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Effects of lithium salts on ASR gel composition and expansion of mortars

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Abstract

Suppression of alkali–silica reaction (ASR) expansion in mortar and concrete by the addition of lithium salts has been confirmed by some workers. It has been revealed that lithium hydroxide tended to reduce the reaction between sodium or potassium hydroxide and reactive silica, and that the ASR gel incorporating lithium was less expansive. However, it has not been reported how the addition of a lithium salt influenced the composition of the ASR gel. The calcium in ASR gel is considered to play an important role in the expansion of the gel. Thus, it is significant to characterize ASR gel composition in mortars containing lithium salts by BSE–EDS analysis. This study aims to discuss the mechanisms of suppression of ASR expansion in mortar by lithium salts from the viewpoint of ASR gel composition. The average CaO/SiO_2 ratio in ASR gels decreased with increasing amount of added lithium salts. It should be noted that the extent of variations in the CaO/SiO_2 ratio in ASR gels significantly decreased with increasing amount of lithium salts. The addition of relatively small amounts of LiOH and Li_2CO_3 resulted in increased expansion. We also obtained an unexpected result that ASR gels became homogeneous with respect to their CaO contents at high dosage levels. However, the reduction in average CaO/SiO_2 ratios and the homogenization in the CaO content of ASR gels due to the addition of lithium salts may not be related to the expansion of mortars.

Keywords: Backscattered electron imaging; Alkali–aggregate reaction; Pore solution; Expansion

1. Introduction

Suppression of alkali–silica reaction (ASR) expansion in mortar and concrete by the addition of lithium salts has been confirmed by some workers [1–4]. Lithium hydroxide tended to reduce the reaction between sodium or potassium hydroxide and silica [2]. It has also been reported that ASR gel incorporating lithium was less expansive and that the addition of lithium hydroxide decreased the total amount of ASR gel produced [4]. Recently, it was revealed by transmission soft X-ray microscopy that the formation of the expansive gel by repolymerization may be limited by the presence of lithium [5]. However, the result of the mortar bar expansion test indicated that the addition of small and moderate amounts of LiOH adversely increased expansion [4]. It has been pointed out that the effects of lithium salts on ASR varied for different salts because of differences in the increased level of OH^- ion concentration in the pore solution between different anions concerned. It has been revealed that lithium salts increased the OH^- ion concentration in the pore solution [6]. Recently, it was also shown that lithium nitrate did not significantly increase hydroxide ion concentration [7].

However, considering that the calcium in ASR gel may play an important role in the expansion of ASR gels and that ASR gel composition greatly varies even in areas of several tens of micrometers, it is significant to reveal the effects of lithium on the composition of the ASR gel.

This study aims to discuss the mechanisms of suppression of ASR expansion in mortars by the addition of lithium salts from the viewpoint of ASR gel compositions obtained by SEM–EDS analyzing of the pore solutions expressed from the mortars.

2. Experimental outline

Calcined flint with a size fraction of 2.5 to 0.6 mm from Blue Circle was used as a reactive aggregate. Its dissolved silica (Sc) and the reduction in alkalinity (Rc) in ASTM chemical test were 1063 and 70 mmol/l, respectively. A high-

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Table 1
Chemical composition of cement (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Ignition loss
20.1	4.7	3.2	62.5	2.5	3.3	0.41	1.1	1.2

alkali Portland cement with the equivalent Na_2O percentage of 1.12 was used. Its chemical composition is given in Table 1. LiOH and Li_2CO_3 were used as additives for inhibiting the ASR expansion of mortars. The dosage levels of the additives were 0.3%, 0.5%, 1.0% and 1.5% by weight of cement. A series of mortars were prepared with a water/cement ratio of 0.55 and an aggregate/cement ratio of 2. Thirty percent of the total aggregate by weight was replaced by the reactive aggregate. It was confirmed in advance that the 30% replacement of reactive aggregate was the pessimum percentage in this study.

A series of mortar prisms, 40 × 40 × 160 mm, were sealed in vinyl sacks and stored in a moist environment at 38 °C for the measurement of changes in length with time.

