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# Chemical approaches to prevent alkali-silica reaction in concrete – A review

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A B S T R A C T

This study synthesizes the use of chemicals to prevent one of common concrete durability problems, alkali-silica reaction (ASR), and can help researchers (i) identify widely used potential chemicals and evaluate these chemical solutions to prevent ASR with proper understanding of mechanisms, and (ii) to identify the research gaps in order to develop guidelines and implementation plan on the use of these chemicals for future research.



## 1. Introduction

The occurrences of the concrete durability problem, alkali-silica reaction (ASR), have been observed over the years (Stanton, 2008; Thomas et al., 2013; Liu & Mukhopadhyay 2014). ASR has been well known as a chemical reaction between alkali hydroxides in pore solution and the reactive form of silica in aggregates. The product of this reaction is named ASR gel. In presence of sufficient moisture (e.g., 80% RH), gel absorbs moisture and swells leading to tensile stresses in concrete and eventually resulting in concrete cracks (Mukhopadhyay et al., 2009; Mukhopadhyay & Liu, 2014a). The use of fly ash (primarily class F ash) is the common effective remedial practice to prevent this concrete durability problem (Latifee, 2016). However, there is a major concern that fly ash with required quality and quantity will not be available to prevent ASR in the long term as both fly ash quality and quantity is changing due to the controls imposed by the new emission standards (e.g., the change of coal composition along with applying control measures by thermal power plants to reduce environmental pollution) (Shahzad Baig & Yousaf, 2017). Therefore, identifying chemicals alternative to fly ash through detailed and effective research is highly needed in order to address the above concern and ensure long lasting durable concrete in the future. The primary goals of this study are to (i) summarize the use of chemicals (alternative to supplementary cementing materials) to prevent ASR, and (ii) identify the research gaps on the use of these chemicals preventing ASR for future investigations.

## 2. Summary

Based on the literature on the use of chemicals to prevent ASR, the relevant findings on the mechanisms of prevention and effects on concrete properties due to the incorporation of these chemicals as well as their commercial availabilities and guidelines to use are discussed below.

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## *2.1 Use of Chemicals to Prevent ASR*

There are several approaches of preventing ASR in concrete, such as avoidance of reactive aggregates, the use of low alkalinity cement (i.e., < 0.6% $Na_2O_e$), the use of pozzolanic materials, the use of air entrainment, the use of impermeable materials to seal the hardened concrete and coat aggregates (Mukhopadhyay & Liu, 2014b; Turk et al., 2017).

