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Effects of externally supplied lithium on the suppression of ASR expansion in mortars

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Abstract

Lithium salts are being externally supplied for mitigating the progress of deterioration of ASR-affected concrete structures. However, it is not clear whether the sodium or potassium in the ASR gel in concrete is replaced by the lithium supplied from the outside. In this article, we examine changes in the composition of the ASR gel, previously formed in mortar specimens, after they are immersed in LiOH solution, using backscattered electron (BSE) imaging and energy-dispersive X-ray (EDX) analysis, associated with length change measurement of the mortar prisms. The intrusion of lithium ions into mortar specimens containing a reactive aggregate could arrest their further expansion within a relatively short time after immersion in 0.50 N LiOH solution. The alkali ions incorporated in most ASR gels, located not far away from interfaces between the cement paste and reactive aggregate particles, appear to be replaced by the lithium ions supplied from the solution. However, the ASR gel within the reacted aggregate particles did not appear to have been affected by the lithium ions.

Keywords: Backscattered electron imaging; Alkali–aggregate reaction; ASR gel; Lithium; Expansion

1. Introduction

Lithium salts are being externally supplied for mitigating the progress of deterioration of ASR-affected concrete structures. Some workers have confirmed that lithium salts introduced into concrete containing reactive aggregate at the mixing stage suppressed the alkali–silica reaction by producing the nonexpansive lithium-bearing ASR gel in the concrete and retarding or reducing the reaction of sodium hydroxide with silica [1–4]. However, in the repair of ASR-affected concrete structures, the ASR gel has already formed within the concrete before the treatment with lithium salt. It has also been reported that treatment of concrete with LiOH has most effectively arrested development of expansive ASR in the hardened concretes [5].

However, at present, it is not clear whether the sodium or potassium in the ASR gel in concrete is replaced by the lithium supplied from the outside. We have examined changes in the compositions of ASR gels in mortar specimens immersed in LiOH solution by the backscattered electron (BSE) imaging and energy-dispersive X-ray (EDX) analysis, and by measuring length changes of the mortar prisms with time.

2. Experimental work

The calcined flint produced by Blue Circle and a crushed limestone with a size fraction of 0.6–2.5 mm were used as the reactive and the nonreactive aggregate, respectively. In the mortar mixture, the reactive aggregate formed 30% of the total aggregate by mass. NaOH was added at a dosage level equivalent to a cement with 1.2% Na_2O. A series of mortar specimens ($40 \times 40 \times 160$ mm prisms) was prepared with a water/cement ratio of 0.55 and an aggregate/cement ratio of 2.0.

Mortar specimens were immersed in 0.50 N LiOH and 0.50 N NaOH solution, and distilled water after precuring for prescribed periods at 38 °C. Mortar specimens were

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completely sealed in vinyl sacks during precuring. The concentrations of LiOH and NaOH solutions were determined such that the OH^- ion concentration in the solutions was equal to that in the pore solution in the 7-day-old mortar which was 0.50 N. If all the alkali content dissolves in the mixing water, it would give a 0.70 N NaOH at the time of mixing.

The mortar specimens sealed in vinyl sacks started expanding at about 7 days; and 50% and 75% of the ultimate expansion of mortar specimens were attained at 28 and 42 days, respectively. The immersion tests for mortar specimens commenced at the age of 7, 28 and 42 days, to correspond with these levels of initial expansion.

Mortar slices for the BSE-EDX analysis were taken from the two mortar specimens immersed in the solutions for 35 and 78 days after precuring. Mortar slices were cut from portions within about 5 mm from surfaces of mortar prisms. The mortar slices were dried using ethanol replacement, followed by vacuum drying at a room temperature overnight. Dried mortar slices were impregnated with an ultra-low viscosity epoxy resin under vacuum, and then polished by the use of silicon carbide abrasive papers. The final polished surface was sputter coated with about a 30-nm-thick layer of gold–palladium alloy for the BSE-EDX analysis.

