Effect of LiNO$_3$ on Expansion of Alkali–Silica Reaction in Rock Prisms and Concrete Microbars Prepared by Sandstone

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Abstract: The aim of this research is to investigate the effect of LiNO$_3$ on the alkali–silica reaction (ASR) expansion of reactive sandstone and the mechanism through which this occurs. This paper presents the results from tests carried out on rock prisms and concrete microbars prepared by sandstone and LiNO$_3$. The findings show that LiNO$_3$ does not decrease the expansion of these samples unless the molar ratio of [Li]/[Na + K] exceeds 1.66, and the expansion is greatly increased when its concentration is below this critical concentration. The expansion stress test proves that Li$_2$SiO$_3$ is obviously expansive. X-ray diffraction (XRD) and scanning electron microscope (SEM) results indicate that LiNO$_3$ reacts with the microcrystalline quartz inside sandstone, inhibiting the formation of ASR gel, and the formation of Li$_2$SiO$_3$ causes larger expansion. A high concentration of LiNO$_3$ might inhibit the ASR reaction in the early stages, and the formation of Li$_2$SiO$_3$ causes expansion and cracks in concrete after a long period of time.

Keywords: microstructure; deformation; alkali–silica reaction; lithium nitrate

1. Introduction

The alkali–silica reaction (ASR) is one of the main reasons for the decline of concrete durability. Following the discovery of the beneficial effects of lithium ions on ASR-related expansion in 1951, the effects of lithium compounds on ASR have been extensively studied [1]. However, the exact role of Li$^+$ ions in controlling ASR is still unclear [2–5]. Several mechanisms have been proposed, including (i) enhance chemical stability of reactive silica exposed to pore solution [6–8], (ii) formation of less expansive Si–Li reaction products [9–12], (iii) formation of physical barrier by insoluble Si–Li reaction products [11,13,14]. However, the proposed mechanisms have mainly been determined experimentally under specific conditions and are not applicable to the most situations.

Lithium nitrate (LiNO$_3$) is considered to be the most excellent compound for inhibiting ASR in various lithium-containing admixtures. Compared to other lithium-containing admixtures, the major advantage of LiNO$_3$ is that it does not contribute to the increase of hydroxide (OH$^{-}$) ion concentration, which eliminates the pessimum effects of other lithium-containing admixtures [15,16]. LiNO$_3$ is also superior to other lithium-containing admixtures due to its neutrality, high solubility and good effect on concrete deformation. The use of LiNO$_3$ as a lithium-containing admixture significantly reduces the expansion and affects the chemical composition and microstructure of the reaction product in mortar samples [11]. The addition of LiNO$_3$ in the molar ratio of [Li]/[Na + K] at a level of 0.74 can generally reduce the expansion of mortar samples prepared with reactive aggregates to reach a safe and nondestructive level [17].

One of the unresolved issues related to the use of lithium-containing admixtures is related to the determination of the reaction product of the aggregate and the solution. Most previous studies...
did not directly confirm the existence of a production layer as a physical barrier, let alone explain the chemical composition, microstructure or effect of protection [18,19]. Feng X [20] considered that a mixed product made from the reaction of LiNO$_3$ with aggregate included crystalline Li$_2$SiO$_3$ crystals and Li-containing low-Ca silica gel, thereby inhibiting the ASR reaction in concrete. Through MR experiments, Kim T [21] showed that the most likely mechanism to explain the excellent ability of Li$^+$ ions to inhibit ASR involves the dense physical barrier, which is formed by the reaction products covers delimited areas on the exposed surface of the reactive aggregate. Zhou BF [22] found that quartz glass slices immersed in the alkaline solution with LiNO$_3$ and Ca(OH)$_2$ were well protected by a production layer consisting of Li$_2$SiO$_3$ crystals and CSH that densely and firmly covered the surfaces of samples, but seriously corroded in solutions with only LiNO$_3$ or Ca(OH)$_2$.

We studied the expansion of reactive aggregate with the rock prism test and concrete microbar test. XRD and SEM were used to find the reaction product to explain the effect of LiNO$_3$ on the alkali–silica reaction of the reactive aggregate.

2. Materials and Methods

2.1. Aggregate

Sandstone aggregate from the Lianghekou hydropower station in China was used. Figure 1 shows the XRD pattern of sandstone. The chemical composition of sandstone is shown in Table 1.

![Figure 1. XRD pattern of sandstone.](image1)

Table 1. Chemical composition of sandstone.

| Oxide Component | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | K$_2$O | Na$_2$O | LOI |
|-----------------|--------|-------------|-------------|-----|-----|-------|--------|-----|
| Sandstone (wt%) | 53.12  | 17.47       | 5.53        | 5.26| 3.89| 4.04  | 0.715  | 9.15|

We can see a large amount of microcrystalline quartz in the sandstone from the polarizing microscope photograph Figure 2.

