

THE MECHANISMS OF LITHIUM EFFECTS ON ASR

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ABSTRACT

A considerable body of literature attests to the potentially favorable effect of lithium in prevention of ASR damage. The results of new investigations concerning the mechanisms governing such effects are reported. Trials were carried out with mortars prepared using Aalborg white cement of almost zero alkali content. Pore solution studies indicate that LiOH added is rapidly sorbed from solution by hydrating cement components; this effect results in the necessity for larger dosages of lithium for ASR control than would otherwise be needed. LiOH added to mortars containing reactive aggregates in the virtual absence of other alkalis do produce an ASR reaction product, which appears to be non-expansive. LiOH added along with NaOH and KOH is partly incorporated into mixed alkali ASR gels, but at a lower proportion than was added. Even though lithium appears to be incorporated into the reaction product gel, the overall extent of reaction appears to be reduced proportionately to the amount of lithium added, and might be entirely suppressed at a high enough dosage. Paradoxically, while mortar bar tests indicate that expansion is prevented if the dosage of lithium in the mixed alkali mortars is sufficiently high, at intermediate dosage levels greater expansions were recorded than in the absence of lithium treatment.

Introduction

A considerable body of literature, beginning with the classical paper of McCoy and Caldwell (1), suggests that lithium compounds may be useful in the amelioration of distress due to alkali aggregate reactions. Studies by Lawrence and Vivian (2), Verbeck and Gramlich (3), Barneyback (4), and Sakaguchi et al. (5) all point to the reduction in apparent ASR response when lithium compounds of various kinds are added to the mix water in reacting mortars. The present investigations were aimed at elucidating the mechanisms responsible for these favorable effects.

Removal Of LiOH From Solution By Non-Reacting Mortars

Considerable insight has been obtained on various chemical processes in hydrating cement systems by separating the mix solution (or pore solution) at periodic intervals and determining the changes in concentration of various species that may occur. In this part of the work, this technique was used to compare changes taking place in the concentrations of various ions in a mortar to which LiOH had been added at a dosage rate equivalent to that provided by 1% Na<sub>2</sub>O in the cement. No reactive aggregate was present. In particular, our first concern was to establish whether or not significant amounts of Li would be removed from the pore solution by the hydrating cement. In order to eliminate possible effects of competing alkalis, the cement used in this study was an extremely low alkali cement, specifically the white sulfate-resisting cement produced by Aalborg Portland.

Mortars were prepared using this cement (0.067% Na<sub>2</sub>O, 0.024% K<sub>2</sub>O, by AAS) and a pure calcitic limestone ground to the size distribution specified for mortars in ASTM C 227. The water:cement ratio was 0.485, and the aggregate:cement ratio was

2.25. Mixing was carried out according to ASTM C 305, after which the mortars were sealed in individual containers and maintained at 38C.

After periods ranging from 1 to 270 days, individual replicate specimens were removed from their containers and the pore solutions expressed by the method described by Barneyback and Diamond (6). The pore solutions were then analyzed by standard methods. At the same time, the content of bound water (105C) was determined for each mortar. In these sealed systems changes in ion concentrations reflect changes both in water content (progressively reduced by ongoing cement hydration) and changes due to ions entering or being removed from the aqueous phase. It is possible to eliminate the former effect by calculation, if the bound water content at each stage is established. To do this, the observed pore solution concentrations are mathematically adjusted to constant (i.e. initial) water content, as described by Diamond and Barneyback (7). Changes in the adjusted concentrations over time thus reflect only changes due to ion entry or removal from the aqueous phase.

This was done in the present case, and the results for  $\text{Li}^+$  are given in Fig. 1.

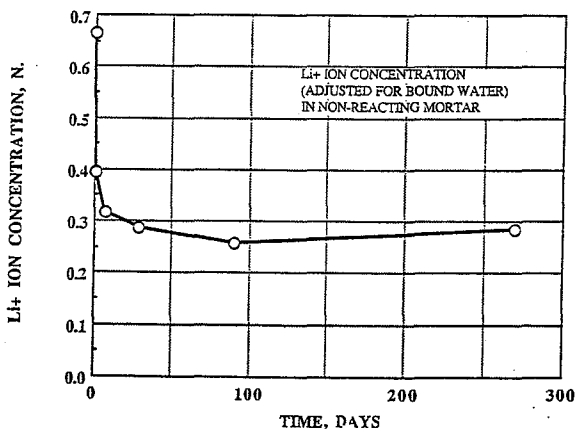


Fig. 1. Lithium ion concentration (adjusted for bound water) in pore solutions expressed from non-reacting mortar treated with LiOH equivalent to 1%  $\text{Na}_2\text{O}$  in the cement.

