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The mechanical and microstructural properties of Li_2SO_4, $LiNO_3$, Li_2CO_3 and LiBr added mortars exposed to alkali-silica reaction

İlhami Demir [a,*], Metin Arslan [b]

[a] *Kırıkkale University, Faculty of Engineering, Dept. of Civil Engineering, Kırıkkale, Turkey*
[b] *Gazi University, Faculty of Technology, Dept. of Civil Engineering, Ankara, Turkey*

HIGHLIGHTS

- This study intends to analyze the effects of lithium additives on cement mortars.
- Optimum additive amount for ASR is calculated based on length changes and mechanical strengths.
- Lithium additives enclosed the alkali products, playing a role in reducing the ASR expansions.
- ASR expansion and strength of reactive aggregates were affected by the type and ratio of additives.

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ABSTRACT

Aim of this study intends analyzing the effects of lithium additives on fresh and hardened cement mortars. In this study, mortar specimens were prepared by adding four types of additives (Li_2SO_4, $LiNO_3$, Li_2CO_3 and LiBr) to the mixing water of the cement at 0.5%, 1%, 1.5%, 2%, 2.5% and 3% proportions by weight. The Alkali-silica reaction (ASR) of these mixtures was explored. The effects of Li_2SO_4, $LiNO_3$, Li_2CO_3 and LİBr, which are used to control ASR induced expansion, on expansion and mechanical properties were determined. ASTM C 1260 experiment standard was used to find out the reactivity of aggregate and cement mixtures. In this experimental study, the morphology and the chemical composition of specimens exposed to ASR effect was examined by means of scanning electron microscope (SEM) and Energy Dispersive Spectroscopy (EDS).

Fourteen-day readings conducted in the experimental study showed that the average maximum length change of the reference mortar bar was 0.34%, whereas the lowest average length change was 0.023% of the mortar bar with 3% Li_2CO_3 additive. Among the mortars that had undergone ASR, mortars containing 3% $LiNO_3$ experienced the least strength loss. As observed in the SEM image, EDX done on dense and wide ASR cracked areas pointed to high ratios of calcium oxide and silica oxide.

1. Introduction

Occurring between alkali oxides that are generally cement induced (Na_2O, K_2O) and aggregates containing reactive silica forms. Alkali-silica reaction (ASR) is a chemical reaction that leads to an expanding effect on the concrete. This reaction causes the formation of a gel, which expands as a result of humidity in concrete and sufficient amounts of alkali effect present at sufficient degree. This volume increase that occurs as a result of swelling in the concrete induces tensile stress, causing cracks in the concrete [1,2].

It is a reaction that takes place between the alkali hydroxides of ASR Portland cement and some minerals (opal, chert, chalcedony, tridymite, cristobalite and quartz, etc.) existing in the aggregate [3].

The conditions required for ASR to take place are the presence of reactive silica in aggregate, pore solution containing high alkali and sufficient humidity in the environment. If any of these conditions is missing, no ASR related expansion will take place. The amount of gel forming in the concrete depends on the type and amount of silica and the alkali hydroxide concentration. ASR development mechanism is as follows [1,4].

$$-\text{Alkali} + \text{Reactive Silica} \rightarrow \text{Alkali Silica Gel Products}$$

$$-\text{Alkali Silica Gel Products} + \text{Humidity} \rightarrow \text{Expansion}$$

Development of internal tensile stress in concrete is not simultaneous with the first stage of gel formation. Thus, the existence of gel does not necessarily mean that severe ASR deformation will take place [1,4].

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* Corresponding author. Tel.: +90 533 768 04 71.
E-mail addresses: ildemir@kku.edu.tr (İ. Demir), metina@gazi.edu.tr (M. Arslan).

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ASR may not pose a serious threat to concrete that has remained dry throughout its service life. ASR occurs in concrete with a relative humidity ratio higher than 80%. If the permeability of the concrete decreases for some reason such as concrete with low water/cement ratio, mineral additives, entering of humidity into concrete or its migration in it will be impeded. It will, therefore, curb the spread of alkalis inside. Increasing heat accelerates the reaction. Indeed, the majority of aggregates demonstrate greater reactivity with increasing heat. Moreover, repeated drying and wetting cycles enhance alkali migration in the concrete, which concentrates alkalis in the drying zones [4].

The use of mineral additives can improve the compressive strength, void structure and permeability of mortar and concrete in time. This is due to the fact that the total volume of voids is reduced following the development of hydration which is owing to the mineral additives [5–9].

