Pergamon

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Cement and Concrete Research 34 (2004) 1403–1415

CEMENT AND CONCRETE RESEARCH

Examination of the effects of LiOH, LiCl, and $LiNO_3$ on alkali–silica reaction

C.L. Collins, J.H. Ideker, G.S. Willis, K.E. Kurtis*

School of Civil and Environmental Engineering, Georgia Institute of Technology, 790 Atlantic Drive, Atlanta, GA 30332-0355, USA

Received 19 November 2002; accepted 5 January 2004

Abstract

Lithium additives have been shown to reduce expansion associated with alkali–silica reaction (ASR), but the mechanism(s) by which they act have not been understood. The aim of this research is to assess the effectiveness of three lithium additives—LiOH, LiCl, and $LiNO_3$—at various dosages, with a broader goal of improving the understanding of the means by which lithium acts. The effect of lithium additives on ASR was assessed using mortar bar expansion testing and quantitative elemental analysis to measure changes in concentrations of solution phase species (Si, Na, Ca, and Li) in filtrates obtained at different times from slurries of silica gel and alkali solution. Results from mortar bar tests indicate that each of the lithium additives tested was effective in reducing expansion below an acceptable limit of 0.05% at 56 days. However, different lithium additive threshold dosages ($[Li_2O]/[Na_2O_e]$) were required to accomplish this reduction in expansion; these were found to be approximately 0.6 for LiOH, 0.8 for $LiNO_3$, and 0.9 for LiCl. Quantitative elemental analysis indicated that sodium and lithium were both bound in reaction products formed within the silica gel slurry. It is also believed that lithium may have been preferentially bound over sodium in at least one of the reaction products because a greater percent decrease in dissolved lithium than dissolved sodium was observed within the first 24 h. It appears that lithium additives either decreased silica dissolution, or promoted precipitation of silica-rich products (some of which may be nonexpansive), because the dissolved silica concentration decreased with increasing dosage of lithium nitrate or lithium chloride additive.

Keywords: Alkali; Alkali–aggregate reaction; Glass; Lithium compounds; Mortar

1. Introduction

Expansion in concrete caused by swelling of the alkali–silica reaction (ASR) gel is a concern in areas of the world where the materials available for concrete include aggregate containing potentially reactive silica and high-alkali cement. ASR occurs when alkalis dissolve into concrete pore solution, indirectly increasing the hydroxyl content, catalyzing the dissolution of silica. After the pore solution becomes saturated with dissolved silica species, silica will precipitate, at the same time binding alkalis, forming alkali–silica gel. This alkali–silica gel is believed to then take in water causing it to swell and exert an internal pressure on the concrete [1,2]. If the internal pressure exceeds the tensile strength of concrete, the concrete may crack.

ASR damage causes a loss in performance. More specifically, cracking reduces strength and stiffness. A network of cracks increases concrete permeability, allowing more water to enter, accelerating ASR damage and making the concrete more vulnerable to other forms of degradation. ASR damage is particularly detrimental in dams where the expansion can cause moving components to function improperly [3–5]. In severe cases, the reaction can be so damaging that the affected structure has to be replaced.

Common methods for avoiding ASR in new construction include using nonreactive aggregate, low-alkali cement, lower water-to-cement ratio (w/c), decreasing cement content, and incorporating mineral admixtures. In some locations, however, appropriate aggregate, cement, or mineral admixtures may not be available. The use of chemical additives is an alternative means to avoid damage by ASR in new construction. McCoy and Caldwell [6] first demonstrated that some chemical salts, including

---

* Corresponding author.
E-mail address: kkurtis@ce.gatech.edu (K.E. Kurtis).

0008-8846/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2004.01.011

lithium salts, may decrease expansion in mortars undergoing ASR. Currently, lithium-containing additives are commercially available to control ASR. However, the mechanism by which lithium acts is still unknown. To date, research on lithium additives has not provided a comprehensive understanding of the mechanism or mechanisms by which this type of additive is effective in reducing expansion during the ASR. As a result, it is difficult to identify appropriate lithium compounds and their doses, and predict for what duration lithium additives will act to suppress expansion.

To address, in part, these outstanding questions regarding the use of lithium additives in concrete to avoid or mitigate ASR, a research program was undertaken to better understand the effect of lithium on the ASR. In addition to the more standard measurements of mortar bar expansion, slurries of silica gel and strong alkaline solutions were prepared to simulate the reaction of reactive siliceous aggregate in pore solution. Quantitative elemental analysis was performed on the slurry filtrate to compare reaction chemistry with expansion results. The results will be discussed in the context of the reactions believed to occur during ASR—silica dissolution and reprecipitation, while binding alkalis and calcium (when present), as a potentially expansive gel.

2. Experimental method

2.1. Mortar bar sample preparation

Mortar bar expansion tests were performed to assess expansion control by lithium additives. Mortar bars were prepared with Type I cement and a w/c ratio of 0.37, in accordance with ASTM C 227, with the following exceptions: sodium hydroxide was added to the mix water to increase the percent Na_2O equivalent,[1] traditional aggregate was replaced with crushed graded borosilicate glass, and various lithium additives were added to the mix water. Cement composition, determined by oxide analysis, is shown in Table 1. Three mortar bars were prepared with each additive at each additive dose according to the adapted ASTM C 227, which requires a cement Na_2O_e of greater than 0.60 wt.%. A final Na_2O_e of 1.0 wt.% was chosen based on research performed by McCoy and Caldwell [6], Stark [7], Lumley [8], and Ramachandran [9]. To raise the Na_2O_e from 0.51 to 1.0 wt.%, sodium hydroxide was added to the mix water based on ASTM C 1293. Crushed borosilicate glass with a fineness modulus of 2.81 was graded according to ASTM C 227 and used in place of traditional aggregate to increase reactivity, based on ASTM PS 81 and ASTM C 441. Table 2 shows the composition of a typical borosilicate glass and Fig. 1 shows the gradation curves for the aggregates. The crushed glass was made from two sizes of Pyrex brand glass tubing from Fisher Scientific with wall thickness measurements of 1.0 and 2.4 mm.

Table 1
Cement oxide analysis

	wt.%
Oxide analysis	
SiO_2	19.85
Al_2O_3	5.67
Fe_2O_3	2.69
CaO	64.81
MgO	0.78
Na_2O	0.19
K_2O	0.49
Na_2O equivalent	0.51
TiO_2	0.51
Mn_2O_3	0.05
P_2O_5	0.19
SrO	0.22
BaO	0.00
SO_3	3.15
Loss on ignition	1.44
Insoluble residue	0.17
Potential composition	
C_3S	62.07
C_3A	10.46
C_2S	10.10
C_4AF	8.20

In addition to sodium hydroxide, each sample contained a specific lithium additive (i.e., LiOH, $LiNO_3$, or LiCl) added by molar concentration to the mix water, so the effect of each respective additive could be compared [10]. The concentration of lithium additive was selected based primarily upon findings presented by other researchers [11–13].

In addition to the control sample, which contained no lithium additive, various additive doses were tested as the ratio of the molar concentration of lithium oxide to the molar concentration of sodium oxide equivalent ($[Li_2O]/[Na_2O_e]=[Li]/[Na_e]$).[2] Using molar proportioning rather than proportioning by weight allows the effects of different compounds to be compared. The dosages tested were as follows: $[Li]/[Na_e]=0$, 0.1 ($LiNO_3$ only), 0.25 ($LiNO_3$ only), 0.5, 1, and 1.5. Table 3 shows the $LiNO_3$ mortar bar components. Three mortar bars were prepared using each molar concentration of each lithium additive. Samples were allowed to cure in a humid container at room temperature and were demolded after 24 ± 2 h and stored in humid metal containers, RH ≈ 90%, at 38.0 ± 2.0 °C per ASTM C 227. Length change measurements were

---

[1] Percent Na_2O equivalent $(Na_2O_e)=Na_2O+0.658K_2O$

[2] $[Li_2O]/[Na_2O_e]$ was found to equal $[Li]/[Na_e]$ by converting each species within this formula, using mole ratios (i.e., 2 mol Li/1 mol Li_2O). From this point on, $[Li]/[Na_e]$ will be used interchangeably with $[Li_2O]/[Na_2O_e]$. Other authors use the convention $[Li]/[Na+K]$, which is not the same because it is a simple alkali ratio not accounting for the 0.658 multiplication factor in front of K_2O.

Table 2
Composition of a typical borosilicate glass

Component	Concentration (wt.%)
Na	5.4
Si	33.7
K	0.7
Ca	0.3
Al	3.5

taken using a length comparator with a digital gage at 1 day (24 h), 14 days (336 h), 28 days (672 h), and 56 days (1344 h).

