

RELATIONSHIPS BETWEEN ALKALI CONTENT, EXPANSION AND PORE SOLUTION COMPOSITION IN OPAL-BEARING MORTARS IMMERSSED IN NaCl SOLUTION

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This study aims at revealing the behavior of OH^- and Cl^- ions in the pore solution in opal-bearing mortars during the NaCl solution immersion and correlating the results to the expansive behavior of the mortars in NaCl solution. The expansion of mortars containing the opaline aggregate was extremely sensitive to alkali content in the mortars. Considerable amounts of $\text{Ca}(\text{OH})_2$ are dissipated during the immersion in NaCl solution in all mortars with opal, but not in mortars without the reactive aggregate. Great amounts of Cl^- ions were dissipated from the pore solution in most opal-bearing mortars during 1 N NaCl solution immersion. Some chemical reactions, in which greater amounts of Cl^- ions are consumed and greater amounts of OH^- ions released, seems to occur within some opal-bearing mortars immersed in the NaCl solution.

INTRODUCTION

Recently, Kawamura and Diamond (1) found that great amounts of chloride-bearing ettringite and Friedel's salt existed within mortar specimens containing a Japanese opal stored in 1 N NaCl solution at 38° C for longer than one year. At present it is ambiguous whether the formation of the chloride-bearing ettringite is related to the expansion of the mortars in the NaCl solution.

Effects of NaCl used as a deicing agent on the expansion of concrete due to the alkali-silica reaction have been pointed out by several workers (2). Nishibayashi and Yamura (3) also found that mortars with added NaOH expanded greatly in sea water at 40° C. However, it is uncertain whether sea water affects the deterioration of actual concrete structures due to the alkali-silica reaction. In this situation, further studies concerning the mechanisms which are responsible for the promotion of expansion of mortars with reactive aggregate in NaCl solution have to be carried out.

This study aims at revealing time-dependent changes in OH^- and Cl^- ion concentration in the pore solution and $\text{Ca}(\text{OH})_2$ content in opal-bearing mortars immersed in 1 N NaCl solution and correlating the results obtained to the expansive behavior of the mortars in the NaCl solution. In this paper, the expansive behavior of the opal-bearing mortars immersed in several NaCl solutions with various concentrations is also discussed.

EXPERIMENTAL DETAILS

Materials

The reactive aggregate used was an opaline rock from the Akase opal mine in Ishikawa Prefecture in Japan. The powder X-ray diffraction pattern for this opal showed the existence of α -cristobalite and quartz. Bulk specific gravity and absorption capacity of the reactive aggregate are 2.29 and 1.79 %, respectively. The opaline rock blocks were crushed and sieved so as to obtain a fine aggregate with the size fraction of 1.2 mm to 0.3 mm. The Japanese standard siliceous sand was used as a non-reactive aggregate. Two ordinary Portland cements with the equivalent Na_2O

TABLE 1 - Chemical Analyses of a High - and a Low -Alkali Cement (Wt.%)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	Ig. loss
High -Alkali Cement	21.1	4.9	3.1	65.1	1.4	2.0	0.50	0.72	0.28	0.7
Low -Alkali Cement	21.9	5.5	2.9	63.1	1.7	2.3	0.29	0.29	0.35	1.3

percentage of 0.97 and 0.48 were used to prepare mortars having various alkali/opal ratios. Their chemical compositions are given in Table 1.

Mix Proportions of Mortars, Expansion Test, Pore Solution Expression and Thermal Analysis of Ca(OH)₂ Content in Mortars

Two series of mortars (Series I and II) for expansion test were prepared. Total aggregate /cement ratio was fixed at 0.75 and water/cement ratio at 0.4. In Series I, mix proportions of mortars with various alkali/opal ratios were determined by varying the replacement level of the non-reactive sand by the opaline aggregate. In Series II, opal /total aggregate ratio was fixed at 0.26 and a series of mortars with various alkali/opal ratios were prepared by diluting the high-alkali cement with the low-alkali cement in the range of relatively low alkali/opal ratios not exceeding 0.05 and by adding NaOH in the range of high alkali/opal ratio above 0.068.