At 7, 35 and 98 days after the initiation of measurements of expansion, mortar slices for BSE–EDS analysis were cut from the middle portion of mortar prisms with and without lithium salts, and then dried using ethanol replacement, followed by vacuum drying at room temperature overnight. Dried mortar slices were impregnated with an ultralow 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 30-nm-thick layer of gold–palladium alloy.

The polished mortar samples were examined with a Hitachi S-2250N SEM equipped with a backscatter detector and a Horiba EMAX5770W energy dispersive X-ray analyzer. The SEM was operated at 25 keV. A standard magnification of 500 was used in EDS analyses at 10 to 20 spots selected within ASR gel areas, 10 to 20 μm wide and about 150 μm long, within cracks in reactive aggregate particles in mortars.

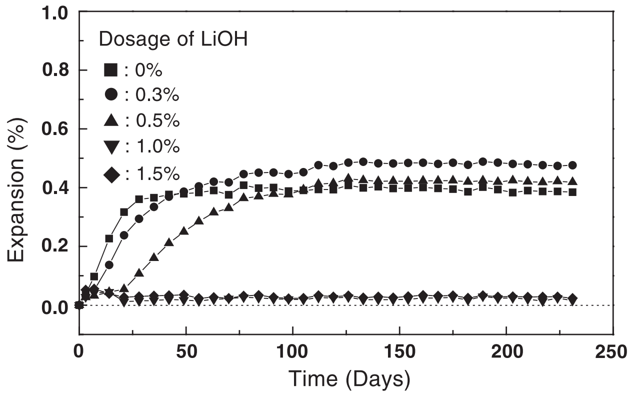

Fig. 1. Expansion curves of mortars with LiOH.

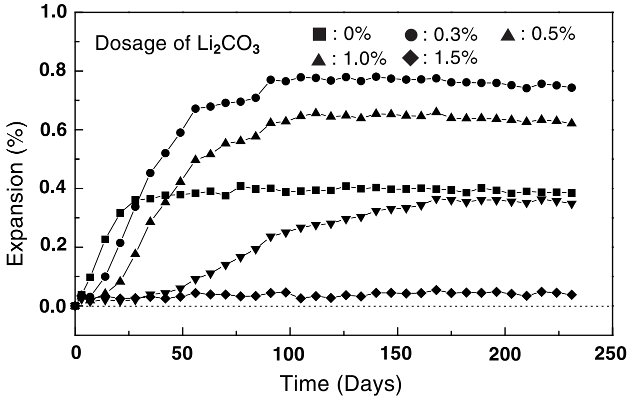

Fig. 2. Expansion curves of mortars with Li_2CO_3.

The Na^+, K^+ and Li^+ ion concentrations in pore solutions expressed from the same mortars as used in the expansion tests were determined by atomic absorption, and the OH^- and SO_4^{2-} ion concentrations were determined by titration with HCl and ion chromatography, respectively. All the ion concentrations have been obtained by adjusting for bound water [8].

3. Results

3.1. Expansion of mortars with and without lithium salts

Measured expansions for mortars with and without LiOH are plotted against time, as shown in Fig. 1. Immediately after the initiation of the expansion test, mortars without additive rapidly expanded up to about 28 days, and thereafter showed little expansion. It is also shown in Fig. 1 that mortars with 0.3% LiOH showed a similar expansion curve to that of mortars without additive. There were only small differences in measured expansions between both throughout the expansion test. The mortar with 0.5% LiOH started expanding after about 28 days, and a little more slowly expanded than the

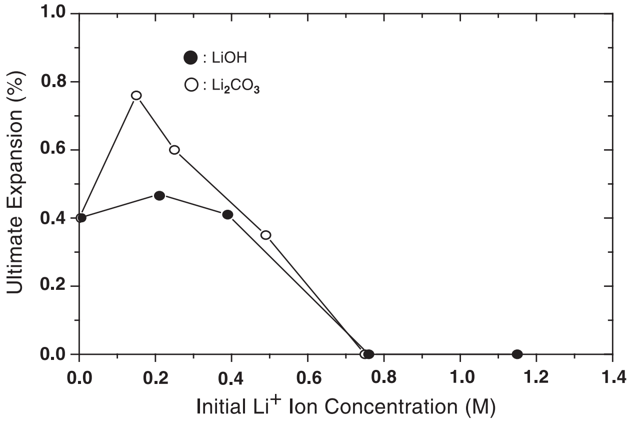

Fig. 3. Relation between initial Li^+ ion concentration and ultimate expansion of mortars.