2.2. Silica gel slurry sample preparation

Silica gel slurry samples were prepared to examine the role of lithium in the ASR. Concentrations of solution phase species (Si, Na, Ca, and Li) were measured over time by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Silica gel slurries were prepared by adding various additives, and chromatograph grade silica gel (100–200 mesh), at the pessimum proportion ($SiO_2/Na_2O \approx 4.8$, per Dent Glasser and Kataoka [14]), to 0.7 M NaOH (pH 13.8) solution made with deaired low resistivity (18.2 MΩ cm) deionized water. The deaired water contributed negligible amounts of Si to the solution. The pessimum proportion, in this case, refers to the proportion of SiO_2 to Na_2O in solution at which gel expansion is maximized [14]. The effect of lithium additives (LiOH, LiCl, or $LiNO_3$) and calcium additives [$Ca(NO_3)_2$ $4H_2O$ or $Ca(OH)_2$] were examined in the slurry samples.

Table 4 shows the composition of the two types of silica gel slurries prepared, those without calcium and those containing calcium. Lithium compounds and dosages were chosen to correspond with the mortar bars prepared as described in Section 2.1. The calcium additive amounts were determined by multiplying the soluble mass of each additive by a factor. The factors were determined such that the slurry would be undersaturated [0.5 times the solubility of $Ca(OH)_2$], saturated [1 times the solubility of $Ca(OH)_2$], or in excess [0.021 and 0.5 times the solubility of $Ca(NO_3)_2{\cdot}4H_2O$ and 2 times the solubility of $Ca(OH)_2$] with respect to $Ca(OH)_2$. At 25 °C, the solubility of $Ca(NO_3)_2{\cdot}4H_2O$ is 58 g/100 g solution and the solubility of $Ca(OH)_2$ is 0.159 g/100 g solution [15].

Initially, only $Ca(NO_3)_2{\cdot}4H_2O$ was tested, but upon addition to the solution, a precipitate believed to be $Ca(OH)_2$ formed [Note: the precipitate was believed to be $Ca(OH)_2$ because mixing $Ca(NO_3)_2$ and NaOH results in $Ca(OH)_2$ precipitate and $NaNO_3$. Also, the precipitate was not believed to be $CaCO_3$ because it did not form when $Ca(OH)_2$ was added in place of $Ca(NO_3)_2{\cdot}4H_2O$]. Because $Ca(OH)_2$ was believed to have been precipitated, Ca, in effect, was in excess in all samples prepared with $Ca(NO_3)_2{\cdot}4H_2O$. Therefore, slurries containing $Ca(OH)_2$ were prepared as well. For $Ca(NO_3)_2{\cdot}4H_2O$, the value of 0.021 times the solubility was chosen to be approximately comparable to twice the solubility of $Ca(OH)_2$, assuming not all of the calcium precipitated as $Ca(OH)_2$. These quantities in which Ca was in excess, including 0.5 times the solubility of $Ca(NO_3)_2{\cdot}4H_2O$, were chosen to replicate the conditions in concrete where dissolution of the poorly soluble hydration product $Ca(OH)_2$ makes calcium available over time.

The slurries were initially shaken, but then were allowed to react without stirring in sealed polyethylene centrifuge tubes at room temperature. For most slurries without calcium, four samples were prepared, with measurements made at 0, 24, 336 (14 days), and 672 h (28 days). For most calcium-containing slurries, three samples were prepared, with measurements at 0, 24, and 336 h (14 days). Slurries to be analyzed at 0 h were prepared without silica gel so that the ASR would not have occurred and the initial state could be measured. To address effects initially occurring within the $LiNO_3$ slurries without calcium and the calcium-containing $Ca(OH)_2$ slurries, samples were also prepared for analysis at 5 and 12 h. Prior to analysis, each sample was filtered with a 0.45 μm Millipore filter and the filtrate was diluted 1000 × . A Thermo Jarrell Ash Iris Model ICP-OES was used for quantitative elemental analysis of the slurry samples. The instrument was calibrated using 1, 5, 10, 20, and 50 ppm mixtures of Na-, Si-, Li-, and Ca-certified reference standards in low-resistivity water. Calibration was performed before and after 10 sample analyses. Each sample was analyzed for Na, Si, Li, and Ca as an unknown and the final element concentrations were determined using the calibration curves created from the calibration standards. Wavelengths used to analyze the elements are listed in Table 5. Thus, the data presented for average concentration of Si, Na, and Li

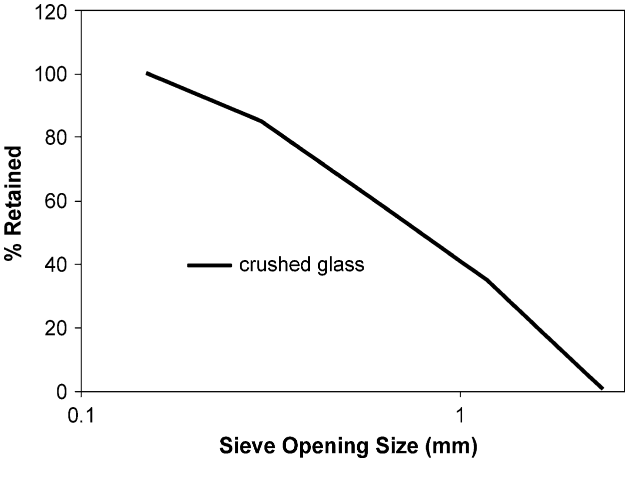

Fig. 1. Glass aggregate gradation.

Table 3
$LiNO_3$ mortar bar components

Li/Na_{eq}	Cement (g)	NaOH (g)	Graded aggregate (g)	Na_{eq} (mol)	Li added (mol)	Additive (g)	Water (g)
0	150	0.945	337.5	0.043	0	0	55.5
0.5	150	0.945	337.5	0.043	0.022	1.489	55.5
1.0	150	0.945	337.5	0.043	0.043	2.978	55.5
1.5	150	0.945	337.5	0.043	0.065	4.468	55.5

Table 4
Slurry sample components

Slurries without Ca

Step 1: Alkali	Step 2: Li addition		Step 3: silica gel
	Additive	Li/Na_e	
0.7 M NaOH	$LiOH \cdot H_2O$	0 (control)	$SiO_2/Na_2O = 4.8$
		0.5	
		1	
		1.5	
	LiCl	0	
		0.5	
		1	
		1.5	
	$LiNO_3$	0	
		0.25	
		0.5	
		1	
		1.5	

Calcium-containing slurries

Step 1: Alkali	Step 2: Ca addition		Step 3: $LiNO_3$ addition	Step 4: silica gel
	Additive	Quantity	Li/Na_e	
0.7 M NaOH	$Ca(NO_3)_2 \cdot 4H_2O$	0.21 times $Ca(NO_3)_2 \cdot 4H_2O$ solubility	0	$SiO_2/Na_2O = 4.8$
			0.25	
			0.5	
			1	
			1.5	
		0.5 times $Ca(NO_3)_2 \cdot 4H_2O$ solubility	0	
			0.25	
			0.5	
			1	
			1.5	
	$Ca(OH)_2$	0.5 times $Ca(OH)_2$ solubility	0	
			0.25	
			0.5	
			1	
			1.5	
		1 times $Ca(OH)_2$ solubility	0	
			0.25	
			0.5	
			1	
			1.5	
		2 times $Ca(OH)_2$ solubility	0	
			0.25	
			0.5	
			1	
			1.5	

obtained by quantitative elemental analysis are based upon two replicates at each wavelength.

3. Results and discussion

3.1. Mortar bar expansion

Mortar bars were prepared to monitor the effectiveness and to determine the optimal dosages of the lithium additives—LiOH, LiCl, and $LiNO_3$—on reducing expansion due to ASR. In addition, the results of these routine expansion tests can be used to interpret data obtained from elemental analysis. Fig. 2a shows the expansion of mortar bars prepared with LiOH compared to the expansion of the control mortar bars prepared without lithium additive. At all dosages tested, mortar bars prepared with LiOH showed little expansion. The least expansion was seen in mortar bars prepared with LiOH at a $[Li]/[Na_e]$ of 1.5. This trend was also observed for LiOH by Thomas et al. [13]. However, Diamond [16] did not observe a continuous reduction in expansion with increasing dosages of LiOH. Rather, Diamond [16] reported a pessimum proportion of LiOH in which doses less than 1.5 resulted in expansion greater than that seen in the control. According to graphical results presented by Diamond [16], the pessimum proportion of LiOH was between 0.4 and 0.8 $[LiOH]/[Na_2O_e]$ (or 0.2 and 0.4 $[Li_2O]/[Na_2O_e]$ or $[Li]/[Na_e]$) in molar concentration. Thomas et al. [13] also found a pessimum proportion of LiOH, $[Li]/[Na+K] = 0.34$, in samples prepared with greywacke aggregate. In accordance with results presented by

Table 5
Wavelengths used to analyze slurry filtrates

Element	Wavelength (nm)
Li	670.784
Na	588.995
Na	589.592
Si	221.667
Si	250.690
Si	251.612
Ca	184.006
Ca	315.887
Ca	317.933
Ca	393.366

