



# The effects of lithium ions on chemical sequence of alkali-silica reaction



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## ARTICLE INFO

### Article history:

Received 31 January 2015  
Accepted 16 September 2015  
Available online 4 October 2015

### Keywords:

Alkali-Aggregate Reaction (C)  
Alkalis (C)  
Lithium compounds (D)  
Pore solution (B)

## ABSTRACT

This paper presents the results of the investigation on the effects of  $\text{Li}^+$  ions on the chemical and physical changes in the cementitious system undergoing alkali-silica reaction (ASR). Specifically, this paper focuses on determining which chemical steps of ASR processes are affected by the presence of  $\text{Li}^+$  ions in the pore solution in order to provide better understanding of the role of  $\text{Li}^+$  ions in the mitigation process of ASR.

The results presented in this paper strongly support the hypothesis that the  $\text{Li}^+$  ions facilitate the formation of a physical barrier on the surface of reactive silica, and thus prevent further attack on the reactive sites by hydroxyl ions.

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## 1. Introduction

Numerous researchers have investigated the use of lithium compounds to mitigate alkali-silica reaction (ASR) ever since the first report of beneficial effects of lithium ions ( $\text{Li}^+$ ) on ASR-caused expansion was published by McCoy and Caldwell [1]. Although the exact nature of the role of lithium ions in controlling ASR is still not clearly understood, several different mechanisms have been proposed. These include: (a) formation of physical barrier by insoluble silicon-lithium (Si-Li) reaction products [2–5], (b) the formation of less expansive Si-Li reaction products [5–10], and (c) increased chemical stability of reactive silica exposed to pore solution [2,11–13]. Brief discussion of each of the mechanisms is presented below:

Several researchers postulated that insoluble Si-Li reaction products may be deposited on the surface of the reactive aggregate particles and act like a physical barrier to prevent further attack of siloxane (Si-O-Si) groups by alkalis. Lawrence and Vivian [2] suggested that the Si-Li complex which formed in the presence of lithium hydroxide (LiOH) and opal had low solubility and thus produced insoluble coating on the surface of the reactive silica particles effectively protecting them from further participation in ASR. Mitchell et al. [3] found that opal particles immersed in  $1 \text{ mol} \cdot \text{L}^{-1}$  LiOH solution saturated with calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ] were covered with a reaction product. In the study by Feng et al. [4], the formation of Si-Li crystals and Li bearing ASR gel was observed in a scanning electron microscope (SEM) images of Vycor<sup>TM</sup> glass disks immersed in solution containing sodium hydroxide (NaOH), lithium nitrate ( $\text{LiNO}_3$ ), and calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ]. The authors suggested that once formed, the layer of Li-Si crystals acts as a diffusion barrier and protects the reactive aggregate particles from further attack

by alkalis [4]. Leemann et al. [5] noticed that the morphology of reaction product transformed from the plate-like product present in system without lithium to the dense product observed in the system with lithium. They suggested that this dense lithium bearing reaction products form a protective barrier that prevents further participation of the reactive aggregate in the ASR process.

The ability of a reactive systems containing lithium admixtures to form less expansive (compared to system without lithium) Si-Li reaction product is also often used to explain the beneficial effects of lithium addition [5,7,10,14]. However, as mentioned in the previous paragraph, it is quite possible that this less expansive Si-Li reaction product might also act as the barrier which slows down the diffusion of ions from pore solution toward the surface of the aggregate. In that sense, the formation of the barrier by insoluble Li-Si reaction product and creation of less expansive reaction product might be, in fact, a part of the same protective mechanism. Several researchers [5,8,11,15,16] observed that the concentration of  $\text{Li}^+$  ions in pore solution extracted from mortars decreased with time while concentration of sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) ions remained more or less the same. These results lead to the conclusion that Si-Li reaction is more preferential than Na/K-silica reaction and indicate that non-expansive lithium-bearing product may form instead of classic expansive ASR gel containing sodium and potassium. Diamond and Ong [7] also confirmed formation of a non-expansive lithium silicate gel in mortar bars incorporating LiOH and reactive aggregates which did not exhibit expansion. Kawamura and Fuwa [14] found that the Ca content in ASR gels decreased by addition of Li salts and that the ASR gel became homogeneous at the high dosage of lithium salts. They further suggested that this more homogeneous ASR gel might be less expansive. The low content of Ca in reaction products was also confirmed in the extensive study by Leemann et al. [5]. Based on the investigation conducted on their model system and mortar samples, these authors suggested that Ca can be replaced by lithium

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and produce the reaction products which are less-expensive and denser than the ASR gel without lithium [5]. Collins et al. [12] and Mo et al. [17] also observed lithium bearing products in specimens incorporating lithium and reactive aggregate.

