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Dual effectiveness of lithium salt in controlling both delayed ettringite formation and ASR in concretes

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Abstract

The influence of lithium nitrate on expansions due to delayed ettringite formation (DEF) and alkali-silica reaction (ASR) has been investigated. Effects of the lithium salt were examined in heat-cured mortars and concretes containing one or both damage mechanisms. The mortars and concretes made using reactive and/or non-reactive aggregates were subjected to heat treatment consisting of a hydration delay period of 4 h at 23 °C followed by steam-curing at 95 °C and then stored in limewater. Results showed that the lithium salt admixture was able to reduce the occurrence of deleterious expansion due to delayed ettringite formation in addition to controlling alkali-silica reaction in cementitious systems containing one or both mechanisms. In concretes made using non-reactive limestone aggregates, incorporation of lithium nitrate in a proportion of 0.74 M ratio of Li to (Na+K) was found to control delayed ettringite formation during the one-year period of this study.

By analyzing the leaching properties of lithium and other alkalis from mortars during storage, it was found that a substantial amount of lithium was retained in the cementitious system in a slightly soluble form, and is expected to be responsible for reducing DEF.

Keywords: Delayed ettringite formation; Alkali-silica reaction; Lithium; Heat treatment; Alkalis

1. Introduction

1.1. Coexistence of alkali-silica reaction and delayed ettringite formation

The coexistence of ASR and DEF mechanisms has been controversial both in practice and research especially in the earlier days when the DEF phenomenon was not well understood. To date the two coexisting damage mechanisms remain much of a problem due to extreme difficulty in isolating and defining the roles played by each of the mechanisms in concrete deterioration. A case in point is the failure of 56 out of 59 prestressed concrete box beams belonging to the Texas Department of Transportation (TXDOT) where heat treatment was not used but the beams were subject to extremely warm, ambient temperatures. TXDOT blamed DEF for the damage while the cement supplier diagnosed ASR as the main source of damage with ettringite playing only a secondary role [1].

Heat-cured concrete railway ties have been reportedly vulnerable to damage involving the presence of both ASR and DEF. Conflicting conclusions were reached in an investigation of damaged concrete railway sleepers in Finland when Tepponen and Ericksson [2] reportedly found that DEF was responsible for the deterioration. About 10 years later, Shayan and Quick [3] examined the same damaged prestressed precast railway sleepers and arrived at the conclusion that alkali-aggregate reaction could have been the primary cause of damage and that DEF could have occurred at the last stages of deterioration crystallizing in pre-existing cracks rather than being the cause of cracking. A similar situation occurred with concrete railway sleepers in Australia at about the same time [4]. Cases of deterioration involving concrete railway ties have been reported in several countries including, Germany [5,6], South Africa [7] and United States of America [8] among others.

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As demonstrated by cases mentioned above, determining the roles played by ASR and DEF in concrete deterioration has been one of the most controversial aspects of ASR and DEF coexistence in concrete. Pettifer and Nixon [9] suggested that the occurrence of sulfate attack promotes ASR by increasing alkalinity of the pore solution. This of course assumes that DEF occurs at least earlier than or simultaneously with ASR. However, later studies appear to suggest that ASR may occur first partly enhanced by heat treatment followed by crystallization of ettringite in cracks already formed [10]. It has also been shown that ettringite formation is hindered by high alkalinity, implying that the consumption of pore solution alkalis during ASR will have a chemical effect of inducing ettringite crystallization therefore promoting DEF formation [11]. Shayan and Ivanusec [12] concluded that where ASR and DEF coexist, ASR plays the main role of inducing cracks.

1.2. Use of lithium salts to control alkali-silica reaction

Lithium salts are now well recognized as effective chemical compounds for controlling ASR in concretes. Their use for this purpose was first reported by McCoy and Caldwell [14]. Since then, lithium use has been widely investigated for research and practical field applications. Presently in North America, lithium in forms of lithium nitrate ($LiNO_3$) and lithium hydroxide (LiOH), is commercially manufactured for use in repair of ASR damaged concretes and infrastructure systems. It has been used in field repair applications including dams, bridges, buildings, pavements and related structures [13]. McCoy and Caldwell [14] also found that a 0.74 M ratio of Li: (Na+K) was necessary for suppression of ASR. This has stood the test of time and still remains the acceptable dosage in practice when using $LiNO_3$.