3. Results and discussion

Figs. 1–3 show expansion curves for mortar specimens which were immersed in 0.50 N LiOH, 0.50 N NaOH solution and in water at the age of 7, 28 and 42 days, respectively, after casting, along with those for the mortar specimens cured in vinyl sacks at 38 °C. Only little differences were found in measured expansions between mortar specimens immersed in the LiOH and in water (Fig. 1). Fig. 4 shows that the OH ion concentration of the pore solution did not change appreciably due to the immersion in the LiOH solution, whereas it dropped rapidly due to the immersion in water. The Na + K ion concentration dropped rapidly in both cases. This was compensated for a similar increase in Li concentration in the case of LiOH immersion, and perhaps by Ca ions in the case of water immersion. The extraction of OH^- and alkali ions over a period of 35 days from mortar specimens in water moderated the alkali–silica reaction after this period (Fig. 1). Almost the same expansion was exhibited by mortar specimens immersed in the LiOH solution (Fig. 1). As the OH ion concentration was unchanged for the specimens immersed in the LiOH solution, the lack of further expansion (compared to the specimens immersed in the NaOH

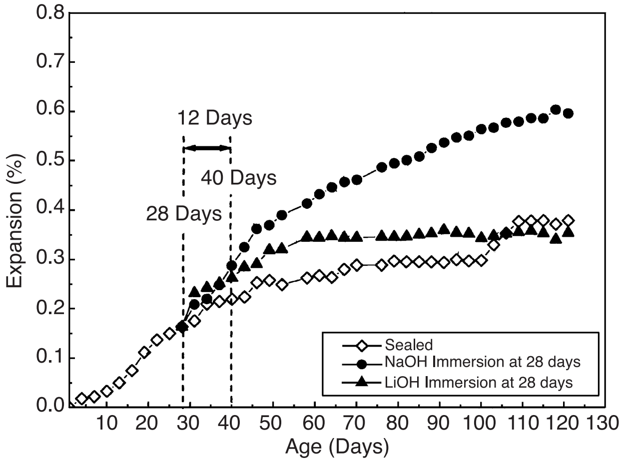

Fig. 2. Expansion curves for mortar prisms immersed in solution at the age of 28 days.

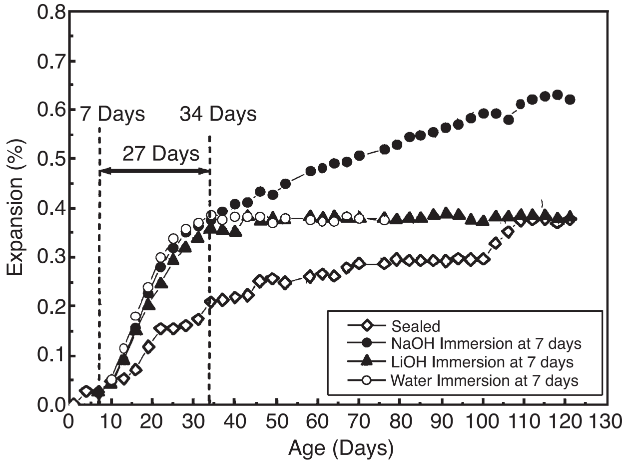

Fig. 1. Expansion curves for mortar prisms immersed in solution at the age of 7 days.

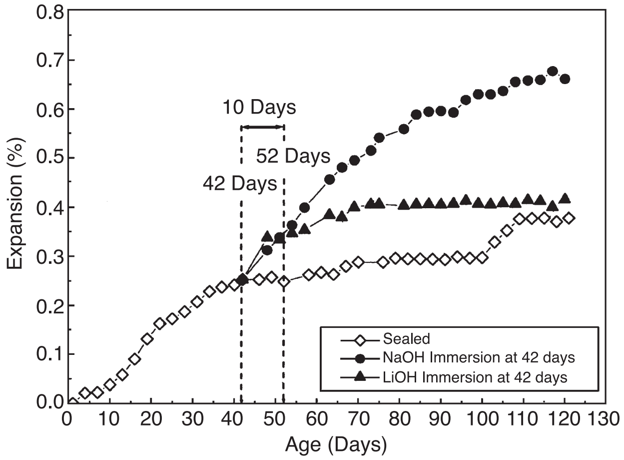

Fig. 3. Expansion curves for mortar prisms immersed in solution at the age of 42 days.