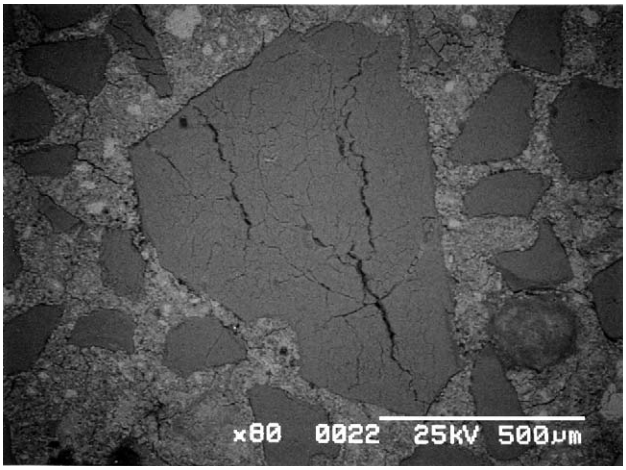

Fig. 4. BSE micrograph for a reactive aggregate particle in mortars without additive.

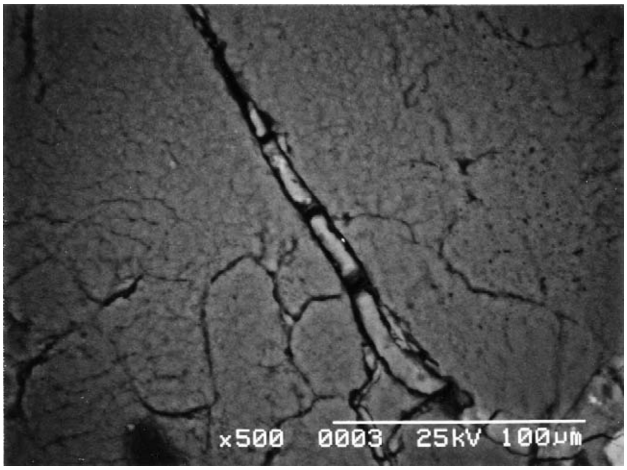

Fig. 6. BSE micrograph for the massive gels in 35-day-old mortar with 0.3% LiOH.

mortar with 0.3% LiOH, reaching almost the same level of expansion as the mortar without additive. Fig. 1 also shows that the expansions of mortars were completely suppressed by the addition of 1.0% and 1.5% LiOH.

Fig. 2 shows expansion curves for mortars with various amounts of Li_2CO_3. The expansion behavior of mortars with Li_2CO_3 at the dosage level of 0.3% and 0.5% is found to be greatly different from that of mortars with LiOH in that the ultimate expansions of mortars with 0.3% and 0.5% Li_2CO_3 were considerably greater than that of the additive-free mortar. The addition of 1% Li_2CO_3 could not suppress expansion in the mortars, the ultimate expansions of which were almost the same as that of the additive-free mortar. Lithium salt content in mortar is expressed as the mole concentration of Li^+ ion in mixing water. Fig. 3 shows the relation between the ultimate expansion of mortars and the initial Li^+ ion concentration. It is found from Fig. 3 that the threshold dosage level of Li^+ ion was about 0.75 M as the initial Li^+ ion concentration in both mortars with LiOH and Li_2CO_3.