The starting concentration of LiOH in the mix water was 0.665N. It is seen that a significant portion of the  $\text{Li}^+$ , about 40%, has been removed from solution by the first day (adjusted concentration 0.4N), and significant further uptake followed over the first month. This uptake of LiOH from solution is apparently due to absorption of LiOH by the products of cement hydration. If these results are characteristic for hydrating cements in general, it would appear that a substantial portion of LiOH added to concrete as an admixture for the prevention of ASR damage would become unavailable for that purpose because of prior uptake by the hydrating cement itself.

Parallel experiments were carried out with NaOH and with KOH, both added at the same dosage level equivalent to 1.0%  $\text{Na}_2\text{O}$ . There was some uptake of both alkalis, amounting to about 25% of the added Na and about 20% of the added K. In all of these experiments it was found that the uptake of the alkali ions from solution was accompanied by uptake of  $\text{OH}^-$  ions. Indeed the reduction in  $\text{OH}^-$  ion concentration in each case was greater than that of the alkalis. Neutrality in the solution was preserved by  $\text{SO}_4^{2-}$  ions, appreciable concentrations of which were brought into solution from the cement,

and which were retained in solution indefinitely. Sulfate ions are usually completely removed from cement paste pore solutions by the end of the first day's hydration, as a result of ettringite formation.

Removal Of LiOH From Solution By ASR Reaction

Experiments parallel to those described above were carried out with mortars identical to those above except that they contained an approximately pessimum proportion of alkali-reactive aggregate replacing an equal mass of the inert limestone. One series contained Beltane opal at a proportion of 4.5% by weight of the total aggregate; another contained cristobalite ("calcined flint" from Blue Circle Industries PLC) at a proportion of 30% by weight. Both series had LiOH equivalent to 1% Na<sub>2</sub>O in the cement added to the mix water.

In Fig. 2 we plot the Li<sup>+</sup> concentrations (adjusted for bound water) for mortars of both series, along with the previous data for the non-ASR reactive mortar. The mortars containing reactive aggregate both showed greater removal of Li<sup>+</sup> ions from the pore solution over the 270-day period studied. We interpret this augmented uptake of Li<sup>+</sup> as evidence of an alkali silica reaction with Li, in the same manner that augmented uptake of Na<sup>+</sup> or K<sup>+</sup> ions would be interpreted as evidence of the formation of ASR gel in conventional ASR reactions. The Beltane opal is seen to react much faster than cristobalite, and it appears to have been fully reacted by 90 days.

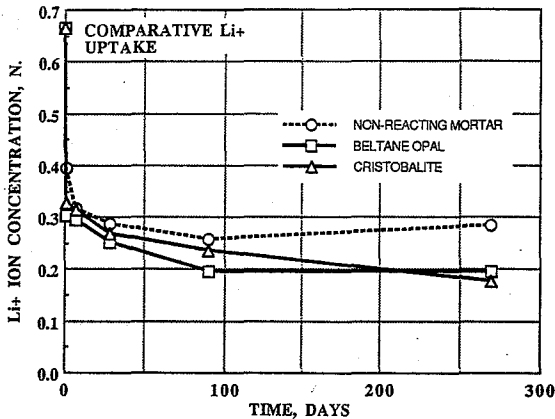


Fig. 2. Lithium ion concentrations (adjusted for bound water) in pore solutions expressed from LiOH-treated mortars containing Beltane opal and cristobalite compared with those from non-reactive mortar.

This interpretation of the pore solution data appeared to be confirmed by examination of fracture surfaces of the Beltane opal - LiOH mortar in UV light after the uranyl acetate treatment described by Naitesayer and Hover (8). Definite indication of the presence of a gel capable of absorbing uranyl ions and fluorescing were found.

To assess the relative amount of the ASR gel formed with LiOH compared to what would be formed with NaOH or KOH, parallel experiments were conducted with reactive mortars to which NaOH or KOH had been added to the mix water at the same 1% Na<sub>2</sub>O equivalent dosage level. Data for the NaOH-bearing mortars are shown in Fig. 3. The augmented uptake of Na<sup>+</sup> found in this NaOH-ASR reaction is much greater

than that of  $\text{Li}^+$  in the  $\text{LiOH}$ -ASR reactions of Fig. 2. The corresponding  $\text{KOH}$  response (not shown) was even greater. Thus it appears that while  $\text{LiOH}$  produces an ASR reaction product gel, the amount formed is substantially less than that formed with  $\text{NaOH}$  or  $\text{KOH}$  at the same starting concentration.

