Chemical additives to control expansion of alkali-silica reaction gel: proposed mechanisms of control

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Calcium chloride, lithium chloride, and acetone have previously been shown to affect expansion caused by alkali-silica reaction (ASR), a deleterious reaction occurring between reactive siliceous minerals present in some aggregate and the strongly alkaline pore solution in concrete. Here, the effect of these chemical additives was examined by transmission soft X-ray microscopy and a quantitative elemental analysis, using ICP-OES. In examining the effect of calcium chloride on ASR gels, the formation of a calcium silicate product, believed to be non-expansive, was identified by X-ray microscopy. Additionally, the elemental analysis results suggest that the concentration of calcium ions in the pore solution, which is dependent upon the solubility of the chemical additive and the percent addition, relative to the concentration of silica species in solution is an important parameter for effective control of expansion associated with ASR. In examining the effect of lithium chloride, quantitative elemental analysis showed silica dissolution in solutions of 0.7 M NaOH + 0.1 M LiCl, but with silicon present in slightly lower concentrations than in 0.7 M NaOH solutions alone. However, X-ray microscopy showed less evidence of repolymerization of the dissolved silica into an expansive gel in the presence of lithium chloride as compared to the reaction of the ASR gel in alkaline (0.7 M NaOH) solutions without lithium. With acetone, the results, including X-ray images showing the formation of repolymerized gel in 0.7 M NaOH solution containing 10% v/v acetone, indicate that the use of acetone as a chemical additive may not be as effective as once believed in preventing expansion caused by ASR. It is proposed that any reduction in expansion by use of acetone is temporary and diminishes over time. © *2003 Kluwer Academic Publishers*

1. Introduction

Infrastructure damage resulting from the alkali-silica reaction (ASR) has been reported in nearly every country in the world and in many types of concrete structures, including dams, spillways, bridges, rigid pavements, buildings, and railroad sleepers [1–3]. ASR is a deleterious reaction that occurs between reactive silica or silicates present in some aggregate and alkalis (K_2O and Na_2O) present in the pore solution. The alkalis are contributed by the cement during hydration or may permeate the concrete from the surrounding environment (e.g., seawater, de-icing agents). The product of the reaction is an alkali-silica gel that is believed to expand by osmotic swelling in the presence of water. Because of the low tensile capacity of concrete, tensile strains of 0.04–0.05% or more are significant enough to crack the concrete [4]. Thus, material properties that are essential for satisfactory performance of the structure in service, including impermeability, strength, and stiffness, are compromised when expansion of ASR gel occurs in concrete.

Three components are required for damage to result from the alkali-silica reaction: the presence of a sufficient amount of alkalis, reactive silica, and water. In the construction of new structures, a holistic approach, may be adopted by specifying low-alkali cement (proportioned to produce a low-alkali concrete), non-reactive aggregate, and by reducing the permeability of the concrete through proper mixture proportioning (including the use of pozzolanic materials) and good construction

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practices [5–7]. While these traditional methods for preventing damage caused by ASR are well recognized, implementation may not always be possible. For example, low alkali cement and non-reactive aggregate may not be locally available at reasonable cost. In addition, this holistic approach can only be applied in new construction. In the absence of a practical means to arrest the reaction and halt damage in existing structures experiencing ASR, costly repair and rehabilitation strategies, sometimes employing extreme measures (e.g., slot cutting), may be required to 'control' damage caused by expansion.

The need for alternative means to avoid damage by ASR has driven research toward the use of chemical additives. McCoy and Caldwell [8] first investigated the use of a range of chemical salts and organic compounds to inhibit expansion in mortar bars. This initial research and subsequent studies have shown that certain chemicals, including lithium salts, calcium salts, and acetone, may reduce expansion caused by ASR. Lack of understanding of the mechanism or mechanisms by which these chemicals reduce expansion is perhaps the most fundamental impedance to the practical use of such chemical additives. Without knowing the mechanism of control, it is difficult to predict the effectiveness of a chemical additive, to foresee the duration of its control, to recommend a dosage, or to devise a practical delivery system.

The goal of this research, then, is to understand how the use of each of three chemical additives—LiCl, $CaCl_2$, and acetone—affects the alkali silica reaction gel expansion. There are several possible mechanisms, which may or may not be valid or may act in combination (see Section 2.0 for a review of the fundamental ASR chemistry). These potential mechanisms include: (1) the additive promotes silica dissolution, but inhibits repolymerization, (2) the additive suppresses silica dissolution, thereby lessening the amount of product formed, (3) the additive interacts with the dissolving silica to form non-expansive or less-expansive products, (4) the additive interacts with a potentially expansive product, rendering it less expansive, and (5) the additive interacts with the dissolving silica to form products which slow the progress of the reaction (i.e., armoring precipitates or semi-permeable membranes).

To gain insight into the mechanisms of control of ASR-induced expansion through the use of LiCl, $CaCl_2$, and acetone, a two-pronged investigation was undertaken. The effects of these three chemical additives on the alkali-silica reaction were studied using transmission soft X-ray microscopy and quantitative elemental analysis. X-ray microscopy was used to examine *in situ* the morphology of any reaction products formed during the reaction of an alkali-silicate gel in sodium hydroxide solution (an idealized pore solution) in the presence of each of three additives. These X-ray images can be compared to images of the alkali-silica gel in sodium hydroxide solution, without the additives, to qualitatively assess the effects of calcium chloride, lithium chloride, and acetone. To aid in the interpretation of the X-ray images, filtrates from companion slurry samples were examined by inductively

coupled plasma optical emission spectroscopy (ICP-OES) to measure the concentration of silicon, calcium, lithium, and sodium ions in solution. Results of the quantitative elemental analysis can be used to assess the effect of these chemical additives on silica dissolution and the incorporation of those elements into the reaction product.

