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Principal Investigator: Kurtis, Kimberly E.
Organization: GA Tech Res Corp - GIT
Title:
POWRE: Examination of the Mechanisms of ASR Gel Expansion Control by Lithium Additive in Concrete

Project Participants

Senior Personnel
Name: Kurtis, Kimberly
Worked for more than 160 Hours: Yes
Contribution to Project:

Post-doc

Graduate Student
Name: Lloyd Collins, Courtney
Worked for more than 160 Hours: Yes
Contribution to Project:

Undergraduate Student

Technician, Programmer
Name: Brooks, Paal
Worked for more than 160 Hours: No
Contribution to Project:
Dr. Brooks, in the School of Environmental Science, Policy, and Management at University of California at Berkeley, taught Ms. Collins to use the ICP-OES and supervised her work there.

Other Participant
Name: Zhu, Guangxuan
Worked for more than 160 Hours: No
Contribution to Project:

Research Experience for Undergraduates
Name: Willis, Gayle
Worked for more than 160 Hours: Yes
Contribution to Project:
Ms. Willis prepared samples, performed tests and microscopy, lead the development of tutorials, and worked on publications
Years of schooling completed: Other
Home Institution: Same as Research Site
Home Institution if Other:
Home Institution Highest Degree Granted(in fields supported by NSF): Doctoral Degree
Fiscal year(s) REU Participant supported: 2002 2001
REU Funding: REU supplement
Organizational Partners

Other Collaborators or Contacts

Dr. Guangxuan Zhu is a Research Scientist in the Environmental Engineering Group of Georgia Tech's School of Civil and Environmental Engineering. Dr. Zhu has trained the graduate student to use the flame AAS and ICP-MS in his laboratory. With his background in analytical chemistry, he has helped the PI and graduate student to develop QA/QC protocols to assure the accuracy of their analyses.

Dr. Paul Brooks, a spectroscopist at University of California at Berkeley’s Environmental Science Policy and Management Dept, made their ICP-OES available for this research and instructed the graduate student in operating the equipment. The ICP-OES work at Berkeley was necessary to collect [Li] data.

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)

Findings:
Findings have been described in the previously attached document describing activities.

Training and Development:
Training and Development

One graduate student, Ms. Collins, and three undergraduate students, Mr. Jason Ideker, Ms. Gayle Willis, and Ms. Jessica Hurst, have been involved in the research funded under this POWRE Award (CMS-0074874). A chemical engineer by undergraduate education, Ms. Collins had no prior experience with concrete. Ms. Collins gained considerable background in concrete technology through her ongoing involvement in this project and by enrolling CEE8525 ‘Materials Science of Concrete’, a graduate course taught by the PI. In this course, Ms. Collins prepared a critical review detailing the state-of-the-art in current understanding of the alkali-silica reaction and the effect of lithium additives. In addition to gaining experience and knowledge in the field of concrete technology (i.e., reviewing literature, preparing samples, testing), the
graduate student has developed a 'through aggregate' imaging technique using confocal microscopy and has learned image analysis and chemical analysis using flame AAS and ICP-OES, as described in the 'Activities' section of this report.

In addition to the graduate student, three undergraduate students have been involved in this project. Gayle Willis started work on this project as a junior and continued through her graduation in Civil and Environmental Engineering at Georgia Tech in May 2002. Her tasks included coding the project web page, developing tutorials, reviewing ASR literature, sample preparation and testing, and report writing. Jason Ideker started work on this project as a senior and continued through his graduation in Civil and Environmental Engineering at Georgia Tech in May 2002. In addition to completing the PI's graduate-level Materials Science of Concrete course, Mr. Ideker's involvement also included sample and materials preparation, literature review, microscopy, testing, and report writing. Jessica Hurst started on this project during her senior year as an Industrial Design student in the College of Architecture at Georgia Tech. Her work included development of the tutorials, including interactive AVI files, and building a three-dimensional model for teaching.

Outreach Activities:
A website and 3 tutorials have been developed and are available at http://www.ce.gatech.edu/~kkurtis/gwillis/index.htm

Journal Publications


Books or Other One-time Publications

Web/Internet Site
URL(s):
http://www.ce.gatech.edu/~kkurtis/gwillis/index.htm
and related sites
Description:
This site is the framework for three tutorials developed for pre-college and college students as well as a description of ASR and the research.

Other Specific Products

Product Type: poster
Product Description:
A poster describing preliminary results was prepared in May 2002 by Collins, Ideker, Willis, and Kurtis
Sharing Information:
This poster was presented at the 2002 Gordon Research Conference for Physics and Chemistry of Cement-based Materials.

