

ALKALI-SILICA REACTION IN REACTIVE AGGREGATE-CEMENT PASTE INTERFACIAL REGIONS

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ABSTRACT

The microhardness and chemical compositions within reactive opaline rocks in model concrete specimens under a saline environment at an elevated temperature of 40 °C were investigated by using microhardness measurements, X-ray diffraction and X-ray fluorescence analysis. The model concrete specimen was placed on the setup so as to be in contact with 1 N NaCl solution at 40 °C for 19 weeks. The specimen as the reference was stored in a moist container at 40 °C and > 95% R.H. for 19 weeks. It was found from microhardness measurements that the portion of about 950 μm away from the interface within the opaline rock showed drastically higher microhardness in the specimen contacted with NaCl solution than in the specimen stored in a moist environment. The X-ray diffraction analyses showed that there were no differences in the diffraction patterns for the affected portions within the opaline rock between the two different storage conditions. It was also found from the X-ray fluorescence analyses that the different storage conditions resulted in different distributions of sodium, potassium, calcium, sulphur, aluminium, and chlorine concentration in portions up to about 1200 μm away from the interface within the opaline rock block.

Keywords: Alkali-silica reaction, Microhardness, Sodium chloride, X-ray diffraction, X-ray fluorescence analysis.

INTRODUCTION

It is well known that, in some cases, NaCl from the surrounding media extremely promotes the expansion of mortars containing reactive aggregate. Kawamura et al. found that the microhardness in regions of about 100 μm to 200 μm away from the interface within reactive calcined flint grains in mortars immersed in 1 N NaCl solution at 38 °C drastically increased with time (Kawamura et al. 1994). A similar rise in microhardness was also found within reactive opal grains in mortars immersed in 1 N NaCl solution at 38 °C (Sugiyama. 1993). These findings indicate that the intrusion of NaCl into reactive aggregate-bearing mortars at an elevated temperature may affect reaction products formed within reactive aggregate grains. In the quantitative analyses in these studies, variations of concentration of elements in a spot within a small reacting grain in mortars were considerably great because of the inhomogeneous textures of reactive aggregate grains. It is rather appropriate to analyse wide areas in order to obtain concentrations of various elements on average.

This study aims at elucidating the microhardness and chemical composition within a relatively large block of a reactive opaline rock in model concrete specimens.

EXPERIMENTAL DETAILS

Materials

Table 1 Chemical composition of cement and opaline rock used.

	Cement	Opaline rock
Ig. loss (%)	0.5	1.9
SiO ₂ (%)	21.2	92.6
Al ₂ O ₃ (%)	5.0	1.9
Fe ₂ O ₃ (%)	3.1	0.5
CaO (%)	64.9	—
MgO (%)	1.5	1.1
SO ₃ (%)	1.9	—
Na ₂ O (%)	0.51	0.4
K ₂ O (%)	0.70	0.7
Total (%)	99.31	99.1

An ordinary Portland cement with an equivalent Na₂O percentage of 0.97 was used. Its specific gravity and Blaine fineness were 3.16 and 3050 cm²/g, respectively. The reactive aggregate used was an opaline rock from Akase opal mine in Ishikawa Prefecture in Japan. An X-ray diffraction pattern for the opaline rock showed the existence of cristobalite and quartz. The reduction in alkalinity (Rc) and the dissolved silica (Sc) of the opaline rock determined in accordance with ASTM C289 test were 158 mM/l and 558 mM/l, and its specific gravity and absorption capacity were 2.36 and 2.65%, respectively. The chemical composition of the cement and the opaline rock is presented in Table 1.

Preparation of specimens

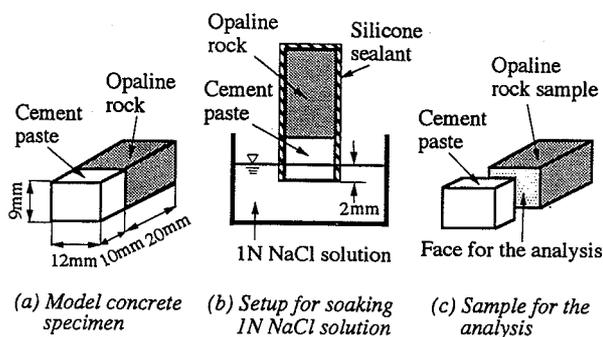


Fig. 1 Model concrete specimen for the microhardness test and X-ray analysis.