2. Review of ASR chemistry

Potassium (K) and sodium (Na) are the only elements of the alkali metals that are found in concrete pore solution in appreciable concentrations [9]. Together, the oxides of these metals, Na_2O and K_2O, are referred to generically as 'the alkalis' within the concrete industry. Alkalis can be introduced to the concrete by the cement and, in some cases, by the aggregate. In addition, during service, alkalis present in the environment, such as in seawater or deicing salts, may ingress into the concrete. In the concrete pore solution, dissociation occurs, i.e.,

$$K_2O + H_2O \rightarrow 2K^+ + 2OH^-$$

$$Na_2O + H_2O \rightarrow 2Na^+ + 2OH^-$$
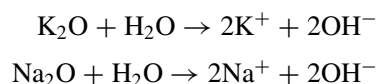
giving a hydroxyl ion (OH^-) concentration sufficient to produce a pH typically in the range 12.5 to 13.5, but reaching as high as 13.9 [10].

The alkali-silica attack in concrete is initiated by the dissolution of silicates present in the aggregate. Those particularly susceptible to attack are rocks containing disordered, amorphous, or strained silicate minerals, including opal, obsidian, cristobalite, tridymite, chalcedony, cherts, cryptocrystalline volcanic rocks (andesites and rhyolites), and strained or metamorphic quartz [11]. Dent Glasser and Kataoka [12, 13] identified two mechanisms that constitute the dissolution silica in the concrete environment: hydroxyl ion attack and reaction of hydroxide ions with silanol groups. Hydroxyl ion attack, alternatively termed hydrolization by some authors [14], occurs by:

$$Si—O—Si + H_2O \rightarrow Si—OH \cdots OH—Si$$
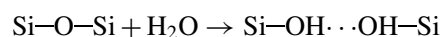
results in the formation of silanol bonds. The reaction of existing silanol groups or silanol groups produced by hydroxyl attack is the second dissolution mechanism and occurs by reaction with hydroxyl ions abundant in cement pore solution:

$$\equiv Si—OH + OH^- \rightarrow \equiv Si—O^- + H_2O$$
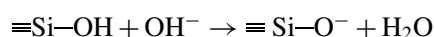
The hydroxyl ions rupture Si—O—Si bonds, loosening the network and producing Si—O$^-$ species. Cations abundant in the pore fluid are attracted to these sites of negative charge and become incorporated into the alkali-silica reaction gel.

While silica solubility is increased in strongly alkaline environments [15] including concrete pore solution, a saturation point will be reached, particularly because diffusion in concrete is limited. Once this point has been reached in a local environment, the dissolved silica repolymerizes into a gel product containing silica,

water, alkalis, and other ions in varying concentrations. This gel product, then, is believed to expand by taking in water, generating an osmotic pressure on the surrounding cement paste and aggregate. While the mechanism for ASR gel expansion is incompletely understood, the pressure generated can be great enough to lead cracking in the paste and aggregate and to expansion of the structure.

A more detailed review of the chemistry of the alkali-silica reaction can be found in [16].

3. Experiment
3.1. Materials
X-ray images were made using finely ground (∼300 sieve) ASR gel obtained from FURNAS Dam, a hydroelectric facility located in Minas Gerais, Brazil. Chemical oxide analysis (Table I) shows that the ASR gel is composed primarily of SiO_2 with K_2O and CaO present in smaller amounts. X-ray diffraction under Cu K_α radiation shows the gel to be largely amorphous, with three very diffuse peaks centered around 4°, 10°, and 27° on the 2θ scale. The XRD pattern for the Brazilian gel can be found in [17]. Because of the large quantity of silica required, samples examined by quantitative elemental analysis were prepared from chemical grade silica gel (60–200 mesh), not ASR gel.

3.2. Transmission soft X-ray microscopy and quantitative elemental analysis
For the samples to be examined by X-ray microscopy, ASR gel was exposed for 7 days to four solutions: (a) 0.7 M NaOH (control/background; pH = 12.6), (b) 0.7 M NaOH + 0.1 M $CaCl_2$ (filtered to 0.45 μm to remove insoluble $CaCO_3$; pH = 12.6), (c) 0.7 M NaOH + 0.1 M LiCl (pH = 12.4) and (d) 0.7 M NaOH + 10% (v/v) acetone (pH = 12.6). The relative proportion of ASR gel added to the solutions was selected to maximize expansivity, as described by Dent Glasser and Kataoka [12, 13] when $SiO_2/Na_2O = 3$. All solutions were made from deionized, low resistivity (17.8 M$\Omega \cdot$cm) water, and all reagents were A.C.S certified and were obtained from Fisher Scientific. Solutions were prepared using Nalgene volumetric flasks (Class B) instead of glassware to avoid the introduction of silicon to the solutions.

The slurries were examined using the XM-1 microscope. XM-1 is operated by the Center for X-ray Optics

T A B L E I Composition by mass of ASR gel from Minas Gerais Dam

Compound	wt%
Loss on Ignition	18.22
SO_3	0.15
MgO	0.96
SiO_2	62.1
Fe_2O_3	0.31
Al_2O_3	2.85
CaO	1.27
MnO	0.013
Na_2O	1.08
K_2O	15.73

on beamline 6.1.2 of the Advanced Light Source, a third generation synchrotron radiation facility operated by the Ernest O. Lawrence Berkeley National Laboratory. The instrument is unique as samples can be observed wet, with high resolution (43 nm), over time, as chemical reactions proceed. Further information about the microscope can be found in [18, 19].