Investigations in the literature on the mechanism of ASR suppression by lithium salts is worth a closer look as it could also give clues of their effect on delayed ettringite formation. Unfortunately, the interaction of lithium with other ions in cementitious systems has not been fully understood and remains a subject of investigation. It has been suggested [15,16,13] that in the presence of lithium salts, a less soluble lithium silicate complex product is formed and that lithium ions partially replace Na^+ and K^+ in ASR gel. This is supported by the findings of Sakaguchi et al. [17] who in their study showed that there was a favourable reaction between silica and lithium hydroxide over silica and the hydroxides of sodium or potassium. By monitoring the concentration of alkalis in pore solution, Sakaguchi et al. [17] found that in the absence of lithium addivites, Na^+ and K^+ decreased during ASR reaction but upon incorporation of lithium additives, the concentration of Na^+ and K^+ remained almost constant while Li^+ concentration steadily decreased with time.

1.3. Adsorption of lithium and other ions on silicates

It is now generally accepted that the adsorption of sulphates on C–S–H in cementitious systems heat treated at temperatures over 70 °C is responsible for the formation of DEF at later ages under moist conditions that inevitably promote the desorption of the sulphates into pore solution. During the process, desorbed sulphates encounter monosulphate and react with it to form ettringite. This formation of ettringite in already hardened concrete later in its life is disruptive and has been referred to as *delayed ettringite formation*.

In cementitious systems containing Li^+, Na^+, K^+ and SO_4^{2-} the ions in solution have to compete for adsorption on the C–S–H surface during hydration with or without heat treatment.

Although some authors have argued otherwise [18], it has been advanced that adsorption of lithium ion is favoured over the adsorption of sodium or potassium ions [17].

1.4. Control of delayed ettringite formation

DEF is a fairly recent deterioration mechanism and a lot about this mechanism is still unknown. However, some control measures have been promoted for prevention of DEF [19]:

- Limiting the maximum curing temperature to ≤ 70 °C.
- Selective use of cement types and their content in concrete. Type 30 cements and the use of high cement contents lead to high DEF susceptible concretes [20,21,1].
- A holistic approach to DEF control by focusing on only three factors: the late SO_4^{2-} release from cements, microcracking, and availability of moisture [22].
- Use of supplementary cementing materials (slag, fly ash, silica fume, natural pozzolans) has been reported to mitigate DEF [23,24].

This paper reports new findings to the effect that lithium nitrate popularly known for controlling ASR were found to be effective in reducing DEF as well. Heat-cured mortars and concretes containing reactive and non-reactive aggregates were used in this investigation. The cementitious systems used were designed to develop the presence of one or both mechanisms. Studies included expansion monitoring, formation of lithium complex products, and leaching of water-soluble alkalis from the pore solution.

2. Experimental

High early strength Portland cement CSA Type 30 was used in this investigation to generate DEF when subjected to heat treatment. Table 1 shows the chemical analysis of a sample of

Table 1
Chemical analysis of CSA Type 30 Portland cement

	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	K_2O	Na_2O	Na_2Oe	LOI	Blaine (cm^2/g)
CSA Type 30	20.38	5.45	2.06	63.41	4.82	1.21	0.10	0.90	0.91	5490

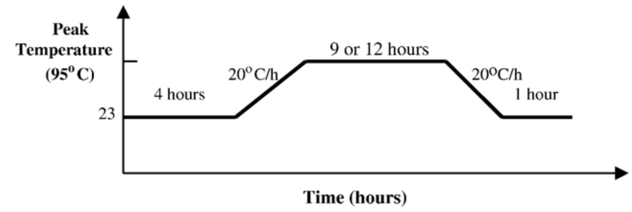

Fig. 1. Conventional 18-hour heat curing cycle applied to mortars and concretes.

cement used. Mortar bars, 25 × 25 × 285 mm were prepared and moist cured at 23 °C or steam-cured at 95 °C. Mortar mixtures consisting of 1:2.25:0.47 cement to sand to water were made using non-reactive 20–30 standard sand as described in ASTM C-778 or crushed Placitas aggregate. The Placitas (from New Mexico, USA) aggregate was of sand and gravel rock type known to contain reactive volcanic glass component [25].

