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Studies on lithium salts to mitigate ASR-induced expansion in new concrete: a critical review

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Abstract

This paper provides a critical review of the research work conducted so far on the suppressive effects of lithium compounds on expansion due to alkali–silica reaction (ASR) in concrete and on the mechanism or mechanisms by which lithium inhibits the expansion. After a thorough examination of the existing literature regarding lithium salts in controlling ASR expansion, a summary of research findings is provided. It shows that all the lithium salts studied, including LiF, LiCl, LiBr, LiOH, $LiOH \cdot H_2O$, $LiNO_3$, $LiNO_2$, Li_2CO_3, Li_2SO_4, Li_2HPO_4, and Li_2SiO_3, are effective in suppressing ASR expansion in new concrete, provided they are used at the appropriate dosages. Among these compounds, $LiNO_3$ appears to be the most promising one. Although the mechanism(s) for the suppressive effects of lithium are not well understood, several mechanisms have been proposed. A detailed discussion about these existing mechanisms is provided in the paper. Finally, some recommendations for future studies are identified.

Keywords: Lithium compounds; Alkali–silica reaction (ASR); Concrete; Mortar

1. Introduction

It is well known that alkali–silica reaction (ASR) can induce cracking and damage in concrete structures, and many attempts have been made to mitigate or prevent ASR in new and existing concrete structures. The three traditional methods used to avoid ASR-induced damage in new concrete include (1) using nonreactive aggregates. This is the most effective way to prevent ASR-induced expansion. However, nonreactive aggregates may not be locally available to the construction sites; and it has been also found that some aggregates, which are not reactive based on the laboratory tests, produce deleterious ASR expansion in the field. (2) Limiting the equivalent sodium oxide content of cement to less than 0.6% by mass, which has been adopted as part of ASTM C 150. This measure is not always effective by itself as certain aggregates can also release alkali ions and cause an increase in the concentration of hydroxyl ions, which may induce deleterious expansions at later ages. (3) Using supplementary cementitious materials (SCM). This procedure has been successfully used in many concrete constructions to mitigate ASR-induced damage. However, not all SCMs are equally effective in this role, and the amount of SCM required to control ASR may not be acceptable for other reasons. A fourth alternative approach to prevent ASR is the introduction of lithium compounds which is the subject of this paper.

In the following sections, a thorough review will be provided on the research work conducted so far on the suppressive effects of lithium on ASR expansion in new concrete and the mechanism(s) by which lithium salts inhibit the expansion.

2. Effects of lithium salts on alkali–silica reaction

2.1. Effects of lithium on ASR-expansion and pore solution

The concept of using lithium salts to inhibit ASR expansion was first reported in 1951 by McCoy and Caldwell

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[1]. In their work, mortar bars were produced with Pyrex glass as the reactive aggregate, and the alkali content of the cement was raised to 1.15% Na_2O by adding NaOH to the mixing water. Over 100 different compounds, including metallic salts, acids, oils, organic chemicals, proteins, and proprietary admixtures, were investigated, among which, LiCl, Li_2CO_3, LiF, Li_2SiO_3, $LiNO_3$, and Li_2SO_4 were found to be the most effective agents to mitigate expansion due to ASR in mortars. A minimum lithium to alkali (potassium plus sodium) molar ratio (expressed as [Li]/[Na+K]) of 0.74 was needed to efficiently suppress expansion.

Later Lawrence and Vivian [2] reported on the use of lithium hydroxide as an inhibitor of expansion. Their studies confirmed the effectiveness of LiOH in preventing abnormal ASR expansion for up to one year when added at rates of 0.5%, 1.0%, or 1.5% by weight of cement, expressed as equivalent sodium hydroxide.