3.3. Quantitative elemental analysis
In the quantitative elemental analysis by ICP-OES (Thermo Jarrell Ash Iris Model), chemical grade silica gel was exposed for 7 days to the same four solutions: 0.7 M NaOH, 0.7 M NaOH + 0. 1 M $CaCl_2$, 0.7 M NaOH + 0.1 M LiCl, and 0.7 M NaOH + 10% acetone. After this exposure period, the samples were filtered and concentrations of Ca, Li, Na, and Si in the filtrate were measured by ICP-OES. This instrument can measure ultratrace, trace, minor, and major concentrations of elements in solution under one set of experimental parameters [20]. Detection limits for the instrument are in the parts per billion range for most elements, including calcium, lithium, sodium, and silicon [21]. In addition, X-ray diffraction (XRD) was performed on the reaction products filtered from the slurries and on the unreacted chemical grade silica gel.

4. Results
Results from the ICP-OES work, and XRD are presented here. The X-ray images will be presented in the "Discussion" section and discussed in context with the results presented below.

4.1. Quantitative elemental analysis
Results from the quantitative elemental analysis are shown in Table II. The results presented are averages calculated from the concentrations measured in duplicate at two (Li, Si) or three (Na, Ca) wavelengths for each sample. Standard deviations have also been calculated and are presented in parenthesis in units of ppm. All solutions and filtrates have been diluted 100×. The results of this analysis indicate the amount of Si in solution and the amount of Ca, Li, and Na incorporated into the reaction product.

Samples diluted from 0.7 M NaOH solution and the filtrate of the 0.7 M NaOH + silica gel slurry serve as the controls in this experiment. For the 0.7 M NaOH sample, the sodium concentration measures 150 ppm, which is somewhat less than the 160.9 ppm expected. In addition, trace amounts of silicon are measured. Because this sample contains no silica gel, the trace amount may have been dissolved in the water used to make the solutions or may simply reflect the error tolerances of the instrument. Silicon concentrations are much higher in the filtrate of the 0.7 M NaOH + silica gel slurry and measure nearly 400 ppm. The sodium concentration is approximately equal to the concentration in the 0.7 M NaOH solution (now diluted 100×). These results indicate that dissolution of the silica gel has occurred in the 0.7 M NaOH solution, but that little

TABLE II Results from quantitative elemental analysis

	Average concentration (ppm) (with standard deviation in ppm)							
	0.7 M NaOH	0.7 M NaOH & silica gel	0.7 M NaOH + 0.1 M CaCl$_2$	0.7 M NaOH + 0.1 M CaCl$_2$ & silica gel	0.7 M NaOH + 0.1 M LiCl	0.7 M NaOH + 0.1 M LiCl & silica gel	0.7 M NaOH + 10% (v/v) acetone	0.7 M NaOH + 10% (v/v) acetone & silica gel
Element								
Ca	0	0.48 (0.061)	0.28 (0.086)	0.20 (0.023)	0	0.39 (0.054)	0	0.0038 (0.010)
Li	0	0	0	0	7.46 (2.28)	6.48 (1.44)	0	0
Na	150.13 (6.67)	147.61 (10.12)	157.78 (3.78)	126.15 (7.76)	152.30 (9.94)	137.98 (5.66)	140.65 (23.43)	104.03 (6.02)
Si	0.17 (0.084)	397.00 (31.33)	0.22 (0.15)	215.42 (10.74)	0.047 (0.010)	339.48 (19.58)	0.048 (0.010)	207.06 (21.85)

sodium, if any (depending on instrument error), from the solution has been adsorbed onto the silica gel or incorporated into an alkali-silica gel.

In the diluted 0.7 M NaOH + 0.1 M CaCl$_2$ and 0.7 M NaOH + 0.1 M LiCl solutions, the sodium concentration measures 158 ppm and 152 ppm, respectively. These concentrations are approximately the same as in the 0.7 M NaOH solution and are close to the expected sodium concentration (i.e., 160.9 ppm), demonstrating the accuracy of the experiment methodology. The sodium concentration of the 0.7 M NaOH + 10% (v/v) acetone solution measures 141 ppm and reflects the inclusion of 10% acetone by volume in the 0.7 M NaOH. In all of these solutions, only trace amounts of silicon are measured.
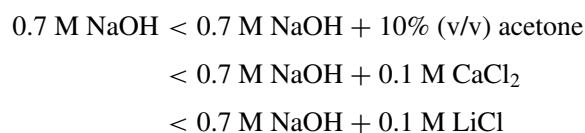
In the diluted 0.7 M NaOH + 0.1 M CaCl$_2$ solution, the calcium concentration measured (0.28 ppm) is significantly lower than expected. Calcium may have been removed as CaCO$_3$ during filtration of the solution. As compared to the 0.7 M NaOH + 0.1 M CaCl$_2$ solution, sodium and calcium concentrations are decreased in the filtrate from the 0.7 M NaOH + 0.1 M CaCl$_2$ + silica gel slurry. Silicon concentration measured approximately 215 ppm, which is 46% less than in the 0.7 M NaOH + silica gel control. These results indicate that less silica is present in solution in the presence of calcium chloride, and that the product of the reaction of silica gel in the 0.7 M NaOH + 0.1 M CaCl$_2$ solution contains some sodium and calcium or that sodium and calcium have been adsorbed to the silica gel surface.

In the diluted 0.7 M NaOH + 0.1 M LiCl solution, lithium concentration measures 7.5 ppm; for this dilution the expected nominal lithium concentration is 6.9 ppm. In the dilution from the slurry of 0.7 M NaOH + 0.1 M LiCl + silica gel, lithium concentration measures 6.5 ppm. Measurements of lithium by ICP-OES are known to drift, as is evidenced by the relatively high standard deviations for these measurements. As a result, no conclusions can be drawn from these measurements. However, silicon and sodium concentration in the diluted filtrate are 15% and 6.8% less than in the 0.7 M NaOH + silica gel control sample. These results indicate that less silica is present in solution in the presence of lithium chloride, and that the product of the reaction of silica gel in the 0.7 M NaOH + 0.1 M LiCl
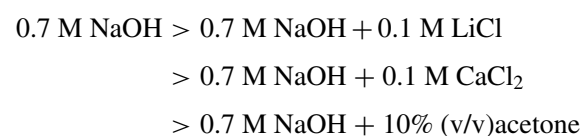
solution contains some sodium or that sodium has been adsorbed at the silica gel surface. However, the amount of sodium in the product or adsorbed is less than was measured in the 0.7 M NaOH + 0.1 M CaCl$_2$ solution.