Product Type: Teaching aids
Product Description:
A hand-built model, constructed from foam, Lexan, and paint, was built. The model shows aggregate, ASR gel, and cracking in concrete. The model can be taken apart- encouraging active learning.
Sharing Information:
The model can be used to illustrate the damage caused by ASR in concrete.

**Contributions**

**Contributions within Discipline:**

A 'through-aggregate' imaging method was developed using LSCM; this technique is useful for examining in situ reactions in concrete. This technique overcomes some difficulties traditionally associated with characterization of cement-based materials, in that artefacts due to sample preparation requirements are largely avoided by through depth characterization at normal temperatures and pressures and with hydrated samples.

Formation of lathlike structures in the presence of Li were observed using the through-aggregate imaging technique. These structures were not apparent in the absence of Li. This observation, with ICP-OES results suggesting Li binding with time, substantiates the hypothesis that a less expansive or non-expansive Li-Si and possibly Li-Si-Ca complex forms and reduces expansion in ASR-affected concrete. The further development of this hypothesized mechanism for lithium action provides a broader foundation for its practical use. However, further research is needed to establish a duration of control.

**Contributions to Other Disciplines:**

The through-aggregate imaging technique might find applications in other fields where complex materials containing transparent and opaque materials are of interest.

**Contributions to Human Resource Development:**

This research project contributes to education in that an interactive web site with alkali-silica reaction tutorials, incorporating 3-D images from the confocal microscope, is being created for pre-college and college students.

Three REU students were supported on this research. One, Ms. Gayle Willis, has since received an NSF graduate fellowship and is working toward her Ph.D. in Civil and Environmental Engineering at Georgia Tech under Dr. Mike Bergin. Her work involves air quality. Mr. Jason Ideker is also continuing his study toward a Ph.D. under the supervision of Dr. Kevin Folliard at Univ. of Texas at Austin. Jason will continue to study ASR and work in the field of concrete. Ms. Jessica Hurst found employment in the field of industrial design following her graduation from Georgia Tech in May 2002. She found her interdisciplinary research experience to be valuable to potential employers.

The graduate student, Ms. Courtney Collins, earned her MS Env from Georgia Tech in May 2002 and is working as a consulting engineer at an environmental firm in Atlanta, GA. She also received much positive feedback from potential employers regarding her interdisciplinary research work.

**Contributions to Resources for Research and Education:**

**MICROSCOPY**

The development of confocal microscopy to examine concrete samples, particularly through-aggregate examination of concrete, provides a new tool for characterization of cement-based materials.

The PI has been asked to give a keynote lecture at an upcoming conference describing 'Advances in Microscopy of Cement-based Materials'. The techniques developed under this grant will be described.

**ALKALI-SILICA REACTION**

The web-based tutorials are available on line.

Material from the tutorials and this research is being incorporated into part of an FHWA workshop 'Guidelines for the use of lithium to mitigate or prevent ASR in concrete'. The PI's continued work in this area lead to her recruitment by The Transtec Group Inc. as an instructor for this workshop series.

**Contributions Beyond Science and Engineering:**

The PI's participation as an instructor at the upcoming FHWA workshops on the use of lithium in concrete will allow this research to be known by practicing engineers, particularly those from the Army Corps and State DOT's who routinely must mitigate ASR damage in concrete.

**Categories for which nothing is reported:**

Organizational Partners
Use of Lithium Additives to Mitigate Alkali-Silica Reaction in Concrete: Examining the Mechanisms of Expansion Control

Courtney Lloyd Collins,
Jason Ideker,
Gayle Willis,
Jessica Hurst, and
Dr. Kimberly Kurtis

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NSF POWRE Award CMS-0074874
Objectives

- Assess effectiveness of LiCl, LiOH, and LiNO$_3$ at various dosages
- Gain an improved understanding of the means by which lithium additives reduce ASR-induced expansion
Alkalis + Reactive Silica + Moisture

ASR Gel which expands

Concrete expansion and cracking

Possible ASR damage on concrete retaining wall
Mortar Bar Expansion Results

Results show a minimum threshold for \([\text{Li}_2\text{O}] / [\text{Na}_2\text{O}_{\text{eq}}]\): 0.6 for LiOH, 0.8 for LiNO\(_3\), and 0.9 for LiCl.

