed in NaCl solution till the age of 120 days. On the other hand, it is confirmed that gel in NaOH solution was carried outside the reactive aggregate grains as a result of its low viscosity.

The CaO content of the gel was also investigated, and shown to be the same level in both NaCl and NaOH immersion. This demonstrates that CaO content has little effect on the expansion behavior of mortars. In a separate study [9] the authors confirm this limited effect of CaO content in the ASR gel on the expansion of mortar.



(a) NaCl solution

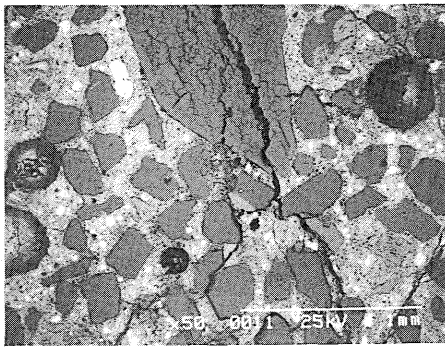
(b) NaOH solution

Photograph 2 SEM micrographs for ordinary cement mortars immersed in NaCl solution and NaOH solution for 120 days

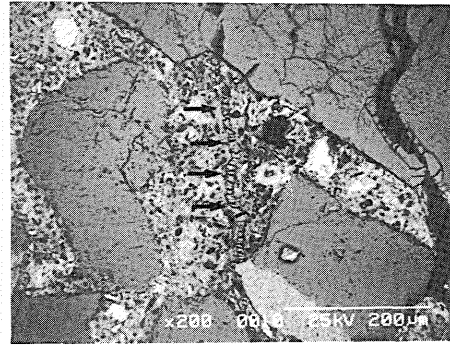
3.3 Microstructural features of Cement Paste in Mortars in NaCl Solution

SEM observations turned up no particularly characteristic features in the microstructure of cement paste in mortars immersed in NaCl solution for 14 days. However, after 56 days in NaCl solution, many ASR-induced microcracks were found to be partly filled with ettringite. In the BSE images in Photograph 3, belts of ettringite are seen in cracks approximately 10 μm wide by 50-200 μm long. No rim cracks filled with ettringite were found around aggregate particles, and particles of ettringite appear to partly fill ASR-induced cracks propagating through the cement paste. However, not all cracks were filled with ettringite, although cracks caused by ASR cannot be differentiated from those caused by sample preparation.

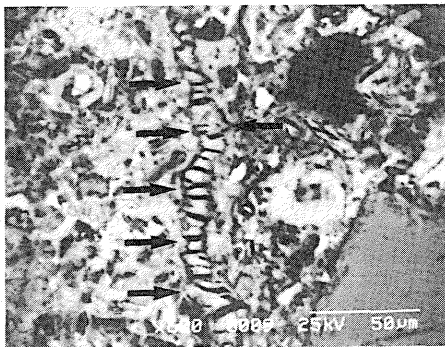
We looked at 10 different areas of ettringite deposits and carried out EDS analysis for about 5 spots in each individual area for a total of about 50 spot analyses of ettringite deposits in the polished face of a mortar sample. A typical EDS result was that relatively large amounts of $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ were detected when analyzing string-like ettringite areas. The mole percentages of $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ and SiO_2 obtained by EDS analysis are plotted in Fig. 5. Part of the SiO_2 and $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ content may result from some contamination that occurred during analysis. It should be noted that the alkali contents obtained in these analyses were considerably higher than the 2% found as an impurity in ettringite [11]. The CaO, Al_2O_3 , and SO_3 contents, obtained by excluding other elements being normalized to 100 percent, are plotted in a ternary phase diagram shown in Fig. 6. The plots lay on and around a line connecting the stoichiometric composition of ettringite with points obtained for ASR gel in air voids within the mortars. Thus, these results show that string-like ettringite deposits found in cracks are mixtures of ettringite and ASR gel. The movement of plotted points towards the CaO apex over time means that the proportion of ASR gel in the string-like deposits and/or the CaO content of the ASR gel itself increases with time. It should be noted that we found no such ettringite deposits in ASR-induced cracks in the sulfate-resisting cement mortars.



(a) reactive aggregate particle



(b) cracks filled with ettringite deposits



(c) ettringite

Photograph 3 BSE micrographs for ordinary cement mortar immersed in NaCl solution for 56 days