It seems that the research on lithium and its impact on ASR virtually ceased after these early studies, although the initial findings were quite promising. It was not until the early 1990s that interest in lithium as an admixture for concrete was renewed. In 1989, Sakaguchi et al. [3] used Pyrex glass and a known reactive andesite sand as the reactive aggregates. $LiOH \cdot H_2O$, $LiNO_2$, and Li_2CO_3 were added to the mortar bars. All of the lithium compounds were effective in reducing expansion. The results also indicated that the effect of lithium salts varies with lithium to alkali molar ratios. The threshold lithium to alkali molar ratio to completely suppress ASR expansion was 0.9. Sakaguchi et al. [3] also found from expression of pore solutions from mortar bars made with $LiNO_2$ that the concentration of lithium ions decreased with time while that of sodium and potassium remained nearly constant. This was in contrast to tests without lithium where a decrease in both the sodium and potassium concentration was observed.

Stark [4] et al. [5] also confirmed the suppressive effects of lithium fluoride and lithium carbonate by following the procedures of ASTM test method C 227 and that of lithium hydroxide by following ASTM C1260. They used a highly reactive natural aggregate (rhyolite) as the reactive aggregate and found that the effective lithium to alkali molar ratio was 0.6, 0.92, and 0.67 for LiF, Li_2CO_3, and LiOH, respectively. One of the important observations from Stark's work was that an insufficient dosage of lithium actually resulted in an increase in expansion compared to the control mortar without lithium; this is known as the "pessimum effect". The pessimum effect was also confirmed by Diamond and Ong [6]. The reason for this pessimum effect may be attributed to an increase in the alkalinity (OH^-) of the pore solution caused by the addition of lithium, especially LiOH. Most other forms of lithium also increase the pH of the pore solution. But $LiNO_3$ is virtually unique in that it does not tend to increase the pH, thereby eliminating the pessimum effect [7].

In Lumley's work [8], expansion of concrete prisms containing calcined flint (cristobalite) as the reactive aggregate, and different amounts of $LiOH \cdot H_2O$, LiF, and Li_2CO_3 were studied. The results indicate that lithium compounds are all effective, provided that the lithium to equivalent soda ratio Li_2O/Na_2Oe is ≥ 0.33 or the molar ratio $[Li]/[Na+K] \geq 0.62$.

Durand [9] did an extensive study on concrete prisms containing three different reactive aggregates from Canada (Sudbury greywacke, Potsdam sandstone, and a siliceous limestone from Sherbrooke) and four different lithium salts ($LiOH \cdot H_2O$, Li_2CO_3, LiF, and $LiNO_3$) at a broad range of [Li]/[Na+K] molar ratios of 0.41, 0.83, 1.24, and 1.66. The findings suggest that when using the Sudbury aggregate, a threshold [Li]/[Na+K] molar ratio of 0.83 for $LiOH \cdot H_2O$, LiF, and Li_2CO_3 was required, and a smaller [Li]/[Na+K] molar ratio of 0.72 was required for $LiNO_3$. When using Potsdam aggregate, only $LiOH \cdot H_2O$ and LiF at a [Li]/[Na+K] molar ratio of 1.66 are able to inhibit the deleterious expansion. None of the four lithium compounds was completely effective in suppressing the expansion with the siliceous limestone. These findings indicate that the suppressive effects of lithium compounds on ASR expansion depend strongly on the kind of lithium compounds used, the [Li]/[Na+K] molar ratio, and on the nature of the reactive aggregate. These observations were also confirmed by other researchers [10] where expansion of mortar bars containing a high-alkali cement of 1.1% Na_2Oe and a highly reactive aggregate were studied. The threshold dosage level of Li^+ ion for both LiOH and Li_2CO_3 was about 0.75. Kawamura and Fuwa [10] also noted the pessimum effect occurred with both of the lithium salts studied. Collins et al. [11] reached a similar conclusion as Durand [9] based on their work with LiOH, LiCl, and $LiNO_3$. The threshold [Li]/[Na+K] molar ratio was found to be 0.6 for LiOH, 0.8 for $LiNO_3$, and 0.9 for LiCl.

A recent work by Berra et al. [12] found a linear relationship between the effective dosage of $LiNO_3$ in terms of [Li]/[Na+K] molar ratio and the difference between the concrete alkali content and the threshold alkali level of the aggregate (alkali reactivity level). They also demonstrated that $LiNO_3$ was effective regardless of whether the concrete prisms were stored in a moisture room at 38 °C or soaked in alkaline solutions at 150 °C. However, Li_2CO_3 was only effective when the concrete prisms were stored in a moisture room at 38 °C.