In the diluted 0.7 M NaOH + acetone solution, silicon and sodium concentration in the diluted filtrate are 48% and 30% less than in the 0.7 M + silica gel control sample. These results indicate that less silica is present in solution in the presence of acetone, and that the product of the reaction of silica gel in the 0.7 M NaOH + acetone solution contains some sodium or that sodium has been adsorbed to the silica gel surface. However, the amount of sodium in the product or adsorbed is greater than in the 0.7 M NaOH + 0.1 M CaCl$_2$ solution and the 0.7 M NaOH + 0.1 M LiCl solution.

Overall, for the filtrates of the samples *containing silica gel*, silicon concentration in solution increases in the order:

$$0.7 \text{ M NaOH} < 0.7 \text{ M NaOH} + 10\% \text{ (v/v) acetone}$$
$$< 0.7 \text{ M NaOH} + 0.1 \text{ M CaCl}_2$$
$$< 0.7 \text{ M NaOH} + 0.1 \text{ M LiCl}$$

In these same filtrates, sodium concentration in solution decreases in the order:

$$0.7 \text{ M NaOH} > 0.7 \text{ M NaOH} + 0.1 \text{ M LiCl}$$
$$> 0.7 \text{ M NaOH} + 0.1 \text{ M CaCl}_2$$
$$> 0.7 \text{ M NaOH} + 10\% \text{ (v/v) acetone}$$

Measurements of silicon concentration in solution may be interpreted simply as indicators of dissolution. However, when accompanied by a significant decrease in alkali concentration, repolymerization of an alkali-silicate gel product may be indicated.

4.2. XRD

X-ray diffraction under Cu K$_\alpha$ radiation shows that the silica gel itself and the products are amorphous with a diffuse peak present at approximately 20–25 degrees on the 2θ scale (Fig. 1). The peak is slightly broader for
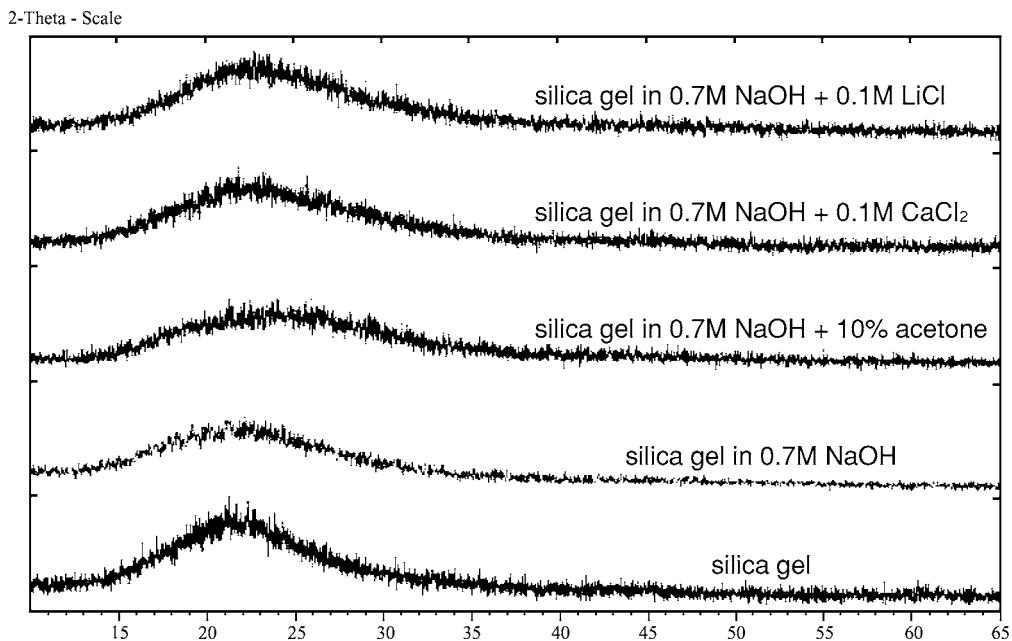
Figure 1 X-ray diffraction patterns for the reaction products filtered from the slurries of chemical grade silica gel in 0.7 M NaOH, 0.7 M NaOH + 10% acetone, 0.7 M NaOH + 0.1 M LiCl, and 0.7 M NaOH + 0.1 M CaCl₂ as compared to the pattern for the unreacted silica gel, bottom.

the products of the reactions, particularly for the silica gel in 0.7 M NaOH + 10% (v/v) acetone solution, as compared to the unreacted silica gel. Also, the peaks for the product of reactions where LiCl and CaCl$_2$ were present are shifted slightly as compared to the product of the reaction of silica gel in 0.7 M NaOH. However, the effects are slight and are difficult to interpret from the XRD patterns.