**Table 1.** Dosage, effects and mechanisms of different chemical admixtures to prevent ASR

| Chemicals | Observations on dosage and effects | Mechanisms |
|---|---|---|
| **Lithium salt** | LiOH:<br>[Li]/[Na] = 0.67-1<br>(Sakaguchi, 1989)<br>LiOH ≥ 0.7% by wt. of cement (Ohama et al., 1989, 1992)<br>[Li]/[Na+K] > 1.2<br>(Diamond & Ong, 1992)<br>[Li]/[Na+K] ≥ 0.75-1<br>(Stark et al., 1993; Stark 1993)<br>[Li]/[Na+K] ≥ 0.62<br>(Lumley, 1997)<br>[Li]/[Na+K] > 0.85<br>(Thomas & Stokes, 1999; Durand, 2000)<br>[Li]/[Na+K] ≥ 0.6<br>(Collins et al., 2004)<br>[Li]/[Na+K] = 1 to 1.11<br>(Fournier et al., 2003) | • Alternate the gel composition<br>• Reduce silica dissolution<br>• Decrease re-polymerization<br>• Reduce the repulsive forces within product<br>• Form dense products protecting reactive minerals from further reaction (Leemann et al. 2015)<br><br>The requirements of a suitable Li-based admixture should be (i) reacting to produce an insoluble silicate, (ii) no interference with or modification with the cement hydration, (iii) no participation in the ASR formation to form expansive materials, and (iv) providing small, high-valence cations. |
| | $LiNO_3$:<br>[Li]/[Na] = 0.67-1<br>(Sakaguchi, 1989)<br>[Li]/[Na+K] > 0.7<br>(Thomas & Stokes, 1999)<br>[Li]/[Na+K] ≥ 0.92<br>(Stark, et al., 1993; Stark, 1993)<br>[Li]/[Na+K] > 0.72<br>(Durand 2000)<br>[Li]/[Na+K] ≥ 0.8<br>(Collins et al. 2004)<br>[Li]/[Na+K] = 0.74 to 0.93 (Fournier et al., 2003)<br>[Li]/[Na+K] ≥ 0.8<br>(Qinghan et al. 1995)<br>[Li]/[Na+K] = 0.56 to 1.11 (Tremblay et al., 2004) | |
| | $Li_2CO_3$ (Note 1): more effective to decrease ASR expansion than LiOH and $LiNO_3$<br>(Vivian, 1947; Sakaguchi, 1989)<br>[Li]/[Na] = 0.67-1<br>(Sakaguchi 1989)<br>$Li_2CO_3$ = 1.0% by wt. of cement (Ohama et al,. 1989)<br>[Li]/[Na+K] ≥ 0.62<br>(Lumley 1997)<br>[Li]/[Na+K] > 0.85<br>(Durand 2000)<br>[Li]/[Na+K] ≥ 0.74<br>(McCoy & Caldwell, 1951) | |
| | LiF:<br>LiF ≥ 0.5% by wt. of cement (Ohama et al., 1989, 1992)<br>[Li]/[Na+K] ≥ 0.6<br>(Stark et al. 1993, Stark 1993)<br>[Li]/[Na+K] ≥ 0.62<br>(Lumley 1997)<br>[Li]/[Na+K] > 0.85<br>(Durand 2000)<br>[Li]/[Na+K] ≥ 0.74<br>(McCoy & Caldwell, 1951) | |
| | LiCl:<br>[Li]/[Na+K] ≥ 0.9<br>(Collins et al. 2004) | |
| **Use of air-entraining admixtures (AEA)** | A 3.6% AEA can cause a 60% reduction in ASR expansion<br>(Ohama et al. 1992).<br>A 4% AEA concrete could reduce ASR expansion by 40%<br>(Ratinov & Rosenberg, 1989). | The entrained air bubbles can accommodate the pressures developed by the formed ASR products and thus the stress in concrete is low<br>(Gudmundsson & Asgeirsson, 1983; Nakajima, et al., 1992; Gillott & Wang, 1993). |
| **Hydration controller** | ASR expansion is lower in the present of retarders than air entrainments<br>(Hobbs, 1988; Ekolu et al., 2007). | • Change the availability of alkali and lime<br>• Change the calcium-silica phase<br>• Delay the rigid-phase formation in the cement paste |
| **Silanes, siloxanes, and silicofluorides** | ASR expansion is lower in the present of siloxanes and silanes than silicoflurides. Siloxanes are more effective than lithium compounds in preventing ASR expansion<br>(Nakajima et al,. 1992; Saucier & Neeley 1993). | Water repellence |
| **Phosphate** | ASR-reactive aggregate with phosphate treatment for one minute shows no expansion at 28 days (Diamond & Ong, 1992). | • Interfere with the silica dissolution and the ASR gel formation<br>• Reduce the osmotic potential and the expansive pressure in the ASR gel |

Note 1: The use of $Li_2CO_3$ induces the problems of (i) acceleration of both initial and final setting times at dosages > 1% by wt. of cement and (ii) $Li_2CO_3$ decreases compressive strength at all levels of dosages.

Although, lowering water-cement ratio (w/c) results reduction in porosity and mobility of alkali ions, but it increases the alkali concentration in pore solution (Chen & Brouwers, 2010) which enhances ASR potential. Chemical admixtures to control ASR were introduced in the 1990s (Stark, 1993). It has shown that lithium nitrate ($LiNO_3$), lithium carbonate ($Li_2CO_3$), lithium hydroxide (LiOH), lithium aluminum silicate ($LiAlSi_2O_6$), and barium salts suppress ASR in laboratory tests (Sakaguchi, 1989; Thomas & Stokes, 1999; Zapała-Sławeta & Owsiak, 2017). The effects of chemicals retarding or inhibiting the ASR reaction are summarized in Table 1. Table 2 lists the use of commercially available ASR chemicals, and the current test methods for assessing ASR chemical dosages (particularly lithium salt) are summarized in Table 3.