3.2. Composition of ASR gels in mortars with and without lithium salts

Fig. 4 shows a BSE micrograph for a reactive aggregate particle in mortars without additive. An enlarged BSE image for the massive ASR gels found in a reactive aggregate particle is given in Fig. 5. From SEM examinations throughout the polished surfaces of mortar samples, we found that the massive ASR gels existed in relatively wide cracks within reactive aggregate particles only in additive-free, mortars containing 0.3% and 0.5% LiOH-containing mortars which showed great expansions. Two BSE micrographs for the typical massive ASR gels found in reactive aggregate particles in 35-day-old mortars with 0.3% LiOH and 98-day-old mortars with 0.5% LiOH are given in Figs. 6 and 7, respectively.

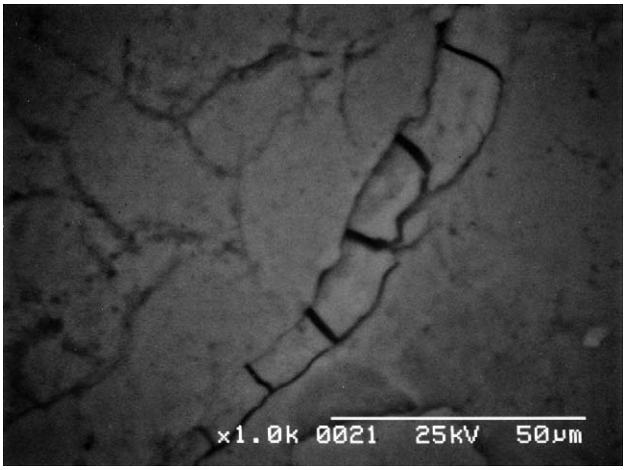

Fig. 5. BSE micrograph for the massive ASR gels in a reactive particle in Fig. 4.

Fig. 7. BSE micrograph for the massive gels in 98-day-old mortar with 0.5% LiOH.

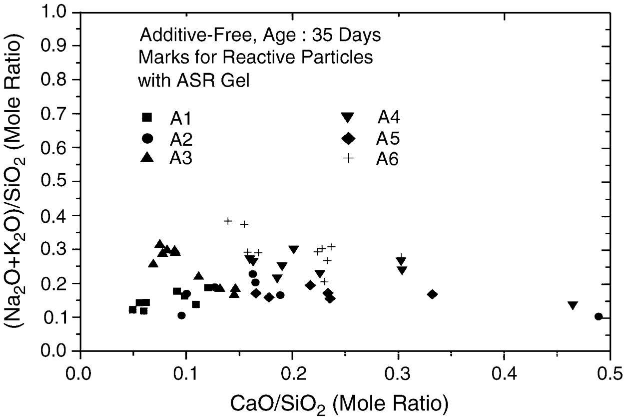

Fig. 8. EDS analysis for ASR gels in 35-day-old mortar without additive.

The presence of many fissures in the original reactive aggregate particles has been confirmed by Lumley [9]. It has been also reported, as a characteristic of the ASR process in mortars with the reactive aggregate, that ASR gels were produced within the fissures, and the expansion of the gels widened the fissures, leading to the overall expansion of mortar prisms [10].

In Fig. 8, $(Na_2O+K_2O)/SiO_2$ mole ratios are plotted against CaO/SiO_2 mole ratios, using the data obtained by EDS spot analyses for the massive gels in cracks within reactive aggregate particles in mortars without additive, at the age of 35 days. In these analyses, five different reactive aggregate particles with wide cracks partly filled with the massive gels were selected. Figs. 9 and 10 present the plots for mortars with 0.3% and 0.5% LiOH. It is seen in Figs. 8–10 that the CaO/SiO ratio in the gels varied widely, and the $(Na_2O+K_2O)/Si_2O$ ratio did to some extent. Fig. 11 was obtained by plotting all the results of analyses. The most noticeable indication obtained from Fig. 11 is that the average value and the extent of variations of CaO/SiO_2 ratio decreased with increasing dosage level of LiOH. The analyses at the age of 98 days are plotted in Fig. 12. The reduction in the average value and the extent of variations of CaO/SiO_2 ratio in mortars with 0.5% LiOH at the age of 98 days is more conspicuous than at the age of 35 days.