5. Discussion

In the presence of 0.7 M NaOH, Kurtis *et al.* [17, 22] found that ASR gel partially dissolves and repolymerizes as a potentially expansive gel. Morphological comparison between Fig. 2 of dry (or unreacted) ASR gel and Fig. 3 of ASR gel in 0.7 M NaOH solution shows repolymerization of the ASR gel occurs in the alkaline solution. These images can be compared to images of the alkali-silicate gel in sodium hydroxide solution in the
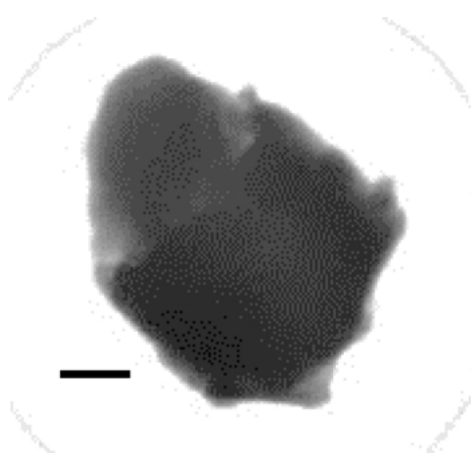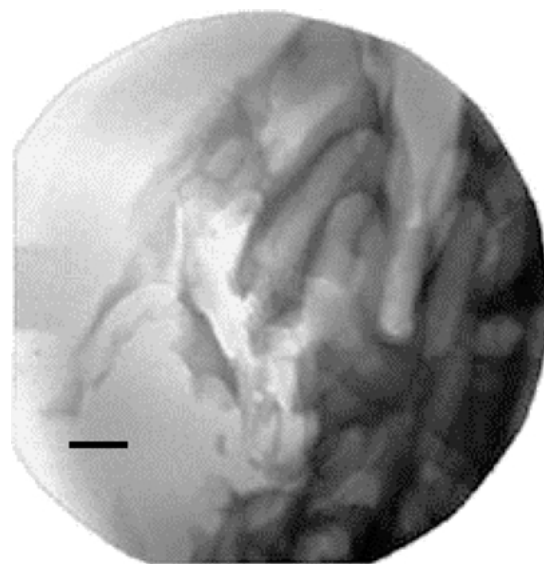

Figure 3 X-ray image of the pessimum proportion of alkali-silicate gel in 0.7 M NaOH after 1 week. The image was taken with a 7.099 s exposure time and a beam current of 210.8 mA at an original magnification of 2400×. Scalebar = 1 μm · 71015031.

presence of each of the additives to qualitatively assess the effects of calcium chloride, lithium chloride, and acetone. In addition, these images will be considered in light of the more quantitative data from ICP-OES and XRD to give a broader impression about the mechanisms underlying the changes induced in the ASR gel as a result of the chemical additive's presence.

5.1. Effect of calcium chloride

X-ray images show that the reaction of the alkali-silicate gel in 0.7 M NaOH + 0.1 M CaCl$_2$ solution results in the formation of spherulitic product composed of lath-like structures (Fig. 4). The morphology is very similar to the 'sheaf-of-wheat' structures produced by
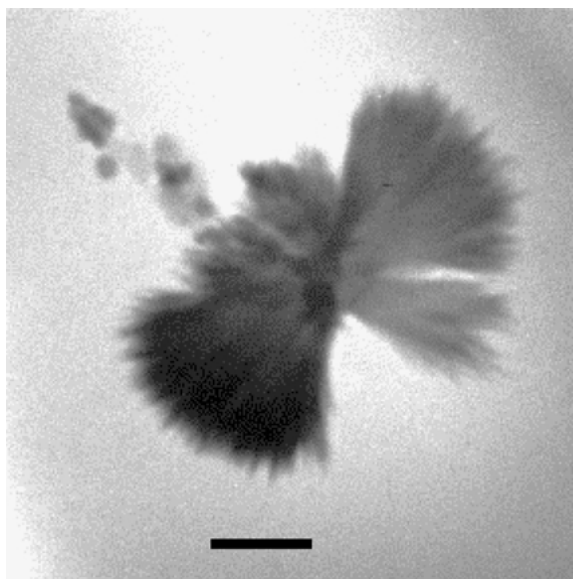

Figure 2 X-ray image of dry alkali-silicate gel. The image was taken with a 20.000 s exposure time and a beam current of 376.0 mA at an original magnification of 2400×. Scalebar = 1 μm · 70213008.

Figure 4 X-ray image of alkali-silicate gel in 0.7 M NaOH + 0.1 M CaCl$_2$. The image was taken with a 14.858 s exposure time with a beam current of 201.3 mA at an original magnification of 2400×. Scalebar = 1 μm · 71121019.

the reaction of the ASR gel in saturated Ca(OH)$_2$ solution [17, 22] which have been described in the literature as calcium silicate hydrates or precursors [23].

The identification of such products during alkali-silica reactions in the presence of calcium is important in understanding the role of calcium in the reaction. Principles from electrical double layer theory have been proposed to explain the expansion of the ASR gel product and the mechanism by which chemical salts reduce expansion [24, 25]. When applying these principles, the ASR gel is assumed to act as a colloid composed of negatively charged particles, and swelling of the gel is attributed to double-layer repulsion effects. The presence of trivalent or bivalent cations (like Ca^{++}) provided by chemical salts has been theorized to lower surface charge density of the ASR gel as compared to systems where more monovalent cations are present, and Prezzi *et al.* [25] provided experimental data in agreement with this predicted behavior. However, since the Gouy-Chapman double layer theory does not take chemical interactions into account, and because the X-ray images clearly show that chemical interactions (i.e., those which result in the formation of calcium silicate hydrates) do appear to be significant in this system, other mechanisms which may affect the expansion of the ASR gel occur must simultaneously in this system where calcium ions are present.

It is also interesting that in this investigation no repolymerized gel was evident as a reaction product in the in 0.7 M NaOH + 0.1 M CaCl$_2$ solution. Previously [17], the reaction of the ASR gel in a solution of saturated Ca(OH)$_2$ containing 0.01 M NaOH was examined, and the product of that reaction contained both lath-like structures and repolymerized alkali-silicate gel. The repolymerized gel is apparently of decreased density, as compared to the original particles of ASR gel, and is believed to be the source of expansion. The quantitative elemental analysis, Table I, shows that silica dissolution occurs when the pessimum proportion

of silica is present in 0.7 M + 0.1 M CaCl$_2$ solution. Thus, in a system composed of silica and alkalis in pessimum amounts with calcium ions, the reaction to form calcium silicate hydrate or a C–S–H precursor may be limited by the amount of calcium ions available for a through solution reaction.