Mortar bars prepared and tested according to ASTM C227, PS 81 and C1293.
Motivation for Research

Without understanding the mechanism of control, it may be difficult

- to predict the effectiveness of a particular chemical additive
- to predict the effectiveness of a particular dosage
- and to foresee the duration of its control.
Motivation for Research

TXRM image of alkali-silica reaction in absence of Li
TXRM image of alkali-silica reaction in presence of LiCl
Methods

- Mortar bar expansion tests
- Microscopy: stereomicroscopy, SEM, and laser scanning confocal microscopy
- Quantitative elemental analysis by ICP-OES
Effect of Lithium on Silica Dissolution

- For LiCl and LiNO$_3$, [Si] decreases with increasing [Li].
- Opposite trend is apparent for LiOH, but LiOH still reduces expansion.
Effect of Lithium on Microstructure

- Immediate drop in [Na] and [Li] concentration apparent by ICP-OES
- Appearance of dendritic products at aggregate/paste interface in presence of lithium

Proposed mechanism:
Binding of alkalis and lithium in a non-expansive or less-expansive reaction product
Alkali-Silica Reaction

Continuing work:

• Investigation of alkali-silica reactivity of lightweight aggregate (for 3M)
• Instructor in FHWA workshops on use of lithium to control ASR damage
1. Introduction

Alkali silica reaction (ASR) occurs in concrete between reactive siliceous components in the aggregate and alkalis present in the pore solution, resulting in the formation of a potentially expansive gel product, which may cause concrete to 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.

Common methods for avoiding ASR in new construction include using non-reactive aggregate, low alkali cement, lower water-to-cement ratio, and/or incorporating supplementary cementitious materials [Ramachandran, 1998; Stark, 1992]. In some locations, however, appropriate aggregate, cement, or supplementary cementitious materials may not be available. Also, tests for potential reactivity of aggregate may be unreliable. The use of chemical additives is an alternative means to avoid damage by ASR in new construction. McCoy and Caldwell [1951] first demonstrated that some chemical salts, including lithium salts, might decrease expansion in mortars undergoing 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 alkali-silica reaction. 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 alkali-silica reaction. The effectiveness of three lithium additives - LiOH, LiCl, and LiNO₃ - at various dosages, was assessed by comprehensive microscopy of mortar samples, mortar bar expansion analysis, and quantitative elemental analysis of silica gel and alkali solution slurries.

2. Research Activities and Results

2.1 Microscopy

In order to be able to observe the formation and evolution of alkali-silicate reaction product over time in a non-destructive manner, a new technique to image into concrete through alkali-reactive glass aggregate by LSCM (laser scanning confocal microscopy) and to produce 3-dimensional (3D) virtual representations of the material was developed. The method proved to be effective in qualitatively monitoring crack formation and growth and product formation, within cracks and at the paste/aggregate interface. This LSCM technique was then utilized in conjunction with stereo microscopy to monitor the progress of alkali-silica reaction in mortar samples prepared with glass aggregate both in the presence and absence of lithium additives: LiNO₃, LiCl, or LiOH. Various quantities of these lithium additives, expressed as Li/Naₑ, were tested.
Microscopy analyses corroborate the beneficial effects of the lithium additives at the dosage range investigated (i.e. $[\text{Li}] / [\text{Na}] = 0.5, 1.0, \text{ and } 1.5$). Mortar microscopy samples showed damage due to ASR only in mortars prepared without lithium additive. No physical manifestations of damage were observed in the microscopy samples prepared with lithium. However, reaction products with dendritic structure were observed at the aggregate/paste interface. Figure 1 shows a random crack pattern, typically associated with ASR damage, observed in the mortars prepared without Li. Gel rings and debonding were also observed around some aggregates in the absence of Li, Figure 2. Intensity maps, such as that shown in Figure 2, were plotted to distinguish between different materials in the mortars. Reaction products at the paste/aggregate interface were also observable by LSCM, Figure 3. In this case, reaction products that appear to be crystalline were seen in mortars prepared with Li. Another type of image obtained by LSCM is the 3D rotational image, Figure 4, of glass aggregate in mortar.

2.2 Mortar Bar Expansion
To assess the effectiveness of the various lithium additives (i.e. LiOH, LiCl, or LiNO$_3$) and dosages on expansion control, mortar bars, containing glass aggregate, were prepared to measure expansion over time.

All mortar bars prepared with lithium additive reduced expansion below that of the reference mortar prepared without lithium. More specifically, as lithium dosage was increased, expansion decreased. Figures 5 and 6 show expansion in mortars prepared with LiOH and LiNO$_3$ (these graphs represents the trends observed with LiCl as well). Figure 7 shows that a minimum threshold lithium dosage, different for each additive, appears to exist below which expansion is not effectively reduced. More specifically, to reduce expansion below an acceptable level of 0.05% using LiOH a dosage greater than 0.6 would be required, for LiNO$_3$ a dosage greater than 0.8, and for LiCl a dosage greater than 0.9.