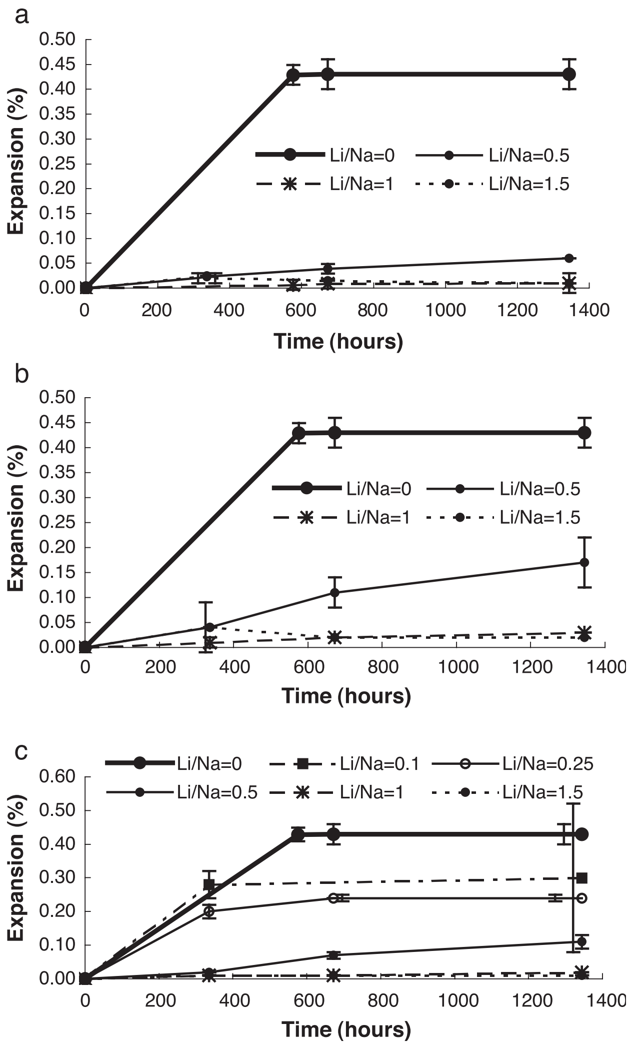

Fig. 2. Expansion of mortar bars over time with and without (a) LiOH, (b) LiCl, and (c) $LiNO_3$.

Lumley [8], Fig. 2a shows no such pessimum proportion. Lumley [8] found that expansion of mortar bars prepared with LiOH decreased with an increase in dose. Mortar bars prepared by Lumley contained Mountsorrel granodiorite coarse aggregate and lithium doses of $[\mathrm{Li_2O}]/[\mathrm{Na_2O_e}]=$ 0.19, 0.39, and 0.58. Thomas et al. [13] also saw no pessimum proportion of LiOH when flint sand was used as the aggregate. It is unclear why pessimum behavior for LiOH dosages is reported by some, while other data, including the results presented here, do not indicate such behavior. This may be due to the variations in the LiOH dosages (particularly with respect to pessimum proportion), the type and grading of aggregate tested, the water-to-cement ratio used, and/or exposure conditions.

Fig. 2b shows the expansion of mortar bars prepared with LiCl compared to the expansion of the control mortar bars prepared without lithium additive. The results demonstrate that the samples with LiCl reduced expansion in comparison to the control samples. Doses of $[\mathrm{Li}]/[\mathrm{Na_e}]=1$ and 1.5 appear to be effective in minimizing expansion over the time period tested, whereas, at a dosage of 0.5, expansion gradually increased over time. For example, at a dosage of 0.5, expansion increased up to 0.17% at 56 days, and at dosages of 1 and 1.5, expansion was measured at 0.03% and 0.02%, respectively. Again, at a lithium dose of 1.5, the least expansion was seen.

In Fig. 2c, the expansion of mortar bars prepared with $LiNO_3$ is depicted. Once again, all samples prepared with lithium showed a reduction in expansion. Additional dosages, $[\mathrm{Li}]/[\mathrm{Na_e}]$ of 0.1 and 0.25, of $LiNO_3$ were tested to see if expansion would continue to increase as the dosage of additive was decreased. Lower concentrations of additives resulted in a general trend of increased expansion. In the samples prepared with $LiNO_3$, as in the mortar bars prepared with LiOH and LiCl, expansion was reduced as the ratio of Li to Na was increased.

However, mortar bars prepared with LiOH, LiCl, or $LiNO_3$ showed very little difference in expansion between $[\mathrm{Li}]/[\mathrm{Na_e}]$ dosages of 1 and 1.5. This may indicate that there is an upper bound for each lithium additive above which mortar bar expansion does not continue to decrease, over the time period examined here [8]. Over the time period tested, at a dosage of $[\mathrm{Li}]/[\mathrm{Na_e}]=1$, expansion increased with the following additive order: $\mathrm{LiOH} < \mathrm{LiNO_3} < \mathrm{LiCl}$. Whereas, Fig. 3 shows that at the largest lithium dose examined (i.e., $[\mathrm{Li}]/[\mathrm{Na_e}]=1.5$), expansion increased with the following additive order: $\mathrm{LiNO_3} \cong \mathrm{LiOH} < \mathrm{LiCl}$.

From the results presented above, it is evident that a minimum or threshold dosage, different for each additive, exists to effectively reduce expansion below an acceptable level. According to ASTM C 33, expansion is acceptable if it is less than 0.05% at 3 months, or less than 0.1% at 6 months. An acceptable level of 0.05% will be assumed in this case.

Fig. 4 shows that the minimum dosage for all three additives tested lies approximately between the lithium and sodium equivalent, [Li] to [Na$_e$], molar ratios of 0.60 to 0.93. Assuming linear behavior between data points in Fig. 4 to reduce expansion to an acceptable level using LiOH, a dosage greater than 0.60 would be required, for $LiNO_3$, a dosage greater than 0.83, and for LiCl, a dosage greater than 0.93. The concept of a threshold lithium

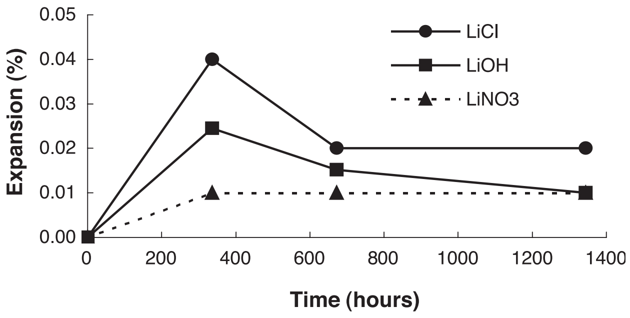

Fig. 3. Comparison of different lithium additives on mortar bar expansion at $\mathrm{Li/Na_{eq}}=1.5$.

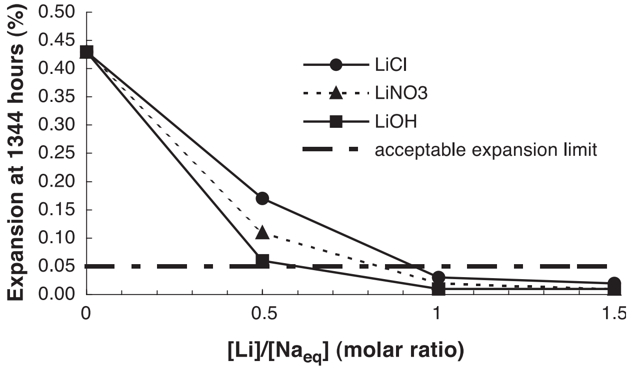

Fig. 4. Threshold lithium additive required to reduce expansion to an acceptable level.

additive dosage has been previously considered by other researchers such as Thomas et al. [13] and Stark [7]. Results shown in Fig. 4 are similar to those found by Thomas et al. [13], where it was found that a lithium-to-alkali molar ratio greater than 0.51 (or [Li]/[Na$_e$] >0.65) was necessary to reduce expansion below 0.04% at 3 years in mortar bars prepared with LiOH and greywacke aggregate. When siltstone was used as the aggregate, and either LiOH or LiNO$_3$ as the additive, a lithium-to-alkali molar ratio greater than 0.70 (or [Li]/[Na$_e$] >0.89) was necessary. The discrepancy in results shown in Fig. 4 and those found by Thomas et al. [13] could be the result of the different aggregates used in testing or testing parameters, including a longer sampling period and storage of the mortar bars in moist toweling where leaching may have occurred.

3.2. Quantitative elemental analysis

For comparison with mortar bar expansion results and to characterize the effect of lithium on the chemistry of the ASR, quantitative elemental analysis by ICP-OES was performed on slurries prepared with silica gel in sodium hydroxide solution and various additives described in Table 4. First, filtrates from silica gel slurries without calcium additive prepared with 0.7 M NaOH solution, SiO_2/Na_2O of 4.8, and LiOH, LiCl, or LiNO$_3$ were analyzed. Also, filtrates from calcium-containing slurries prepared with 0.7 M NaOH solution, SiO_2/Na_2O of 4.8, either $Ca(OH)_2$ or $Ca(NO_3)_2{\cdot}4H_2O$, and LiNO$_3$ were analyzed. These results for filtrates of both sets of slurries will be considered within the context of the reactions known to occur during ASR: initial dissolution of reactive siliceous aggregate and eventual precipitation of alkali–silica products and, in the presence of calcium, alkali–silica–calcium products.