Therefore, it is proposed that both the solubility of the calcium-containing chemical additive and the percent addition are critical parameters for control of expansion by ASR gel with calcium salts. For instance, calcium hydroxide is only slightly soluble in water ($K_{sp} = 8 \times 10^{-6}$ at 22°C). When comparing equal volumes of saturated (0.0126 M) Ca(OH)$_2$ solution and 0.1 M CaCl$_2$ solution, the concentration of calcium ions is an order of magnitude less in Ca(OH)$_2$ solution. Indeed, McCoy and Caldwell [8] found that 10% by weight of cement addition of CaCO$_3$, which is nearly insoluble ($K_{sp} = 2.8 \times 10^{-9}$ at 25°C), did not reduce expansion in mortar bars after 8 weeks. McCoy and Caldwell [8] also reported that 1% by weight of cement addition of CaCl$_2$ was not effective. In contrast, Prezzi *et al.* [25] found expansion due to ASR in mortar bars was decreased when the mix water contained 1 M and 2 M concentrations of CaCl$_2$. Reaction between calcium ions and carbon dioxide, in the air or dissolved in the mix water, to produce poorly soluble calcium carbonate should also be considered when selecting calcium-containing additives and dosages.

5.2. Effect of lithium chloride

X-ray images of alkali-silicate gel in 0.7 M NaOH + 0.1 M LiCl solution are shown in Figs 5 and 6. The images show products of varying morphology. In Fig. 6, a relatively large particle, for this sample, is shown. It appears that some repolymerization has occurred near the perimeter of the particle, but the volume of gel appears to be less than in the 0.7 M NaOH solution alone
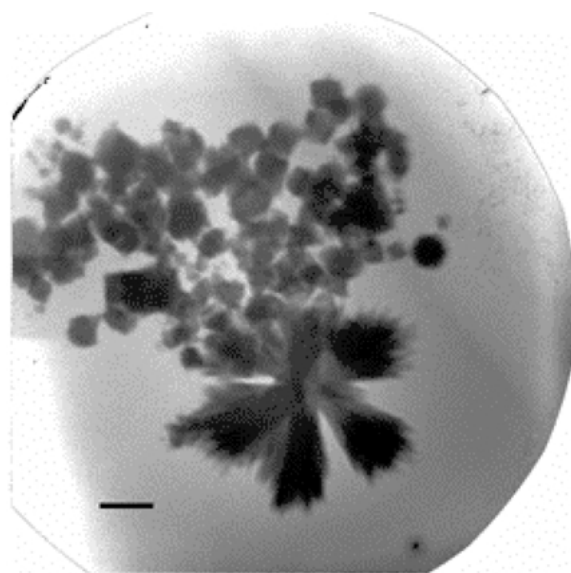

Figure 5 X-ray image of alkali-silicate gel in 0.7 M NaOH + 0.1 M LiCl. The image was taken with a 8.237 s exposure time with a beam current of 361.5 mA at an original magnification of 2400×. Scalebar = 1 μm · 71121034.
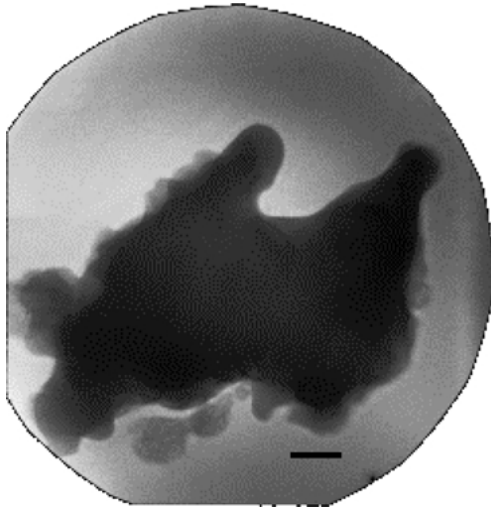
Figure 6 X-Ray image of alkali-silicate gel after 1 week in 0.7 M NaOH + 0.1 M LiCl. The image was taken with a 8.460 s exposure time with a beam current of 235.1 mA at an original magnification of 2400×. Scalebar = 1 μM · 71015028.

(Fig. 3). The small particles, seen in Fig. 5, are more typical of this sample, and these range from approximately 0.25 μm to 3 μm in size, which is smaller than the original particle size. The particle edges are well-defined and little, if any, repolymerized gel is evident. It appears in this image, as in others, that the smaller particles have a tendency to aggregate. In addition, structures similar to the spherulitic structures produced by the reaction of the ASR gel with calcium are apparent in Fig. 5. The presence of the lath-like spherulites implies that the ASR gel has dissolved in the 0.7 M NaOH + 0.1 M LiCl solution, and that calcium present in the alkali-silicate gel (Table I) has reacted with the dissolved silicate species to form the sheaf-of-wheat structures. The presence of repolymerized gel and the general smaller size of the gel particles as compared to dry gel particles indicate that dissolution of the ASR gel has occurred. Results from quantitative elemental analysis, Table II, confirm that silica dissolution occurs in the 0.7 M NaOH + 0.1 M LiCl solution.