2.3 Silica Gel Slurries
Silica gel slurries were prepared to examine the role of lithium in the alkali-silica reaction. Concentrations of solution phase species (Si, Na, Ca, and Li) in slurry filtrates were measured over time by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). First, filtrates from silica gel slurries without calcium additive prepared with 0.7 M NaOH solution, SiO$_2$/Na$_2$O 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$_2$O of 4.8, either Ca(OH)$_2$ or Ca(NO$_3$)$_2$ · 4H$_2$O, and LiNO$_3$ were analyzed. The calcium-containing slurries should more closely represent the reactions occurring in the pore solution of concrete. The results for filtrates of both sets of slurries were 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.

2.3.A Silica Gel Slurries Without Ca
In all slurries prepared without Ca, dissolved silica concentration in the filtrates increased up to 336 hours (14 days). However, after 336 hours, some slurries showed a decrease in dissolved [Si]. More specifically, this decrease was observed in slurries
prepared with: LiOH at a dosage of Li/Na_e=1.5 (Figure 8), LiCl at dosages of Li/Na_e=1 and 1.5, and LiNO_3 at dosages of Li/Na_e=0.5 and 1.5 (Figure 9). 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 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 slurries prepared with LiOH, Figure 8, dissolved silica concentration generally increased as the amount of LiOH was increased, due presumably to a corresponding increase in OH^- [Diamond, 1999], while the opposite trend was apparent for those samples prepared with LiCl and LiNO_3. 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 (Figure 9). 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].

A large (11 % to 42 %) initial decline in dissolved Na was observed for all lithium additives at all lithium dosages over the first 24 hours. Figure 10 shows the concentration of Na in solution filtrates from slurries prepared with LiNO_3. 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.

The dissolved Li concentration in all slurries undergoes an even larger initial drop (ranging from 23 % to 57 %) than Na over the first 24 hours and then remains relatively steady over the observation period. The concentration of Li in solution in slurries prepared with LiNO_3 is shown in Figure 11. 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 appear to be no correlation between the trends of Li concentration and Na concentration.

2.3.B Calcium-containing Silica Gel Slurries

In all slurries containing calcium, dissolved [Si] was greatest in either the sample prepared without Li or the sample prepared with LiNO_3 at a dose of [Li]/[Na_e]=0.25, the
lowest dosage examined. Generally, as Li dose increased, dissolved [Si] decreased. Figure 12 represents the trends observed in all slurries containing calcium.

Comparing Si concentration in samples prepared with calcium, Figure 12 (under saturated with respect to Ca) and Figure 13 (excess Ca conditions), to samples prepared without Ca, Figure 9, shows that, overall, less silicon is in solution in the calcium-containing slurries. This decrease in [Si] in solution is believed to indicate the formation of calcium-containing silicates such as C-S-H. In the slurries prepared with excess Ca(OH)$_2$, Figure 13, the amount of dissolved silica at 336 hours was not as great as in the saturated and under saturated (Figure 12) 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 (Figure 12), C-S-H formation will continue as silica dissolves and the alkali-silica reaction will proceed. Thus, the relative amount of calcium available for reaction appears to be directly related to the amount of silica in solution.

A reaction layer, believed to be C-S-H, that 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 and sometimes formed beneath the layer, above the remaining silica gel. This buoyant reaction product 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 under saturated with respect to Ca than in slurries with excess calcium.

Quantitative elemental analysis of the solution layers above and below the reaction product shell was performed on some of the 9.7 M NaOH silica gel slurries prepared with under saturated and excess Ca(OH)$_2$ with and without LiNO$_3$. In agreement with Dent Glasser and Kataoka [1982], 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.

Like the slurries prepared without calcium (Figure 10), most slurry samples containing Ca also experienced an initial drop in Na in solution (7% - 44%) over the first 24 hours, likely due to the binding of Na at the silicate surface and within reaction product. 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.

