

## USE OF LITHIUM-CONTAINING COMPOUNDS TO CONTROL EXPANSION IN CONCRETE DUE TO ALKALI-SILICA REACTION

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### ABSTRACT

This paper reports results from an experimental study aimed at evaluating the efficacy of lithium-containing compounds in controlling alkali-silica reaction (ASR) and establishing appropriate dosage levels for use with reactive U.K. aggregates. Two chemical compounds, lithium hydroxide monohydrate ( $LiOH.H_2O$ ) and lithium nitrate ( $LiNO_3$ ), and three reactive aggregates (flint sand, greywacke and siltstone) were used in the study. Expansion tests were carried out on concrete prisms stored at 38°C and large concrete blocks (300 x 300 x 500 mm) stored on an outdoor exposure site in southeast England.

Expansion data for concrete containing  $LiOH.H_2O$  show that the level of lithium required to control expansion to an acceptable level (i.e.  $\leq 0.04\%$ ) increases with the amount of alkali present and varies with different aggregates. Generally, the data to 54 months indicate that a level of 1.0 kg of  $LiOH.H_2O$  for each 1.0 kg of equivalent sodium oxide ( $Na_2O_e$ ) is sufficient for the flint sand and greywacke aggregates. This is equivalent to a lithium to alkali molar ratio of  $[Li]/[Na+K] = 0.74$ . Higher levels of lithium are required with the siltstone aggregate. The incorporation of fly ash in the concrete mix may reduce the level of lithium required to control expansion. Lower levels of  $LiOH.H_2O$  may actually increase expansion above that of control mixes without lithium. Pore solution studies indicate that lithium does not necessarily prevent reaction between the alkalis and silica, but may change the nature of the reaction product.

Keywords: Alkali-silica reaction, concrete, fly ash, lithium, pore solution, prevention

## INTRODUCTION

Interest in the development of chemical admixtures to control expansion due to alkali-silica reaction (ASR) dates back almost half-a-century. McCoy and Caldwell (1951) carried out mortar-bar expansion tests using Pyrex glass as a reactive aggregate to assess the effect of more than 100 different compounds (including metallic salts, acids, oils, organic chemicals, proteins and proprietary admixtures) on ASR expansion. The most promising chemicals were various lithium-containing compounds ( $LiCl$ ,  $Li_2CO_3$ ,  $LiF$ ,  $Li_2SiO_3$ ,  $LiNO_3$ , and  $LiSO_4$ ), which virtually eliminated expansion after 8 weeks storage at 38°C provided they were used in sufficient quantity.

Despite the encouraging data published by McCoy and Caldwell, more than 40 years elapsed before lithium was given serious consideration as a practical remedy for ASR. There now exists a substantial body of data (Blackwell et al. 1997; Lumley, 1997; Ohama et al. 1989; Sakaguchi, 1989; Stark, 1992; Stark et al. 1993) to demonstrate the efficacy of lithium compounds in controlling ASR in concrete. The level of lithium required to suppress damaging expansion in mortar and concrete increases as the quantity of alkali in the mix increases; for most aggregates it appears to be sufficient to ensure a lithium to alkali molar ratio,  $[Li]/[Na+K]$ , in the range 0.70 to 0.80 (Blackwell et al. 1997). Lower levels of certain lithium compounds (e.g.  $LiOH$ ,  $LiCl$ ,  $Li_2CO_3$ ,  $LiF$ ) may actually increase expansion above that of control mixes without lithium (Diamond and Ong, 1992; Stark et al. 1993). This pessimum effect is deemed to be the result of increased pore solution pH when these compounds are used (e.g.  $2LiCl + Ca(OH)_2 \rightarrow CaCl_2 + 2LiOH$ ). Lithium nitrate ( $LiNO_3$ ) does not cause this effect due to the high solubility of calcium nitrate and the addition of  $LiNO_3$  to cement paste has been found to increase the lithium and nitrate ion concentrations of the pore solution with no significant augmentation of the hydroxyl ion concentration (Stokes et al. 1997). For this reason lithium nitrate does not exhibit a pessimum effect; i.e. low dosages do not lead to higher expansions.