2.5 by 2.5 by 28.5 cm mortar bars for expansion test were prepared. Mortar specimens with a given alkali/opal ratio were molded in duplicate. After about 24 hours curing at 20° C, the specimens were demolded, and then stored in the fog box maintained at 38° C for 27 days. These 28 days old specimens were immersed in 1, 3 N and the saturated NaCl solution at 38° C. Measurements of their length changes commenced immediately after demolding. The concentration of the NaCl solutions was controlled by replacing the old solution by the new one so that the reduction in their Cl⁻ ion concentration were within 5 percent.

Pore solutions were expressed by the high pressure apparatus from ϕ 5 by 10 cm mortar cylinders which were cured in the fog box at 38° C for 28 days being sealed tight in vinyl sack. Pore solutions squeezed from the mortar cylinders which were immersed in 1 N NaCl solution for 14 and 62 days after 28 days curing in the fog box, were also analyzed.

Additional 25.3 by 25.3 by 28.5 mm mortar bars produced for the thermal analysis were stored in the fog box for 28 days, and then immersed in 1 N NaCl solution at 38° C for 45 days. Portions up to the depth of 5 mm from the surfaces of the specimens were cut off, and then dried for several days in the vacuum drying oven at a room temperature. A quantitative thermal analysis of the combined method of TG and DSC was applied to the determination of Ca(OH)₂ content in mortars (6). The TG-DSC apparatus manufactured by Rigakudenki Co. Ltd. was used at the heating rate of 10° K/ min., with about 50 mg sample. Calcined aluminum oxide was used as the reference material.

RESULTS AND DISCUSSION

Relationship between Alkali/Opal Ratio and Expansion

Figs. 1 and 2 show the relationship between alkali/opal ratio and expansion in opal-bearing mortars immersed in 1 N NaCl solution at various immersion periods in Series I and II mortars, respectively. As shown in Figs. 1 and 2, the pessimum alkali/opal ratio in Series I and II mortars cured for 28 days in the fog box at 38° C is about 0.05 and 0.1, respectively. The pessimum value decreased with time during the immersion in 1 N NaCl solution. Around 100 days after the start of immersion in the solution, Series I and II mortars showed the maximum expansion at the alkali/opal

ratio of 0.015 and 0.03, respectively. It was also found from Fig. 1 that Series I mortars with the alkali/opal ratio smaller than 0.01 did not expand at all during the storage in both the fog box and 1 N NaCl solution. The Series II mortars with the alkali/opal ratio of 0.02 and 0.03 showed greatly delayed expansion. However, once these mortars started to expand, their expansion rapidly increased with time. Furthermore, it should be noted that the pessimum alkali/opal ratio in Series I mortars immersed in 1 N NaCl solution during a relatively long period is adjacent to the critical alkali/opal ratio below which mortars showed no expansion at all. Such extremely sensitive response of the expansion of mortars in NaCl solution to OH^- ion concentration of the pore solution in mortars have been also found by one of the present authors (4).

As shown in Fig. 2, in Series II mortars, the continuous decrease in expansion with increasing alkali/opal ratio in the range of low alkali/opal ratio was interrupted at 0.05. This discontinuity in the relationships between alkali/opal ratio and expansion at the alkali/opal ratio of 0.05 may be attributed to the addition of NaOH in mortars with the alkali/opal ratio greater than 0.05.

Effects of the Concentration of NaCl Solution on Expansion

Fig. 3 shows expansion curves for the Series I mortar specimens with the alkali/opal ratio of 0.01 and 0.0064 in 1N, 3N and the saturated NaCl solution. These mortars were made with the low-alkali cement. The mortars with the alkali/opal ratio of 0.01 and 0.0064 showed little expansion during both the first 28 days moist curing and the immersion in 1 N NaCl solution. However, the mortar with the alkali/opal ratio of 0.01 started to expand around 20 days after the immersion in 3 N and the saturated NaCl solution. Particularly, the expansion of the mortar with the alkali/opal ratio of 0.01 in 3 N NaCl solution was significantly great compared to that in the saturated NaCl solution. Even the mortar with the smallest alkali/opal ratio of 0.0064 started to slowly expand around 20 days after the immersion in 3 N and the saturated NaCl solution.