Concrete mixtures were made at 0.45 water–cement ratio and used to cast 75 × 75 × 285 mm prisms. Glacial sand and 10 mm crushed dolomitic stone were used for non-reactive aggregates while the highly reactive Placitas coarse aggregate [25] was used in concrete mixtures to generate ASR. The effects of lithium were studied using lithium nitrate commercially available in North America. A dosage of 0.74 M ratio of Li to (Na + K) was added. No air entrainment or other admixtures were used in the mortar or concrete mixtures.

Concrete prisms and mortars were cast in steel moulds and heat-cured at 95 °C. Steam-curing of concretes was made according to a conventional 18-hour curing cycle using a programmable environmental chamber. The cycle applied consisted of 4 h delay (preset) period, temperature rising at 20 °C/h, then the maximum temperature of 95 °C was maintained for 9 h followed by cooling back to 23 °C as shown in Fig. 1. The curing cycle used for mortars was the same as that described for concretes except that a longer period of 12 h was maintained at 95 °C during steam-curing of mortar bars. Specimens were demoulded after heat treatment and stored in limewater.

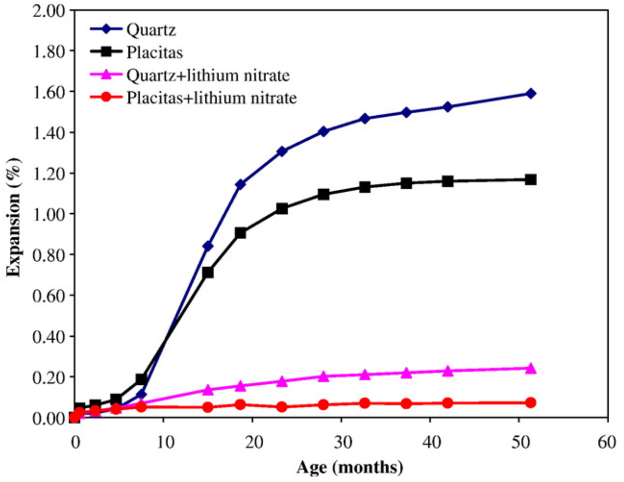

Fig. 2. Mitigation of expansion by admixed $LiNO_3$ in mortars made using reactive Placitas and non-reactive quartz aggregates. The mortars were stored in limewater at room temperature.

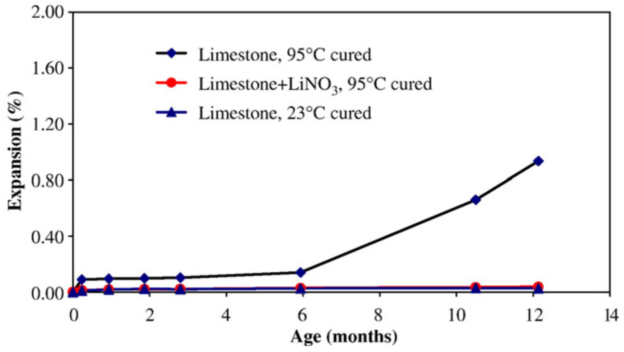

Fig. 3. Lithium ameliorates DEF expansion in heat-cured concretes made using non-reactive limestone aggregates and stored in limewater at room temperature.

3. Results

3.1. Expansion measurements

The length change of mortar bars and concrete prisms was monitored for different storage conditions. All measurements were taken at room temperature and used to calculate expansion. Fig. 2 gives the effect of using lithium nitrate on heat-cured mortars made using non-reactive 20–30 standard sand (Ottawa sand) and highly reactive crushed Placitas aggregate. Mortar specimens were stored in limewater to maximize delayed ettringite formation. Cement alkalis (Na^+, K^+), being highly water-soluble were substantially leached out in the early ages of storage (as seen in Fig. 6) and this would diminish expansion due to ASR. The observed expansion is likely to have been primarily due to delayed ettringite formation. The two aggregate types had different effects on DEF expansion with the quartz (standard sand) aggregates showing a higher expansion than Placitas. Different aggregate types are known to give varied effects on DEF [26,27]. This is attributed to the varied weaknesses of aggregate/paste bond and possible chemical reaction between cement paste and some types of aggregates. Interestingly, the use of $LiNO_3$ showed a significant impact of mitigating DEF expansion in both aggregate types for a period of monitoring of up to almost two years.