**Table 2.** List of commercially available ASR chemicals

| Product | Suggested dosage | Compatibility | Note |
|---|---|---|---|
| **$LiNO_3$** | 4.6 liters (L) for every kilogram (kg) of $Na_2O_e$ by the cement; subtract 0.85 L of water for each liter of $LiNO_3$ added (SiKa 2018 (accessed 03.14.18)) | • SCMs<br>• Other chemical admixtures | • Add at the end of the batching cycle<br>• A minor set acceleration and small amount of water reduction<br>• Determine dosage according to CRD-C662 (Aggregates 2010) in Table 3 |
| | (Amount of cement (kg/m$^3$) x $Na_2O_e$ x 1.62)/100 in L/m$^3$; subtract 0.84 L of water for each liter of $LiNO_3$ added (Grace 2018 (accessed 03.14.18)) | • SCMs<br>• Other chemical admixtures | • Add at the end of the batching cycle<br>• May accelerate the initial setting time<br>• No effects on concrete hardened properties<br>• Determine dosage according to CRD-C662 and ASTM C1293 (ASTM 2015) |
| **Lithium-based, ASTM C494/494M Type S (ASTM 2016)** | (Amount of cement (kg/m$^3$) x $Na_2O_e$ x 1.62)/100 in L/m$^3$; subtract 0.8 L of water for each liter of inhibitors added (BASF 2018 (accessed 03.14.18)) | • SCMs<br>• Other chemical admixtures | • Accelerate the initial setting time by 5-20%<br>• No effects on concrete hardened properties<br>• Not require low-alkali cement |

**Table 3.** Summary of the current test methods for assessing ASR chemical dosages

| Method | Test condition | Performance evaluation |
|---|---|---|
| **Storks et al. (Stokes et al. 2003) (mortar bar and concrete prism)** | 0-100% (depends on the alkali aggregate reactivity) of the recommended dose of 4.6 L of $LiNO_3$ for each kg of $Na_2O_e$ in the mortar or concrete<br>[Li]/[Na+K] = 0.74 in mixing water<br>[Li]/[Na] = 0.74 in soak solution | ASTM C1260 (ASTM 2014) @28-days<br>ASTM C1293@2-year |
| **Folliard et al. (Folliard, Thomas et al. 2006) (concrete prism)** | [Li]/[Na+K] = 0.51 - 0.8 in mixing water | ASTM C1293@2-year |
| **TxDOT (TxDOT 2009) (mortar bar)** | [Li]/[Na+K] = 0.74 in mixing water<br>[Li]/[Na] = 0.148 in soak solution | • ASTM C1260@28-day<br>• If ((E2-E1)/E1) ≥ 0.1, use ASTM C1293 to determine Li dosage<br>E1: 28-day expansion of control mix<br>E2: 28-day expansion of the Li mix |
| **CRD-C662 (Aggregates 2010) (mortar bar)** | Li dose% x 0.0493 wt. of cement in mixing water<br>Li dose% x 71 ml of $LiNO_3$ in 1N NaOH in soak solution | ASTM C1260@30-day |
| **Wingard et al. (Wingard et al. 2012) (mortar bar)** | [Li]/[Na] = 0.74 in mixing water<br>[Li]/[Na] = 0.37 in soak solution | ASTM C1567 (ASTM 2013) @14-day |

## 3. Discussion

Based on Tables 1 and 2, the main observations on the effects of ASR inhibitors due to incorporation of chemical admixtures are concluded.

- Limited research on the use of AEA + retarder, silanes / siloxanes / silicofluorides and phosphates to control ASR. Although research has shown some promises but these are not commercially available products.
- Only the lithium salts directly control ASR. $LiNO_3$ is a good candidate for use as an effective ASR inhibitor as (i) it is the most common commercially available lithium compound, (ii)

need a low dosage (i.e., lower molar ratio of [Li]/[Na+K]) to suppress ASR, (iii) the properties are not altered significantly by the use of $LiNO_3$, (iv) it is compatible with other chemical admixtures, and (v) it does not raise the pH value of pore solution (Zapała-Sławeta & Owsiak, 2017).

*3.1 Current test methods commonly used for accessing $LiNO_3$ dosages*

Based on Table 3, an expansion criterion to evaluate the ASR performance has been assigned in the current test methods, such as concrete prism test (CPT) and accelerated mortar bar tests (AMBT). However, different studies have indicated that (i) the use of current ASR test methods (AMBT and CPT) have limitations and drawbacks (e.g., alkali leaching, aggregate crushing, long test duration, etc.) (Swamy, 2002; Marks, 1996; Mukhopadhyay et al., 2009; Liu & Mukhopadhyay, 2014a,b) and (ii) a single value of expansion from AMBT and CPT is not an appropriate criteria to assess ASR potential (Shon, 2008). Therefore, the demand for developing rapid and reliable ASR test methods is high.