One of the methods to quickly study ASR expansion is to expose the mortars to an autoclave treatment. Ohama et al. [13] studied the efficacy of $LiOH \cdot H_2O$, LiF, and Li_2CO_3 in mortar bars containing an amorphous opaline silica as the reactive aggregate. The bars were autoclaved at 128 °C under a pressure of 245 kPa for 4 h after the first 24 h curing at 20 °C and 100% RH. LiF and $LiOH \cdot H_2O$ reduced the expansion by half, while Li_2CO_3 only slightly reduced expansion. Bian et al. [14] used the same autoclave procedure and studied the suppressive effect of $LiNO_2$. An andesite sand from Japan was used as the reactive aggregate. It was concluded that the effective [Li]/[Na+K] ratio depends on the Na_2Oe content of mortar mixtures. When the Na_2Oe content in the mortar is greater than 2.0% by mass, a [Li]/[Na+K] molar ratio of 0.8 can efficiently suppress the deleterious expansion, while at a lower Na_2Oe content, e.g., 0.5% Na_2Oe, a smaller [Li]/[Na+K] molar ratio of 0.1 is enough to keep the expansion innocuous. Bian et al. [15] also studied the suppressive effects of many different lithium salts, LiF, LiCl, LiBr, $LiNO_3$, Li_2SO_4, LiH_2PO_4, Li_2CO_3, LiOH, and a commercial $LiNO_2$ solution, at the same [Li]/[Na+K] molar ratio of 0.8. They found LiCl, LiBr, $LiNO_2$, $LiNO_3$, Li_2SO_4, and LiH_2PO_4 produced similar suppressive effects on ASR expansion, whereas Li_2CO_3, LiOH, and LiF only exhibited certain effects. Mo et al. [16] used the same autoclave procedure to study the long-term effectiveness of LiOH in inhibiting ASR. The results show that LiOH at an appropriate dosage can effectively inhibit the ASR expansion during the whole experimental period up to 3 years. It should be noted that all of these results are obtained from autoclave treatment, and the results are not directly comparable with data from studies at lower temperatures and pressures.

Diamond and Ong [6] conducted testing on cristobalite and Beltane opal in mortar bars containing LiOH. They reported that a minimum [Li]/[Na+K] molar ratio of 1.2, a higher threshold than the reports from other studies, was required to inhibit the deleterious expansion. From the pore solution analysis data, the authors concluded that even in nonreactive aggregate mortars, after only 1 day of hydration, about 40% of the LiOH added to the mortars was absorbed by the products of cement hydration, which means a substantial portion of LiOH added is not available for combating ASR. In comparison, the proportion of NaOH and KOH consumed by the hydrating cement is 25% and 20%, respectively. The greater affinity of C–S–H for lithium over other alkali ions was also reported by Bhatty and Greening [17] and Stade [18]. Those researchers found that the lower the calcium to silica ratio of the C–S–H, the greater the retention of alkali and that more lithium enters C–S–H than sodium or potassium. From studies on the synthesized gel slurries containing lithium salts, Collins et al. [11] also verified that, in the presence of other alkalis, lithium is preferentially bound within at least one of the reaction products because the decrease in lithium concentration was typically greater than that of sodium.

Lane's work [19,20] on LiOH and a commercial $LiNO_3$ solution again confirmed Durand's [9] findings. Concrete prisms containing Pyrex glass and some Virginia reactive aggregates containing microcrystalline and strained quartz, which are considerably less reactive than Pyrex glass, were studied. Lane [19,20] reported that lithium doses of [Li]/[Na+K]=0.925 were required for the two aggregates, and that both lithium compounds are not as effective in preventing the expansions of slowly reactive aggregates as appears to be the case with highly reactive aggregates.