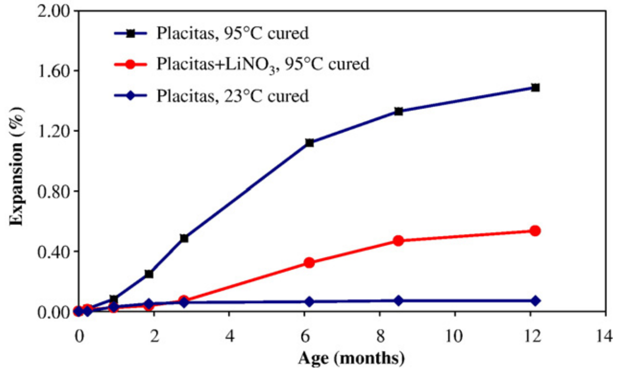

Fig. 4. Mitigation of expansion by $LiNO_3$ in concretes containing both DEF and ASR. The concretes were made using Placitas coarse aggregates and stored over water at 38 °C (ASTM C-1293).

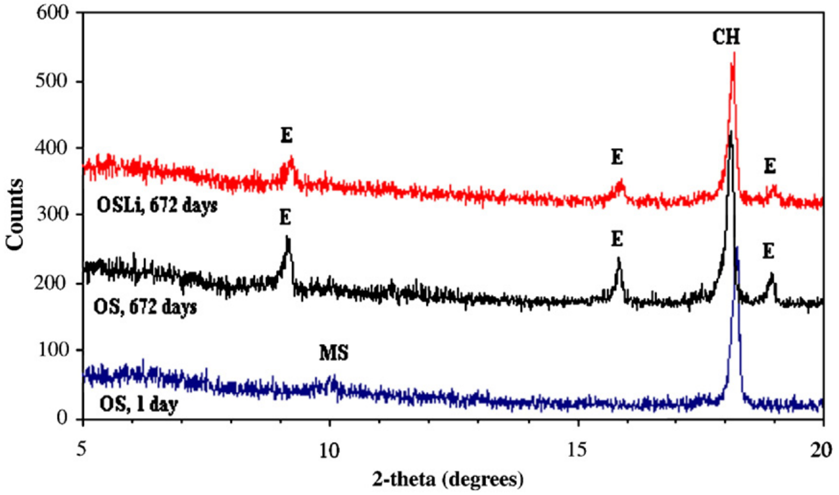

Fig. 5. XRD patterns of heat-cured mortars, OS — quartz (Ottawa sand), Li — lithium, MS — monosulphate, E — ettringite, CH — calcium hydroxide.

Similar observations were obtained in concretes made using limestone aggregate as shown in Fig. 3. Heat-cured concrete specimens free of lithium salt exhibited high expansions due to DEF but the corresponding concretes containing $LiNO_3$ had not shown expansion by the time of compiling this report. Additional experiments were conducted using heat-cured concretes made with Placitas as coarse aggregate in order to produce ASR. Storage at 38 °C over water as recommended in ASTM C-1293 was used to ensure alkalis remain in the concretes and participate in ongoing reactions. Results in Fig. 4 show that expansion in moist cured concretes free of lithium was around 0.07%. For corresponding heat-cured concretes free of lithium however, there was a steady increase in expansion throughout the period of monitoring reaching 1.49% in one-year. It is likely that some or most ASR already took place during heat treatment under restraint provided by steel moulds leaving little or no alkalis available during storage for alkali-silica reaction. It follows that most of the expansion observed later was due to DEF. Indeed, Diamond and Ong [10] reiterated that in a cementitious system where both mechanisms exist, ASR occurs earlier and most expansion observed in the long-term is due to DEF.

The ASR-DEF concrete system containing lithium salt addition again showed mitigation of expansion at early ages but some expansion occurred later. This observed late expansion seemed to have the same character as that of the corresponding lithium-free concretes. This implies that there was insufficient dosage to control both mechanisms. Since ASR occurs earlier than DEF, most of the lithium present in the system was consumed during ASR and the amount of lithium left afterwards, if any, was insufficient to control DEF. This appears to be a reasonable argument given that the dosage of 0.74 M ratio of Li: (Na+K) used for the lithium salt is considered sufficient for (only) ASR control. It follows that a higher dosage of $LiNO_3$ would be required to ameliorate expansion in a system containing both ASR and DEF.