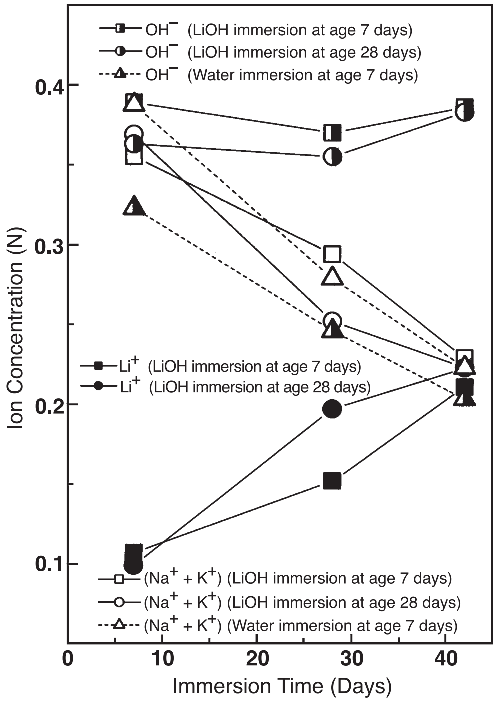

Fig. 4. Changes in Na^+, K^+, Li^+, OH^- ion concentration of the pore solution with time.

solution) must have resulted from the depletion of Na + K and enrichment with Li in the pore solution, which would, in turn, affect the nature of the ASR gel products. The considerably lower expansion in the sealed mortar specimens may be due to the limitation of available water. Figs. 1–3 indicate that the intrusion of lithium into mortar specimens with the reactive aggregate could suppress further expansion shortly after immersion in the LiOH solution. Measured expansion from the time of immersion to the time when no further expansion takes place is probably due to the consumption of the available OH^- and alkali ions and the effect of the ASR gel already formed before the lithium from the outside acted on the ASR gel. As shown in Figs. 1–3, expansion curves of mortar specimens in the LiOH solution started being differentiated from those of specimens in NaOH solution at relatively short times after immersion. Presumably, after immersion in solution, the lithium appears to have acted on the ASR gel as it intruded into mortar prisms. Figs. 1–3 show that expansion of mortar specimens immersed in the LiOH at the age of 7, 28 and 42 days started decreasing after 27, 12 and 10 days after immersion in the LiOH solution, respectively (i.e., expansion of mortar specimens started decreasing earlier in specimens precured in vinyl sacks for longer periods). This is due to the fact that the remaining expansion of the latter specimens would be smaller, as most of OH^- and alkali ions would have been consumed in the longer reaction period.

It was observed in earlier work [6] that sufficient ASR gel forms in relatively wide cracks in reacted