Another approach to the attempts toward reducing ASR is the use of lithium containing additives. Lithium salts could be added to the concrete mixture against the reactivity of the aggregate. Mc Joy and Caldwell [10] are the first to prove that some chemical salts containing lithium salt reduce expansion in mortars exposed to ASR. Today, lithium containing additives that can be used to control ASR are available on the market. The studies that have been carried out so far on lithium additives could not actually clarify the mechanism or shed light upon the mechanisms with which such additives reduce ASR expansion. It may be considered difficult to predict for how long the lithium additives can prevent expansion by determining the optimum lithium compound and dosage [3,11,12].

The approaches to the prevention of ASR generally focus on directly preventing ASR or altering the chemical environment in which it occurs, thus on reducing the expansion of gel. Some examples to this approach are avoiding reactive aggregates, using low alkali cement, using mineral additives or lithium containing additives [13,14].

Although the studies carried out so far have indicated that lithium containing additives are effective in reducing ASR, it is also highlighted that it is not possible to predict the long term effects of lithium additives without a comprehensive approach [15].

A variety of studies have indicated that using lithium additives at suitable dosages reduce concrete expansion that occurs as a result of ASR [11,16–18]. As most of the aforementioned studies, the results of which were analyzed, demonstrate, the principles indicated in ASTM C 1260 could be applied in ASR determination methods.

Yet in another study, it was noted that lithium additives, due to delayed ettringite formation, reduce detrimental expansion, as well as regulating the ASR effect in the concrete [19].

Some studies examining the SEM and ASR morphology in mortars with lithium hydroxide additives revealed that protective layers form on the surface of opal. It was observed that these protective layers reduce ASR [12,20,21].

Studies examining the composition and morphology of ASR products using scanning electron microscope and Energy Dispersive Spectroscopy have gained importance in the recent years. Several studies exist examining the microstructural properties of ASR [22,23].

Also some experimental results exist showing that use of LiOH and Li_2CO_3 at optimum dosages increase ASR expansion [24,25].

It was thought that replacement of Li+ in lithium containing additives with K+ or Na+ took place in the ASR gel. The (K+, Na+) proportion of Li+ ions, a part of gel, to regular alkali ions is a function related to the ions in the solution. Thus, the effectiveness of the lithium activity basically depends on lithium's maintaining its high proportion to other cations in the solution. It was determined out that the Li/(K + Na) mol ratio exceeding the 0.6–0.9 range was required in order to eliminate entirely ASR expansion. At this point, ion concentration, as an outcome of LiOH behavior, has a potential to increase the already high OH− ion concentration. That is why utmost care is needed when less amount of lithium compound is used. ASR expansion attenuated by LiOH can be retarded, and the expansion can be decreased by using a higher Li/(Na + K) molar ratio. However, together with this positive effect, mortar strength will decrease as a result of LiOH addition. As the amount of LiOH increases, strength is bound to be reduced more. When LiOH is added, the final and initial setting time of the cement will shorten. There is a gap in the literature in terms of the

Table 1
The chemical and mineralogical properties of the aggregate.

Chemical properties		Mineralogical properties	
Compound	Amount (%)	Compound	Amount (%)
SiO_2	65.5	Quartz	42.67
Al_2O_3	5.6	Albite	12.40
Fe_2O_3	6.2	Dolomite	0.16
CaO	19.1	Calcite	4.72
K_2O	2.6	Muscovite	28.67
TiO_2	0.6	Chlorite	2.08
MnO	0.1	Anorthite	9.31
BaO	0.2		
Tm_2O_3	0.1		
SrO	0.03		
Rb_2O	0.01		

Table 2
The grading of the aggregate used.

Sieve size	Amount in between two sieves (%)
4.75 mm (No: 4)–2.36 mm (No: 8)	10
2.36 mm (No: 8)–1.18 mm (No: 16)	25
1.18 mm (No: 16)–600 μm (No: 30)	25
600 μm (No: 30)–300 μm (No: 50)	25
300 μm (No: 50)–150 μm (No: 100)	15

Table 3
The chemical and physical properties of CEM I 42.5 R cement.

Chemical compound	CEM I 42.5 R
SiO_2 (%)	21.01
Al_2O_3 (%)	5.39
Fe_2O_3 (%)	3.23
CaO (%)	62.11
MgO (%)	1.98
Na_2O (%)	0.38
K_2O (%)	0.82
SO_3 (%)	3.1
Specific gravity	3.18
Blaine fineness (cm^2/g)	3352
Loss of ignition (%)	2.38
$Na_2O + 0.658\times K_2O$	0.92
Initial set (min)	155
Final set (min)	195
Volumetric expansion (mm)	2

Table 4
Mixture ratio in mortar specimen with lithium additives.

Materials (g)	0%	0.5%	1.0%	1.5%	2.0%	2.5%	3.0%
Cement	440	440	440	440	440	440	440
Lithium additive	0	2.2	4.4	6.6	8.8	11	13.2
Aggregate	990	990	990	990	990	990	990
Water	206.8	206.8	206.8	206.8	206.8	206.8	206.8