3.2.1. Silica gel slurries without calcium

In the samples prepared with LiOH, the dissolved silica concentration, [Si], in the filtrates increased up to 336 h (14 days), as shown in Fig. 5a, presumably due to near-surface silica being dissolved into solution. Also up to 336 h, silica dissolution increased as the amount of LiOH was increased, due presumably to a corresponding increase in OH^- [16]. However, after 336 h, there is a 3% decrease in [Si] for the slurry prepared with [Li]/[Na$_e$] = 1.5. This decline in dissolved Si was observed after 336 h in some of the LiCl and LiNO$_3$ samples as well. Fig. 5b shows that with LiCl doses of [Li]/[Na$_e$] = 1 and 1.5, the Si concentration decreases after 336 h. In the LiNO$_3$ slurries, shown in Fig. 5c, doses of [Li]/[Na$_e$] = 0.5 and 1.5 result in a decrease in [Si] after 336 days. In these slurries, the silica gel was allowed to react without stirring. Therefore, dissolution of silica was dependent on rate-limited diffusion through the bed of silica gel and the reaction products forming near the surface. At the same time, Si was precipitated from solution to form reaction products. Therefore, the competing effects of Si dissolution

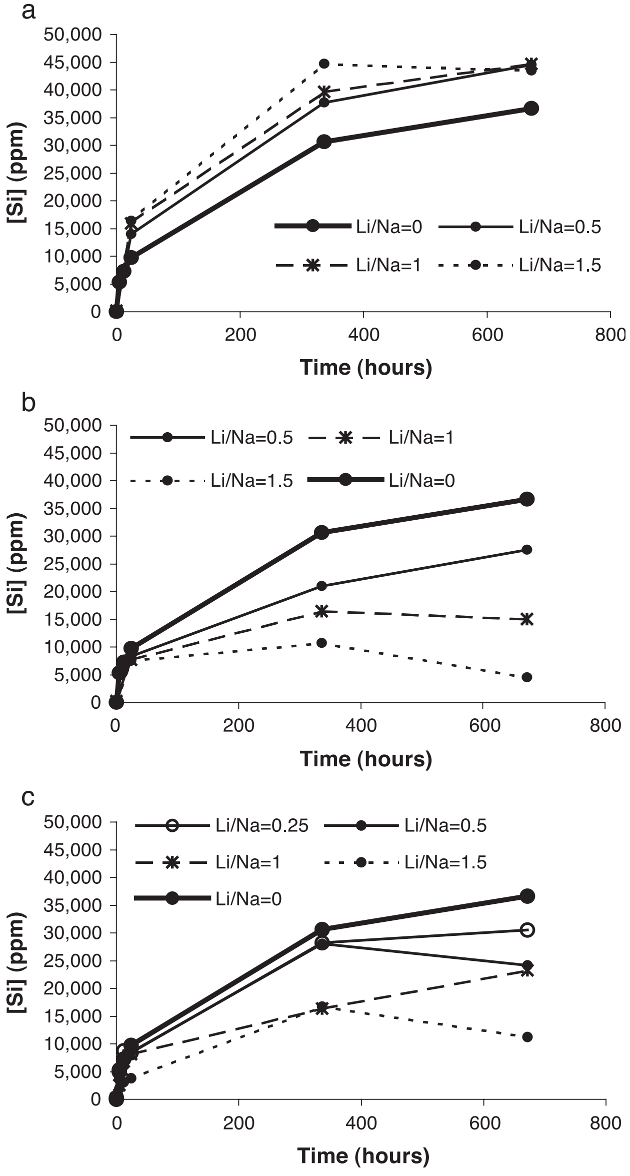

Fig. 5. Dissolved Si concentration in slurry filtrates without Ca prepared with (a) LiOH, (b) LiCl, and (c) LiNO$_3$.

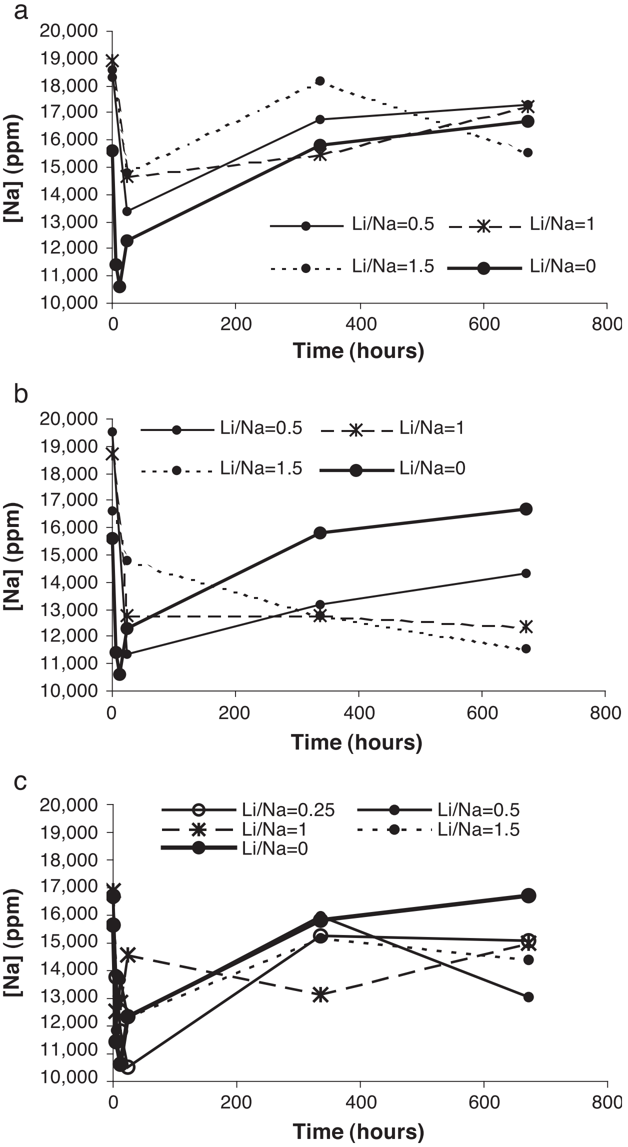

Fig. 6. Dissolved Na concentration in slurry filtrates without Ca prepared with (a) LiOH, (b) LiCl, and (c) $LiNO_3$.

and product formation, both of which can occur at different rates depending upon the alkalinity of the solution and the [Li], can produce different results for the different slurries examined. Therefore, it is proposed that the dissolved [Si] fluctuates due to the competing effects of two processes: (1) dissolution and diffusion of Si species into the solution initially, and (2) at later ages the precipitation of lithium–alkali silicate or another lithium-containing reaction product whose presence may limit the rate of ion dissolution/ diffusion.

In the presence of LiOH, Si in solution was found to increase with an increase in [Li] (Fig. 5a), while the opposite trend was apparent for those samples prepared with LiCl and $LiNO_3$ (Fig. 5b and c). That is, the dissolved Si, which was initially approximately equal at different Li concentrations, decreased with an increase in [Li] for those samples prepared with LiCl and $LiNO_3$. It would appear that the increase in OH^-, contributed to the solution by LiOH, increases the rate of dissolution of silica or the solubility of silica in solution, or perhaps both. Another possible explanation for the dissolved silicon trend reversal in slurries prepared with LiCl and $LiNO_3$ is that increasing [Li] suppresses silica dissolution when the OH^- remains constant. In slurries prepared with LiOH, this suppression of dissolved silicon by Li may compete with the increasing tendency toward silicon dissolution in the presence of greater OH^- concentrations. Another potential explanation is that more silicate reaction product is formed with an increase in [Li].