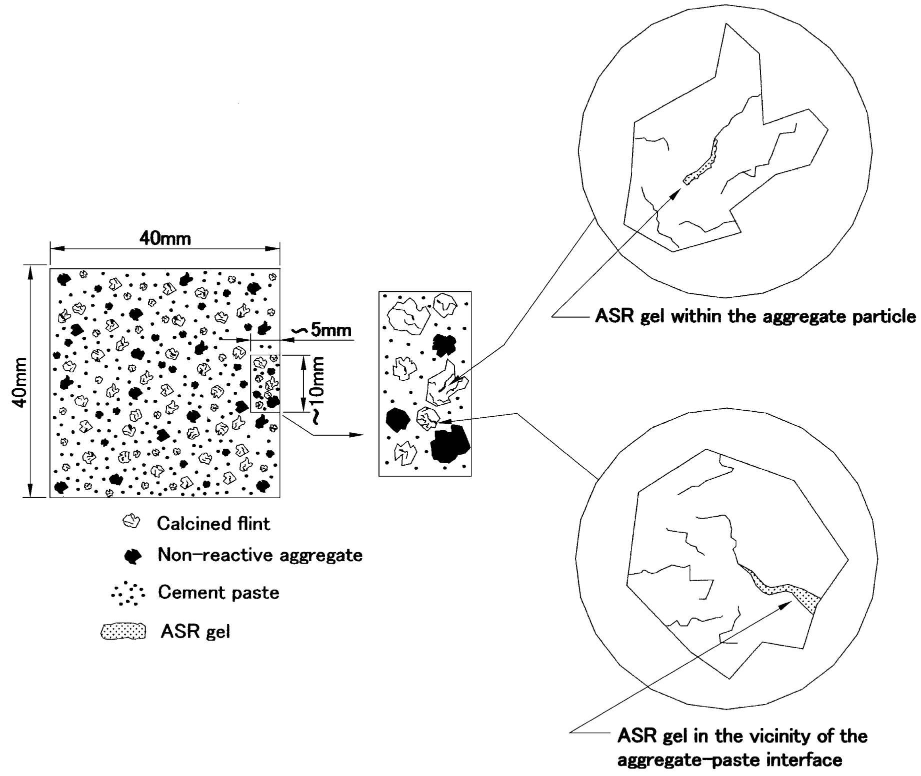

Fig. 5. Schematic sketch of the cross-section of a mortar bar and locations of EDX analysis for the ASR gel areas.

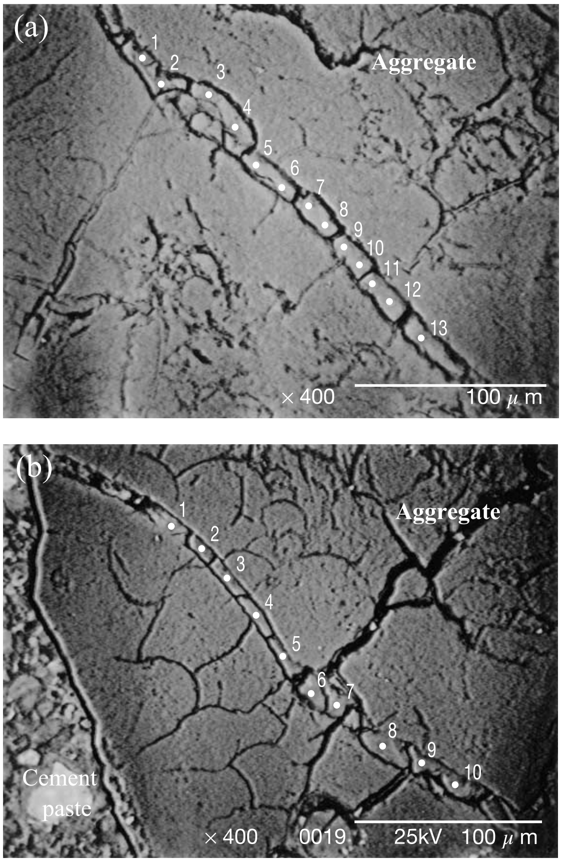

Fig. 6. SEM images for ASR gels. (a) ASR gel within the aggregate particle; (b) ASR gel in the vicinity of the aggregate–paste interface.

calcined flint aggregate to allow its analysis by EDX. A schematic sketch of the cross-section of the mortar and locations of EDX analysis is presented in Fig. 5. SEM images for the ASR gel areas are given in Fig. 6, and the results of EDX spot analyses within the ASR gel areas are presented in Figs. 7 and 8. These diagrams present the average of results obtained by EDX analyses at 10 to 13 spots in an ASR gel area. At the time of immersion of mortar specimens in the LiOH solution, considerable amounts of ASR gel were considered to have already formed within reactive aggregate particles during precuring.

The results of EDX analyses for ASR gel areas within the aggregate particles are given in Fig. 7. Alkali contents in most ASR gel areas in the mortar specimens were found to be as high as about 20%. It is assumed from these results that the lithium ions have not reached the ASR gel areas located within the aggregate and away from interfaces in mortar samples.

The results of EDX analyses for ASR gel areas in the vicinity of interfaces between the cement paste and the reactive aggregate were plotted in the phase diagram in Fig. 8. We found that there were a number of spots showing alkali contents of less than 10% in the ASR gel areas, largely for the specimens stored in the LiOH solution. However, as also shown in Fig. 8, all the ASR gels found in areas in the vicinity of interfaces in the samples sliced from mortar prisms immersed in NaOH solution and in water, and sealed mortar prisms contained about 20% alkalis. Moreover, even in ASR gel areas in the vicinity of interfaces, several spots showing alkalis contents of 15–20% were found. This is because some of the points analyzed in this region were in fact within the aggregate particle, and not close to the cement paste, so that the results were similar to the points shown in Fig. 6(a). The lithium ions could probably not reach the gel areas within the aggregate particles which are away from the interface with the cement paste. These results suggest that the alkalis in ASR gels not far away from the