An initial decrease (ranging from to 20% to 69%) in [Li] in solution was observed over the first 24 hours in most samples prepared with Ca. The larger percent decrease in Li than Na, which was also observed in the absence of Ca (Figure 11), may indicate that Li is preferentially bound. In the slurries prepared with excess Ca(OH)$_2$, the concentration of Li in solution is less than the concentration of Li in corresponding samples prepared without Ca. This data indicates that Li may be bound within the C-S-H, as was also observed by Diamond [1999].
2.3.C Results Synthesis

Mortar bar results show that expansion was reduced with increasing Li additive concentration, with all additives tested. Slurries prepared with Ca showed that dissolved Si decreased with an increase in LiNO₃ as was observed in slurries prepared without Ca. However, relative Si concentration was lower in calcium-containing slurries due to C-S-H formation. In comparing the slurry results to mortar bar results, it appears that lower concentrations of Si in solution indicate reduced expansion. However, the mechanism by which an increase in Li results in a decrease in Si remains uncertain, but it is proposed, based upon these results, that this may be due to either suppression of Si dissolution or the precipitation of a non-expansive lithium bearing silicate [Mo et al., 2002].

Microscopic characterization of companion samples [Collins, 2002; Collins et al., submitted] has shown the presence of gel-like reaction products, present in mortars prepared with reactive aggregate in the absence and presence of lithium additives, as well as dendritic reaction products. 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 non-expansive (as proposed by Laurence and Vivian [1961]), or their formation near the reactive silicate surface may limit silica dissolution or may restrict expansion.

2.4 Educational Tools

In addition to research, educational tools were developed to teach some about concrete materials and ASR to youth and other individuals who don’t know much about it. A power point tutorial described: basic principles of the alkali-silica reaction, expansion theories, lithium control theories, and research methods and results. This tutorial, in addition to other ASR information, has been made widely accessible by being put on a website (registered with search engines). A three-dimensional foam model of ASR occurring in concrete was also created to enhance visualization of the process. All materials can be accessed via the web page http://www.ce.gatech.edu/~kkurtis/gwillis/index.htm

3. Conclusions

3.1 Microscopy

- “Through aggregate” imaging by laser scanning confocal microscopy (LSCM), a technique for imaging reactions in concrete through glass aggregate, was developed and was shown to be effective for examining alkali-silica reaction in situ.
- Three-dimensional representations of the aggregate, images of reaction product both within cracks and at the paste/aggregate interface, and quantitative measurement of gel ring thickness at the surface are all examples of types of information gained by LSCM that have not, at this point in time, been possible with other microscopy methods.
• LSCM and stereo microscopy images showed definitive evidence that ASR occurred in the sample prepared without lithium additive, characteristic crack patterns, gel rings, common reaction products, and debonding were observed.
• Samples prepared with lithium showed no evidence of ASR. However, through aggregate imaging showed reaction product formation occurring at the paste/aggregate interface in which apparently crystalline reaction products were formed. The formation of this type of product at the aggregate/paste interface was observed only in the presence of lithium, indicating that its formation may be key to the suppression of ASR-induced damage with lithium additives.

3.2 Mortar Bar Expansion
• 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 [Li₂O]/[Na₂O₃] for each additive used.
• 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]/[Na₃] dose of 1.5 for all additives tested.

3.3 Silica Gel Slurries
• A sharp decline in dissolved Na and Li concentration was observed over the first 24 hours 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 LiNO₃ 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 LiNO₃, 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 alkali-silica reaction, 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 non-expansive lithium-silicate complex, which is substantiated by microscopy work.

4. References


Fig. 1. Random cracking pattern in mortar prepared without Li

Fig. 2. LSCM image and intensity map of reaction product in mortar without Li
Fig. 3. LSCM images of the pasteaggregate interface in the mortar prepared with LiOH, [Li]/[Na] = 0.5 at (a) 1, and (b) 7 days

Fig. 4. 3D LSCM rotational image of glass bead aggregate in microscopy mortar sample (a) x-y plane, (b) rotation, (c) rotation, (d) rotation, (e) y-z plane
Fig. 5. Expansion of mortar bars over time with and without LiOH

Fig. 6. Expansion of mortar bars over time with and without LiNO₃
Fig. 7. Threshold lithium additive required to reduce expansion to an acceptable level
Fig. 8. Dissolved Si concentration in slurry filtrates without Ca prepared with LiOH

Fig. 9. Dissolved Si concentration in slurry filtrates without Ca prepared with LiNO₃
Fig. 10. Dissolved Na concentration in slurry filtrates without Ca prepared LiNO₃

Fig. 11. Dissolved Li concentration in slurry filtrates without Ca prepared with LiNO₃
Fig. 12. Dissolved [Si] in slurry filtrates with LiNO₃ and under saturated with respect to calcium

Fig. 13. Dissolved [Si] in slurry filtrates with LiNO₃ and excess calcium