Influence of Exposure Conditions on the Efficacy of Lithium Nitrate in Mitigating Alkali Silica Reaction

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Abstract. Lithium nitrate is known to have the highest potential to inhibit alkali silica reaction in concrete. It is well soluble in water and does not increase the pH of concrete pore solution. The extent to which the alkali silica reaction is mitigated is affected by the amount of the applied lithium ions, exposure conditions and by the kind of reactive aggregate. It is known that some lithium compounds such as lithium carbonate or lithium fluoride, when used in insufficient amount, may increase expansion due to alkali silica reaction. This effect was not detected in the presence of lithium nitrate. The aim of this study was to determine the effect of lithium nitrate on alkali silica reaction in mortars exposed to different conditions. Expansion studies were conducted in accordance with the accelerated mortar bar test (ASTM C1260) and the standard mortar bar test (ASTM C227). It was observed that the long-term expansion results are different from the values obtained in the accelerated mortar bar test. Lithium nitrate does not reduce ASR-induced expansion when mortars are stored under conditions specified in ASTM C 227. The microstructure of the mortar samples exposed to different conditions was examined and X-ray microanalysis was performed. The microstructure and compositions of the alkali-silica reaction products varied. The amount of alkali silica gel in mortars with lithium nitrate in which the expansion was high was greater than that in the mortar bars tested by accelerated method.

1. Introduction
The application of lithium compounds to inhibit the destructive reaction between reactive aggregate and alkalis was first suggested by McCoy and Cadwell [1]. It was also discovered that among lithium compounds such as LiF, LiCl, LiBr, LiOH, LiOH-H2O, LiNO3, LiNO2, Li2CO3, Li2SO4, Li2HPO4, and Li2SiO3, the lithium nitrate had the greatest potential to inhibit the alkali-aggregate reaction. Further findings on lithium nitrate indicate that unlike lithium fluoride, carbonate or hydroxide, this compound does not raise the pH value [2-4]. Since pH does not grow after introducing lithium nitrate into the mix, the destruction of materials associated with the pessimum effect should not take place. Lithium ions introduced into the mix are balanced almost entirely by nitrate anions and only to a small extent by hydroxyl ions [5]. Lithium nitrate is also effective in controlling delayed ettringite formation (DEF) in concrete [6].

Many laboratory studies have focused on the use of lithium nitrate to control alkali silica reaction [7]. The accelerated method of aggregate alkaline reactivity testing (ASTM C1260), which is a fast indicator of sensitivity of aggregates to potential destructive expansion, has to be modified by adding LiNO3 to the soak solution. This modification is important to prevent leaching of lithium ions from the mortar bars [8]. It also follows from the author’s previous studies that the efficacy of inhibitors
depends on both the amount of lithium ions introduced and the presence of lithium nitrate in the soak solution [9, 10]. An appropriate dosage of lithium salt providing enough lithium ions to suppress ASR induced expansion is often determined by this modified accelerated mortar bar test [11].

In the standard mortar bar test (ASTM C227) high alkali cement mortars are stored at 38°C and over 95% humidity. But because alkali leaching, this standard test method is not recommended for use in determining the dosage of inhibitors required to suppress expansion [12]. Additionally, slowly reactive rocks may not expand in this test but if the aggregate is very reactive, expansion of the mortars is observed after a relatively short time. The findings from a series of standard and accelerated tests of the mortars containing rhyolite and lithium nitrate were in good agreement. For mortar bars tested in accordance with the standard mortar bar test, expansion was suppressed even when only 75% of the recommended dosage of lithium ions was added (standard [Li]/[Na+K] molar ratio is 0.74), but expansion occurred in the mortar bars stored under the conditions specified in the accelerated method [8].

This study was carried out to provide more experimental data with regard to lithium nitrate potential to suppress ASR induced expansion under different exposure conditions.

2. Materials

The tests were carried out on mortars in accordance with the methodology included in ASTM C1260 [13] and ASTM C227 [14]. Portland cement CEMI 42.5R was used in the experiments. Cement chemical analysis results are shown in Table 1. The content of sodium and potassium, calculated as Na$_2$O$_{eq}$ was 0.66%.