The Building Research Establishment (BRE), U.K., in partnership with FMC Corporation (a producer of lithium salts), initiated studies on the effect of lithium salts on ASR in 1994. Preliminary tests were concerned with determining the effect of lithium on the expansion of concrete with U.K. aggregates since previous research had been confined to tests on mortar and had indicated that the efficacy of lithium depended on the nature of the reactive aggregate. A previous publication (Blackwell et al. 1997) reported on the effect of lithium hydroxide monohydrate ( $LiOH.H_2O$ ) on the expansion of concrete prisms containing either reactive flint sand or reactive siltstone aggregate; data to 12 months were presented. This program was later expanded to include a third reactive aggregate (a greywacke) and an alternative form of lithium, namely a solution of lithium nitrate (30%  $LiNO_3$ ).

This paper presents long-term expansion data for concrete prisms stored under laboratory conditions and larger blocks stored under field conditions for mixes containing different reactive aggregates and various levels of  $LiOH.H_2O$ . Some data for fly ash concrete are also reported. The paper also presents preliminary data (i.e. up to eighteen months) for concrete mixes containing  $LiNO_3$ .

## EXPERIMENTAL PROGRAM

### Materials

The materials used for the tests reported here included high-alkali portland cement (1.15%  $\text{Na}_2\text{O}_e$ ), fly ash, lithium hydroxide monohydrate ( $\text{LiOH}\cdot\text{H}_2\text{O}$ ), lithium nitrate solution (30%  $\text{LiNO}_3$ ), three reactive aggregates, and a non-reactive limestone. The chemical composition of the cement and fly ash is given in Table 1.

TABLE 1: Results of Chemical Analyses of Cementitious Materials

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{Na}_2\text{O}_e$	$\text{SO}_3$	LOI
Cement	20.7	4.90	3.30	62.9	2.70	1.10	0.43	1.15	2.9	1.15
Fly Ash	53.8	27.8	8.84	2.49	1.27	3.54	1.13	3.46	3.6	3.46

The reactive aggregates used were a river sand, a crushed siltstone and a crushed greywacke. The sand was comprised of 50% alkali-reactive flint with lesser amounts of quartz, meta-quartzite, and carbonates. Previous experience has shown that maximum concrete expansion occurs when the flint content is approximately 10% to 15% of the total aggregate. Consequently, the sand proportion used was 25% by mass of the total aggregate (i.e. 12.5% flint). The siltstone contains a mixed lithology cemented together by microcrystalline quartz; the cementing silica is the reactive constituent of this aggregate. The greywacke used was a crushed rock from Northern Ireland. Both the siltstone and greywacke were used as the coarse aggregate in concrete mixtures (i.e. approximately 65% by mass of total aggregate). A "non-reactive" carboniferous limestone from the west of England (Cheddar) was used both as a coarse and fine aggregate to vary the amounts of reactive constituents in the concretes. The total silica content of this limestone is less than 1.0% and the material is considered to be non-reactive by all existing testing criteria.

### Expansion Tests on Concrete

Almost 200 concrete mixes have been cast as part of the BRE study and only selected data are presented here. Variables include cement content, use of fly ash or slag, type of reactive aggregate, and level and form of lithium compound.

Lithium hydroxide monohydrate ( $\text{LiOH}\cdot\text{H}_2\text{O}$ ) was added as a powder to the mixing water of the concrete mix. The recommended dosage for this material is generally 1.0 kg of  $\text{LiOH}\cdot\text{H}_2\text{O}$  for every 1.0 kg of equivalent soda ( $\text{Na}_2\text{O}_e$ ); this yields a lithium to alkali molar ratio of  $[\text{Li}]/[\text{Na}+\text{K}] = 0.74$ . For mixes containing lithium nitrate, a 30%- $\text{LiNO}_3$  solution was added during mixing, with appropriate corrections being made to maintain the desired mixing water content. The recommended dosage for this solution is generally 4.6 litres of solution for every 1.0 kg of equivalent soda ( $\text{Na}_2\text{O}_e$ ); this also yields a lithium to alkali molar ratio of  $[\text{Li}]/[\text{Na}+\text{K}] = 0.74$ . The majority of mixes cast with lithium employed the recommended doses although mixes were cast with higher and lower lithium levels.

At least three concrete prisms (75 x 75 x 200 mm) with stainless-steel inserts for length measurements were cast for each mixture. The prisms were demolded at 24 hours and stored in plastic containers at 20°C/100% RH. At 7 days, all prisms were measured prior to being

wrapped in moist toweling and polyethylene. The wrapped prisms were then returned to the containers and stored at 38°C. Length measurements were made on the prisms periodically; prisms were allowed to stabilize at 20°C/100% RH for 24 hours prior to length measurements being made.