Fig. 6a–c show the concentration of Na in solution filtrates from slurries prepared with LiOH, LiCl, and $LiNO_3$. The initial ($t=0$) sodium concentration in all slurries should have been approximately 16,000 ppm, however, the initial

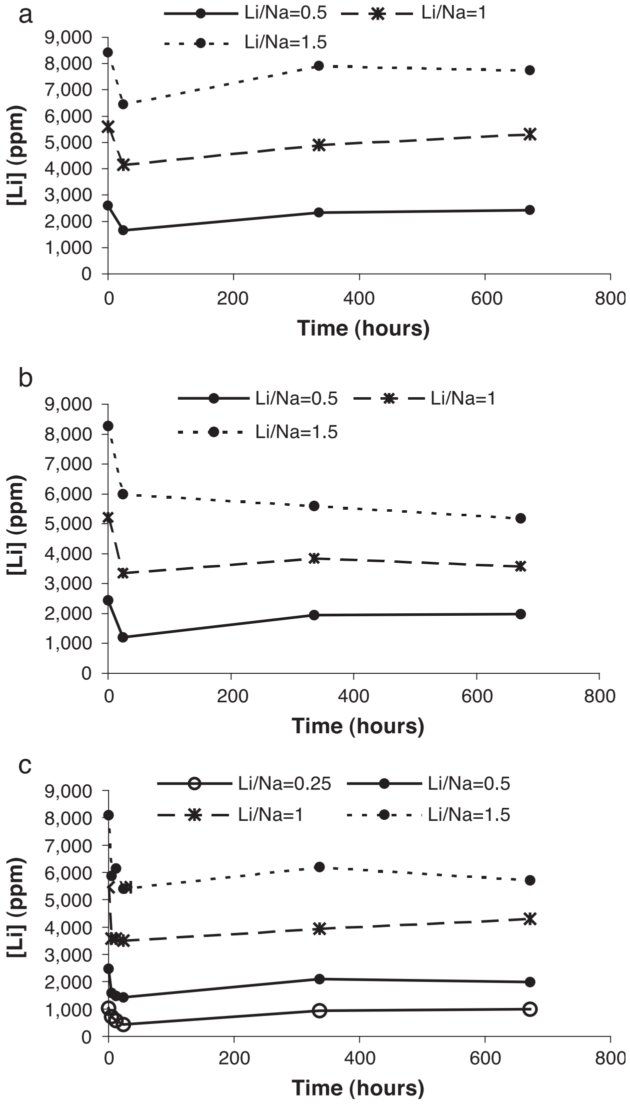

Fig. 7. Dissolved Li concentration in slurry filtrates without Ca prepared with (a) LiOH, (b) LiCl, and (c) $LiNO_3$.

concentrations deviated from the expected value by an average of 1620 ppm. This discrepancy may be due to the significant dilution necessary for the filtrate concentration to be within a readable range by the ICP-OES. A large (11–42%) initial decline in dissolved Na was observed at all lithium dosages over the first 24 h. The rapid initial decrease is likely due to sodium binding to the negatively charged silicate surface and/or being incorporated into sodium–silicate product. After the initial decline, no distinct trends are apparent in [Na] in solution over time in the presence of the different additives. It is proposed that this variation is once again likely a result of limited ion mobility through the silica bed and/or reaction product layer. However, it does appear that there is, in general, less dissolved Na in samples prepared with LiCl and $LiNO_3$ than LiOH, with [Na] generally being the lowest in the presence of LiCl.

The dissolved Li concentration in all slurries, shown in Fig. 7a–c, undergoes an even larger initial drop (ranging from 23% to 57%) than Na over the first 24 h and then remains relatively steady over the observation period. The larger initial drop in Li could be due to Li being preferentially bound over Na in the reaction product. Other than both ions showing an initial decrease, there appears to be no correlation between the trends of Li concentration and Na concentration.

3.2.2. Calcium-containing silica gel slurries

Slurry samples of silica gel in 0.7 M NaOH prepared with Ca additives, $Ca(NO_3)_2 \cdot 4H_2O$ or $Ca(OH)_2$, and $LiNO_3$ were examined to assess the effect of lithium addition in solutions most closely representing pore solution in concrete.

In all slurries containing calcium, dissolved [Si], depicted in Fig. 8a–e, was greatest in either the samples prepared without Li or the samples prepared with $LiNO_3$ at a dose of $[Li]/[Na_{eq}] = 0.25$, the lowest dosage examined. Generally, as Li dose increased, dissolved [Si] decreased.

Comparing Si concentration in samples prepared with calcium (Fig. 8) to samples prepared without Ca (Fig. 5) shows that, overall, less silicon is in solution in the calcium-containing slurries. For example, the maximum [Si] found in the slurries containing calcium was approx-

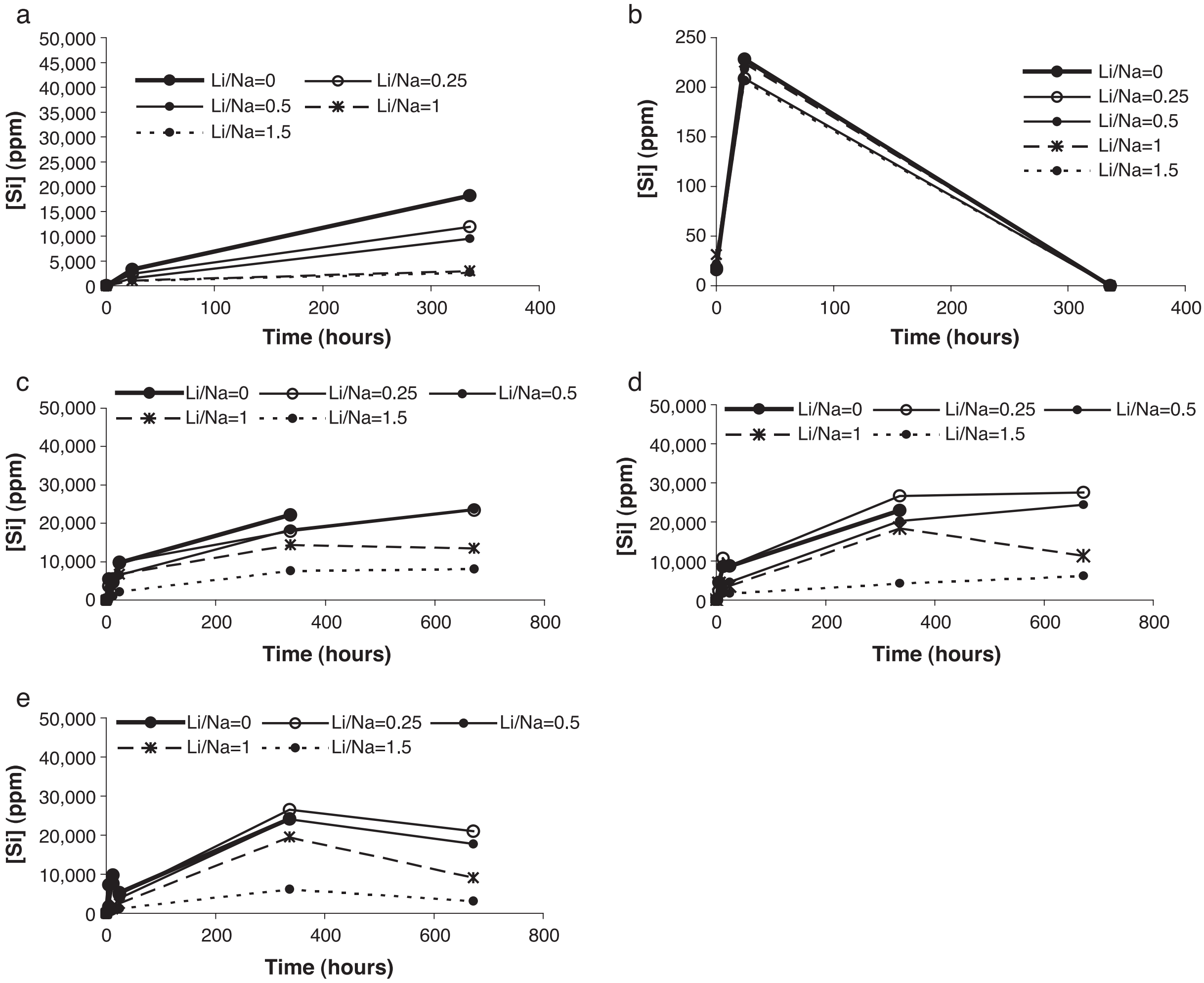

Fig. 8. Dissolved Si concentration in slurry filtrates with $LiNO_3$ and calcium (a) 0.021 times the solubility of $Ca(NO_3)_2 \cdot 4H_2O$, (b) 0.5 times the solubility of $Ca(NO_3)_2 \cdot 4H_2O$, (c) 0.5 times the solubility of $Ca(OH)_2$, (d) 1 times the solubility of $Ca(OH)_2$, and (e) 2 times the solubility of $Ca(OH)_2$.

imately 27,000 ppm in slurries prepared with 1 times the solubility of $Ca(OH)_2$, compared to 37,000 ppm in the reference slurries without calcium. This decrease in [Si] in solution is believed to indicate the formation of calcium-containing silicates such as C-S-H. Silica concentration in solution was less for slurries prepared with $Ca(NO_3)_2{\cdot}4H_2O$ (Fig. 8a and b) than slurries prepared with $Ca(OH)_2$ (Fig. 8c–e) over the time period examined. And, in the slurries prepared with excess $Ca(OH)_2$ (Fig. 8e), the amount of dissolved silica at 336 h was not as great as in the saturated (Fig. 8d) and undersaturated (Fig. 8c) slurries prepared with $Ca(OH)_2$, indicating C-S-H is forming more quickly than silica is dissolving. However, if C-S-H formation is slower than silica dissolution, due to limited Ca, C-S-H formation will continue as silica dissolves and the ASR will proceed. This would be the case in the undersaturated samples (Fig. 8c) in which the amount of dissolved silica increases over the testing period, in contrast to the oversaturated case (Fig. 8e) where the amount of silica in solution decreases at later times (i.e., between 672 and 336 h). Thus, the relative amount of calcium available for reaction appears to be directly related to the amount of silica in solution.