Several researchers [3,5,18] have studied the effects of lithium on the chemical structure of ASR gels using the nuclear magnetic resonance (NMR) spectroscopy. These NMR studies showed that the incorporation of  $\text{Li}^+$  ions into the ASR gel changes its structure from a product containing mainly  $\text{Q}^3$  sites to a product with more disordered networks containing mainly  $\text{Q}^1$  and  $\text{Q}^2$  sites. It was previously reported that the layered silicates and gels which can expand by absorbing water typically contain significant amount of  $\text{Q}^3$  sites [19,20]. Therefore, the reduction in the number of  $\text{Q}^3$  sites observed in the presence of lithium ions implies the formation of less expansive ASR gel.

It has also been observed that the rate of silica dissolution decreases in systems with lithium admixtures, even though the pH values of the pore solution remain essentially unchanged [2,11–13]. This implies that the presence of lithium ions somehow increases the chemical stability of the silica, although the exact nature of this mechanism is still unknown. The increased chemical stability of silica will, in turn, result in smaller amount of expansive gel and lower degree of damage. Lawrence and Vivian [2] found that dissolution of reactive silica strongly depended on the type of alkali hydroxides (i.e. NaOH, KOH, or LiOH) present in the system. These authors found that the rate of silica dissolution was the smallest for LiOH and the highest for KOH. Wijnen et al. [13] also found similar pattern for the dissolution of reactive silica and suggested that the dissolution rate decreased with an increase in the ionic radius of the alkaline species (i.e. it followed the order  $\text{K}^+ < \text{Na}^+ < \text{Li}^+$ ). Collins et al. [12] observed that the dissolution of silica decreased in solutions with  $\text{LiNO}_3$  and  $\text{LiCl}$  but it increased in the presence of LiOH. This increased dissolution of silica in the presence of LiOH appears to be caused by the increase in the pH values due to addition of hydroxyl ions from LiOH. Feng et al. [21] observed significant reduction of silica dissolution in the presence of  $\text{LiNO}_3$ . Based on their extensive studies, Tremblay et al. [11] concluded that the beneficial effects of  $\text{LiNO}_3$  in controlling ASR may be most reasonably explained by the increased chemical stability of reactive silica.

In their 2003 study, Kurtis and Monteiro [22] investigated the effects of both, the 0.7 M solution of NaOH and 0.7 M NaOH plus 0.1 M  $\text{LiCl}$  on the properties of the ASR gel using the soft X-ray microscopy and quantitative elemental analysis. In contrast to the test results discussed in the previous paragraph, the data collected by Kurtis and Monteiro [21] indicated that the presence of the lithium chloride in the solution did not prevent the dissolution of the silica gel (although the analytical amounts of the silicon in the  $\text{LiCl}$  contacting system was lower than that observed in the 0.7 M NaOH solution alone). These authors concluded that while not necessarily significantly limiting the silica dissolution, the presence of lithium ions reduces the repolymerization into an expansive gel (due to strong field interaction between Li and Si) and reduces expansive behavior due to changes in surface charge of small gel particles.

The present paper aims to improve the understanding of the role of lithium ions in controlling the ASR using the results of various studies which were conducted on both reactive and non-reactive systems and with and without the addition of  $\text{LiNO}_3$ . These studies included: (a) the model reactant (MR) experiments simulating ASR during exposure of reactive aggregate to the potassium hydroxide (KOH) solution [23–25], (b) the analysis of pore solution from mortars containing the reactive aggregate (Jobe sand) or non-reactive aggregate (Ottawa sand) with three different dosages of  $\text{LiNO}_3$  (molar ratio of lithium to alkali ions of, respectively, 0, 0.26, and 0.74), and (c) the mortar bar expansion tests performed on specimens containing the same three different dosages of  $\text{LiNO}_3$  as those mentioned in point (b).