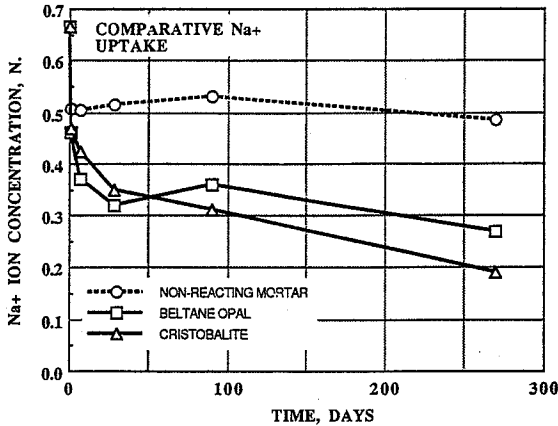


Fig. 3. Sodium ion concentrations (adjusted for bound water) in pore solutions expressed from mortars treated with  $\text{NaOH}$  equivalent to 1%  $\text{Na}_2\text{O}$  in the cement.

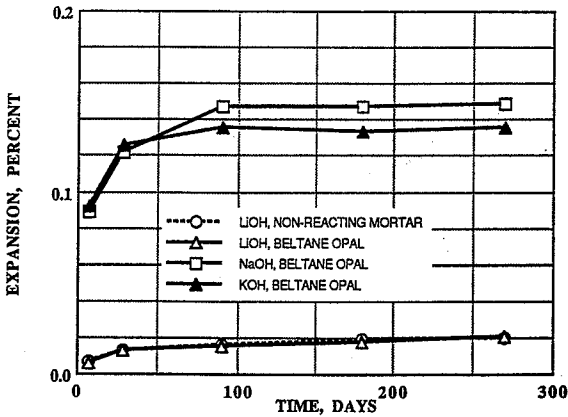


Fig. 4. Measured expansions for non-reactive mortars treated with  $\text{LiOH}$ , and for mortars containing Beltane opal treated with  $\text{LiOH}$ ,  $\text{NaOH}$ , and  $\text{KOH}$ , all at dosages equivalent to 1%  $\text{Na}_2\text{O}$  in the cement.

Mortar bars of the same compositions as cited above were prepared as standard ASTM C 227 bars and exposed to the specified test conditions of 100% RH at 38°C. The expansion data are shown in Fig. 4. No significant expansion was found for the Li-bearing mortars, despite the previously cited evidence that ASR reaction had taken place.

The LiOH mortar bars showed no surface gel deposits or cracks. In contrast, surface gel deposits and extensive cracking were observed for the Na- and K-bearing mortars.

It should be pointed out that the expansions recorded for the Na- and K-bearing mortar bars in these tests, while significant, were much smaller than expected. The details of the exposure as presently specified in the present ASTM test (C 227-90) requires that wicking material be maintained at no more than 30 mm distance from each surface of the mortar bars. Unfortunately, this leads to extensive leaching of the alkali hydroxide from the mortar bars, and thus to reduced expansions.

#### LiOH Effects In Mixed Alkali Hydroxide Systems

The above responses were derived from mortars in which LiOH was added to an almost alkali-free cement. In using lithium as a chemical admixture to mitigate ASR, one would naturally expect to employ it only with high alkali cements, i.e. cements capable of generating substantial concentrations of NaOH or KOH (or both) in the pore solutions.

To model this state of affairs, new mortars were prepared from the same cement, but the LiOH added along with fixed high dosages of NaOH and KOH. The latter were added in amounts equivalent to 0.5% Na<sub>2</sub>O in the cement for each alkali, i.e. to a total Na<sub>2</sub>O equivalent of 1.0%. The LiOH was added at three levels: a low dose level, corresponding to 0.4% Na<sub>2</sub>O equivalent; an intermediate dose level, corresponding to 0.8% Na<sub>2</sub>O equivalent; and a high dosage level, corresponding to 1.2% Na<sub>2</sub>O equivalent. The corresponding initial Li<sup>+</sup> concentrations in the mix water were 0.266N, 0.532N, and 0.798 N. As before, non-reacting mortars containing only limestone, and mortars containing Beltane opal and cristobalite were prepared.