Urhan [17,18] presents a possible explanation that C-S-H formation can block silica dissolution if C-S-H formation occurs at a faster reaction rate than silica dissolution. In the slurries with excess Ca, the dissolved Si can be consumed in C-S-H and/or alkali–silica gel formation. Also, formation of a C-S-H layer near the site of silica dissolution could slow the rate of dissolution and/or limit the amount of silica going into solution. A reaction layer, believed to be C-S-H, which formed at the surface of the silica gel, was evident in all slurries prepared with $Ca(OH)_2$. Slurries that developed a reaction layer also contained a buoyant reaction product that floated above the reaction layer, labeled as "diffuse layer (above shell)" in Fig. 9. A similar product also sometimes formed beneath the layer, above the remaining silica gel. This buoyant reaction product, evident in Fig. 9, is believed to be the alkali–silica (possibly calcium- and lithium-containing) reaction gel. At 14 days, upon visual inspection, the layer of buoyant reaction product was thicker in slurries undersaturated with respect to Ca than in slurries with excess calcium. Dent Glasser and Kataoka [19] also observed a "shell" and white precipitate when a lump of silica gel was reacted with $Ca(OH)_2$ and sodium hydroxide or potassium hydroxide. Analysis of the dissolved ion concentration inside and outside the shell over 3 days showed that the shell acted as a semipermeable membrane initially allowing more K^+ and Si species to penetrate than Ca^{2+} and OH^-. However, it was found that by the third day, the concentrations inside and outside the shell had converged [19].

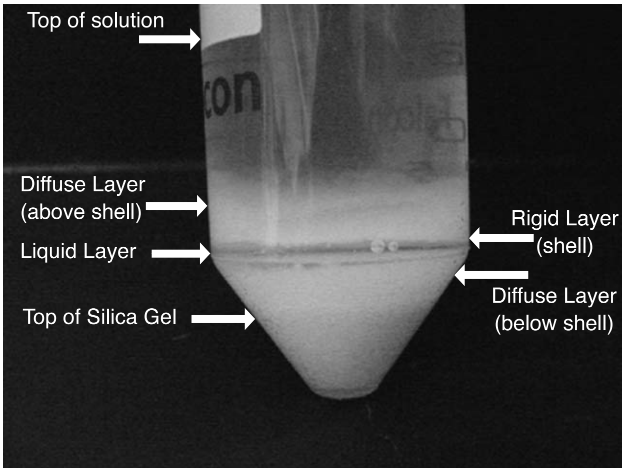

Fig. 9. Layered slurry sample containing Ca.

Here, quantitative elemental analysis of the solution layers above and below the reaction product shell was performed on some of the 0.7 M NaOH silica gel slurries prepared with 0.5 and 2 times the solubility of $Ca(OH)_2$ with and without $LiNO_3$. Fig. 10a shows that the highest concentration of dissolved silica occurred close to the reaction layer, either above or below. In agreement with Dent Glasser and Kataoka [19], in slurries prepared without lithium, the dissolved silica concentration was generally greater below the shell. This may suggest that the reaction product layer initially hindered diffusion of dissolved silica into the upper solution. However, as the concentration of $LiNO_3$ increased, the difference between dissolved silica concentration above and below the reaction layer was diminished. Dissolved sodium and lithium concentrations above and below the shell (Fig. 10b and c) are approximately equal at 6 days, which indicates that their concentrations above and below the layer have converged.

Like the samples prepared without calcium (Figs. 5–7), most slurry samples in Fig. 11a, c, d, and e also experienced an initial drop in Na in solution (7–44%) over the first 24 h, likely due to the binding of Na at the silicate surface and within reaction product. In some slurries prepared with 0.5 times the solubility of $Ca(NO_3)_2{\cdot}4H_2O$ [in excess with respect to $Ca(OH)_2$; Fig. 11b], an initial increase in dissolved Na was observed between 0 and 24 h. It is proposed that Na, initially bound within the large quantity of precipitate that formed upon addition of Ca at 0.5 times the solubility of $Ca(NO_3)_2{\cdot}4H_2O$, was released over time as precipitate dissolution occurred. Dissolved calcium being utilized in the formation of a calcium–silicate product would drive this dissolution of the $Ca(OH)_2$ initially precipitated. Dissolved Na did not show an initial increase in the slurries prepared with 0.021 times the solubility of $Ca(NO_3)_2{\cdot}4H_2O$, possibly because less precipitate formed initially upon addition of $Ca(NO_3)_2{\cdot}4H_2O$. In slurries prepared with Ca, in addition to rate-limited diffusion and alkali–lithium–silicate reaction product formation, C-S-H formation also plays a role in the change in solution phase Na. As in slurries prepared without calcium, there were no other distinct trends observed in the dissolved Na concentration.

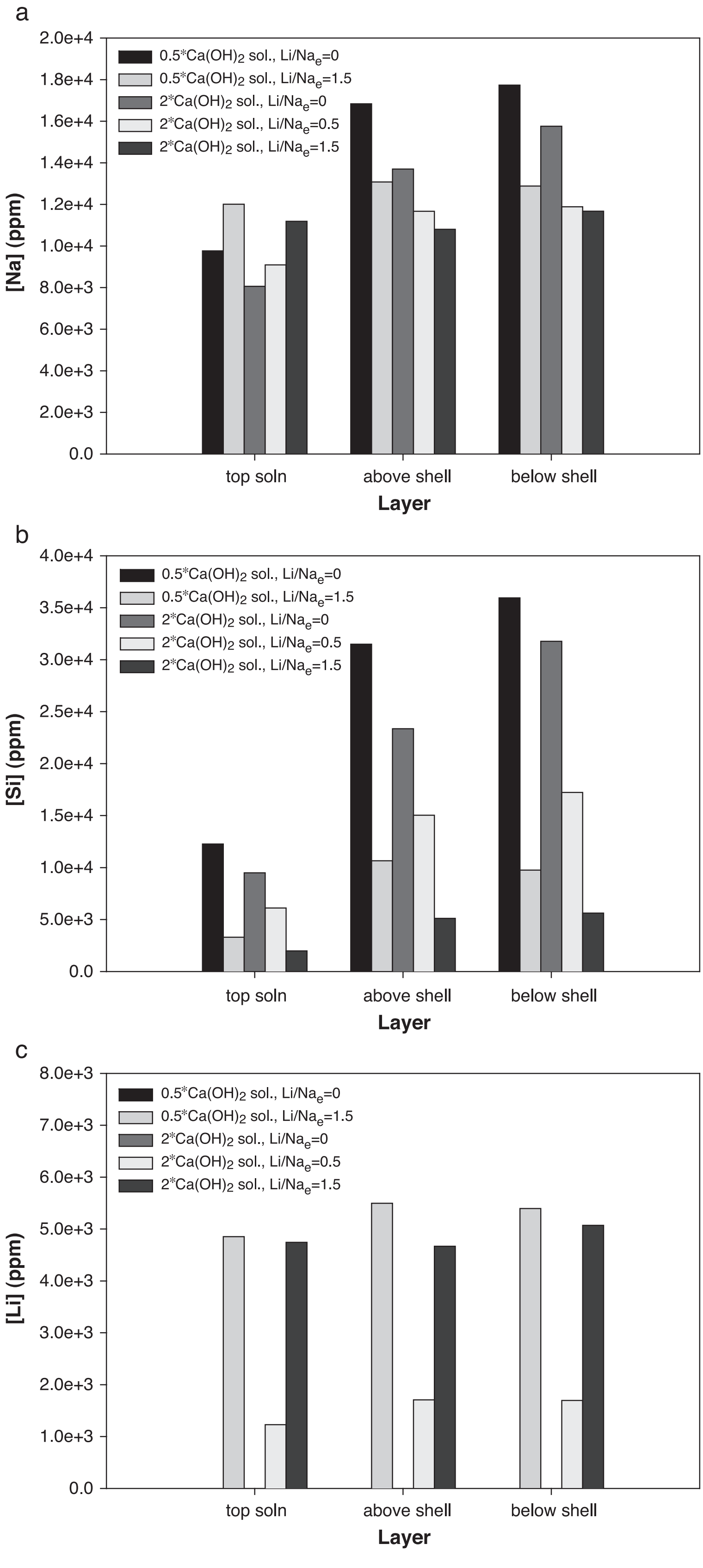

Fig. 10. Analysis of dissolved (a) Si, (b) Na, and (c) Li in slurry solutions above and below the reaction layer at 6 days.