The MR experiments allowed for determination of chemical and physical changes in the closed reactive system consisting of the mixture of the reactive silica mineral, the alkaline solution (KOH), the solid  $\text{Ca}(\text{OH})_2$ , and  $\text{LiNO}_3$ . The results obtained from the MR experiment

were supported by the studies of the effects of  $\text{Li}^+$  ions on the chemistry of the pore solution obtained from the actual cementitious system [experiments (b) and (c)].

## 2. Materials and experimental methods

### 2.1. Materials

The reactive silica mineral used for the MR experiments was  $\alpha$ -cristobalite, which is a well-defined crystallographic form of silica. The previous study of this mineral [26] using SEM aided by the energy-dispersive spectrometry indicated that it was ~99% pure silica and that its microstructure appeared to contain large number of microcracks. This silica was ground to obtain the size fraction between 0.297 mm (No. 50 sieve) and 0.595 mm (No. 30 sieve). Resulting material was then extensively cleaned ultrasonically in deionized water to remove fine particles. The specific surface area measured by Brunauer–Emmett–Teller (BET) method (nitrogen adsorption isotherm) was  $1430 \text{ cm}^2 \cdot \text{g}^{-1}$ . The value of the loss of ignition, determined using the thermogravimetric analysis (TGA) method was about 0.02%.

The potassium hydroxide solution was prepared by diluting commercial standard of  $1.0 \text{ mol} \cdot \text{L}^{-1}$  KOH solution with deionized water. The reagent grade  $\text{LiNO}_3$  and  $\text{Ca}(\text{OH})_2$  were used as the source of  $\text{Li}^+$  and  $\text{Ca}^{2+}$ , respectively.

The mortar test specimens were prepared using high-alkali Type I Portland cement ( $1.04 \text{ Na}_2\text{O}_{\text{eq}}$ ). The composition of the cement is summarized in Table 1. One non-reactive (NR) aggregate (ASTM C 778 standard Ottawa graded sand) from Illinois and one reactive (R) aggregate (Jobe sand) from the quarry in El Paso, Texas were used to prepare mortar specimens. Petrographic examination of the Jobe sand revealed that it mostly consisted of fragments of weathered to sound granitic rock, coarse to fine-grained sodium and potassium feldspars, volcanic rocks, chert, quartzite, and other rock fragments. The most reactive minerals among the above components of the Jobe sand included andesite, chert, quartzite, and volcanic rock fragments that contained cristobalite. As such, although one cannot completely eliminate potential contribution of feldspars to the total alkali content of the pore solution, it is believed that (given a presence of the other, highly reactive minerals and relatively short duration of the experiments) such contribution (if any) was likely relatively small. The specific gravities of non-reactive (NR) sand and reactive (R) sand were, respectively, 2.65 and 2.55, their absorptions were, respectively, 0.0% and 1.0%, and their loss of ignition (the ratio of the ignited mass of aggregate to the oven-dried mass of aggregate) were, respectively, 0.9991 and 0.9950.

**Table 1**  
Properties of type I Portland cement used in the preparation of mortars.

Chemical composition	Cement (%)
Silicon dioxide, $\text{Si}_2\text{O}$	20.1
Aluminum oxide, $\text{Al}_2\text{O}_3$	5.2
Ferric oxide, $\text{Fe}_2\text{O}_3$	2.1
Calcium oxide, CaO	61.8
Magnesium oxide, MgO	3.7
Sulfur trioxide, $\text{SO}_3$	3.6
Carbon dioxide, $\text{CO}_2$	–
Limestone %	–
Loss of ignition	1.2
Total alkali as Sodium Oxide, $\text{Na}_2\text{O}_{\text{eq}}$	1.04
Compounds	
Tricalcium silicate, $\text{C}_3\text{S}$	50.6
Dicalcium silicate, $\text{C}_2\text{S}$	19.7
Tricalcium aluminate, $\text{C}_3\text{A}$	10.2
Tetracalcium aluminoferrite, $\text{C}_4\text{AF}$	6.4
Fineness	
Blain fineness ( $\text{m}^2 \cdot \text{kg}^{-1}$ )	400

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