The expansion curves of the mortars with the alkali/opal ratio of 0.03 and 0.076 presented in Fig. 4 are typical ones for mortars with a relatively low and high alkali/opal ratio in Series II, respectively. The mortar with the alkali/opal ratio of 0.03 showed no expansion during the first 28 days moist curing. However, immediately after the mortar specimens were immersed in 3N and the saturated NaCl solution, they started to expand. The expansion of mortars immersed in 1N NaCl solution was delayed by about one month. Once the mortar specimens in 1N NaCl solution started to expand, the progress of their expansions was so rapid that expansions of the mortar specimens in 1N NaCl solution exceeded those of the ones in the saturated NaCl solution around 60 days after the start of immersion. This fact indicates that the concentration of NaCl solution affects the expansion of mortars with the reactive aggregate in NaCl solution at a relatively low alkali/opal ratio ranging from 0.025 to 0.05. On the other hand, the expansion of the mortar with a relatively high alkali/opal ratio of 0.076 reached as much as 0.4% at the end of 28 days moist curing, showing almost the same expansion curves in the three different NaCl solutions.

Fig. 5 shows the relationships between alkali/opal ratio and expansion in mortars at 132 days after the start of immersion in 1N, 3N and the saturated NaCl solution. The pessimum value of alkali/opal ratio in 1N, 3N and the saturated NaCl solution was 0.03, 0.04 and 0.076, respectively, although the expansion of mortars in the saturated NaCl solution only a little varied with alkali/opal ratio. It is also found from Fig. 5 that the difference in expansion between the different NaCl solutions at a relatively low alkali/opal ratio ranging from 0.025 to 0.05 is considerably greater than at a relatively high alkali/opal ratio ranging from 0.076 to 0.15 except the mortar with the alkali/opal ratio of 0.15 showing a considerably great expansion in 1N NaCl solution.

Analogical Inferences on Characteristics of ASR Deterioration in Concrete in Saline Environments

The results obtained in a series of expansion tests suggest the occurrence of the following phenomena as characteristics of ASR deterioration in concretes in the environments where NaCl is supplied. (1) A little change in a reactive component content, alkali concentration and local environments where concrete structures are located, brings about a drastic change in the degree of damage due to the alkali-silica reaction. (2) In concretes with a greater amount of alkali than the

critical value, the smaller the alkali content in concrete, the more serious the damage in concrete caused by the supply of NaCl. (3) NaCl concentration of solutions supplied to concrete also affects the degree of deterioration of the concrete due to the alkali-silica reaction, depending on the alkali content of the concrete. (4) Even reactive aggregate-bearing concretes with a considerably small amount of alkali may be damaged in a saline environment.

Changes in Pore Solution Composition with Time in Mortars in NaCl Solution

Fig. 6 shows the relationships between alkali/opal ratio and OH^- ion concentration in the pore solutions expressed from mortars cured in the fog box at 38°C for 28 days and the ones immersed in 1N NaCl solution during the periods prescribed. As shown in Fig. 6, OH^- ion concentration in the pore solution in both mortars with and without the reactive aggregate cured in the fog box at 38°C for 28 days proportionally increases with increasing alkali/opal ratio, although mortars with the alkali/opal ratio smaller than 0.05 immersed in the NaCl solution for 14 days show a higher value of OH^- ion concentration than that expected from the plots for the alkali/opal ratio greater than 0.05. This disorder in the proportionality at the alkali/opal ratio of 0.05 is supposed to reflect the addition of NaOH in the preparation of mortars. The proportional relation between OH^- ion concentration in the pore solution and alkali content in cement pastes without reactive aggregate has been demonstrated by Diamond (5).