The work conducted by Thomas et al. [21] on $LiOH \cdot H_2O$ and $LiNO_3$ agree well with published data from other researchers. A [Li]/[Na+K] molar ratio of 0.74 for $LiNO_3$ can sufficiently suppress the ASR-induced expansion with most aggregates. While $LiOH \cdot H_2O$ is less efficient in concrete prisms containing a crushed siltstone aggregate, a higher ratio of [Li]/[Na+K]=0.85 is required to inhibit the deleterious ASR expansion.

Although both LiOH and $LiNO_3$ are good inhibitors for suppressing ASR-induced expansion, $LiNO_3$ is a better choice compared to LiOH. LiOH raises the OH^- ion concentration of the pore solution, increasing the challenge for lithium. Furthermore, the caustic nature of LiOH poses some safety concerns. The findings on $LiNO_3$ indicate that $LiNO_3$ does not introduce more OH^- ions in the pore solution, and it is fully soluble, and of neutral pH, making it convenient and safe to handle. $LiNO_3$ also has a benign effect on the concrete properties of strength, electrical resistance, drying shrinkage, and resistance to freezing and thawing, whereas LiOH can retard the strength development [20]. Studies also show that $LiNO_3$ is compatible with other chemical admixtures [22]. Thus, $LiNO_3$ has become the most promising lithium salt for suppressing ASR expansion [23].

2.2. Summary of research findings

A summary of the above research findings is given in Table 1. From the work conducted so far, some general facts regarding the effects of lithium in controlling ASR expansion can be drawn, which are as follows:

1. All 11 types of lithium salts studied, including LiF, LiCl, LiBr, LiOH, $LiOH \cdot H_2O$, $LiNO_3$, $LiNO_2$, Li_2CO_3, Li_2SO_4, Li_2HPO_4, and Li_2SiO_3, have shown some suppressive effects in controlling ASR-induced expansion in fresh concrete, provided they are present at appropriate dosages.
2. The efficacy of lithium in suppressing expansion due to ASR strongly depends on the nature or reactivity of the aggregate, the form of lithium, and the amount of alkalis present.
3. About half the amount of the lithium added to suppress ASR-induced expansion is adsorbed by the hydrating cement, and the uptake of lithium by C–S–H is more than that of sodium and potassium. Hence, only half of the lithium added is available for the suppressive purpose.
4. The minimum lithium to alkali molar ratio to efficiently inhibit deleterious ASR expansion is generally in the range of 0.67−1.20 for most of the lithium salts studied and 0.72−0.93 for $LiNO_3$.
5. Both LiOH and $LiNO_3$ are more effective in preventing the expansion of highly reactive aggregates than of slowly reactive aggregate.
6. The benefit of using $LiNO_3$ to inhibit ASR expansion over other lithium salts is that $LiNO_3$ does not increase the OH^- ion concentration of the pore solution, thus