The uptake of Li<sup>+</sup> from the pore solutions of non-reactive mixed alkali mortars is shown in Fig. 5. In this figure the circles denoting the initial Li<sup>+</sup> concentrations in the mix water are filled. In each case the hydrating cement has effectively removed a substantial portion of the added Li<sup>+</sup>. It is evident that the presence of the other alkalis does not inhibit the uptake of LiOH by the hydrating cement.

In Fig. 6 we plot the adjusted Li<sup>+</sup> ion concentrations of high-LiOH dosage mortar containing Beltane opal with those of the corresponding non-reacting mortar. It is evident that incorporation of the Beltane opal has caused a much enhanced removal of Li<sup>+</sup> ions from the pore solution. In the usual manner, we attribute this augmentation to incorporation of Li<sup>+</sup> ions into the ASR reaction product. Similar results were obtained for the cristobalite-bearing mortar, and for mortars of lower starting lithium dose level.

The comparative augmentation of Li removal in this mixed alkali system is much greater than that previously presented in Fig. 2, where only LiOH was added. With NaOH and KOH available as well as LiOH, one might expect a considerable increase in the total extent of ASR reaction and gel formation, i.e. an enhanced opportunity for Li<sup>+</sup> to be incorporated in ASR gel.

It appears from Fig. 6 that the enhanced uptake of Li<sup>+</sup> ions from this mixed pore solution in the presence of Beltane opal may have come at the expense of the expected uptake of alkali ions. Comparison of the existing data for the augmented uptake of Na<sup>+</sup> and of K<sup>+</sup> in these lithium-bearing mixed alkali mortars with data for augmented uptake of Na<sup>+</sup> and K<sup>+</sup> ions in the "pure" NaOH and KOH treated mortars, confirms this. The implication of this finding is that Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> can all be seen as competing for incorporation in the ASR reaction product being formed in the mixed alkali systems.

However, it is a considerable oversimplification only to consider the uptake of these cations as determining the composition of the ASR gel. ASR gels also incorporate

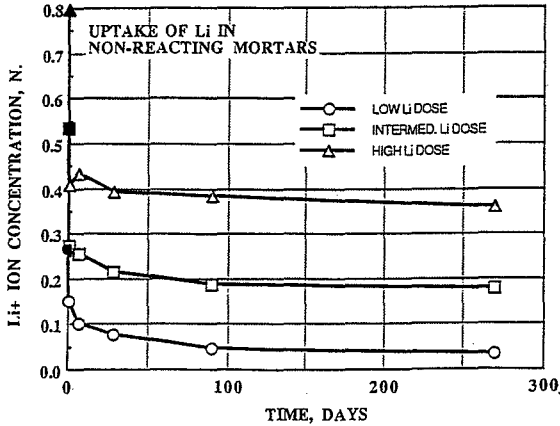


Fig. 5. Lithium ion concentrations (adjusted for bound water) in pore solutions of non-reactive mortars, all treated with 0.5% Na<sub>2</sub>O equivalent each of NaOH and KOH, but with varying dosage levels of LiOH.

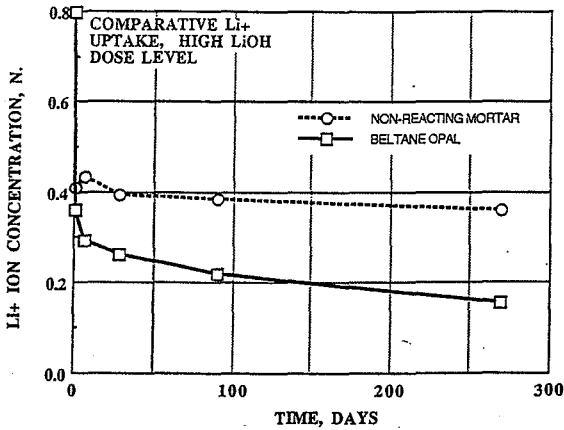


Fig. 6. Lithium ion concentrations (adjusted for bound water) in pore solutions of non-reactive and of Beltane opal containing mortars, treated with 0.5% Na<sub>2</sub>O equivalent each of NaOH and KOH, and 1.2% Na<sub>2</sub>O equivalent of LiOH.

significant amounts of calcium and often some aluminum, and also vary in composition from place to place within a given reacting concrete or mortar.

