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Experimental study and empirical modeling of lithium nitrate for alkali-silica reactivity

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HIGHLIGHTS

- Proposed an empirical model to predict optimum Li dosages for suppressing ASR.
- The predicted Li dosages were compared with experimental values at 14, 28 and 56 days.
- A good agreement existed between the optimum experimental and analytical Li dosages.
- The model may be used to select a trial Li dosage to suppress excessive expansion of reactive aggregate.

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ABSTRACT

The influence of various dosages of lithium nitrate salt to inhibit the ASR-induced expansions of six reactive aggregates was studied. ASTM C 1260 (commonly known as Accelerated Mortar Bar Test (AMBT)), and modified AMBT were used to measure linear expansions of control mortar bars containing no lithium content and those of the mortar bars treated with up to six dosages of lithium-to-alkali molar ratios of 0.59, 0.74, 0.89, 1.04, 1.19 and 1.33, respectively. An empirical model to predict the minimums dosages of lithium salt required to suppress the excess mortar expansion below the prescribed failure limits at 14, 28 and 56 days was developed. The study revealed that a good correlation existed between the optimum lithium content obtained by the experimental procedures and that evaluated by the proposed model. It was also found that the amount of lithium nitrate salt needed to suppress ASR-induced mortar expansion varied depending upon the extent of aggregate reactivity, the mineralogy of the aggregates, and the test duration.

1. Introduction

Alkali-silica reaction (ASR) is one of the major durability problems, discovered in [38], which is the most prevalent cause of premature deterioration in concrete structures. Although the ASR reaction is very complex, there are some fundamental agreements in the reaction chemistry and mechanisms [41,10,20]. ASR is the chemical process in which, in the presence of sufficient moisture, certain minerals of some aggregate groups react with the hydroxyl ions of alkalis present in concrete. The resulting product (gel) expands and creates tensile stresses forces in concrete resulting in extensive cracks and damages on structural members.

The most effective practice to prevent concrete damages caused by the alkali-silica reaction is through the use of innocuous aggregates. However, if non-reactive aggregates are not be available, the reactive aggregates can also be used in concrete without affecting the ASR-induced damages by using various mitigation techniques. One of the methodologies to suppress excessive ASR-induced expansion is the use of lithium compounds in concrete. The idea was first reported by McCoy and Caldwell [29]. For the next four decades, a few studies were reported on the use of lithium salts to control ASR. Since 1990, the awareness of utilizing lithium bearing compounds in new concrete for ASR suppressive purposes has been increased.

Lithium salts do not react with concrete in the same manner as pozzolanic materials do. The mechanisms by which the lithium salts reduce ASR expansion are still unclear. However, some researchers [12,11,34,42] have proposed that lithium may either reduce silica dissolution, or it may decrease the repolymerization of silica and silicates. When lithium compounds are used to suppress the ASR-induced expansion of a reactive aggregate, the structure of the silica governs the rate and/or amount of silica dissolution in the ASR reaction [12]. Poorly crystalline or

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amorphous silica is much more prone to ASR than well-crystallized or dense forms of silica [43], and the dissolution rate of well-crystallized silica only occurs in a very slow rate at the surface [12]. Since aggregate mineralogy solely depends on the amount and structure of silica, it can affect the extent to which lithium salt is able to control ASR expansion.

The amount of lithium salts required to inhibit the ASR-related damages in fresh concrete is a function of the equivalent alkali [sodium oxide (Na_2O_{eq})] available in the cementitious materials and the amount of cementitious materials used per cubic yard (or cubic meter) of concrete [12,5]. As reported in this study, the appropriate dosages of lithium salt to inhibit ASR expansion were mostly based on the Accelerated Mortar Bar Test (AMBT). The standard lithium dose (sometimes referred as 100% Li) is the amount of lithium admixture that supplies enough Li ion to achieve a lithium-to-alkali molar ratio [Li:(Na + K)] (LAMR) of 0.74 [30,11]. More research studies also showed that the standard lithium dose of 0.74 is adequate to inhibit the excessive expansion of most aggregates caused by alkali-silica reaction [9,32]. Conversely, some highly reactive aggregates require considerably extra dosage of lithium salt [40,8,13] and some less reactive aggregates may need less [24,28,46,6,36].

The efficacy of lithium in suppressing alkali-silica reactivity depends on the nature of aggregate [8,22,34,10,19], form of lithium [8,22,6,34,23], and the use of supplementary cementitious materials and the total amount of alkalis present in concrete [6,10,34,5,23]. Among the lithium admixtures utilized in concrete, lithium nitrate is the most commonly used, because it is safe, environmentally benign, and easy to handle [30,46,1,12]. Lithium nitrate salt does not increase the pH of pore solution [24,44,12,32,13], and it has no significant effect on concrete properties [24,31,5].