Table 1
Summary of findings on lithium salts in suppressing ASR expansion

Research work	Testing method	Reactive aggregate	w/c ratio by mass	Total Na_2Oe %, by mass	Lithium salt (s) studied	Minimum lithium to alkali molar ratio
McCoy and Caldwell [1]	ASTM C 227	Pyrex glass		1.15	LiCl, LiF, Li_2CO_3, Li_2SiO3, Li_2SO_4, $LiNO_3$	0.74
Lawrence and Vivian [2]	ASTM C 227	Opaline rock	0.5	0.5–1.5	LiOH	
Sakaguchi et al. [3]	ASTM C 227	Pyrex glass	0.55	0.8–1.0	$LiOH \cdot H_2O$, $LiNO_2$, Li_2CO_3	0.9
		Andesite sand		1.2	$LiOH \cdot H_2O$	0.9
Stark [4]	ASTM C 227	Andesite			LiF, Li_2CO_3	0.67 (LiF), 0.92 (Li_2CO_3),
Stark et al. [5]	ASTM C P 214	Rhyolite Granite gneiss			$LiOH \cdot H_2O$	0.75–1.0 (LiOH)
Diamond and Ong [6]	ASTM C 227	Cristobalite	0.485	1	LiOH	1.2 (Cristobalite,
		Beltane opal	0.485	1	LiOH	more for opal)
Durand [9]	ASTM C 1293	Sudbury Potsdam Sherbrooke	0.405	0.88–1.25	$LiOH \cdot H_2O$, LiF, Li_2CO_3 $LiNO_3$	With Sudbury: 0.72 for $LiNO_3$ 0.82 for other three
Lane [19,20]	ASTM C 1260 ASTM C 1293	Pyrex glass Quartz	0.45	0.75–1.25	$LiOH \cdot H_2O$, $LiNO_3$	0.925 for $LiNO_3$
Lumley [8]	ASTM C 1293	Cristobalite	0.5	0.86–1.13	$LiOH \cdot H_2O$, LiF, Li_2CO_3	0.62
Thomas et al. [21]	ASTM C 1293	UK aggregates			$LiOH \cdot H_2O$, $LiNO_3$	0.74 for $LiNO_3$ 0.85 for $LiOH \cdot H_2O$
Collins et al. [11]	ASTM C 227	Borosilicate glass	0.37	1	LiOH, LiCl, $LiNO_3$	0.6 for LiOH, 0.9 for LiCl 0.8 for $LiNO_3$
Kawamura et al. [10]	ASTM C 227	Calcined flint	0.55	1.12	LiOH, Li_2CO_3	0.75 M
Berra et al. [12]	ASTM C 1293	Siliceous aggregate	0.44	2.3–9 kg/m3	$LiNO_3$, Li_2CO_3	
Ohama et al. [13]	Autoclave	Opaline amorphous silica	0.63–0.78	2	$LiOH \cdot H_2O$, LiF, Li_2CO_3	0.5% wt for LiF 0.7% wt for $LiOH \cdot H_2O$
Bian et al. [14]	Autoclave	Andesite sand	0.5	0.5–3.5	LiF, LiCl, LiBr. $LiNO_3$, LiOH Li_2SO_4, Li_2CO_3, LiH_2PO_4,	0.8
Mo et al. [16]	Autoclave	Microcrystalline Quartz		1.5–3	$LiOH \cdot H_2O$	≥0.3 for Na_2Oe≤2.5% ≥0.6 for Na_2Oe=3%

there is no pessimum effect. Its benign effect on concrete properties, its neutrality, and high solubility all provide it with a unique response in controlling ASR expansion.

(7) Although autoclaving offers a method for accelerating ASR and decreasing the duration of testing, the results from autoclave expansion tests involving lithium are not directly comparable to those from studies at lower temperatures and pressures.

3. Mechanism of lithium salts on ASR

Although lithium-bearing admixtures have shown to be an effective method to mitigate the expansion due to ASR, the mechanism or mechanisms by which lithium salts inhibit expansion has not been unequivocally established. A better understanding of the mechanism(s) will help significantly in identifying the effectiveness of a particular lithium salt and its dosage and predicting the duration of its control on ASR expansion. Several existing mechanisms have been proposed. Some are focused on the nature of the reaction products produced, some are focused on silica dissolution, or ASR gel repolymerization, while others are based on colloid and surface chemistry theory. Details of the proposed mechanisms are discussed next.

3.1. Effects of lithium on alkali–silica-reaction products

The ability of lithium to change the nature of the reaction products was first proposed by Lawrence and Vivian [2] and is now the most commonly recognized mechanism regarding the suppressive effect of lithium compounds. Lawrence and Vivian [2] studied the reactions of different alkali solutions, including NaOH, KOH, LiOH, and a mixture of those three alkalis, with finely divided, precipitated silica. A gelatin product was observed in all of the reaction systems, but the gel product in the presence of lithium ion was different from that when only sodium or potassium was present. This suggests that the lithium–silica complex is less soluble and more stable and thus is capable of protecting silica from further attack by other alkalis.

A similar ASR reaction product was found by Sakaguchi et al. [3] by observing the interface between Pyrex glass and hardened cement paste by means of energy dispersive X-ray spectrometry. No visible ASR gel at the interface was found;

instead, a kind of lithium silicate, which hardly swells and dissolves, was produced at the surface of aggregates. This lithium–alkali (and possibly calcium) silicate must contain a minimum proportion of lithium to be nonexpansive because of the pessimum effect of lithium dosages on controlling ASR expansion as observed by Stark [4].