Large concrete blocks (300 x 300 x 500 mm) were also cast from some of these mixtures and were placed on an outdoor exposure site at BRE to simulate field conditions. These blocks were placed upright in shallow plastic trays containing water to a depth of approximately 25 to 50 mm. Length measurements were made annually using reference points attached to the surface of the blocks.

### Pore Solution Tests on Mortars

Mortars were cast using materials from the same sources as those used in the concrete study. Mortars were cast with an aggregate to cement ratio of 2.25 and a water to cement ratio of 0.50. Coarse aggregate was crushed and all aggregates were graded to meet the requirements of ASTM C 227. Mortars were cast in sealed cylindrical containers (50 mm diameter x 100 mm), rotated for the first 24 hours to avoid segregation and then stored in the sealed containers over water at 23°C. Pore solution was extracted at various ages and the solution analyzed for hydroxyl ions by titration and for alkali ions (lithium, sodium and potassium) using flame photometry.

## DISCUSSION OF RESULTS

The expansion data presented here refer either to prisms stored at 38°C or larger blocks stored under field conditions. For the purposes of this paper, significant or damaging expansion refers to expansion in excess of 0.04% as this value is generally consistent with the onset of cracking and has been adopted as a limit in a number of specifications.

Figure 1 shows the expansion of concrete prisms containing 550 kg/m<sup>3</sup> of high-alkali cement (equivalent to 6.33 kg/m<sup>3</sup> Na<sub>2</sub>O<sub>e</sub>), reactive flint sand and various levels of LiOH.H<sub>2</sub>O. It is clear that lithium hydroxide is able to suppress damaging expansion with this aggregate provided it is used in sufficient quantity. Concrete with at least 75% of the recommended dose of LiOH.H<sub>2</sub>O (i.e. [Li]/[Na+K] = 0.55) showed no significant expansion after 39 months. Concrete with only half the recommended dose (i.e. [Li]/[Na+K] = 0.37) did undergo expansion and cracking although the level of expansion was somewhat less than the control mix without lithium. In other words, no pessimum was observed with low levels of lithium and this aggregate.

In November of 1994, a number of large concrete blocks were cast with the same flint sand and various cement contents. Some of these blocks also contained the recommended dose of LiOH.H<sub>2</sub>O. Figure 2 shows the expansion of the blocks, measured in April 1999 (i.e. at approximately 54 months of age), as a function of the total cement alkalis in the concrete. Blocks with less than 5.0 kg/m<sup>3</sup> Na<sub>2</sub>O<sub>e</sub> did not expand or crack regardless of the presence of lithium, however, for concrete with 5.46 or 6.33 kg/m<sup>3</sup> Na<sub>2</sub>O<sub>e</sub>, considerable expansion accompanied by extensive cracking was observed at this time. None of the blocks containing lithium hydroxide have exhibited any distress to date. Indeed, expansion measurements reveal that the lithium-containing blocks have actually undergone a net shrinkage during storage.