Nevertheless, it is of interest to attempt to compare the proportion of Li to the sum of Li + Na + K ions added in the mix water to the proportion that appears to have been taken up in ASR gel formation. Table 1 contains such a comparison for the 90 day data for both the Beltane opal- and the cristobalite- bearing mortars, each at the low, intermediate, and high dose levels.

Table 1. Analysis of the Augmented Uptake of Lithium, Sodium, And Potassium Ions In Reacting Mortars (at 90 Days).

Mortar	Ratio of Li to Total Alkali Ions Added In Mix Solution (%)	Ratio of Li to Total Alkali Ions in Augmented Uptake by Reacting Mortars (%)
Low Li Dose Level, Beltane Opal	28.6	15.1
Low Li Dose Level, Cristobalite	28.6	16.0
Intermediate Li Dose Level, Beltane Opal	44.4	32.6
Intermediate Li Dose Level, Cristobalite	44.4	40.4
High Li Dose Level, Beltane Opal	54.5	34.2
High Li Dose Level, Cristobalite	54.5	36.2

It is seen that there are only minor differences in the latter between the Beltane opal mortars and the cristobalite mortars at a given Li dosage level.

At the low dosage level, the data suggest that the proportion of lithium incorporated in the reaction product is only about half the proportion of lithium added. This appears to be a reflection of the prior high uptake of lithium by the hydrating cement itself; when only a little LiOH is added, much of it is picked up by cement hydration before ASR can be significantly established.

At the intermediate dose level, the proportion of lithium apparently incorporated into the ASR product is significantly higher, and nearly reflects the proportion added to the mortar. But surprisingly, there is no further increase for the high lithium dose level. This observation was unexpected and no explanation is forthcoming.

Thus far, the data for the augmented uptake of the several ions in these mixed alkali mortars has been interpreted from the point of view of assessing the competition among the different alkalis for inclusion in the reaction product gel. From another point of view, the total of such augmentation in a given case might be used to provide a comparative indication of how much gel is being formed.

In Fig. 7 the total augmented uptake of all three alkali ions are plotted as functions of the starting lithium ion concentration, for both Beltane opal- and cristobalite-bearing mortars at 270 days. There is a progressive decline apparent with increasing lithium dosage level. The trends are remarkably similar for both reactive aggregates, and are approximately linear. Projections of the trend lines suggest that a starting  $\text{Li}^+$  ion concentration of about 1.5N might entirely suppress the ASR gel formation in these mixed alkali systems.

A plot for 90 day results gave an entirely similar trend, again projecting to suppression of uptake at a starting  $\text{Li}^+$  concentration of 1.5 N.

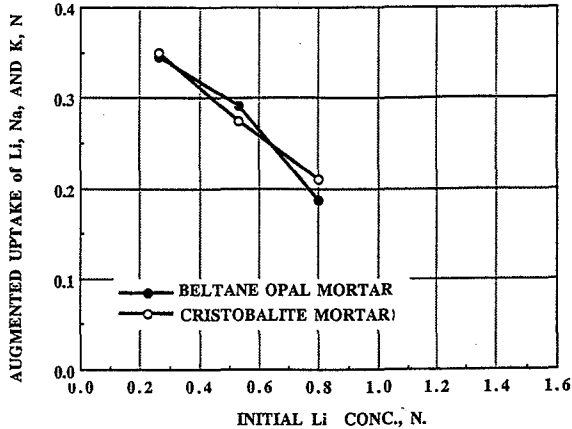


Fig. 7. The sum of the apparent augmented uptake of lithium, sodium, and potassium cations at 90 days as functions of the initial lithium concentration level in the mix water, for Beltane opal- and cristobalite-bearing mortars.

This trend is quite remarkable, especially in view of the fact that since Li has been added as LiOH, increasing Li dosage also results in increased  $\text{OH}^-$  ion concentration. The actual measured  $\text{OH}^-$  ion concentrations of the pore solutions at 1 day for the non-reacting mortars of this series were 0.46N, 0.54N, and 0.66N, respectively for the low, medium, and high lithium dose levels. It should be noted that these concentrations, while increasing with increasing LiOH dose level, are much lower than the total concentrations of the lithium and other alkali cation concentrations present; as indicated earlier, the difference is made up by  $\text{SO}_4^{2-}$  ions.