The indication that the alkali-silica reaction has progressed in all opal-bearing mortars during the first 28 days curing in the fog box is obtained from the fact that OH^- ion concentration in the pore solution in opal-bearing mortars is considerably lower than in the corresponding standard sand mortars. Fig. 6 also shows that OH^- ion concentration in both mortars with and without opal decreased with time during the immersion in the NaCl solution. It should be noted that, after 14 days immersion in 1N NaCl solution, OH^- ion concentration in the pore solution in mortars without the reactive aggregate is higher than in mortars with the reactive aggregate except that at the alkali/opal ratio of 0.04, but that, after 62 days, OH^- ion concentration in the former is a little lower than in the latter at the alkali/opal ratio greater than 0.05. This fact shows that some reactions releasing greater amounts of OH^- ions into the pore solution occurred within at least these mortars containing the reactive aggregate during the immersion period from 14 to 62 days in 1N NaCl solution.

Fig. 7 shows the relationship between alkali/opal ratio and Cl^- ion concentration in the pore solution in mortars immersed in 1N NaCl solution for 14 and 62 days after the curing in the fog box for 28 days. As shown in Fig. 7, Cl^- ion concentration in the pore solution in opal-bearing mortars immersed in 1N NaCl solution for 14 and 62 days is lower than in the controls at the alkali/opal ratio greater than 0.03 and 0.06, respectively. This fact indicates that greater amounts of Cl^- ions were dissipated from the pore solution in these opal-bearing mortars than in the controls during the period from 14 to 62 days after the start of immersion in NaCl solution. On the other hand, as shown in Fig. 2, all mortars except those with the alkali/opal ratio of 0.025 and 0.35 greatly expanded by 62 days after the start of immersion in the NaCl solution. Thus, the dissipation of greater amounts of Cl^- ions from the pore solution in these opal-bearing mortars than in the controls appears not to be related to the expansion of the mortars in the NaCl solution.

$\text{Ca}(\text{OH})_2$ Content in Various Mortars

Fig. 8 shows the relationship between $\text{Ca}(\text{OH})_2$ content and alkali/opal ratio in mortars with and without the opaline aggregate cured in the fog box maintained at 38°C for 28 days and in those immersed in 1 NaCl solution for 45 days after the 28 days moist curing. As shown in Fig. 8, as a whole, there is only a little difference in $\text{Ca}(\text{OH})_2$ content in the standard sand mortars between the specimens cured in the fog box for 28 days and those stored in 1N NaCl solution for additional 45 days, although $\text{Ca}(\text{OH})_2$ content in the latter is a little greater than in the former at the alkali/opal ratio greater than 0.1. However, $\text{Ca}(\text{OH})_2$ content in all mortars containing opal stored in 1 N NaCl solution for 45 days is considerably lower than in those only cured in the fog box for 28

days. It is found from these results that considerable amounts of $\text{Ca}(\text{OH})_2$ were dissipated during the immersion in NaCl solution in all mortars with opal, but that $\text{Ca}(\text{OH})_2$ content little changed in mortars without the opal. If the alkali-silica reaction progressed within mortars with the reactive aggregate during the immersion in the NaCl solution, at least a part of $\text{Ca}(\text{OH})_2$ dissipated may be consumed in the process of the reaction, as has already been confirmed by Diamond (7) and Wei & Glasser (8). However, the mechanisms responsible for the dissipation of considerable amounts of $\text{Ca}(\text{OH})_2$ within the reactive aggregate-bearing mortars in the NaCl solution can not be explicitly explained at present.

CONCLUSIONS

The results obtained in the discussion on the relationships between the expansive behavior and the pore solution composition in mortars with various alkali contents immersed in various NaCl solutions with different concentration are summarized as follows;

(1) The expansion of mortars containing the opaline aggregate in 1N NaCl solution was extremely sensitive to the alkali/opal ratio in mortars.

(2) The concentration of NaCl solution in which mortar specimens were immersed, greatly influenced the expansion of mortars with a relatively low alkali/opal ratio. However, in the range of high alkali/opal ratio, the concentration of the NaCl solution little influenced the expansion of mortars.

(3) A chemical reaction, in which Cl^- ions are consumed and OH^- ions released, seems to occur within some opal-bearing mortars during the immersion in 1N NaCl solution. However, this phenomenon appears not to be related to the expansion of the mortars in the NaCl solution.