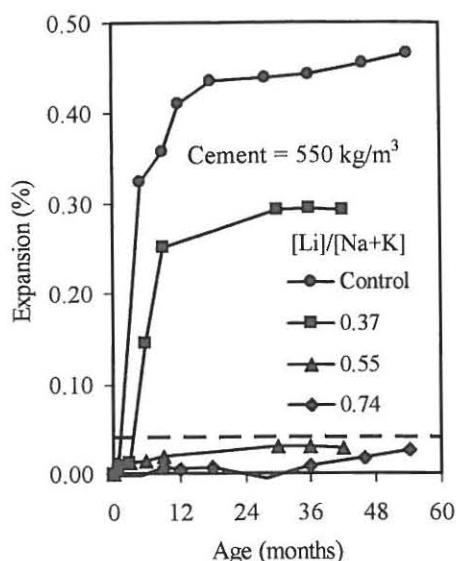


Fig 1 Expansion of Concrete Prisms with Flint Sand and LiOH

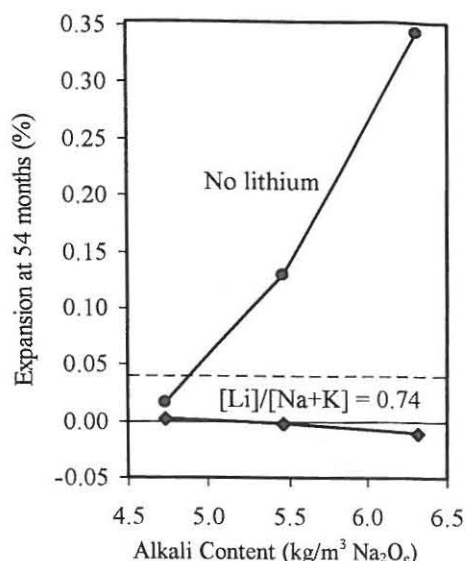


Fig 2 Expansion of Outdoor Blocks with Flint Sand and LiOH

Figure 3 shows the effect of  $\text{LiOH} \cdot \text{H}_2\text{O}$  on the expansion of concrete prisms with  $550 \text{ kg/m}^3$  of high-alkali cement and greywacke aggregate. No expansion was observed for concretes containing lithium hydroxide provided the lithium to alkali molar ratio,  $[\text{Li}]/[\text{Na}+\text{K}]$ , was at least 0.51. However, it is interesting to observe with this aggregate that there is a pessimum effect with the lower dose of lithium,  $[\text{Li}]/[\text{Na}+\text{K}] = 0.34$ , actually resulting in increased expansion compared with the control mix without lithium. The expansion of concrete with  $500 \text{ kg/m}^3$  of high-alkali cement was also increased by low doses of lithium hydroxide as shown in Figure 4, and a minimum level of lithium, i.e.  $[\text{Li}]/[\text{Na}+\text{K}] > 0.51$ , is required to suppress expansion to less than 0.04% at 3 years. Figure 4 shows that concrete with  $450 \text{ kg/m}^3$  of high-alkali cement did not exhibit significant expansion regardless of the presence or level of lithium. This might indicate that although a small amount of  $\text{LiOH}$  may exacerbate expansion, it may not initiate damaging reaction if there is insufficient alkali ( $\text{Na}$  or  $\text{K}$ ) present from the cement already.

Figure 5 shows the effect of combinations of lithium hydroxide and fly ash on the expansion of concrete containing reactive siltstone aggregate and  $450 \text{ kg/m}^3$  of high-alkali cement. These results show that neither the addition of fly ash nor the recommended dose of  $\text{LiOH} \cdot \text{H}_2\text{O}$  is totally effective in limiting the long-term expansion to less than 0.04%, although both measures substantially reduce the expansion compared with the control concrete. The combined addition of fly ash and  $\text{LiOH} \cdot \text{H}_2\text{O}$  reduces expansion further, but the expansion still exceeds 0.04% after 54 months. It should be noted that the fly ash here was used as an addition to the high-alkali cement rather than as a partial replacement for the cement. The control mix in Figure 5 has  $450 \text{ kg/m}^3$  of high-alkali cement and the fly ash mix has  $450 \text{ kg/m}^3$  of high-alkali cement plus  $150 \text{ kg/m}^3$  of low-calcium fly ash (i.e. 25% fly ash by mass of total cementitious material). Figure 6 shows the expansion at 54 months plotted against the total alkali contributed by the cement. The alkali content has little effect on the long-term expansion across the range studied ( $4.03$  to  $5.18 \text{ kg/m}^3 \text{ Na}_2\text{O}_e$ ) and significant expansion occurs at the lowest alkali level even in the presence of 25% fly ash and  $\text{LiOH} \cdot \text{H}_2\text{O}$ .