With the evidence of dissolution, the formation of a relatively small amount of repolymerized gel is remarkable. Of the alkali metal cations, lithium is unique because it stabilizes colloids and prevents gelling [26]. In a system containing both Na$^+$ and Li$^+$, such as the one under investigation, the alkalis compete for adsorption at negatively charged sites on the silicate surface. Since adsorption affinity increases with cation radius, it is expected that sodium adsorption with be preferential to lithium adsorption. However, measurements of the concentration of alkali ions in expressed pore solution show that over time the Li$^+$ concentration decreased while the Na$^+$ and K$^+$ concentration remained constant [27]. The Eisenman model of cation exchange includes a limiting case, the *strong field* case, where cations are in direct contact with the surface [28]. Because of strong field exchange behavior, the negatively charged surface of iron oxide, for example, exhibits a preference for smaller cations, with a stronger attraction for Li$^+$ as compared to K$^+$. Thus, the apparent preference of the alkali silica reaction gel for Li$^+$ as compared

to Na$^+$ and K$^+$, as described by [27] may be the result of strong field exchange behavior. If lithium adsorption is more favorable than Na$^+$ and K$^+$ adsorption, a physical mechanism for prevention of gel repolymerization may exist. Iler [26] postulates that the highly hydrated lithium ions (hydrated ion radius = 0.36 nm) are not adsorbed as near to the silicate surface as a cation with smaller hydrated radius, such as sodium or potassium (with radii of 0.24 and 0.133 nm, respectively). Thus, the net repulsion between the silicate particles remains high and repolymerization does not occur. The effect of the lithium would be dependent upon its relative concentration in the solution. In this system, the concentration of Na$^+$ is five times greater than the concentration of Li$^+$, indicating that some repolymerization will occur, but the amount of gel repolymerization may be decreased by the presence of the lithium-containing additive.

While the formation of the expansive gel by repolymerization may be limited by the presence of lithium, aggregation of 0.25–1 μm particles occurs. In a system with both sodium and lithium ions present, lithium may reduce the surface charge density of alkali-silicate gel. If this occurs, the repulsion forces between colloids gel particles will be reduced. In accordance with double layer theory, the decrease in surface charge density will result in a reduction expansive pressure generated by swelling of the gel.

Thus, interpretations of the X-ray images in consideration of surface chemistry principles suggests two mechanisms by which lithium may act to reduce expansion of alkali-silicate gel. First, lithium may limit repolymerization, effectively reducing the potential for expansion. Second, lithium seems to promote the aggregation of relatively larger particles, but the potential expansion may be decreased because of a reduction in surface charge density of the alkali-silicate gel which occurs in the presence of lithium.

5.3. Effect of acetone

X-ray images of the alkali-silicate gel in 0.7 M NaOH + 10% (v/v) acetone are shown in Figs 7 and 8. The images show regions of varying density, similar to the repolymerized alkali-silicate product resulting from the reaction of the ASR gel in 0.7 M NaOH solution (Fig. 3). Quantitative elemental analysis shows a 26% decrease in alkali concentration in the filtrate from the 0.7 M NaOH + 10% (v/v) acetone solution containing silica gel, as compared to the 0.7 M NaOH + 10% (v/v) acetone solution (Table II). The decrease in alkali concentration coupled with the evidence of silica dissolution and the presence of the repolymerized gel in the X-ray images suggests that acetone may not be an effective chemical additive for controlling expansion caused by the alkali-silica reaction.

Initially, these results appear to contradict the findings of McCoy and Caldwell [8] who reported that a 1% by weight of cement addition of acetone reduced the expansion of mortar bars by 16% in 8 weeks. Closer inspection of their data reveals that effect of the acetone addition in controlling expansion decreased over time. At two weeks, this dosage resulted in a 43% reduction
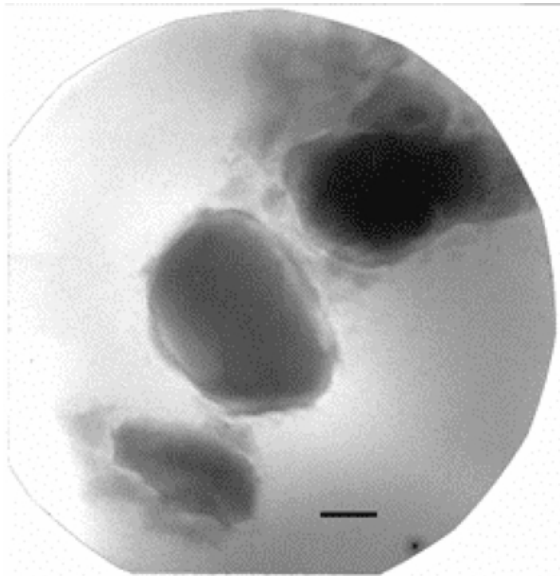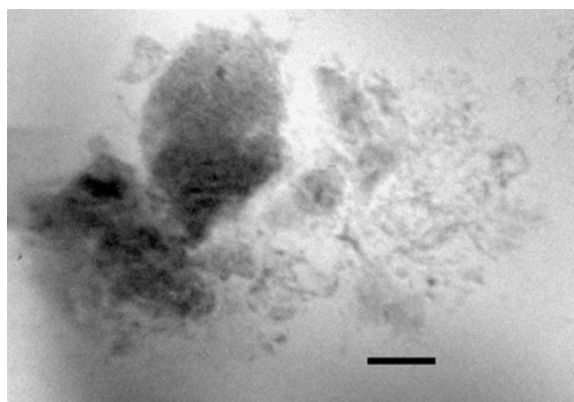
Figure 7 X-ray image of alkali-silicate gel in 0.7 M NaOH + 10% acetone by volume. The image was taken with a 10.924 s exposure time with a beam current of 183.2 mA at an original magnification of 2400×. scalebar = 1 μm · 71024034.


Figure 8 X-ray image of alkali-silicate gel in 0.7 M NaOH + 10% acetone by volume. The image was taken with a 8.978 s exposure time with a beam current of 222.3 mA at an original magnification of 2400×. Scalebar = 1 μm · 71024010.

in expansion, but this effect decreases to 28% at 4 weeks and 15% at 6 weeks [8]. A comparison of the results of McCoy and Caldwell [8] with the results of this investigation suggest the effectiveness of this additive to control expansion may be time-dependent.