(4) Considerable amounts of $\text{Ca}(\text{OH})_2$ are dissipated during the immersion in 1 N NaCl solution in all mortars with opal, but not in mortars without the reactive aggregate.

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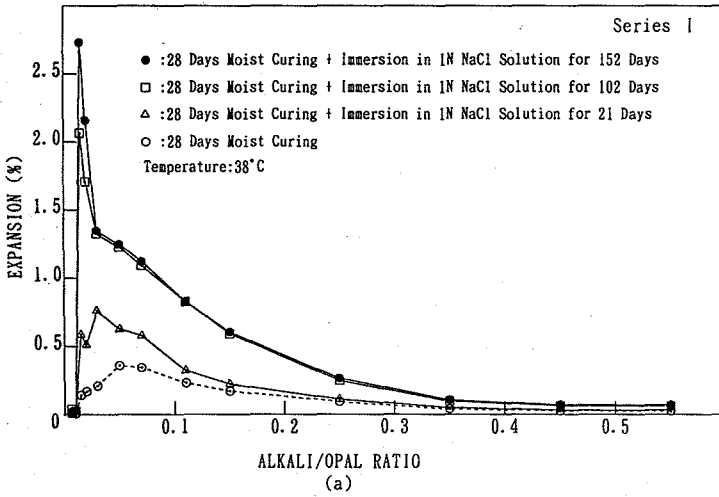


Figure 1 Relationships between expansion and alkali/opal ratio in Series I mortars with opal in 1N NaCl solution.

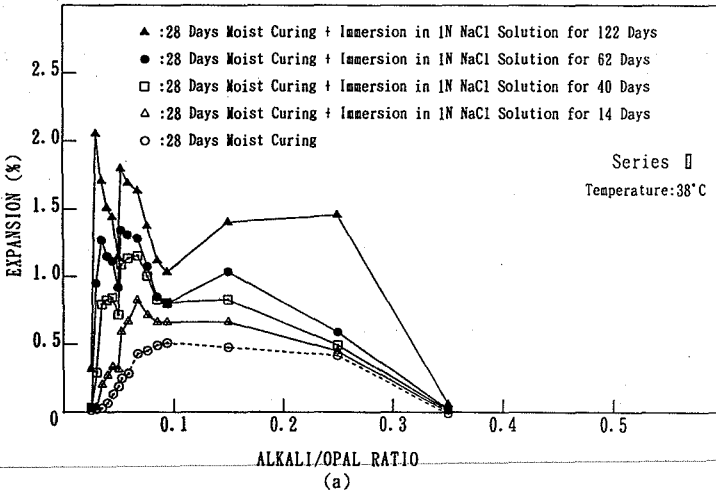


Figure 2 Relationships between expansion and alkali/opal ratio in Series II mortars with opal in 1N NaCl solution.

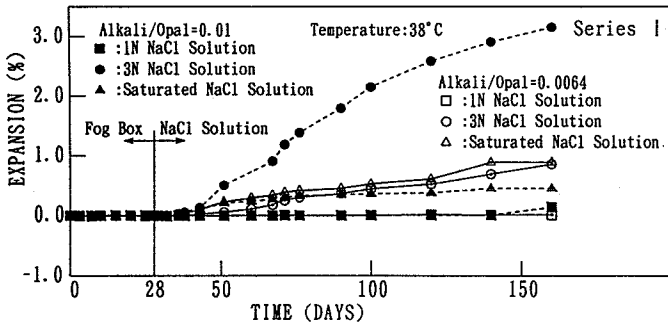


Figure 3 Expansion curves for Series I mortars with opal in 1N, 3N and the saturated NaCl solution.