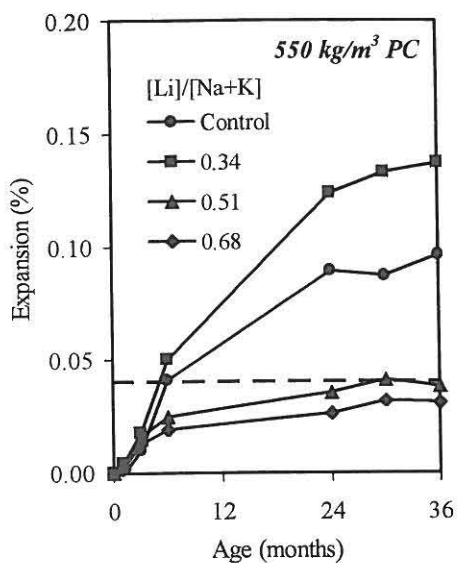


Fig 3 Expansion of Concrete Prisms with Greywacke and LiOH

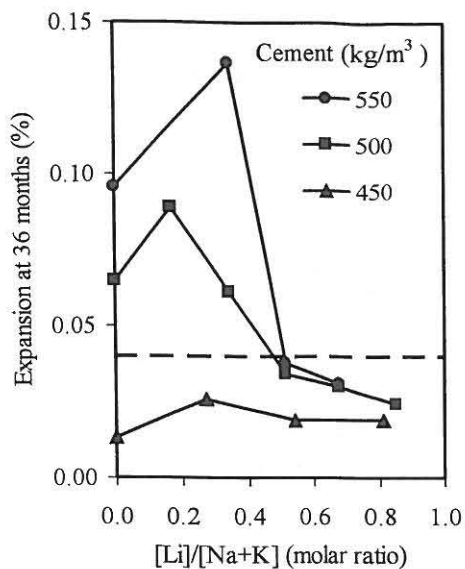


Fig 4 Expansion of Concrete Prisms with Greywacke and LiOH

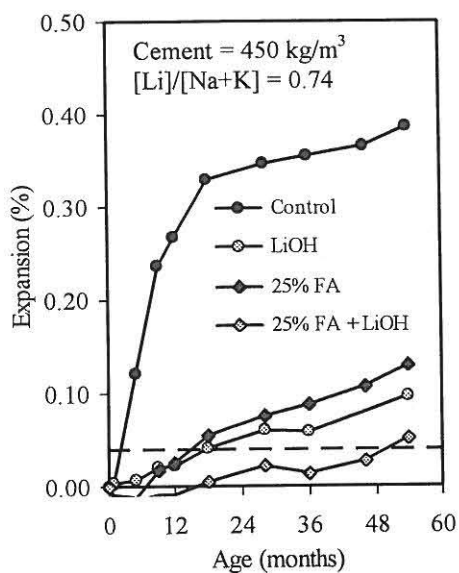


Fig 5 Expansion of Concrete Prisms with Siltstone and LiOH

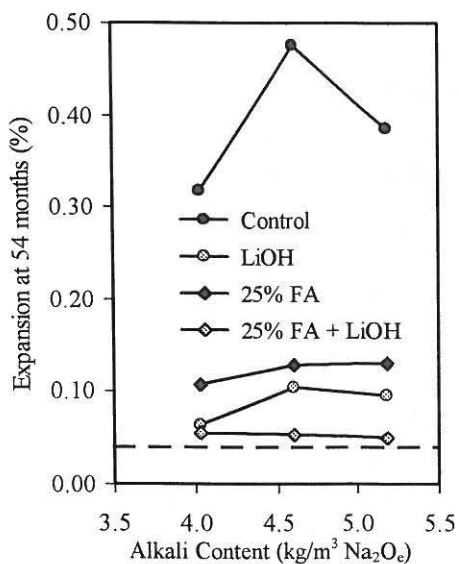


Fig 6 Expansion of Concrete Prisms with Siltstone and LiOH

This aggregate is very reactive and previous studies (Thomas et al. 1996) have shown that preventive measures found to be effective with other U.K. aggregates (e.g. use of 25% low-calcium fly ash) may not be sufficient to completely suppress damaging expansion with the siltstone. Figure 7 shows the effect of the amount of lithium on the expansion at 36 months for concretes with the siltstone aggregate and three different amounts of high-alkali cement. The expansion is effectively suppressed (i.e.  $< 0.04\%$ ) at this age by slightly increasing the lithium dosage from the recommended level of  $[Li]/[Na+K] = 0.74$  to just 0.85. Longer-term data are required to determine whether the prevention is permanent. Further testing of this aggregate with various levels of fly ash, slag and lithium have since commenced, but the tests are not sufficiently advanced for inclusion in the present paper.