9 × 12 × 30 mm model concrete specimens were made by bonding a 9 × 12 × 20 mm reactive opaline rock prism to a cement paste prism with a water-cement ratio of 0.4, as shown in Fig. 1(a). The rock prisms were carefully cut from a rock block with a wafering blade saw. The surfaces of rock prisms were polished by hand on smooth iron and glass plates using water and five carborundum powders of #60, #100, #180, #400, and #800. Megascopic observations on the opaline rock showed that there might be faint stratiform heterogeneity in the rock. In order to remove the effect of the heterogeneity of the rock on the results of microhardness measurements, the direction of the stratum was perpendicular to the rock-cement paste interface in the preparation of model concrete specimens. The rock prisms had been stored in water for 24 hours before the cement paste was cast on them.

The surfaces of rock prisms were polished by hand on smooth iron and glass plates using water and five

A cement paste was cast in the special steel mould inlaid with a opaline rock prism. A vibrator with a $\phi 2$ mm vibrating head was used for the compaction of cement paste. The model concrete specimens were stored in a room maintained at 20 °C and about 85% R.H. for 24 hours in the moulds, and then demoulded. Immediately after demoulding, 5 faces of the model concrete specimens except the cement paste face of 9×12 mm were coated with a silicone sealant to obtain the one-dimensionally modeled concrete specimens. Thereafter, the model concrete specimens were cured under the following two conditions; placed on the setup so as to be in contact with 1 N NaCl solution at 40 °C for 19 weeks (Fig. 1(b)) and stored in a moist container at 40 °C and > 95% R.H. for 19 weeks. The latter curing condition was applied to the reference.

Microhardness test

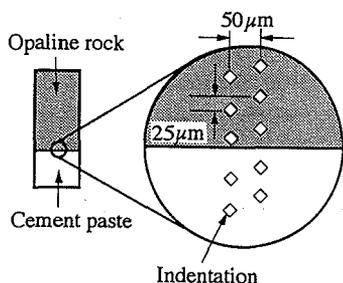


Fig. 2 Spots for the microhardness measurements.

After curing, the silicone coating on the 5 faces of the model concrete specimens was removed, and then their opposite faces of casting faces were polished on a rotating wheel using ten successively finer emery papers; #150, #240, #320, #400, #600, #800, #1000, #1500, #2000, and finally #3000. The time for polishing with each emery paper was about 40 seconds.

The microhardness tester with a Vickers indenter was used to measure microhardness. The microhardness measurements were made in cement paste regions near the rock-cement paste interface and in rock regions up to about 1100

μm away from the interface on the polished surface of specimens. For the purpose of facilitating the measurements of the diagonal length of indentations in the microhardness measurements, areas of 1×2 mm on the polished surface of rocks were stained with blue oily ink. Spots for the measurements were spaced as shown in Fig. 2 to exclude the effect of the preceding indentation on the later one.

X-ray diffraction and X-ray fluorescence analysis

After completion of microhardness measurements, the model concrete specimens were subjected to flexural loads to produce rock samples for X-ray analysis. Failure of the model concrete specimen stored in a moist environment occurred at the interface, and the rock sample as shown in Fig. 1(c) was obtained. On the other hand, the model concrete specimen in contact with NaCl solution failed at the cement paste portion near the interface. Thus, the remainder of the cement paste on the rock surface was removed by abrasion with #240 and #400 emery papers to produce the same rock sample as that in Fig. 1(c). Because of the abrasion for preparing the rock sample, the first X-ray analysis in this series was made at the surface of about $10 \mu\text{m}$ away from the interface, not at the immediate surface of the interface.