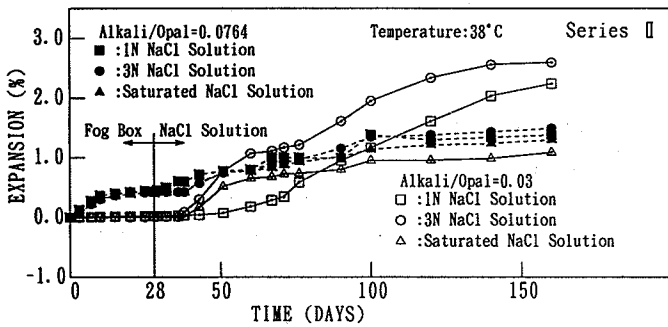


Figure 4 Expansion curves for Series II mortars with opal in 1N, 3N and the saturated NaCl solution.

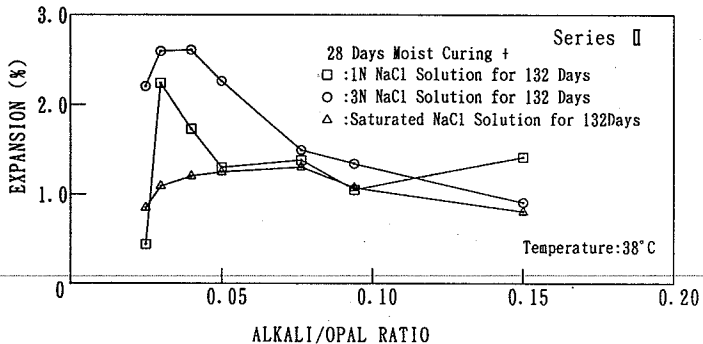


Figure 5 Relationships between expansion and alkali/opal ratio in mortars with opal in 1N, 3N and the saturated NaCl solution.

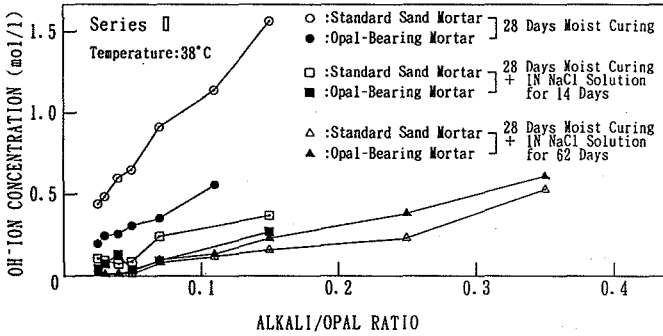


Figure 6 Relationships between OH⁻ ion concentration and alkali/opal ratio in mortars with and without opal immersed in 1N NaCl solution.

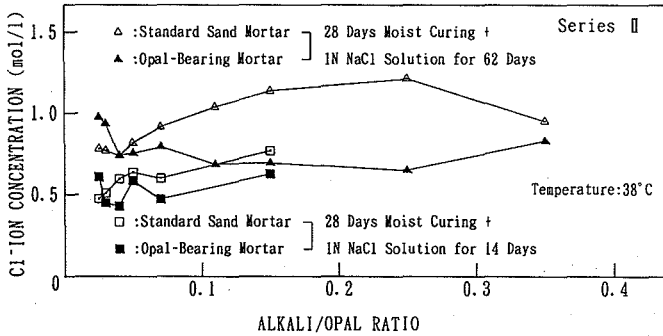


Figure 7 Relationships between Cl⁻ ion concentration and alkali/opal ratio in mortars with and without opal immersed in 1N NaCl solution.

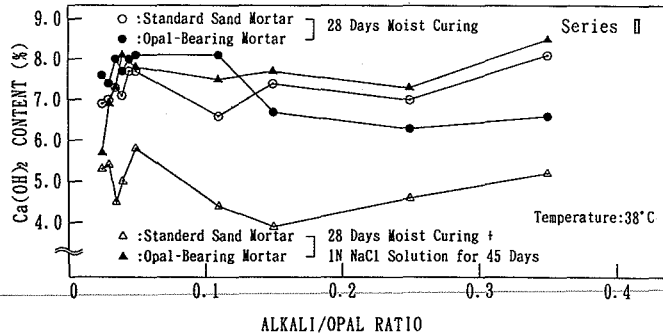


Figure 8 Relationships between Ca(OH)₂ content and alkali/opal ratio in mortars with and without opal.