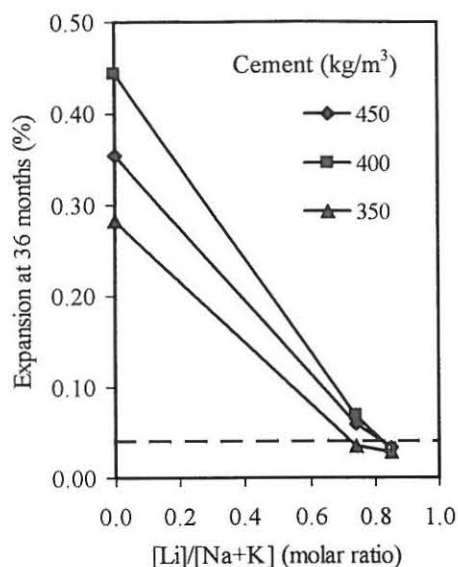


Fig 7 Expansion of Concrete Prism with Siltstone and LiOH

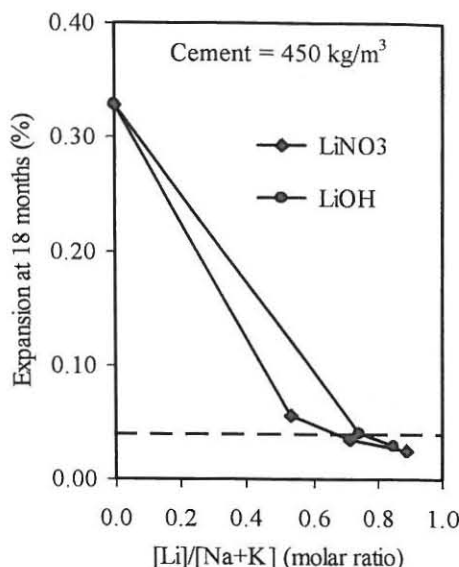


Fig 8 Effect of Form of Lithium on Expansion with Siltstone

Concrete mixes were also cast recently using this aggregate together with lithium nitrate solution. Although at the time of writing data were only available for specimens up to 18 months of age, some results are shown in Figure 8 to permit comparison between the different forms of lithium. There is no indication from these results that  $LiNO_3$  is significantly more efficient than  $LiOH.H_2O$  in controlling expansion with this aggregate; with both compounds it appears to be necessary to achieve a lithium to alkali molar ratio of  $[Li]/[Na+K] > 0.70$  to limit expansion to less than  $0.04\%$  at 18 months. It is possible that the nitrate form is more effective in controlling the long-term expansion. Other investigators have observed an increased efficacy when  $LiNO_3$  is used with a highly-reactive rhyolite from New Mexico (Stokes, private communication). Also it has been reported (Stokes et al. 1997) that the nitrate form will not be susceptible to the pessimum behaviour displayed by lithium hydroxide when used with the greywacke aggregate (Figure 4). This will be investigated as more data become available in this study.

Figure 9 shows results from pore solution studies on four different mortars. The left-hand graph compares two mortars without lithium, one of which contains a non-reactive limestone and the other reactive flint sand. The right-hand graph compares similar mortars that contain a quantity of lithium hydroxide monohydrate such that  $[Li]/[Na+K] = 0.74$ . The presence of reactive aggregate in mortars without lithium results in a reduction in the alkalinity of the pore solution, i.e.  $Na$ ,  $K$  and  $OH$  reduce with time. When lithium hydroxide is added to mortars much of the lithium goes into the pore solution and there is a concomitant increase in the hydroxyl ion concentration. The presence of reactive aggregate in lithium-containing mortars also reduces the alkalinity of the pore solution and the lithium concentration reduces with time together with the other ions.