More recently, Collins et al. [24] observed the formation of a crystalline product at the paste/aggregate interface as early as 1 day of age by laser scanning confocal microscopy (LSCM). Mo et al. [16] also reported significant crystalline products in the lithium-bearing specimens by SEM examination. The EDS analysis showed that this crystalline product contained large amounts of Ca and Si but less K than that in a typical ASR gel. Diamond and Ong [6] also revealed from the pore solution responses and the ultraviolet (UV) observation that LiOH added to mortars containing reactive aggregates in the virtual absence of other alkalis produces an ASR reaction product, which appears to be nonexpansive; the length change measurements on mortar bars confirmed that this lithium gel in the near absence of sodium and potassium does not induce expansion. They also found that when lithium is present with other alkalis, each at about 0.25% of the mass of the cement, the ASR gel contained all of the ions and was less expansive than the pure sodium or potassium gel alone. Hence, it is suggested that, at a sufficiently high lithium dosage, the formation of ASR gel might be entirely avoided.

Kawamura and Fuwa's SEM–EDS results [10] revealed that there are typical massive ASR gels existing in the mortars with lower lithium dosages, which showed great expansions. However, no gel was observed in mortars with greater than the threshold dosage level of a lithium salt. The EDS results also showed that the average CaO/SiO_2 ratio of the gel decreased with increasing amounts of lithium salts added, and that the composition of ASR gels became homogeneous at a high dosage level. However, there was no direct correlation between expansion of mortar bars and the CaO/SiO_2 ratio in ASR gels. Other workers have demonstrated that a minimum level of CaO is required to produce a gel capable of disrupting concrete [25].

Consequently, there is another question derived from this theory: in the presence of sodium and potassium, is the reaction between lithium and silica more favorable than the reaction between sodium, potassium, and silica? Lawrence and Vivian's study [2] showed that increasing LiOH concentrations up to 2N LiOH equivalent in 2N NaOH solution resulted in a greatly decreased tendency for NaOH to react with silica gels. Sakaguchi et al's work [3] on expressed pore solution analyses also demonstrated that the lithium–silica reaction is more favorable than the sodium–silica or potassium–silica reaction.

However, Chatterji [26] argued that when lithium is present with sodium and potassium, the alkalis would compete for adsorption at negatively charged sites on the silicate surface. Since adsorption affinity increases with ionic radius, the sodium adsorption will be preferential to lithium adsorption based on the data of Table 2. But Iler [27] has already postulated that, of the alkali metal cations, lithium is unique because it stabilizes colloids and prevents gelling, so the highly hydrated lithium ions are not adsorbed as near to the silicate surface as a cation with smaller hydrated radius, such as sodium or potassium. Further research on this topic is necessary.

3.2. Effects of lithium on silica dissolution

Some researchers suggest that the suppressive effect of lithium on ASR expansion may be attributed to the decrease in silica dissolution, thereby lessening the rate of product formation and eventually decreasing the potential for expansion. This is based on the findings by Lawrence and Vivian [2] and Wijnen et al. [29]; that is, among LiOH, NaOH, and KOH, the rate of silica dissolution is the slowest for LiOH and fastest for KOH.

Recently, Collins et al. [11] and Kurtis et al. [30,31] conducted studies to examine the reaction of silica gel in simulated pore solutions with and without lithium salts. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to quantitively measure the ion concentrations of silicon, calcium, lithium, and sodium in the filtrates obtained from the slurry samples. In the slurries prepared with LiCl and $LiNO_3$, the dissolved Si concentration decreased with increasing lithium dosages, again suggesting that lithium could suppress silica dissolution. However, in the same work with LiOH, in contrast to the slurries with LiCl and $LiNO_3$, the slurry with LiOH showed an increase in silica dissolution with increasing lithium dosage, implying that LiOH actually accelerates silica dissolution. This increase in silica dissolution by LiOH was contrary to other researchers' results [2,29]. However, from mortar bar expansion tests, this increase in silica dissolution did not translate to an increase in mortar bar expansion tests.