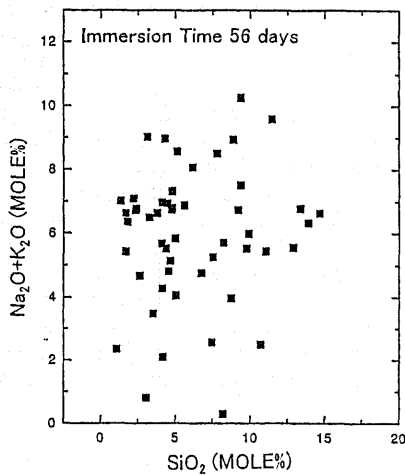


Fig.5 Alkali and silica contents of ettringite deposits in cracks

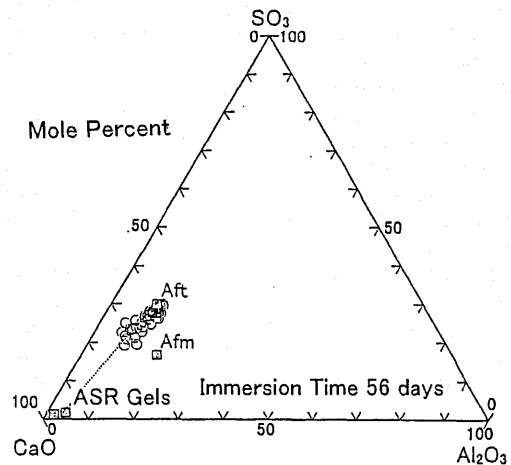


Fig.6 Ternary phase diagram of ettringite in cracks

4. DISCUSSION

As observed above, some cracks in the cement paste phase were filled with ettringite. The formation of ettringite like this requires a supply of Ca^{2+} , SO_4^{2-} , and $\text{Al}(\text{OH})_4^-$ ions. It has been shown that the solubility of ettringite in the system consisting of ettringite-water-NaCl is about three times that in the ettringite-water system, and that monosulfate-water-NaCl systems are less stable than ettringite-water-NaCl systems [12]. It

Table 2 Expansion, Ettringite Formation in Cracks, ASR Gel Composition, Width and Length of String-like Ettringite Areas in Ordinary Portland Cement Mortars

Time(Days)	0	14	56	119	266	406
Expansion	None	Very Active	Very Active	Very Active	Slowly	Very Slowly
String-like Ettringite in Cracks	None	None	Present	Present	Present	Present
Average Width of Band Areas of Ettringite	None	None	9.4 μ m	12.4 μ m	17.8 μ m	14.0 μ m
Average Length of Band Areas of Ettringite	None	None	370 μ m	234 μ m	272 μ m	213 μ m
State of ASR Gel	Solid	Solid	Solid	Solid	Partly Evacuated	Mostly Evacuated

is known that SO_4^{2-} ions are released during the conversion of the monosulfate to Friedel's salt under NaCl attack. So, taking into consideration the fact that secondary ettringite deposits were hardly found in cracks in the cement mortar samples made with a sulfate-resisting cement, despite immersion in NaCl solution up to 406 days, the monosulfate can be concluded to be a major source of SO_4^{2-} ions.

As shown in Fig.1, the expansion of the sulfate-resisting cement mortar was much less than that of mortar containing ordinary cement. The equivalent percentages of Na₂O in the two types of cement are little different, but the amount of unreacted C₃A in the sulfate-resisting mortar when immersion began would have been much less than in the latter. As a result, it is impossible to infer whether the much lower expansion of sulfate-resisting cement mortar in NaCl solution was due to the absence of secondary ettringite formation or not.

In order to elucidate the role of ettringite formation in the expansion of mortars, we tabulate the rate of expansion, ettringite formation, average width and length of ettringite-filled cracks, and the state of ASR gel within aggregate particles for various immersion times in Table 2. The width and length values given in this table are averages of 10 measurements for different cracks filled with ettringite. The width of these ettringite-filled cracks appears to increase with increasing expansion. However, even after immersion for 406 days, an expansive ASR gel with relatively low alkali content was present within reactive aggregate particles, although a great portion of this gel had been evacuated from some of the particles. Thus, it is unclear if secondary ettringite formation led to increased mortar expansion. Grattan-Bellow [13] and Davis & Oberholster [14] have reported that the increased expansion in concrete supplied with NaCl is induced not only by ASR as promoted by the increasing concentration of Na⁺ and OH⁻ ions formed in the reaction between NaCl and C₃A or Ca(OH)₂, but also by the production of expansive monochloro-aluminate and chloro-surfo-aluminate. As far as these results of immersion tests in NaCl solution up to 406 days are concerned, it is not possible to infer whether the formation of secondary ettringite in many pre-existing ASR-induced cracks increased mortar expansion or not. The greater expansions of mortars in NaCl solution than in NaOH solution found in this study could result from the production of low-alkali ASR gel with high viscosity, which would give rise to lasting expansive pressure within the mortar over a long period.

5. CONCLUSIONS

The conclusions reached in this investigation can be summarized as follows:

- (1) Mortar immersed in 1M NaCl solution expanded more than that in 0.6M NaOH solution. The greater expansion of mortar in NaCl solution might result from the formation of ASR gel with relatively low alkali content and high viscosity.
- (2) Many ASR-induced micro-cracks were found to be partly filled with ettringite in mortars containing reactive aggregates and immersed in NaCl solution for periods longer than 14 days.
- (3) String-like ettringite deposits found in cracks were mainly a mixture of ettringite and ASR gel.
- (4) From this work, it is impossible to infer whether the formation of ettringite in ASR-induced cracks increases mortar expansion or not.

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