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Effect of sulfate on cement mortars containing Li_2SO_4, $LiNO_3$, Li_2CO_3 and LiBr

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HIGHLIGHTS

- Mechanical properties and expansion characteristics were investigated.
- Initial setting time and final setting time of cement paste were explored.
- Having cured in water and sulfate solution mortars were comparatively investigated.
- The impact of aggressive environment on cement mortars was assessed.

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ABSTRACT

The purpose of this study is to explore the influence of sulfate on the fresh and hardened mortars containing lithium additives added with the aim to prevent alkali-silica reaction (ASR). Four different types of lithium additives (Li_2SO_4, $LiNO_3$, Li_2CO_3 and LiBr) were added to the cement at the ratios of 0.5%, 1%, 1.5%, and 2% by mass in order to produce mortar specimens. Influence of sulfate on the specimens was then investigated. Used in order to keep the expansion under control, expansion characteristics and mechanical properties of Li_2SO_4, $LiNO_3$, Li_2CO_3 and LiBr were defined.

Initial setting and final setting tests were conducted on the cement pastes as per the provisions of TS EN 196-3 standard. Flexure and compressive tests were conducted in accordance with TS 196-1 in order to identify the mechanical properties of cement mortars. Prisms of 25 × 25 × 285 mm in dimension were produced as per ASTM C 1012-95 in order to measure the length change of the cement bars and results were analyzed.

The results showed that Li_2CO_3 among the other lithium additives was effective in shortening the initial setting and final setting times, while $LiNO_3$ and LiBr additives gave the best results in terms of strength and length change when tested for 1% additive ratio by mass. The highest length change was observed for the specimens with Li_2CO_3 cured both in water and sulfate solution. The lowest length change was observed for the specimens with $LiNO_3$ cured both in water and sulfate solution. 1% $LiNO_3$ additive gave the best results under sulfate effect for all test days. The length change of cement mortar with 1% $LiNO_3$ additive was decreased by 53%, 25%, and 41% under sulfate effect for the 90th, 180th, and 360th day, respectively. It is believed that the use of $LiNO_3$ and LiBr additives at the ratio of 1% by mass will reduce the unfavorable influence of sulfate. Li_2CO_3 and $LiSO_4$ should not be used because they have negative effects on mechanical properties and length changes.

1. Introduction

Concrete is widely used in the civil engineering operations thanks to the advances in the concrete technology. It is expected from concrete to be resistant to several environmental effects along with improved compressive strength. Recently, durability of concrete and its resistance to aggressive environments have been receiving interest. Sulfate is the origin of various significant problems in concrete operations. Magnesium sulfate and sodium sulfate are among the most devastating mineral salts (alkalis) which are dissolved and available in the ground and underground waters commonly in contact with concrete. Bonding with the calcium aluminates hydrated in the cement, sulfates form expanding

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crystals. Increasing in time, such an expansion is reported by many authors to lead to cracks in concrete and crumbling [1,2].

Alkali-Silica Reaction (ASR) may prove to be a severe danger for concrete. ASR is a reaction which occurs between alkali hydroxides available in the Portland cement and a number of minerals (such as Opal, chert, chalcedony, tridymite, cristobalite and quartz, etc.) available in the aggregate [3].

ASR may not be a severe danger for concrete which is not exposed to humidity throughout its lifetime. ASR starts in concretes which are exposed to 80% or more relative humidity. If the permeability of concrete is reduced using lower water/cement ratio or with the use of additional cement, mineral additives or any other means, then entry of moisture and its circulation in the concrete are also reduced. Thus, dispersal of alkalis in concrete is also restricted. Reaction rate increases with the increase in temperature. Reactivity of majority of the aggregates increases at higher temperatures. Nevertheless, exposure to repeated drying-wetting cycles facilitates the transportation of alkalis in concrete and it leads to alkali concentration at drying sections [4].

A number of mineral additives are used in order to decrease the ASR. The use of mineral additives improves the compressive strength, pore structure and permeability of mortar and concrete as the total number of pores decrease with the improved hydration thanks to the mineral additive [5–9].

Another approach in the efforts to decrease ASR is the use of lithium-based additives. Lithium salts can be added to the concrete mixture as a neutralizing agent for the reactivity of aggregates. McJoy and Caldwell proved for the first time that some chemical salts containing lithium salts reduces the expansion of mortars exposed to ASR [10].

Today, additives containing lithium which can be used to keep ASR under control are available commercially. Up to date, the research on lithium additives failed to explain the mechanism involved in reducing the ASR expansion or the mechanism in general with the use of such additives. It seems quite hard to predict the extent of expansion prevention when the lithium compound and the additive ratio are defined [11–13].