It seems that different lithium salts yield different influences on silica dissolution, thus it is hard to say that decreasing silica dissolution is the only reason for the suppressive effects of all lithium salts on ASR expansion.

3.3. ASR gel repolymerizaiton

This theory was proposed by Kurtis et al. [30,31]. From the above work on $LiNO_3$, LiCl, and LiOH, they suggested that the suppressive effect of lithium on ASR expansion should not largely depend on the quantity of dissolved silica but should be attributed to the limitation of ASR gel repolymerization. This can be supported from their investigations of ASR gel in simulated pore solutions with and without lithium salts, in which transmission soft X-ray microscopy was employed to image the changes in gel microstructure. The ASR gel obtained from an ASR-affected structure was exposed to NaOH alone and NaOH with LiCl solutions. In the presence of NaOH solution alone, the ASR gel is partially dissolved and repolymerized as a potentially expansive gel. While in the presence of LiCl, a significant dissolution of the original gel particles was observed, but the repolymerization into an expansive gel was decreased as compared to the reaction of the ASR gel in NaOH solution alone. They then proposed that lithium might limit the repolymerization of ASR gel, which can effectively reduce the potential for expansion.

It is noticeable that, in this theory, before adding lithium salts, the alkali–silica reaction has already occurred, and substantial ASR gel exists. It may be difficult to apply this theory to new concrete because according to the previous findings [10], no ASR gel is formed when the lithium dosage is above a certain level. It should also be noted that the observations are based on one particular lithium salt. The situation may be different for other lithium salts. However, this theory may offer an explanation regarding the suppressive effect of lithium on existing concrete structures damaged by ASR expansion.

3.4. Colloid and surface chemistry effects

Some researchers have tried to explain the suppressive effect of lithium on ASR expansion by using the Gouy–Chapman electrical double layer (EDL) theory. This theory was first used to explain the expansion of ASR gel by Prezzi et al. [32], and later was extended to describe the effect of chemical additives, including lithium salts, on inhibiting ASR expansion [33]. According to the EDL theory, an exchange of electrical charges occurs whenever two dissimilar materials are brought in contact, the extent of this exchange depends on the subdivision of the materials and their nature. The ASR gel is assumed to be negatively charged. Due to the charged states, the ASR gel is surrounded by positively charged electrical double layers. These double layers not only determine the type and concentration of the positive ions in them but also affect the ion transport to the ASR gel. The thickness of these double layers can be calculated from the ionic strength and hydrated radius of the cations. Theoretically, cations with larger valence and smaller hydrated ionic radii will result in a thinner double layer, consequently causing a smaller gel expansion. As shown in Table 2, at the same valence level, the hydrated ionic radius of Li^+ ion is larger than those of Na^+ and K^+ ions, which means that lithium should produce greater expansion as compared to sodium and potassium. This is contradictory to the results generally observed in expansion testing. Hence, the EDL theory cannot satisfactorily explain the suppressive effect of lithium in ASR expansion.

Table 2
Chemical information for Li^+, Na^+, and K^+ ions [28]

Ions	Valence	Ionic radius (nm)	Hydrated ionic radius (nm)
Li	1	0.060	0.34
Na	1	0.095	0.276
K	1	0.133	0.232

Other researchers [15] proposed that the suppressive effectiveness of cations depends on the ionic surface charge density (σ). The larger the value of σ of a cation, the greater its electron affinity and thus the stronger the bonding between the cation and anions in the gels, resulting in a more contracted and densified structure, which exhibits less tendency to expand. Therefore, from the information in Table 2, the effectiveness of cations on inhibiting ASR expansion should follow the order: Li>K>Na, which coincides with the expansion testing results. Kurtis et al. [30,31] also reasoned that the suppressive effect of lithium on ASR expansion is attributed to the reduction in surface charge density of the alkali–silicate gel, which may occur in the presence of lithium.