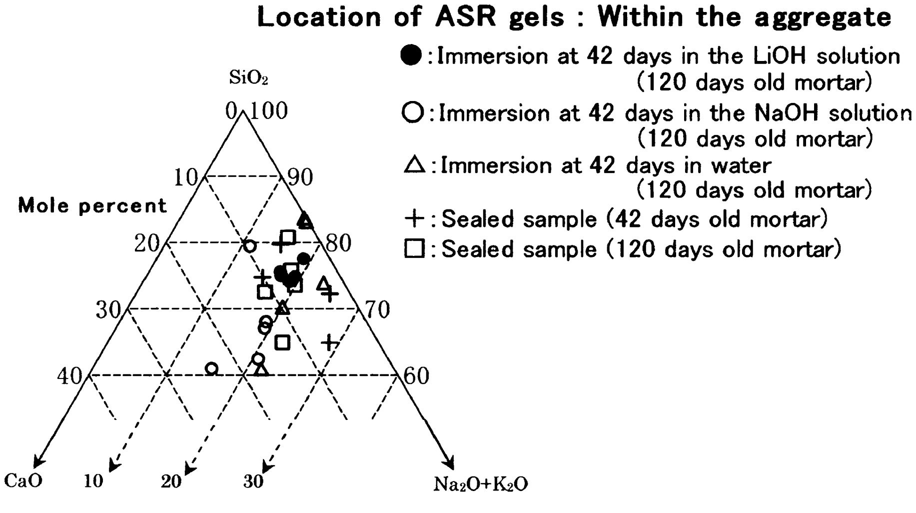

Fig. 7. Ternary phase diagram for ASR gels located within aggregate particle as shown in Fig. 6(a).

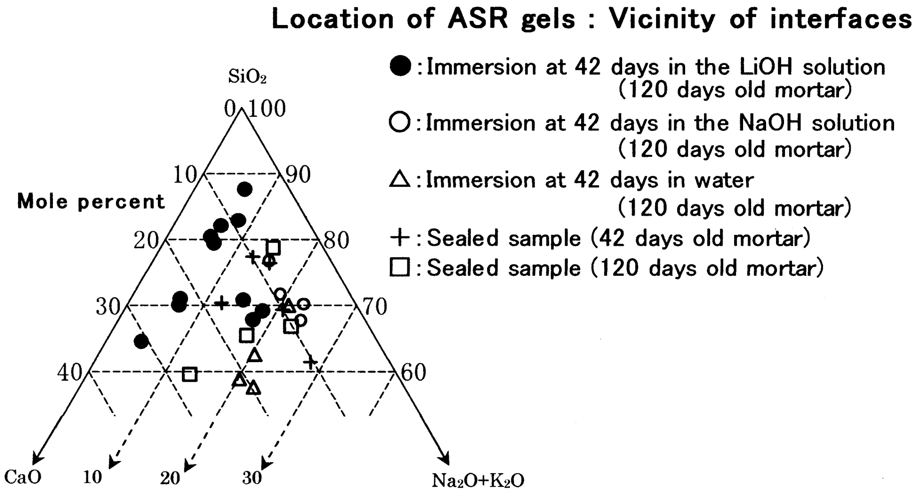

Fig. 8. Ternary phase diagram for ASR gels located in the vicinity of aggregate–paste interfaces as shown in Fig. 6(b).

interfaces were replaced by the lithium ions supplied from the external solution.

4. Conclusions

From the results obtained in this study, the following conclusions are drawn:

(1) The intrusion of lithium ions into mortars with a reactive aggregate could arrest further expansion of mortar bars, relatively shortly after immersion in 0.50 N LiOH solution.
(2) Expansion of mortar specimens continued after immersion in the LiOH solution so far as Na + K hydroxides were available. Consequently, the expansions started decreasing earlier in mortar bars precured in vinyl sack for longer periods; the specimens having undergone most of their expansion potential.
(3) The alkalis in most ASR gels in the vicinity of interfaces between the cement paste and the reactive aggregate particles appear to be replaced by the lithium ions supplied from the external solution.
(4) The ASR gel within the aggregate particles, which is away from the interface with cement paste, is not influenced by the lithium ions.

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