The X-ray diffraction and fluorescence analysis was applied to determine X-ray

diffraction patterns and sodium, potassium, calcium, sulphur, aluminium, and chlorine concentration within the regions up to about 1200 μm away from the interface in the rock samples. Surfaces of the rock samples to be analyzed were prepared by careful step by step abrasion with a # 400 emery paper. The weight of materials removed by abrasion was measured with a balance with 0.05 mg sensitivity. The distance from the interface to the surface to be analyzed was calculated on the basis of the weight of materials removed and the density of rock.

The X-ray fluorescence analyses were made using the Shimadzu X-ray fluorescence spectrometer. The accelerating voltage and electric current intensity used was 45 kV and 50 mA, respectively. Considering the experimental conditions in this study, the analyzable depth for the opaline rock samples is supposed to be at least several μm .

RESULTS AND DISCUSSION

Microhardness distribution within opaline rocks

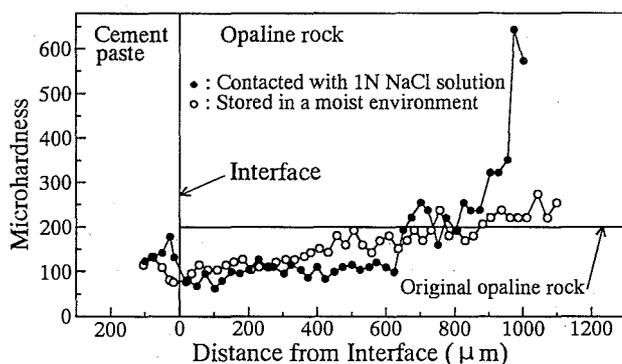


Fig. 3 Microhardness within opaline rocks in the model concrete specimens.

the immediate vicinity of the interface. The microhardness within the rock increases gradually with distance from the interface, as shown in Fig. 3. It is also apparent that the region with the microhardness comparable to the level of the original opaline rock is in the range of about 750 μm to about 1100 μm away from the interface.

It is found from Fig. 3 that in the opaline rock in the model concrete specimen contacted with NaCl solution, the portions up to about 650 μm away from the interface show about half the microhardness of the original opaline rock. The microhardness in the region ranging from about 700 μm to about 900 μm in this series increased to the level of the original opaline rock, although the plots in the region were somewhat scattered. Furthermore, a drastic rise in microhardness is found in the regions from about 900 μm to 1000 μm away from the interface within the opaline rock.

From comparison in microhardness distributions within reactive opaline rocks between model concrete specimens under the two different storage conditions, the

Fig. 3 shows plots of the value of microhardness within the reactive opaline rock in the model concrete specimens contacted with 1 N NaCl solution and stored in a moist environment for 19 weeks. In the opaline rock in the reference model concrete specimen stored in a moist environment, the lowest value of microhardness of about 80 is found in

following results were obtained.

1) The microhardness in the region from about 300 μm to about 650 μm away from the interface decreased significantly, when the specimen was contacted with NaCl solution. This suggests that the alkali-silica reaction has occurred more actively in the interfacial regions in the specimen contacted with NaCl solution than in the specimen stored in a moist environment. The acceleration of the alkali-silica reaction by the intrusion of Cl^- ions was also confirmed in other studies (Kawamura et al. 1994, Kawamura & Takeuchi. 1995).

2) The microhardness in the region from about 900 μm to 1000 μm away from the interface increases in the presence of NaCl. In particular, the portion of about 950 μm away from the interface shows drastically higher microhardness in the specimen contacted with NaCl solution than in the specimen stored in a moist environment, resulting in the production of an extremely hard reaction product.

X-ray diffraction analyses within opaline rocks

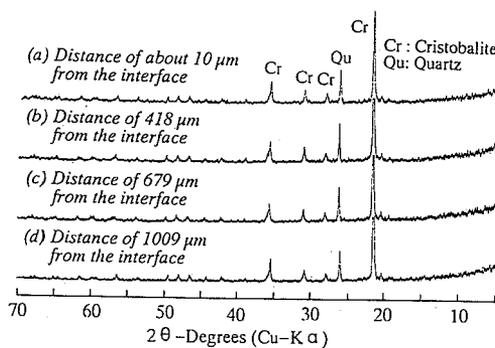


Fig. 4 X-ray diffraction patterns for the surfaces within the opaline rock in the model concrete specimen contacted with 1N NaCl solution.