A more thorough review of the chemistry of the silica-acetone system in an alkaline environment yields insight into the effects of time and pH on the control of gel expansion. Acetone is an organic compound consisting of a polar carbonyl group and two methane groups:

$$H_3C\text{—}\underset{H_3C}{\overset{}{C}}=\ddot{O}:$$
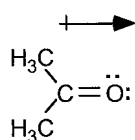
The dielectric constant (ε_s) of acetone is 21, making it a less polar liquid than water which has a dielectric constant of 78.5 [29]. In an investigation of the physical swelling of clays in solvents, including acetone, Murray and Quirk [30] established that the dielectric constant of the solvent is a major determinant in the total swelling of clays and that swelling decreased linearly with decreasing dielectric constant. These results may be applicable to alkali-silicate gel which, like clay, is a silicate and has previously been treated as a colloid by Prezzi *et al.* [24, 25]. It follows, then, that the decrease in mortar bar expansion described by McCoy and Caldwell [8] by using acetone as a chemical additive may be ascribed to the replacement of water, possibly at hydrophobic sites on the bridging oxygens, with acetone. The replacement of water by acetone in the alkali-silicate gel may be supported by findings of Taylor and Turner [31] who reported that acetone replaces bound water, adsorbed water, and some interlayer water in hydrated cement paste. Although no published research describing the replacement of water by acetone in alkali-silicate gels has been located, based upon the work of Murray and Quirk [30] and Taylor and Turner [31] it may be proposed that the decrease in expansion, particularly at early times, is a result of the replacement of water ($\varepsilon_s = 78.5$) with acetone ($\varepsilon_s = 21$).

One explanation for the apparent decreasing effectiveness over time may be the volatilization of the acetone. Another possible explanation is aldol condensation of acetone, a reaction which occurs readily under alkaline conditions at room temperature. Products of the reaction are less volatile than acetone and include mesityl oxide ($(CH_3)_2C\text{=}CHC(O)CH_3$). Using GC/MS to examine the liquid in and surrounding hydrated cement paste soaked in acetone for 30 days, Taylor and Turner [31] identified 14 components in the liquid other than acetone, including mesityl oxide which comprised 21% of the liquid volume and small amounts of phorone ($[(CH_3)_2 \cdot C\text{=}CH]_2 \cdot CO$) and its cyclic isomer iso-phorone, both of which are yellow in color. The 0.7 M NaOH + 10% (v/v) acetone solution used in this investigation developed a yellow color after a period of several months which deepened over time, suggesting that the aldol condensation reaction was occurring. The effect of products of aldol condensation of acetone on the swelling of the ASR gel has not been studied previously. While no details about the polarity of these products are available in the literature, the size and structure of the mesityl oxide molecule suggests that the liquid is less polar than acetone, which may decrease the expansion according to the results of Murray and Quirk [30]. But, the larger size of the molecule suggests that steric hindrance may negatively influence the capacity of the gel for expansion.

6. Conclusions

Calcium chloride, lithium chloride, and acetone have previously been shown to affect expansion caused by ASR. The effect of these chemical additives was examined by transmission soft X-ray microscopy and a quantitative elemental analysis. To examine the effect of some chemical additives, X-ray images were made of the reaction of the pessimum amount of alkali-silicate gel from a Brazilian dam in sodium hydroxide solution, and in 0.7 M NaOH plus 0.1 M CaCl$_2$, 0.1 M LiCl, or

10% (v/v) acetone. Complementary qualitative elemental analysis was performed using pessimum samples of chemical grade silica gel in the same solutions. Interpretations of this data in light of surface science principles yields the following insights on the effect the effect of these three chemical additives on expansion during alkali-silica reaction.

6.1. Calcium chloride
Reaction of the ASR gel in 0.7 M NaOH $+ 0.1$ M CaCl$_2$ solution produced spherulitic structures resembling the distinctive 'sheaf-of-wheat' morphology which is not believed to be expansive. No evidence of repolymerization was found, in contrast to earlier work [17] which showed the repolymerization resulting from the reaction of the ASR gel in saturated calcium hydroxide $+ 0.1$ M NaOH solution. These results suggest that the concentration of calcium ions in the pore solution, which is dependent upon the solubility of the chemical additive and the percent addition, relative to the concentration of silica species in solution is an important parameter for effective control of expansion associated with ASR.

6.2. Lithium chloride
X-ray images of the reaction of the ASR gel in 0.7 M NaOH $+ 0.1$ M LiCl solution showed that dissolution of the original gel particles had occurred, which was supported by the quantitative elemental analysis. However, in the presence of lithium chloride, the repolymerization into an expansive gel was decreased as compared to the reaction of the ASR gel in 0.7 M NaOH solution. Interpretations of the X-ray images in consideration of surface chemistry principles suggests two mechanisms by which lithium may act to reduce expansion of alkali-silicate gel. First, lithium may limit repolymerization, effectively reducing the potential for expansion. Second, lithium seems to promote the aggregation of relatively larger particles, but the potential expansion may be decreased because of a reduction in surface charge density of the alkali-silicate gel which may occur in the presence of lithium.

6.3. Acetone
Despite the interest in using chemical additives to control expansion by ASR, few studies have been directed towards understanding the mechanisms by which certain organic compounds, such as acetone, affect expansion caused by the alkali-silicate reaction. Images of the reaction of the ASR gel in 0.7 M NaOH $+ 10\%$ (v/v) acetone solution showed alkali-silicate gel particles surrounded by repolymerized gel, indicating that the use of acetone as a chemical additive may not be as effective as once believed in preventing expansion caused by ASR. By examining related research performed in the field of surface science, several hypothesis emerge to explain the initial substantial decrease in expansion with time and the subsequent diminishing effectiveness of acetone as reported in the literature. The decreased polarity of acetone as compared to water may be the physical mechanism that initially reduces expansion. Over time, volatilization of the acetone and formation of different products by base-catalyzed aldol condensation may decrease the effectiveness of acetone as an agent for reducing expansion associated with ASR.

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