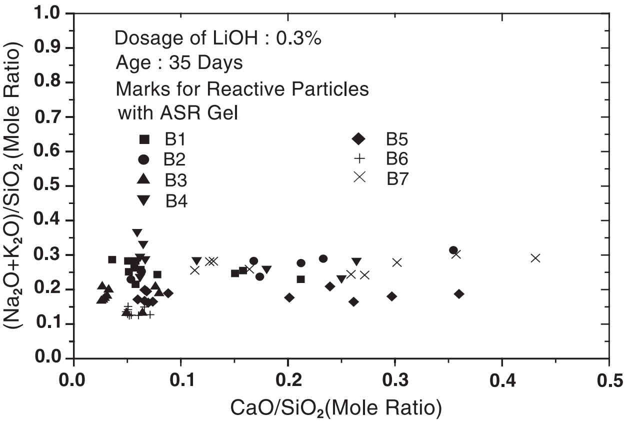

Fig. 9. EDS analysis for ASR gels in 35-day-old mortar with 0.3% LiOH.

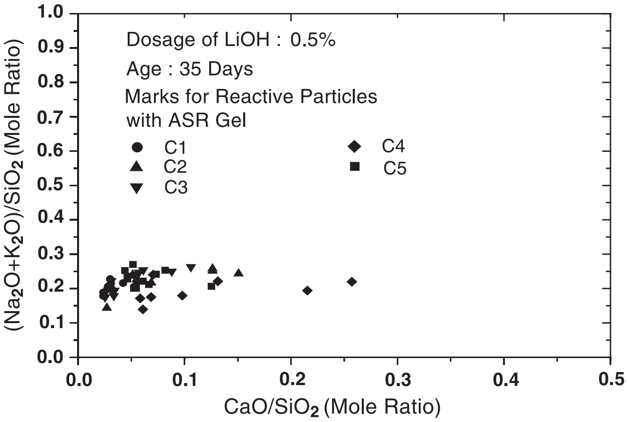

Fig. 10. EDS analysis for ASR gels in 35-day-old mortars with 0.5% LiOH.

Figs. 13 and 14 show plots of all the results of analyses for mortars with and without Li_2CO_3 at the age of 35 and 98 days, respectively. We could find massive ASR gels even in mortars with 1% Li_2CO_3. The trend in changes of CaO/SiO_2 ratio of ASR gels with increasing Li_2CO_3 content looks similar to that in mortars with LiOH. However, it is found from a comparison between plots for mortars with LiOH and Li_2CO_3 at the age of 98 days (Figs. 12 and 14) that the extent of variations of CaO/SiO_2 ratio of ASR gels in mortars with 0.3% Li_2CO_3 was greater than those in mortars without additive, but in mortars with 0.3% LiOH was almost the same as those in additive-free mortars.

4. Discussion

As presented above, the average CaO/SiO_2 ratios in ASR gels produced within reactive aggregate particles decreased with increasing amounts of the lithium salts added at the age of 35 days (Figs. 11 and 13). However,

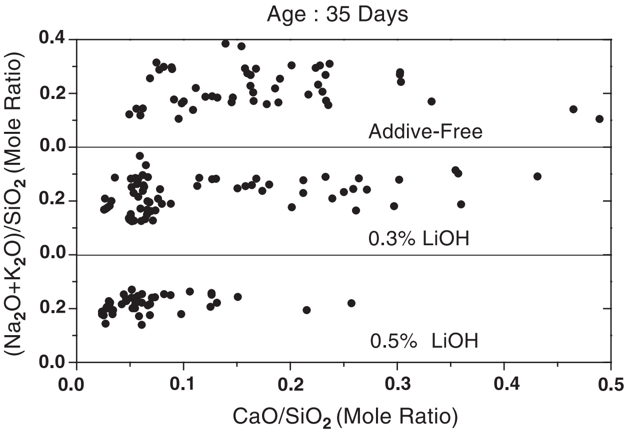

Fig. 11. EDS analysis for ASR gels in 35-day-old mortars with various amounts of LiOH.