3.2. X-ray diffraction

It can be observed from Fig. 5 that upon heat treatment of mortars at 95 °C, ettringite was destroyed or did not form as no ettringite peaks were observed in the one day specimens. Some

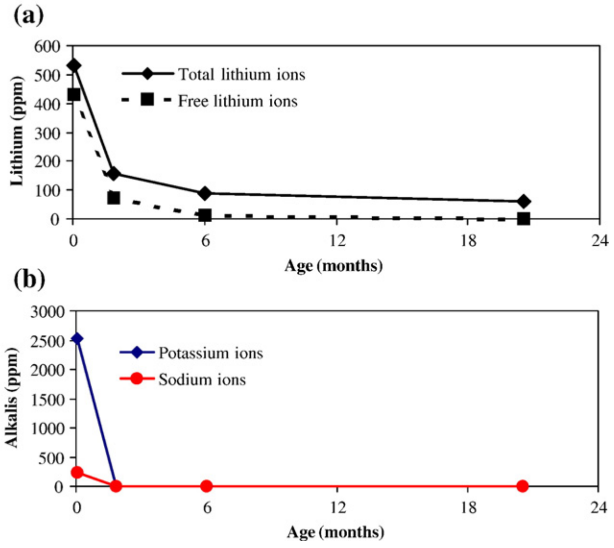

Fig. 6. Alkali leaching from heat-cured quartz mortars stored in limewater at 23 °C (a) total and free lithium ions, (b) sodium and potassium ions.

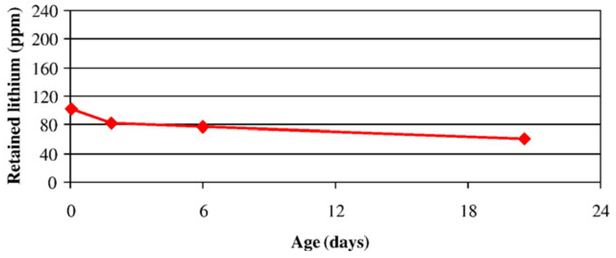

Fig. 7. Monitoring of lithium retained in heat-cured quartz mortars stored in limewater at room temperature.

monosulphate appeared to exist in the system as expected. At the later age of 672 days, there were strong ettringite peaks in lithium-free mortars that accounted for the high expansion of 1.6% given in Fig. 2. For mortars containing lithium salt admixture, ettringite peaks were still formed but had a rather reduced intensity (see Fig. 5).

3.3. Retained lithium

For mortar specimens stored in limewater, the highly water-soluble sodium and potassium ions were leached out of pore solution in the first few weeks, much faster than the leaching of free lithium ions as given in Fig. 6. The acid-soluble (total) lithium and water-soluble lithium ions present in mortars were monitored for a period of 1.7 years. Fig. 7 shows that a substantial amount of lithium ions were retained in the mortars. This retained lithium is suspected to be responsible for the mitigation of DEF expansion. However, the retained lithium given in Fig. 7 appears to be slightly soluble. Fortunately, most field applications involve massive concretes where leaching out of alkalis may not be of significance.

It is possible that lithium may be retained in the cementitious system by mechanism(s) such as chemical sorption, physical adsorption or chemical binding in some form of lithium silicate complex compound as suggested in the literature [28,15,16]. Lithium metasilicate (Li_2SiO_3) and orthosilicate (Li_4SiO_4) are the only known lithium silicate compounds [29]. Lithium aluminosilicate ($LiAlSiO_4$) is the other possible lithium complex compound that may be formed.

They are somehow soluble in cold water and that confirms the leaching studies conducted. But a great deal remains unknown such as the effective dosages for control of DEF depending on the type of lithium salt, aggregate type, the chemical interactions and mechanism itself that ensures the effectiveness of lithium salt.

4. Conclusions

In the wake of coexistence of ASR and DEF in deteriorated field concretes and the associated diagnostic problems, limited investigation of the potential of utilizing lithium salt to mitigate both damage mechanisms was conducted. This was considered important for the fact that uses of lithium salt in such cases would be of double benefit.

1. Indeed, the incorporation of a lithium salt in heat-cured mortars and concretes is effective in reducing expansion due to delayed ettringite formation as it does to alkali-silica reaction although the mechanisms and required dosages in each case may differ.
2. The ettringite peaks formed in heat-cured mortars and concretes containing lithium salt additions appear to be less than the peaks formed in lithium-free cementitious systems and this corresponds well with the observed expansions.
3. The effectiveness of lithium salt in reducing delayed ettringite formation is related to its retention in some form within the cementitious system thereby ensuring its existence in the system. The retained lithium was found to be slightly soluble.

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