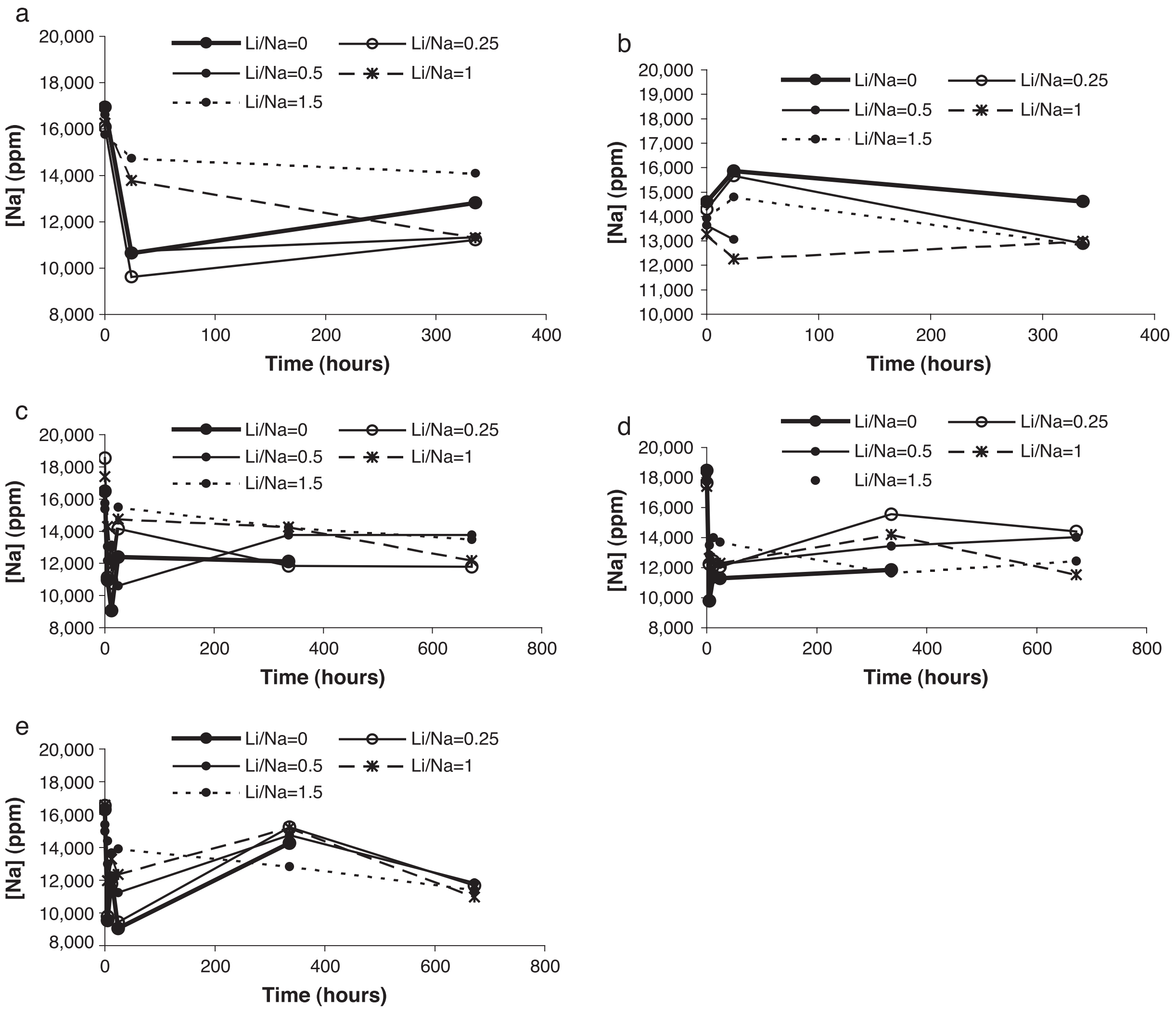

Fig. 11. Dissolved Na concentration in slurry filtrates with $LiNO_3$ and calcium (a) 0.021 times the solubility of $Ca(NO_3)_2{\cdot}4H_2O$, (b) 0.5 times the solubility of $Ca(NO_3)_2{\cdot}4H_2O$, (c) 0.5 times the solubility of $Ca(OH)_2$, (d) 1 times the solubility of $Ca(OH)_2$, and (e) 2 times the solubility of $Ca(OH)_2$.

An initial decrease (ranging from 20% to 69%) in [Li] in solution was observed over the first 24 h in most samples prepared with Ca, as shown in Fig. 12a and b.[3] The larger percent decrease in Li than Na, which was also observed in the absence of Ca, may indicate that Li is preferentially bound. Like Na concentration, slurries prepared with 0.5 times the solubility of $Ca(NO_3)_2{\cdot}4H_2O$ also showed an initial increase in Li, presumably due to the dissolution of precipitate that formed upon addition of $Ca(NO_3)_2{\cdot}4H_2O$. In the sample prepared with 2 times the solubility of $Ca(OH)_2$ (in excess), shown in Fig. 12b, the concentration of Li in solution is less than the concentration of Li in corresponding samples prepared without Ca (Fig. 7c). These data indicate that Li may be bound within the C-S-H, as was also observed by Diamond [16].

3.3. Synthesis of results

To gain a more holistic view of the research presented, mortar bar expansion and slurry solution results will be compared. Mortar bar results show that expansion was reduced with increasing Li additive concentration, for all additives tested, including LiOH. In contrast, dissolved silica concentration decreased with a corresponding increase in lithium in slurries prepared with LiCl or $LiNO_3$, but not LiOH. Therefore, it is proposed that damage during ASR may not be due to an increase in silica concentration in solution, but instead, may be due to the nature of the reaction product.

Slurries prepared with calcium showed that dissolved [Si] decreased with an increase in $LiNO_3$, as was observed in slurries prepared without Ca. However, the relative [Si] was lower in calcium-containing slurries, presumably due to C-S-H formation. These calcium-containing slurries should more closely approximate the conditions in concrete pore solution because of the presence of calcium in addition to

---

[3] In the interest of space, some graphs that show similar trends will be omitted.

alkalis. In comparing the slurry results to mortar bar results with the same lithium additive type and dosage, it appears that lower values for [Si] in solution in the slurry samples, in most cases, matched with reduced mortar bar expansion. While the mechanism by which an increase in [Li] results in a decrease in [Si] cannot be established for certain, based upon these results, it is proposed that this effect may be due to either suppression of Si dissolution or the precipitation of a nonexpansive lithium-bearing silicate product [20].

Microscopic characterization of companion samples [21,22] has given further evidence to suggest the formation of a nonexpansive product in the presence of lithium additives. Gel-like reaction products were observed in companion mortars prepared with reactive aggregate in the absence and presence of LiOH, LiCl, and $LiNO_3$. In the presence of lithium additives, dendritic reaction products were also observed at the aggregate/paste interface (Fig. 13). These dendritic products were only apparent among the gel products in those mortars containing lithium. It is proposed that the dendritic product, formed in the presence of lithium, is key to understanding the mechanisms of ASR expansion control by lithium salts. These products may themselves be nonexpansive (as proposed by Lawrence and Vivian [23]), or their formation near the reactive silicate surface may limit silica dissolution or may restrict expansion. Slurry solution layer analysis showed that a 3.5-fold decrease in dissolved silica near the silica gel surface was observed as the dosage of lithium (Li/Na_e) was increased from 0 to 1.5 (Fig. 10b). While these products have been observed, their composition, stability over time, and role in chemical transport remain unclear.

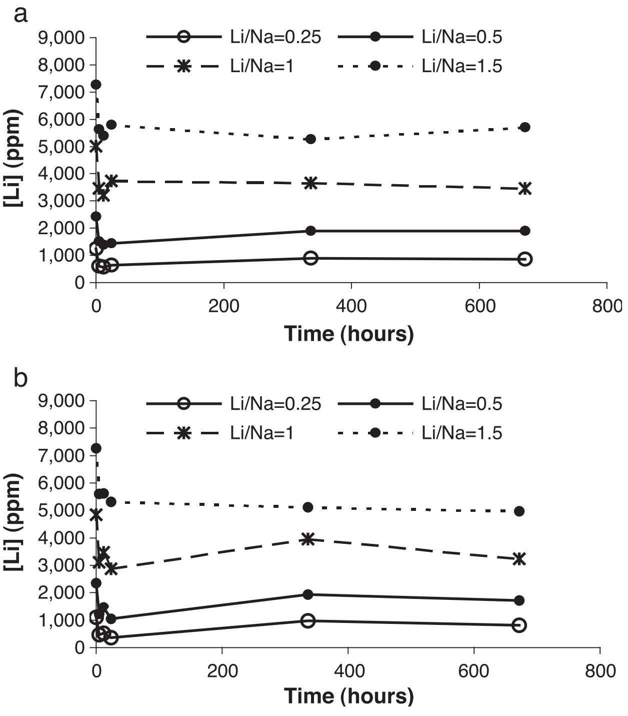

Fig. 12. Dissolved Li concentration in slurry filtrates with $LiNO_3$ and calcium (a) 0.5 times the solubility of $Ca(OH)_2$ and (b) 2 times the solubility of $Ca(OH)_2$.