Table 1. Chemical composition of cement

| Material | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | SO$_3$ | K$_2$O | Na$_2$O | TiO$_2$ | LOI$^a$ | N.s.p.$^b$ |
|----------|--------|------------|------------|-----|-----|--------|-------|-------|--------|--------|----------|
| Cement   | 20.20  | 4.80       | 3.00       | 61.70 | 1.80 | 2.70   | 0.78  | 0.15   | 0.45   | 3.00   | 1.00     |

$^a$LOI – loss of ignition,
$^b$N.s.p – parts non-soluble in HCl and Na$_2$CO$_3$

Silica sand containing 6% of the 0.5-1mm opal was used as reactive silica aggregate. The results of petrographic analyses revealed that the main component of this aggregate was cristobalite/tridymite-like opal. Narrow strips of crystalline chalcedony developed between the opal zones. The opal aggregate had a BET surface area of 5.0m$^2$/g.

The bars with dimensions 25x25x250mm were made with and without lithium nitrate. Lithium nitrate was added to the mixing water at a [Li]/[Na+K] molar ratio of 1.0. The prepared bars were stored at the temperature of 23±2°C and relative humidity of ≥95% for 24 hours and removed from their moulds. Two series of mortar bars tested in the accelerated method were immersed in water at 80±2°C for 24 hours. Mortars with and without lithium nitrate were soaked in a 1M NaOH solution at 80±2°C and the mortar bars with LiNO$_3$ were stored in the soak solution containing lithium nitrate with the same lithium-alkali ratio as that used in the mortar. Expansion measurements were taken for 28 days, every day for 14 days and after this period the frequency was reduced to 7 days. The ASTM C227 tests were conducted for 720 days on another two series of mortar bars (with and without LiNO$_3$) by storing specimens over water in the climatic chamber at 38±2°C and relative humidity exceeding 80%. The measurements were taken at 14 days and every 30 days for the 600 days, then again after 720 days. At 14 and 28 days (ASTM C1260) and 360 and 720 days (ASTM C227) of curing, the pieces of the specimens were examined under the scanning electron microscope coupled with EDS.

3. Results and discussion

3.1. Expansion

The result of linear changes in the mortar bars with and without lithium nitrate, measured to ASTM C1260 are shown in Figure 1a. In the specimens without lithium nitrate, the expansion limit was
exceeded as early as at 24 hours. Bars elongation increased gradually and attained approximately 0.88% at 28 days. In the mortars with lithium nitrate, the elongation of the specimens was limited to the safe level of up to 0.1% also at 14 and 28 days of exposure to the soak solution. The expansion results allow a conclusion that lithium admixture prevents mortars from destructive expansion.

![Graphs showing expansion of mortars with and without lithium nitrate](image)

Figure 1. The expansion of mortars with and without lithium nitrate measured according to (a) ASTM C1260, (b) ASTM C227

Linear changes in the reference mortar bars analysed with ASTM C227 procedure reached 0.16% at 14 reaction days after which the linear dimensions of the bars started increasing slightly, levelling off at 0.17% at 360 and 720 days. The elongation of mortar bars with lithium nitrate was 0.30% at 360 days, thus exceeding the aggregate reactivity threshold set at 0.1%. Expansion of mortars increased, reaching 0.53% at 720 days (Figure 1b). The expansion of mortars with opal aggregate observed in the accelerated test at 14 days, was 4.8 times that recorded at 360 days in the long-term method (standard test). The linear changes in the mortar bars with lithium nitrate observed in the long-term test at 360 days were about 7.5 times the expansion value recorded at 14 days in the accelerated test. In the standard test the expansion curve did not show the shape typical of the reactive aggregate reaction with sodium and potassium hydroxides. Expansion, increasing slightly up to day 90, increased significantly in the period between 90-180 days. After about 420 days, another rapid increase in the linear elongation of mortar bars was recorded.

The expansion process was still proceeding but at a substantially slower pace. A similar plot of curves was observed in the mortars with reactive aggregates but without corrosion inhibitors by Owsiak [15]. The expansion curve, according to the literature on aggregate reactivity, is not characteristic only of the alkali-aggregate reaction [16]. The elongation observed after 420 days on the expansion curve may be associated with DEF. It has to be noted, though, that the investigations available in the literature have not been conducted for mortars with potential corrosion inhibitors.

Moreover, in the mortars with lithium nitrate, increased formation of reaction products of greater solubility (exudations observed on the surface of the mortar bars) than those formed in the reference specimens was noted.