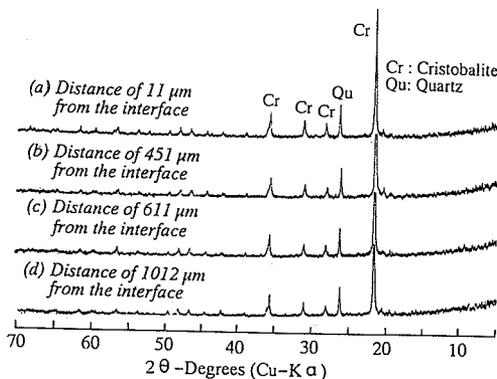


Fig. 5 X-ray diffraction patterns for the surfaces within the opaline rock in the model concrete specimen stored in a moist environment.

The X-ray diffraction patterns for portions up to about 1000 μm away from the interface within the opaline rocks in the model concrete specimens contacted with 1 N NaCl solution and stored in a moist environment are presented in Figs. 4 and 5, respectively. Figs. 4 and 5 show that the diffraction patterns for different distances from the interface are not different from one another. It is also found from the comparison between Fig. 4(d) and Fig. 5(d) that there is no difference in the diffraction patterns for the face of about 1000 μm away from the interface within the opaline rock between the two different storage conditions. This result indicates that the drastic rise in microhardness in the portion of about 950 μm away from the interface within the opaline rock in the presence of NaCl was not responsible for the production of crystalline substances.

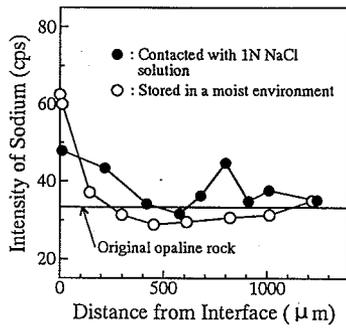
X-ray fluorescence analyses within opaline rocks

Fig. 6 shows plots of the fluorescent X-ray intensity for various elements of sodium, potassium, calcium, sulphur, aluminium, and chlorine obtained by X-ray fluorescence analysis within the opaline rocks in the model concrete specimens contacted with 1 N NaCl solution and stored in a moist environment. As shown in Fig. 6(a), the intensity for sodium within the opaline rock in the model concrete specimen stored in a moist environment is greater at the portions near the interface than in the specimen contacted with NaCl solution, but the intensity for sodium in the latter exceeds that in the former in portions deeper than about 100 μm . A similar distribution pattern is also observed in the intensity for potassium within the opaline rocks (Fig. 6(b)). All the plots in Fig. 6(b) are found to be considerably greater than the level of the intensity for potassium of the original opaline rock, which stands for the base line.

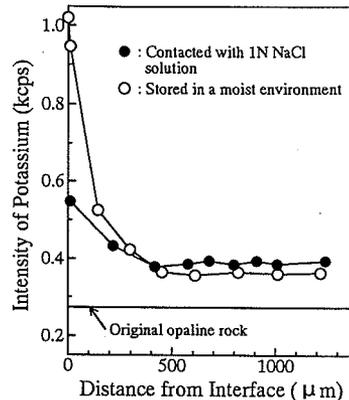
Fig. 6(c) shows that the intensity for calcium at portions near the interface within the opaline rocks in the specimen contacted with NaCl solution was far greater than in the reference, but that there is no difference in the region from about 200 μm to about 1200 μm away from the interface within the rocks between the two different storage conditions. Kawamura et al. found that the intrusion of calcium into the alkali-silica gels formed in reactive opal grains in mortars cured in a moist environment increased the microhardness in the regions (Kawamura et al. 1983). Furthermore, the second author et al. of this paper (Kawamura et al. 1994) reported that a soft reaction product produced within reactive calcined flint grains in mortars was altered into an extremely hard reaction product during the immersion in the 1 N NaCl solution. They deduced that this alteration was related to the intrusion of considerable amounts of calcium into the regions. In this study, from the fact that the intensity for calcium in portions deeper than about 200 μm within the opaline rock in the specimen contacted with NaCl solution is almost the same as in the reference (Fig. 6(c)), it can be mentioned that the drastic rise in microhardness within the opaline rock in this model specimen in the presence of NaCl as previously described is not responsible for the intrusion of calcium.