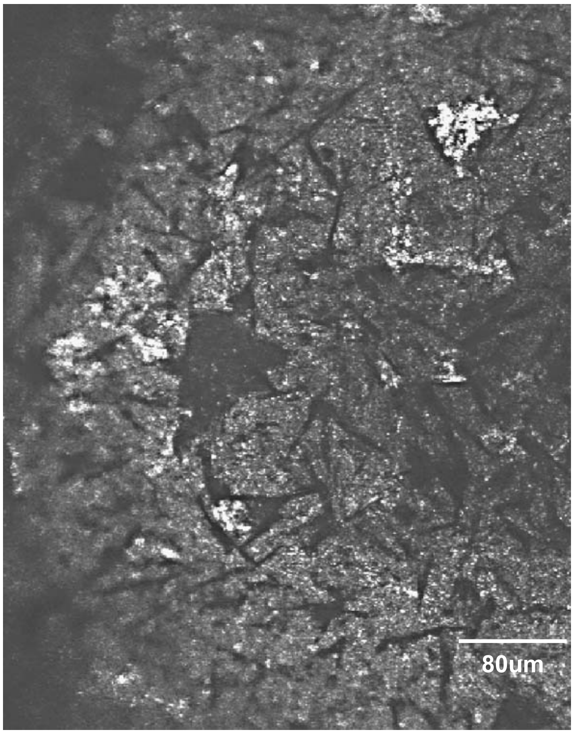

Fig. 13. Image of the paste/aggregate interface in a sample prepared with glass beads as reactive aggregate with LiOH, $[Li_2O]/[Na_2O_{eq}] = 1.5$ and stored in conditions similar to ASTM C 227. Image of the interface was made at 50 days of age by laser scanning confocal microscopy through the transparent aggregate, using a technique described in Ref. [22]. Dendritic, apparently crystalline products are visible at the interface in samples containing lithium.

4. Conclusions

The ASR and the effect of lithium additives on ASR were investigated by performing expansion testing and by quantitative elemental analysis on pessimum proportions slurries of silica gel in 0.7 M NaOH solutions containing LiOH, LiCl, or $LiNO_3$ in varying concentrations in both the absence and presence of calcium ions. To determine effective lithium additives and their doses, expansion tests were performed on mortar bars containing various quantities of LiOH, LiCl, or $LiNO_3$. Key findings were as follows:

- Expansion was reduced as the concentration of lithium additive was increased.
- The minimum threshold concentration of lithium additive varied between 0.5 and 1 molar ratio of $[Li_2O]/[Na_2O_e]$ for each additive examined, with respect to the particular reactive aggregate used in this work.
- A lithium additive upper bound may exist above which expansion no longer decreases. According to mortar bar

expansion results, this upper bound may be around a [Li]/[Na_e] dose of 1.5 for all additives tested, for the particular reactive aggregate examined here.

Slurry samples were prepared to mimic the reactions occurring in concrete undergoing ASR. Chemical analysis of these samples provided data that aided in the interpretation of physical observations made in this investigation and in previous research. The following results were observed in silica gel slurries:

- A sharp decline in dissolved Na and Li concentration was observed over the first 24 h indicating that both alkalis are bound within the reaction products.
- Li may be preferentially bound within at least one of the reaction products because the percent decrease in Li concentration was typically greater than the percent decrease in Na.
- Dissolution of silica and the behavior of Na in the slurries appeared to be rate-limited by diffusion into and out of the thick bed of silica gel and the reaction products.
- The trend of dissolved Si concentration decreasing with an increase in lithium in slurries prepared with LiCl and $LiNO_3$ could be due to lithium suppressing silica dissolution or promoting precipitation of a silica-containing reaction product.
- In contrast to slurries prepared with LiCl and $LiNO_3$, slurries prepared with LiOH showed an increase in silica dissolution with a corresponding increase in additive amount. The increase in silica dissolution with LiOH did not translate to an increase in expansion in mortar bars prepared with LiOH. Therefore, expansion due to ASR, in the presence of lithium, is most likely not largely dependent on the quantity of dissolved silica. In fact, the reduction in expansion in the presence of lithium may be due to the formation of a nonexpansive lithium–silicate complex, which is substantiated by earlier microscopy work.

Acknowledgements

Research was supported by NSF POWRE Award CMS-0074874. Any opinions, findings, and conclusions or recommendations expressed are those of the authors and do no necessarily reflect the views of the National Science Foundation.

References

[1] W.C. Hansen, Studies relating to the mechanism by which the alkali–aggregate reaction produces expansion in concrete, ACI Mater. J. 40 (1944) 213–227.

[2] D.W. Hobbs, Alkali–Silica Reaction in Concrete, Thomas Telford, London, 1988.

[3] R.G. Charlwood, Z.V. Solymar, Long-term management of AAR-affected structures: an international perspective, 2nd International Conference on Alkali–Aggregate Reaction in Hydroelectric Plants and Dams, Chattanooga, TN, 1995. p. 19.

[4] V.A. Newell, C.D. Wagner, A review of the history of alkali–aggregate reaction at three of the Tennessee Valley Authority's dams, 2nd International Conference on Alkali–Aggregate Reaction in Hydroelectric Plants and Dams, Chattanooga, TN, 1995. p. 57.

[5] C.D. Wagner, V.A. Newell, Modifications to Hiawassee Dam and planned modification to Fontana and Chickamauga Dams by the Tennessee Valley authority to manage alkali–aggregate reaction, 2nd International Conference on Alkali–Aggregate Reaction in Hydroelectric Plants and Dams, Chattanooga, TN, 1995. p. 83.

[6] W.J. McCoy, A.G. Caldwell, New approach to inhibiting alkali–aggregate expansion, ACI J. 22 (1951) 693–705.

[7] D. Stark, Lithium salt admixtures—An alternative method to prevent expansive alkali–silica reactivity, Proceedings of the 9th International Conference on Alkali–Aggregate Reaction in Concrete, London, 1992.

[8] J.S. Lumley, ASR suppression by lithium compounds, Cem. Concr. Res. 27 (1997) 235–244.

[9] V.S. Ramachandran, Alkali–aggregate expansion inhibiting admixtures, Cem. Concr. Compos. 20 (1998) 149–161.

[10] M. Prezzi, P.J.M. Monteiro, G. Sposito, The alkali–silica reaction: Part 2. The effect of chemical admixtures, ACI Mater. J. 95 (1998) 3–10.

[11] S. Ong, Study on effects of steam curing and alkali hydroxide additions on pore chemistry, microstructure, and alkali silica reactions, PhD thesis, School of Civil Engineering, Purdue University, 1993.

[12] Y. Sakaguchi, M. Takamura, A. Kitagawa, T. Hori, F. Tomosawa, M. Abe, The inhibiting effect of lithium compounds on alkali–silica reaction, Proceedings of the 8th International Conference on Alkali–Aggregate Reaction, Kyoto, Japan, 1989. pp. 229–234.

[13] M. Thomas, R. Hooper, D. Stokes, Use of lithium-containing compounds to control expansion in concrete due to alkali–silica reaction, Proceedings of the 11th International Conference on Alkali–Aggregate Reaction in Concrete, Centre de Recherche Interuniversitaire sur le Beton (CRIB), Canada, 2000.

[14] L.S. Dent Glasser, N. Kataoka, The chemistry of alkali–aggregate reaction, Cem. Concr. Res. 11 (1981) 1–9.

[15] A. Seidell, Solubilities of Inorganic and Organic Compounds, Van Nostrand-Reinhold, New York, 1928.

[16] S. Diamond, Unique response of $LiNO_3$ as an alkali silica reaction-preventive admixture, Cem. Concr. Res. 29 (1999) 1271–1275.

[17] S. Urhan, Alkali silica and pozzolanic reactions in concrete: Part 1. Interpretation of published results and a hypothesis concerning the mechanism, Cem. Concr. Res. 17 (1987) 141–152.

[18] S. Urhan, Alkali silica and pozzolanic reactions in concrete: Part 2. Observations on expanded perlite aggregate concretes, Cem. Concr. Res. 17 (1987) 141–152.

[19] L.S. Dent Glasser, N. Kataoka, On the role of calcium in the alkali–aggregate reaction, Cem. Concr. Res. 12 (1982) 321–331.

[20] X. Mo, C. Yu, Z. Xu, Long-term effectiveness and mechanism of LiOH in inhibiting alkali–silica reaction, Cem. Concr. Res. 33 (2003) 115–119.

[21] C.L. Collins, Examination if the mechanism by which lithium additives inhibit alkali–silica reaction gel expansion, MS EnvE thesis, School of Civil and Environmental Engineering, Georgia Institute of Technology, 2002.

[22] C.L. Collins, J.H. Ideker, K.E. Kurtis, Laser scanning confocal microscopy for in situ monitoring of alkali–silica reaction, J. Microsc. 213 (2) (2004) 149–157.

[23] M. Lawrence, H.E. Vivian, The reactions of various alkalis with silica, Aust. J. Appl. Sci. 12 (1961) 96–103.