Compared to all lithium compounds utilized in concrete construction, lithium nitrate is shown to be most sufficient to suppress the ASR-induced expansion for most reactive aggregates [8,44,6,11]. Feng et al. [11] investigated the optimum dosages of eleven lithium salts, such as LiBr, LiCl, LiF, $LiNO_3$, $LiNO_2$, LiOH, $LiOH{\cdot}2H_2O$, Li_2HPO_4, Li_2CO_3, Li_2SO_4, and Li_2SiO_3, in suppressing ASR expansion of new concrete prepared with a number of reactive aggregates. The study revealed that the appropriate dosages of LAMR to inhibit ASR expansion were shown to be effective in the range of 0.72–0.93 for $LiNO_3$ and 0.67–1.20 for remaining lithium salts. Among the eleven lithium salts used, lithium nitrate was appeared to be the most effective in controlling the excessive expansion due to alkali-silica reactivity Tremblay et al. [48] examined the $LiNO_3$ dosage to suppress the 14-day mortar expansion of twelve reactive aggregates below 0.10%. The standard lithium dosage of 0.74 was shown to be sufficient in suppressing mortar expansion of six reactive aggregates, and three aggregates were needed a higher $LiNO_3$ dosage of between 0.75 and 1.04. The expansions of the remaining three aggregate groups were not controlled even with the lithium to alkali molar ratio of 1.11. The findings obtained from the past research studies suggested that an extensive range of LAMRs was shown to be effective for inhibiting the concrete damages due to alkali-silica reactivity. They were: 0.72–0.92 [11]; 0.60–0.90 [6]; 0.74–1.04 [15]; 0.74–0.93 [30,14]; 0.74–1.04 [48]; 0.74–1.19 [19], and 0.75–1.00 [40].

Table 1 shows the findings of lithium salts in suppressing ASR expansion of various reactive aggregates having different mineralogy [11]. As can be shown, of the fourteen studies listed in Table 1, most investigations were limited to only one aggregate group, and a few research studies dealt with a maximum of two aggregate groups.

Past investigations on the effect of lithium nitrate salt in arresting the ASR were mostly confined to a limited number of aggregate groups having a narrow range of ASR-induced expansions and the test duration of 14 days. Additionally, they lacked a detailed statistical analysis. As such, an extensive research study was needed to incorporate reactive aggregates having a wide range of ASR expansion, extended test durations of more than 14 days, and detailed statistical analyses.

Table 1
Summary of the findings on lithium salts in suppressing ASR expansion of reactive aggregates having different mineralogy [11].

Research work	ASTM standard	Reactive aggregate	W/C by mass	% Na_2Oe by mass	Lithium salt(s) studied	Minimum lithium to alkali moral ratio
McCoy and Caldwell [29]	C 227	Pyrex glass	–	1.15	LiCl, LiF, Li_2CO_3, Li_2SiO_3, Li_2SO_4, $LiNO_3$	0.74
Sakaguchi et al. [37]	C 227	Pyrex glass	0.55	0.8–1.0	$LiOH{\cdot}H_2O$, $LiNO_2$, Li_2CO_3	0.90
		Andesite sand		1.2	$LiOH{\cdot}H_2O$	0.90
Stark [39]	C 227	Andesite	–	–	LiF, Li_2CO_3	0.67 (LiF), 0.92 (Li_2CO_3)
Stark et al. [40]	C 1293	Rhyolite Granite genesis	–	–	$LiOH{\cdot}H_2O$	0.75–1.0 (LiOH)
Diamond and Ong [7]	C 227	Cristobalite	0.485	1.0	LiOH	1.2 (Cristobalite, more for opal)
		Beltane opal	0.485	1.0	LiOH	
Durand [8]	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 others
Lane [25,26]	C 1260 & C 1293	Pyrex glass Quartz	0.45	0.75–1.25	$LiOH{\cdot}H_2O$, $LiNO_3$	0.925 for $LiNO_3$
Lumley [28]	C 1293	Cristobalite	0.5	0.86–1.13	$LiOH{\cdot}H_2O$, LiF, Li_2CO_3	0.62
Thomas et al. [44]	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. [6]	C 227	Borosilicate glass	0.37	1.0	LiOH, LiCl, $LiNO_3$	0.6 for LiOH, 0.9 for LiCl, 0.8 for $LiNO_3$
Kawamura and Fuwa [22]	C 227	Calcined flint	0.55	1.12	LiOH, Li_2CO_3	0.75 M
Ohama et al. [35]	Autoclave	Opaline amorphous silica	0.63–0.78	2.0	$LiOH{\cdot}H_2O$, LiF, Li_2CO_3	0.5% wt for LiF 0.7% wt for $LiOH{\cdot}H_2O$
Bian et al. [4]	Autoclave	Andesite sand	0.5	0.5–3.5	LiF, LiCl, LiBr, $LiNO_3$, Li_2SO_4, Li_2CO_3 LiH_2PO_4	0.80
Mo et al. [33]	Autoclave	Microcrystalline Quartz	–	1.5–3.0	$LiOH{\cdot}H_2O$	$\geqslant 0.3$ for $Na_2O_{eq} \leqslant 2.5\%$ $\geqslant 0.6$ for $Na_2O_{eq} = 3.0\%$