As shown in Fig. 6(d) and (e), the intensity for sulphur and aluminium within the opaline rock is greater in the specimen contacted with NaCl solution than in the specimen stored in a moist environment. In particular, a relatively high content of aluminium was found in the region from about 1000 μm to about 1200 μm away from the interface in the presence of NaCl (Fig. 6(e)). It is also found from Fig. 6(f) that Cl^- ions intruded into the opaline rock.

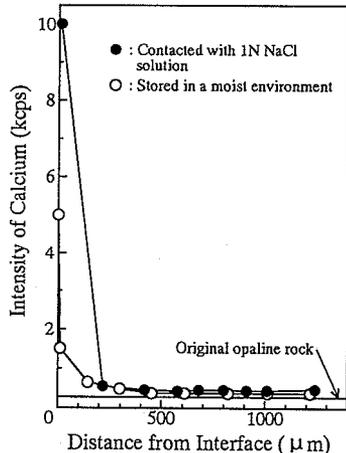
The above results manifest that the inward diffusion of Cl^- ions into the cement paste promoted the diffusion of sodium, potassium, calcium, sulphur, and aluminium into the opaline rock. In particular, it should be noted that the presence of Cl^- ions in the cement paste phase mobilized a relatively large amount of aluminium into the opaline rock phase.



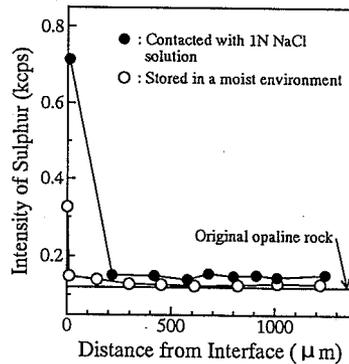
(a) Distribution of sodium



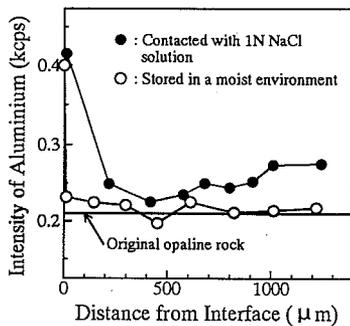
(b) Distribution of potassium



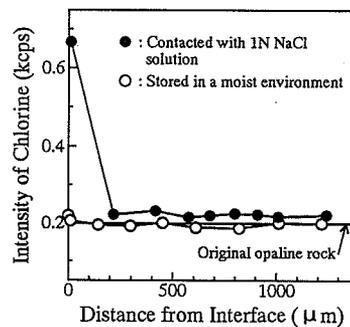
(c) Distribution of calcium



(d) Distribution of sulphur



(e) Distribution of aluminium



(f) Distribution of chlorine

Fig. 6 Distributions of intensity of various elements within the opaline rock in the model concrete specimen.

CONCLUSIONS

The following findings were obtained from this study.

1) The microhardness in the region from about 900 μm to 1000 μm away from the interface within the opaline rock in the model concrete specimen increased in the presence of NaCl. In particular, the portion of about 950 μm away from the interface shows drastically higher microhardness in the specimen contacted with 1 N NaCl solution than in the specimen stored in a moist environment.

2) There is no difference in the X-ray diffraction patterns for the surface of about 1000 μm away from the interface within the opaline rock between the model concrete specimens contacted with 1 N NaCl solution and stored in a moist environment. It seems that the formation of an amorphous reaction product is responsible for the drastic rise in microhardness in the portion of about 950 μm away from the interface within the rock in the presence of NaCl.

3) The inward diffusion of Cl^- ions into the cement paste phase promoted the diffusion of sodium, potassium, calcium, sulphur, and aluminium.

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