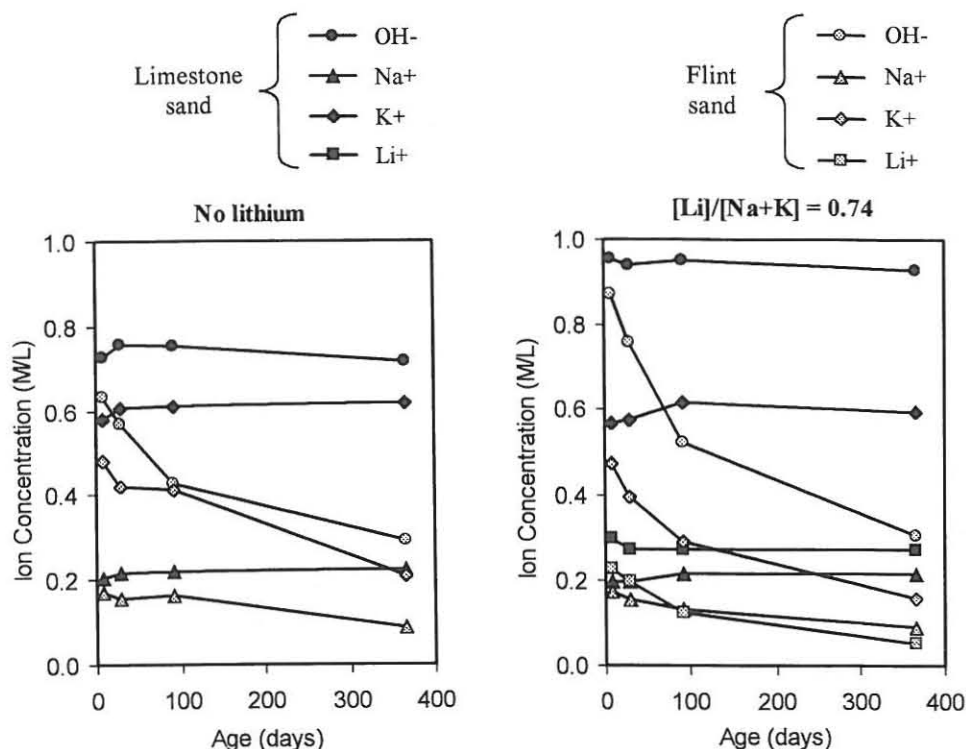


Figure 9 Effect of Lithium Hydroxide and Reactive Sand on Pore Solution Composition

It is reasonable to ascribe the differences between the pore solution composition of mortars with limestone and flint sand to reactions between the ions in solution and the reactive silica in the flint (i.e. alkali-silica reaction). In mortars without lithium, the sum of the sodium and potassium ions in solution at 1 year is 0.840 moles/litre for mortar with limestone sand and 0.295 in mortar with flint sand. The difference (0.545 moles/litre) is presumably consumed by the alkali-silica reaction; there is a slightly smaller difference in the hydroxyl ion concentration between the two mortars. It is interesting to note that there is a very similar change in the sum of potassium and sodium ions due to the presence of flint sand in mortars with lithium; indeed the sum reduces from 0.806 to 0.248 moles/litre, which is a reduction of

0.558 moles/litre. This means that the presence of lithium is not preventing the consumption of sodium and potassium as proposed by Diamond and Ong (1992). The consumption of these alkalis is accompanied by a reduction in lithium from 0.270 moles/litre in mortars with limestone to 0.051 moles/litre in mortars with flint. The difference of 0.219 moles/litre is also presumably due to reaction with the flint sand.

Taken together, the results from concrete prism expansion tests and pore solution studies of mortars indicate that *LiOH* is effective in preventing expansion without necessarily impeding the reaction between the alkalis and silica. In fact, the amount of alkali-silica reaction appears to be enhanced in the mortars containing lithium as there is a consumption of lithium alkalis in addition to that of sodium and potassium. It is possible then that lithium affects expansion by controlling the nature of the alkali-silica product formed rather than preventing its formation. This phenomenon is currently under study at the University of Toronto, and full details of this work and the results of the pore solution studies will be published later.

## CONCLUSIONS

1. Lithium hydroxide monohydrate was effective in controlling long-term expansion in concrete prisms containing a reactive flint sand or a reactive crushed greywacke aggregate provided that the lithium to alkali molar ratio of the mix was 0.51 or higher, i.e.  $[Li]/[Na+K] \geq 0.51$ .
2. At lower levels of lithium (e.g.  $[Li]/[Na+K] = 0.34$  to  $0.37$ ), expansion exceeded 0.04%. In the case of greywacke aggregate, the expansion with this level of lithium actually exceeded that of the control mix without lithium.
3. Concrete blocks (300 x 300 x 500 mm) with 475 or 550 kg/m<sup>3</sup> of high-alkali cement and flint sand exhibited significant expansion and extensive cracking after 3 to 4 years field exposure. No visible distress was apparent in blocks containing lithium hydroxide with the same levels of cement and reactive aggregate after 54 months; the lithium content of these undamaged blocks was  $[Li]/[Na+K] \geq 0.74$ .
4. Lithium hydroxide monohydrate was less efficient in controlling the expansion of prisms with a crushed siltstone aggregate; a lithium to alkali ratio of  $[Li]/[Na+K] = 0.85$  was required to control expansion to less than 0.04% at three years. Lower amounts of lithium may be necessary when used in conjunction with fly ash.
5. Pore solution studies indicated that *LiOH* did not necessarily impede the reaction between alkalis (*Na* and *K*) and silica in mortars containing flint sand. It is suggested that the effect of lithium on expansion may be related to the nature of the reaction product that forms in the presence of lithium.

## ACKNOWLEDGEMENT

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