3.2. Microstructure

Observations of the fractures of the specimens made with LiNO₃, in which the reaction proceeded at an elevated temperature, did not show the presence of sodium-potassium-calcium hydrate silicate gels. The mortars had compact microstructures (Figure 2a). Calcium silicate phases, probably enriched with lithium ions, formed in the cement paste matrix (Figure 2c). In the regions near the interfacial zones, compact, fibrous calcium silicates were observed, probably being enriched with lithium ions (Figure 2b-c). These products may protect the reactive grains against the reaction with sodium and potassium...
hydroxides [17]. In the reference mortars, both crystalline and massive (amorphous) alkali silicate with a high content of sodium was observed to fill the areas of reactive grain (Figure 2d-f). No significant differences between the specimens analysed at 14 and 28 days were noted.

Figure 2. The microstructure of mortars with ASTM C1260: with lithium nitrate after (a) 14 days, (b) 28 days and without lithium compound after (d) 14 days, (e) 28 days; EDS spectrum at location (c) 1-2, (f) 3-4

Substantial amounts of calcium-potassium silicates in the form of massive gels (Figure 3a,3c) were found, both at 360 and at 720 days, in the microstructure of mortars containing lithium nitrate stored over water at 38°C, located mainly in the air voids. The cracks in the reaction products indicated heavy hydration. No cracks were observed around the air voids filled with reaction products. This is probably associated with the accumulation of gels in the large pores. However, numerous corrosion centres were found, along with the microcracks of reactive grains and the surrounding cement paste.
Figure 3. Micrographs showing formation of ASR products after testing with ASTM C227: with lithium nitrate after (a) 360 days, (b) 720 days, (d)-(e) alkali silica gel and fine ettringite, and without LiNO₃ after (g) 360 days, (h) 720 days; EDS spectrum at location (c) 1-2, (f) 3-4, (i) 5-6.
The sodium-calcium silicates with a high potassium content were also observed on the surface of the reactive opal aggregates (Figure 3b-c). In mortars with lithium nitrate no massive ettringite needles were noted in the interface zones between the reactive aggregates and the paste, but very fine ettringite needles were observed in microcracks located in the cement paste near reactive opal aggregate (Figure 3d-f). The presence of accumulated portlandite crystallites was observed in the pores.

In the reference mortars analysed with the standard test, swelling alkali silicate gels were observed (Figure 3g), along with conglomerates of fibrous ettringite and hexagonal portlandite crystals located mainly in the air voids (Figure 3h). The massive alkali silicate gels had high contents of potassium ions (Figure 3i). A significant role of DEF associated with ASR has been widely reported in the literature [18-20]. In the case under analysis, the formation of ettringite in the reference specimens tested with the long-term method had a negligible effect on the expansion observed in the mortars, unlike in the mortars with opal aggregates analysed by Owsiak [21].

4. Conclusions

- Expansion of quartz sand mortars made with 6% reactive aggregates is a function of reaction conditions. At higher temperatures and in the presence of sodium hydroxide source, the specimens expand heavily. The linear changes exceeding the standard-based aggregate reactivity limits indicate an advanced reaction between the opal aggregates and sodium and potassium hydroxides.
- The expansion of mortar bars created with opal was suppressed by lithium nitrate addition, only when the reaction proceeded at 80°C and the external source of lithium nitrate was provided (according to modified ASTM C1260 standard test method).
- The addition of lithium nitrate in the mortars in which the reaction proceeded at 38°C was found to threaten their durability. Expansion of the specimens with LiNO₃ after 360 days was approximately 7.5 times that of mortars determined with the accelerated test after 14 days. The literature on so high expansion growths of mortars/concrete with lithium ions is scarce.
- The microstructural tests of mortars with lithium nitrate that showed small expansion confirmed the absence of destructive reaction products. No microcracks were observed on opal aggregate grains or on the cement matrix, which indicates high efficacy of LiNO₃ as corrosion inhibitors.
- The microstructural tests of mortars with lithium nitrate, analysed with ASTM C227 indicate increased formation of strongly hydrated, mainly amorphous, potassium-calcium silicate gels, located both in the air voids and on the surface of the aggregate grains. Significantly, the reaction products showed greater solubility observed in the form of multiple exudations on the specimen surfaces.
- In the mortars with lithium nitrate, which showed high expansion, no ettringite agglomerates were detected; very fine needles were present in the cracks of the cement paste near the reactive aggregates. Probably the increased gel formation is responsible for the rate of expansion observed. The tests conducted so far do not exclude the possibility of DEF in the mortars with lithium nitrate and its potential effect on the increase in specimen expansion. Nevertheless, this may not be the main cause of the material deterioration. Further investigations into this matter are necessary.

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