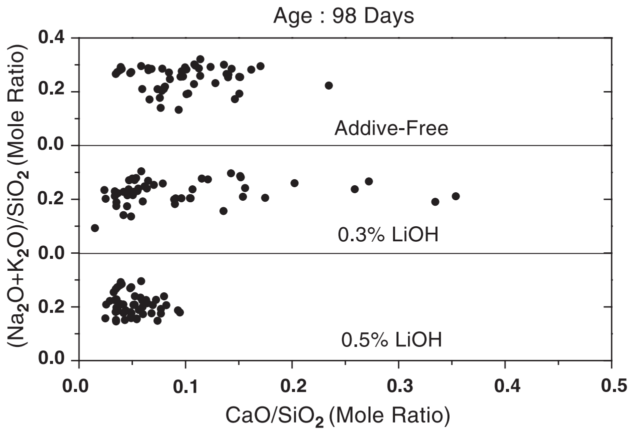

Fig. 12. EDS analysis for ASR gels in 98-day-old mortars with various amounts of LiOH.

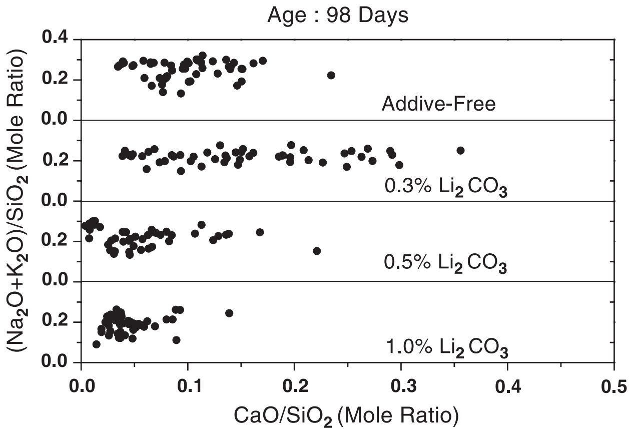

Fig. 14. EDS analysis for ASR gels in 98-day-old mortars with various amounts of Li_2CO_3.

at present, it is not clear whether Li replaced some of the calcium in ASR gels. It was also found from the EDS analyses that the composition of ASR gels became homogenous at the dosage level of 0.5% and 1.0% for mortars with LiOH and Li_2CO_3, respectively. However, the addition of less than 0.5% LiOH and 1.0% Li_2CO_3 could not inhibit expansion of mortars. Expansion was completely suppressed in mortars with greater than the threshold dosage levels of the lithium salts. Adversely, the addition of 0.3% and 0.5% Li_2CO_3 greatly increased the expansion of mortars (Fig. 2). In the SEM examinations, no massive ASR gel was found within reactive aggregate particles in mortars with greater than the threshold dosage level of a lithium salt. However, even in these mortars, ASR gel was detected within fine cracks in reactive particles by fluorescence microscopic examinations of their polished surfaces treated with uranyl acetate. The ultimate expansions of mortars with 0.5% LiOH and 1.0% Li_2CO_3 were almost the same as those of additive-free mortars (Figs. 1 and 2). Thus, the suppression of expansion in mortars with a lithium salt at an amount greater than the threshold dosage level may not be related to the great reduction in the average CaO/SiO_2 ratio and the homogenization in the CaO/SiO_2 ratio of ASR gels.

Recently, on the basis of the experimental results obtained with transmission soft X-ray microscopy, Kurtis et al. [5] proposed that the reduction of ASR expansion by lithium might be attributed to the limitation of repolymerization and the promotion of the aggregation of relatively large particles in ASR gels. It is not clear if such changes in the structure of ASR gels by the addition of lithium are related to the homogenization and the reduction in average CaO/SiO_2 ratio in ASR gel composition.