An indication of the effectiveness (or lack of it) of the different levels of Li treatments in reducing expansion was obtained in modified ASTM C-227 mortar bar testing, the results of which are plotted in Fig. 8. These tests were carried out with mortar bars placed in individual plastic sleeves in the 38C exposure cabinet with a small amount of water added before the sleeves were sealed, as described by Hooton and Rogers (9). In Fig. 8 measured expansion at 270 days are plotted vs. starting  $\text{Li}^+$  ion concentration in the mix water.

The measured expansions of the non-reacting mortar were small (ca. 0.02%) and independent of Li dosage. With both Beltane opal and cristobalite, to our surprise, low and intermediate dose levels of LiOH actually increased expansion. It required the high dose level (equivalent to 1.2%  $\text{Na}_2\text{O}$  in the cement) to effectively reduce expansion, and even here the expansion with Beltane opal was not completely eliminated.

Sakaguchi et al. (5) reported expansion results with LiOH added to a normal Portland cement (with NaOH also added). They found high expansion with their andesite reactive aggregate at an alkali level (not counting Li) of 1.2%  $\text{Na}_2\text{O}$ , for Li:Na mole ratios up to 0.6; for 0.9 and higher, expansion was eliminated. In the present data, the alkali level (not counting Li) is 1%  $\text{Na}_2\text{O}$  and it was found that the high Li dose level, corresponding to a Li:(Na+K) mole ratio of 1.2 apparently eliminated expansion for cristobalite, but was not quite sufficient to eliminate expansion completely for Beltane opal. In any case, a high Li dose is indicated as being required.



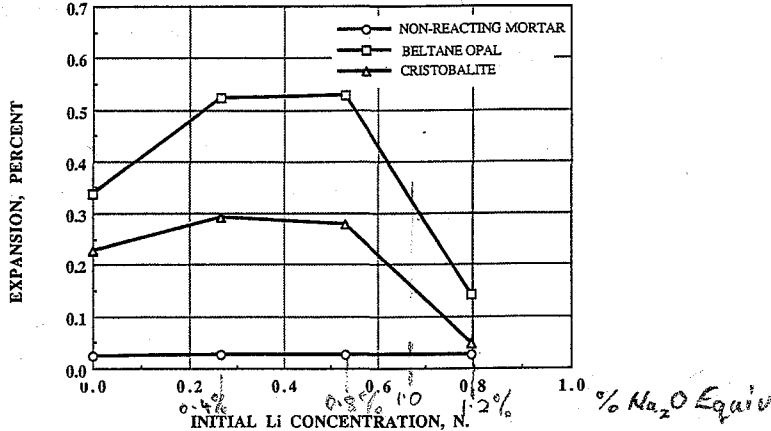


Fig. 8. Measured expansions at 270 days for ASTM C 227 - type mortar bars in sealed bags, for mortars treated with 0.5% Na<sub>2</sub>O equivalent each of NaOH and KOH, and 0.4%, 0.8%, and 1.2% Na<sub>2</sub>O equivalent, respectively of LiOH.

### Conclusions

A number of findings recorded here appear to be of significance, although the total pattern of ASR response to lithium treatment remains complex.

First, it seems clearly established that much more lithium is taken up by cement hydration products than sodium or potassium. This uptake is more rapid than ASR reaction, and it may limit the effectiveness of small doses of lithium compounds added to ameliorate ASR.

Secondly, it is clear, from both Li<sup>+</sup> pore solution responses and from UV observation of uranyl acetate treated mortar that LiOH will induce formation of an ASR reaction product in the absence of other alkalis. This product is non-expansive in character.

Secondly, it appears that when LiOH is added to potentially ASR reactive mortars along with NaOH and KOH, the resulting gel will contain all of the ions. However, the proportion of Li<sup>+</sup> ions included will be much less than the proportion initially present in the mix water, in part due to early absorption of LiOH by the hydrating cement itself.

We have in the past considered that ASR gels incorporating lithium would be less expansive in character than those produced in the absence of lithium, and that the greater the proportion of lithium in the gel, the less expansive they might be expected to be. This interpretation is at variance with the evidence of the mortar bar tests, which indicate that small and moderate doses of LiOH resulted in increased expansion. It appears that a critical lithium dosage is needed to overcome the combined concentrations of NaOH and KOH so as to significantly reduce or eliminate the expansive effect.

Indirect evidence derived from pore solution concentration measurements suggests that in mixed alkali hydroxide systems, the more the LiOH added, the less the

total amount of ASR gel that is produced. Extrapolation of this trend suggests that at a sufficiently high dosage of LiOH, approximately 1.5N, might entirely suppress the formation of gel in high alkali mortars.

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