Apart from the test methods mentioned in Table 3, a chemical test (Liu and Mukhopadhyay 2014a, AASHTO 2017) and a concrete cylinder test (Liu & Mukhopadhyay, 2015) to determine the ASR reactivity and threshold alkalinity (THA) of aggregate followed by determination of concrete alkali loading and mix design validation were developed. Since each aggregate has a unique value of THA, concrete alkali loading is a function of aggregate reactivity and it's THA. The current practice which is to assign a common relatively lower level of alkali loading (e.g., 2.1-2.4 $kg/m^3$) for all concrete mixes irrespective of type of applications such as an example of one size fits for all doesn't necessarily ensure avoiding ASR all the time. As the methods have the capability to determine case specific concrete alkali loading and validate the chemical dosages, the determination of optimum dosage of lithium shall be more accurate than the current approach. As concrete alkali loading varies with aggregate reactivity, the optimum chemical dosage shall also vary accordingly in order to control ASR. Further research shall use this as the basis to develop a powerful approach to determine optimum chemical dosage based on sound scientific concept.

## 4. Recommendations for Future Research

This study reviews and summarizes a wide range of chemicals to solve the concrete durability problem ASR. The effort to identify chemicals compounds both at the national and international level shall continue and research in the following aspects shall be investigated.

- It has been found that the amount of Li-compound addition in soak solution varies with the test methods commonly used. The lithium in soak solution can serve as a reservoir, and the specimen may experience overestimation of lithium effects than the dosage provided in the mix. In order to determine the optimum dosage of lithium to control ASR, it's important to understand the mechanism behind it by studying the microstructural changes by suitable micro-analytical techniques.
- Determination of optimum dosage of commercially available chemicals listed in Table 2 as well as other products listed in Table 1 - According to Table 3, the optimum dosage of commercially available ASR chemicals is determined by AMBT (e.g., ATM C1260) and/or CPT (e.g., ASTM C1293). AMBT is rapid but reliability is questionable (it underestimates). CPT (e.g., ASTM C1293) is reliable but time consuming. The development of a rapid but reliable test to determine the optimum dosage of lithium compounds is needed. The current practice in assigning a lowest possible common concrete alkali loading in order to control ASR in new concrete is a one size fits all approach which doesn't provide a unique solution. Concrete threshold alkali loading (CTAL) is a function of aggregate reactivity and its THA. There is no such procedure currently available to determine CTAL. The need of a procedure to determine CTAL is very high, as determining optimum dosage of lithium based on known cases of specific CTAL shall be

economical and effective. Assigning a high common lithium dosage for all may not be needed for some cases where a minimum dosage (e.g., 75%) is sufficient.

- Development of practice to add the chemicals in a batch plant as well as time in a mixing sequence - According to Table 2, ASR chemicals are added at the end of the batching cycle. However, a practical way to add those chemicals in a batch plant and a mixing sequence is not clear mentioned. The practice to add these chemicals needs to be developed.
- Measurement of fresh/harden properties in order to detect any changes of the fresh/harden concrete properties due to any kind of cement-admixes incompatibility - Based on the literatures searched in this study, different admixtures do not interfere with each other's action in a negative way; however, cement-admixes interaction may sometimes lead to incompatibilities which affect the fresh/harden properties.
- Development of approach and understanding of control mechanisms of combined use of chemicals to obtain the benefits of controlling ASR - In Table 1, each individual chemicals was applied by different researchers to control ASR; however, an approach to combine different chemicals and a clear understanding of controlling mechanisms based on agreed upon facts are yet to be established for some compounds (e.g., AEA + retarder, silanes / siloxanes / silicofluorides and phosphates). Therefore, approach development and a clear understanding of mechanisms are highly needed in order to ensure an effective utilization of a product.
- Development of guidelines on proper utilization of chemicals to improve concrete durability including, but not limited to ASR - guidelines shall aid engineers in making a cost-based decision on the use of ASR chemical admixtures considering factors related to materials, construction, fresh and hardened concrete properties, and ensuring effective durability performance. The guidelines shall include, but not limited to (i) developing best mix design practices - the permissible and optimum levels of replacement of potential chemicals to obtain optimum ASR-resistant performance, (ii) selecting effective chemicals, individually or combined, to control ASR, (iii) selecting the optimum dosage of the selected potential chemicals to control ASR, (iv) the use of effective and innovative approach and methods to evaluate performance of the potential chemicals - overcome the drawbacks and limitations of current modified mortar bar and concrete prism tests, (v) guidelines to check the effect on fresh and hardened concrete properties and planning to avoid those issues due to cement-admixes incompatibility, (vi) best construction practices to ensure successful project using concrete made of appropriate chemicals to control ASR, (vii) a cost and benefits analysis to determine if the use of ASR chemicals is cost effective, and (viii) specification development - the guidelines and specification for use of ASR chemicals need to be developed and incorporated in the construction specifications in different transportation agencies.

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