In addition to the above studies, other investigators [34–36] have studied the mechanism of lithium inhibiting ASR expansion from sol–gel science principles. The silico–alkaline sols and gels were synthesized from silica gel, alkali oxide, and water in the presence and absence of calcium. ^{29}Si-NMR spectroscopy and small-angle X-ray scattering techniques were used to study the silicate and gel formation. It appears that lithium enhances the formation of large silicate species (cyclic molecules and colloidal particles) [34,36]. The gelation time of gels formed by destabilization of lithium silicate solutions or potassium silicate solutions is longer than those obtained from sodium silicate solutions at a constant calcium concentration [35]. Unfortunately, there is no further report on the sol–gel transition process or on the connection with expansion tests.

Recently, Thomas [37] suggested that attention should be paid to the role of calcium in the suppressive effects of lithium on ASR-expansion. In a recent study, on mortars containing reactive flint sand and lithium ([Li]/[Na+K]=0.74), the reaction product was observed to contain K, Na, and Si but with little or no calcium. It was hypothesized that lithium might form a nonswelling lithium–alkali–silica complex instead of the typical swelling ASR gel composed of calcium–alkali–silica complex. However, this is contrary to the EDL theory, which predicts that an ASR gel containing larger concentrations of cations with larger valences will exhibit less expansion. That is, a gel with higher ratio of calcium to monovalent cations (Na^+, K^+, and Li^+) should result in less expansion. Further study is necessary to elucidate the role of calcium.

3.5. Concluding remarks

From the above discussion, it can be said that all of the proposed mechanisms are reasonable under certain conditions, but there are some findings from the previous work on the influences of lithium on ASR that no mechanism totally explains. For example, why lithium salts are more effective with highly reactive aggregates than with slowly reactive aggregates and what is the role of calcium. However, there are some general agreements as follows:

(1) Lithium salts do react with silica to form a lithium-containing gel product in the absence of other alkalis, but this gel does not produce any expansion in mortar bar or concrete tests;
(2) When the lithium is present with other alkalis, the form of reaction product, whether crystalline or gelatinous, significantly depends on the lithium dosage and may also vary with the location and time.

In order to gain a better insight into the mechanism(s) by which lithium salts inhibit the ASR-induced expansion, the following areas are identified for further research:

(1) The composition of the lithium-containing reaction product.There is no report on the composition of this lithium–alkali silicate complex, mainly because there is no suitable analysis technique available. SEM–EDS is a very good quantitative technique to study the ASR gel composition without lithium addition. As lithium is too light for SEM–EDS, a suitable quantitative technique for lithium analysis is required for examining the ASR reaction product in the presence of lithium.
(2) The transition dosage of lithium salts, at which lithium–alkali silicate gels change their expansive behaviors.Based on the above discussion, it seems the expansive behavior of ASR reaction product significantly depends on the lithium dosage. Therefore, there must be a transition dosage, at which a slightly lower or greater change will change the expansive behavior of the reaction product. Then the questions arise: which dosage is the turning point? Why and what happened to the system at this dosage?
(3) The relations between silica dissolution and ASR expansion.The findings on the influence of lithium salts on silica dissolution are contradictory. Why do some lithium salts decrease the silica dissolution, while some have an opposite effect? Why does not this increase in silica dissolution result in an increase in ASR expansion?
(4) The priority of the lithium–silica reaction to sodium or potassium–silica reaction. When lithium is present with other alkalis, is the lithium–silica reaction more favorable than other alkali-silica reaction? Or is the formation of a nonexpansive lithium-containing product favored over the formation of a more expansive product containing relatively greater concentrations of the alkalis, sodium, and potassium? Further work needs to be done both on the experimental and theoretical aspects.
(5) The different effectiveness of lithium on different reactive aggregates.Although it is found that lithium salts are more effective with highly reactive aggregates than with slowly reactive aggregates, there is no explanation for why this should be so. A thorough study is necessary.
(6) Role of calcium.The role of calcium in the suppressive effects of lithium on ASR expansion requires further study.
(7) Kinetic studies of the reaction process.All the alkali ions are involved in the reactions with reactive silica and in binding by C–S–H. In such a complicated system, it is very difficult to conduct kinetic studies for each reaction. But if this type of study is carried out, it should provide a very important insight as to how lithium compounds suppress ASR.

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