Diamond and Ong [4] reported that low and intermediate dosage of LiOH increased expansions of mortars containing Beltane opal and cristobalite. It was also found that increased expansions at relatively low dosage levels of LiOH may be due to the increase in the OH^- ion concentration in the pore solution, and that Li_2CO_3 increased the OH^- ion concentration [6]. In this study, the OH^- and SO_4^{2-} ion concentrations in the pore solution in mortars containing the reactive aggregate were measured at the age of 1 day. In

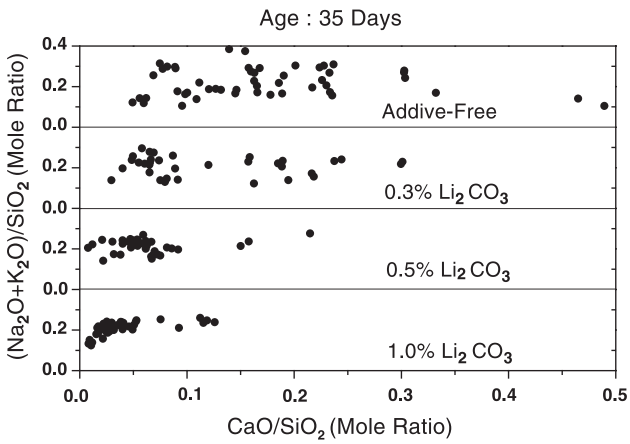

Fig. 13. EDS analysis for ASR gels in 35-day-old mortars with various amounts of Li_2CO_3.

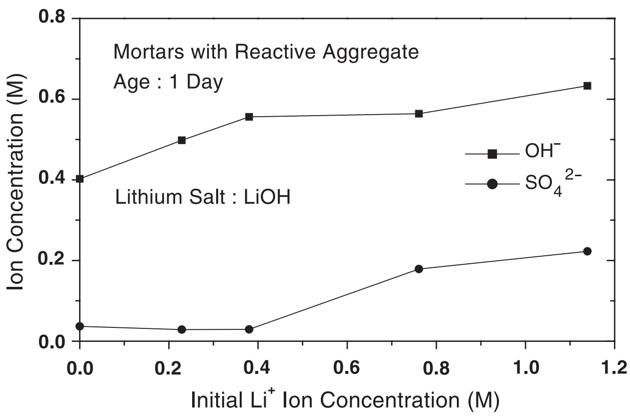

Fig. 15. OH^- and SO_4^{2-} ion concentration in the pore solution in mortars with LiOH.

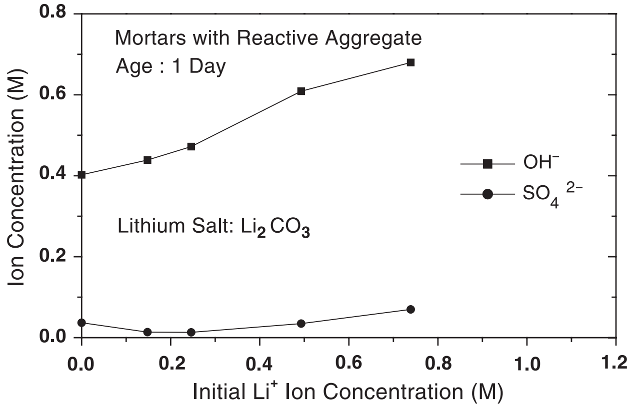

Fig. 16. OH$^-$ and SiO$_4^{2-}$ ion concentration in the pore solution in mortars with Li_2CO_3.

Figs. 15 and 16, the OH$^-$ and SO$_4^{2-}$ ion concentrations are plotted against the initial lithium concentrations expressed in moles per liter. There were little differences in OH$^-$ and SO$_4^{2-}$ ion concentrations in pore solutions between mortars with LiOH and Li_2CO_3 up to the initial lithium ion concentration of about 0.4 M. However, the OH$^-$ ion concentrations in pore solutions in mortars with Li_2CO_3 were higher than in mortars with LiOH at the initial Li$^+$ ion concentrations greater than about 0.4 M. Diamond [6] stated that the mechanism of the increase in OH$^-$ ion concentration in pore solutions in mortars with Li_2CO_3 seemed to involve precipitation of the even more insoluble calcium salt of the anion concerned. Little increase in OH$^-$ ion concentration in mortars with LiOH was also explained by the conversion of some or all of the added lithium hydroxide to lithium sulfate [6].