Although the effectiveness of lithium-based additives in reducing ASR is suggested in research, it was also noted that it will not be possible to predict the long-term effects of lithium additives without an explanatory approach [14]. Several studies reported that the use of lithium additives at specific ratios reduced the expansion on concrete due to ASR [15–17].

It is believed that the partial transformation of Li+ available in lithium-based additives with K+ or Na+ occurs in ASR gel. The ratio of Li+ ions to alkali ions (K+, Na+) is a function of the ions available in the solution. In other words, effectiveness of lithium depends on the higher ratio of Lithium in the solution when compared to other cations. It was found that a Li/(K + Na) mole ratio between 0.6 and 0.9 is required in order to prevent the expansion due to ASR fully. At this point, the effect of high OH− ion concentration due to the LiOH behavior is further increased. Therefore, one should take heed in situations where decreased amounts of lithium compound are use. ASR expansion can be decelerated or reversed with LiOH and such an effect is increased with the increased Li/(Na + K) mole ratio. Although this is a favorable impact, strength of mortar will be reduced with LiOH addition. Increasing the amount of LiOH used decreases the strength. LiOH addition decreases the time necessary for initial setting and final setting of the cement. Literature is limited not only for bringing an explanation to the benefits of Lithium compounds in preventing ASR, but also explaining the effects of similar compounds on the properties of cement such as setting time and strength [18].

It is known that lithium addition reduces the expansion effect of Alkali-Silica Reaction (ASR) in concrete. However, there are no studies in the literature to our knowledge to explore the effects of lithium addition on the setting time of cement mortars and the properties of hardened cement mortars in aggressive environments.

The purpose of this study is to investigate the effects of lithium additives on the durability of cement mortars in sulfate environment. Lithium additives are effectively used in preventing Alkali-Silica reaction. Literature review showed that there are no studies on the effect of sulfate on such additives used to prevent ASR. With this purpose, the effect of the treatment of cements with different lithium-based additives in 5% sulfate solution on their linear length change and mechanical behavior was analyzed. Four different types of lithium additives (Li_2SO_4, $LiNO_3$, Li_2CO_3 and LiBr) were added to the cement at the ratios of 0.5%, 1%, 1.5%, and 2% by mass in order to produce mortar specimens. Length change, setting time, flexural and compressive strengths were investigated for 7, 28, 90, 180 and 360 days with regards to additive type and ratio. Thus, it was possible to compare the linear length change and mechanical behaviors of lithium added cement mortars under sulfate effect.

2. Materials and method

2.1. Materials

Standard sand (Rilem sand) which complies with TS EN 196-1, CEM I 42.5 R cement, drinking water, sodium sulfate and 4 different lithium additives with over 98% purity were used in this research. Among these additives were Li_2SO_4 (Lithium Sulfate), $LiNO_3$ (Lithium Nitrate), Li_2CO_3 (Lithium Carbonate) and LiBr (Lithium Bromide). Drinking water (DW) and 5% sodium sulfate (SS) solution were used as treatment fluids. Physical and chemical properties of the cements used are shown in Table 1.

2.2. Method

Lithium additives were added to the cement paste at the ratios of 0.5%, 1.0%, 1.5%, and 2.0%. Water requirement of cement paste and setting times were defined in accordance with the provisions of TS EN 196-3 [19]. The ratio of standard sand to cement and to water was taken 3:1:0.5 as per the provisions of TS EN 196-1 for cement mortar mixtures [20].

Mortar specimens were produced using molds of 40 × 40 × 160 mm in dimension. For each lithium additive, 4 different mixtures with 0.5%, 1%, 1.5% and 2% addition and 0% reference mixture were prepared. A total number of three specimens were molded for each one of these series. Prisms of 25 × 25 × 285 mm in dimension were produced as per ASTM C 1012-95 in order to detect the length change of cement mortar bars [21].

Cements produced were kept at 20 ± 1 °C and 60% relative humidity for 24 h, and then were taken out of the molds in order to be tested for their length change in water cure (WC) and 5% sodium sulfate (SS) cure at 20 ± 3 °C in 7, 28, 90, 180 and 360 days. Setting time calculations of cement pastes with different additive ratios were performed in accordance with TS-EN 196-3 Standard, while flexural and compressive strength tests were performed in accordance with TS-EN 196-1 Standard for 7th, 28th, 90th, 180th, and 360th day.

Table 1
The chemical and physical properties of CEM I 42.5 R cement.

Chemical compound	CEM I 42.5 R
SiO_2 (%)	22.03
Al_2O_3 (%)	5.37
Fe_2O_3 (%)	3.33
CaO (%)	63.03
MgO (%)	1.98
Na_2O (%)	0.36
K_2O (%)	0.79
SO_3 (%)	3.1
Specific gravity	3.18
Blaine fineness (cm^2/g)	3352
Loss of ignition (%)	2.38
Na_2O +0.658x K_2O	0.88
Volumetric expansion (mm)	1