Figs. 17 and 18 show amounts of Li$^+$ removed from the pore solutions in mortars with LiOH and Li_2CO_3 for a period of 1 to 35 days, respectively. Considering that a great portion of added Li$^+$ ions has been removed in the formation of cement hydration products by 1 day [4], it is seen in Figs. 17 and 18 that eventually as much as about 0.20 M and 0.15 M of Li$^+$ ions were taken up in ASR gel formation in mortars with LiOH and Li_2CO_3, respectively. However, the amounts of Li$^+$ ions removed from the pore solutions in Li_2CO_3-bearing mortars are found to be smaller than in the LiOH-bearing mortars at an initial Li$^+$ ion concentration. Diamond and Ong [4] and Diamond [6] revealed that the increase in expansion at relatively low dosage levels of LiOH and Li_2CO_3 was due to the increase in OH$^-$ ion concentration in the pore solution. The increase in expansion in mortars with 0.3% and 0.5% Li_2CO_3, and the failure in suppression of expansion in mortars with 1.0% Li_2CO_3 and, 0.3% and 0.5% LiOH can be explained in the same way, as stated by Diamond and Ong [4] and Diamond [6]. However, since the OH$^-$ concentrations in mortars with Li_2CO_3 at a low initial Li$^+$ ion concentration are almost the same as in mortars with LiOH (Fig. 3), less effectiveness in the suppression of ASR in mortars with Li_2CO_3 appears to be related to less amounts of Li$^+$ ions removed from the pore solutions in the mortars.

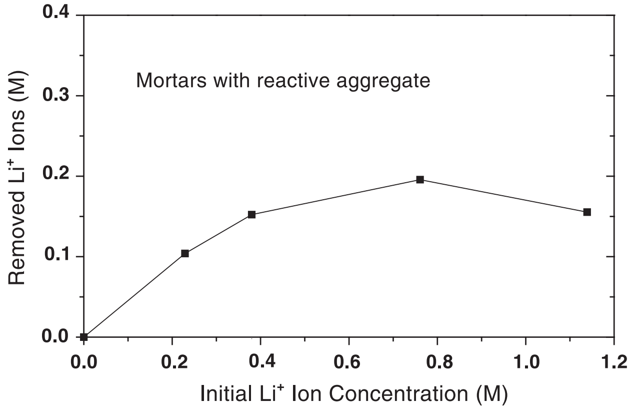

Fig. 17. Amounts of Li$^+$ ions removed for a period of 1 to 35 days in mortars with LiOH.

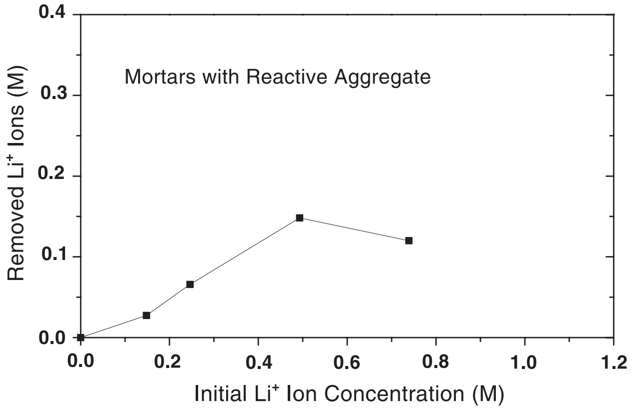

Fig. 18. Amounts of Li$^+$ ions removed for a period of 1 to 35 days in mortars with Li_2CO_3.

5. Conclusions

We obtained the conclusion that the threshold dosage level of Li$^+$ ion for both LiOH and Li_2CO_3 was about 0.75 M in mortars made with a high-alkali cement of 1.1% Na_2O equivalent and a highly reactive aggregate. As to the effects of lithium salts on ASR gel composition, the average CaO/SiO_2 ratio decreased with increasing amount of the lithium salts added. It was also found from EDS analyses that the composition of ASR gels became homogeneous at a high dosage level. However, at present, it is not clear how the reduction in CaO/SiO_2 ratio in ASR gels formed in mortars with a dosage level of lithium salt just slightly lower than the threshold level and the homogenization in CaO content in the ASR gels lead to the formation of nonexpansive ASR gels.

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