![Figure 2. Microstructure of sandstone.](image2)
2.2. Rock Prism Test

The effect of LiNO$_3$ on the expansion of sandstone in different alkali solutions was studied in accordance with ASTM C589. The sandstone was cut into the rock prisms 10 × 10 × 30 mm in size in the same direction. The nail heads were fixed on the ends of the rock prisms with P•II525 Portland cement, and the nail heads were covered at both ends with a damp cloth until the cement hardened. The hardened rock column was cured in clear water for 24 h. The length of every rock prism was measured to be the initial length of the rock prism by a spiral micrometer with an accuracy of 0.001 mm. Then the rock prisms were separately cured in different alkaline solutions at 80 °C. The curing solutions were mixed solutions of NaOH and LiNO$_3$, and the ratios of Li/Na were 0, 0.41, 0.83, 1.24, 1.66, 2, and 3 respectively. The fresh curing solutions were replaced every 28 days. After curing to the set age, all the rock prisms were taken out and cooled to room temperature. Then, we measured the length and recorded the data to calculate the expansion rate at this time.

2.3. Concrete Microbar Test

The concrete microbars of 40 mm × 40 mm × 160 mm in size had a cement: aggregate ratio of 1 and a water: cement ratio of 0.3 according to RILEM AAR-5. Sandstone aggregates with grain sizes of 5 or 10 mm were used. The alkali content of cement was adjusted to 2% Na$_2$O equivalent by adding NaOH into the mixing water. LiNO$_3$ was added to the mixing water in different molar ratios of lithium ions to alkali ions [Li]/[Na + K], such as 0, 0.41, 0.83, 1.24, 1.66, 2, and 3. The fresh curing solutions were replaced every 28 days. NaOH and LiNO$_3$ were added to the curing solutions in the same molar ratio and the concentration of NaOH in every solution was 1 mol/L. After curing to the set age, all concrete microbars were taken out from the curing solutions and cooled to room temperature. Then we measured the length and recorded the data to calculate the expansion rate at this time.

2.4. Expansion Stress Test Apparatus

The expansion stress caused by the activity of SiO$_2$ and LiNO$_3$ was tested by the expansion stress test apparatus which can be seen in Figure 3. We put 50 g SiO$_2$ powder made of quartz glass with granules of less than 80 µm in size into the sample mold and compressed it into a compacted body by a press until the body could hold the pressure of 650 MPa for 5 s. Then, we put the mold into the expansion stress test apparatus with a pressure of 25 ± 0.1 MPa by tightening the nut. The apparatus was cured in a constant temperature curing box in a solution of 1 mol/L NaOH and 0.83 mol/L LiNO$_3$ at 60 °C. Because the expansion of the rock prism and the concrete microbar samples greatly increased at an [Li]/[Na + K] dosages of 0.83 compared to the reference sample, the pressure sensor used in this device is suitable for temperature below 70 °C. The expansion stress was calculated according to Equation (1):

\[ \sigma = \frac{4(F_t - F_0)g}{\pi d^2} \]  

where $\sigma$ is the expansion stress (MPa); $F_t$ is the sensor value at time $t$ (kg); $F_0$ is the initial value of the sensor (kg); $g$ is the acceleration due to gravity and with a value of 9.8 m/s$^2$; $d$ is the inner diameter of the mold with a value of 24 mm; and the value of $\pi$ is 3.14.
3. Results and Discussion

3.1. Rock Prism and Concrete Microbar Deformation

Figure 4 showed the expansion curves of rock prisms cured in solutions with different concentrations of LiNO₃ and 1 mol/L NaOH compared to the reference sample cured in 1 mol/L NaOH solution without lithium additive. LiNO₃ added at Li/Na ratios of 0.41, 0.83, and 1.24 to solutions increased the expansion of samples obviously; the largest expansion was 8.8%, which caused damage to the samples. LiNO₃ added at doses of 2 and 3 decreased the expansion of samples; samples expanded by about 0.25% in comparison to 0.91% in reference samples at 210 days. A dose of 1.66 decreased expansion after 150 days.

The results indicated that LiNO₃ did not decrease the expansion of rock prisms until its concentration exceeded 1.66 mol/L and the expansion was greatly increased when its concentration was below this critical concentration. The expansion must be caused by the formation of other reaction products such as Li₂SiO₃ rather than just ASR. The data from the early days showed that the lower the Li concentration was, the faster the reaction was. The expansion curve of the sample at a dose of 0.41 tended to be gentle after 120 days indicating that the main reaction of the expansion had been completed or the expansion stress had been released from the cracks.

The rock prisms with large expansion at 210 days cracked or were even damaged, showing that the expansion of aggregate contributed greatly to the expansion of concrete made of sandstone. However, we studied the effect of LiNO₃ on concrete microbars using the modified RILEM AAR-5 standard considering the directionality of rock expansion and the limitations of cement on aggregates.
Figure 5 showed the expansion curves of mortar microbars prepared with LiNO$_3$ compared to the reference sample prepared without lithium additive. The results indicated that critical Li concentration for concrete microbars was dose of 2. The samples with LiNO$_3$ at [Li]/[Na + K] ratios of 0.41 and 0.83 increased expansion while samples at doses of 1.66, 2, and 3 decreased expansion in comparison to the reference samples. Doses of 1.66, 2, and 3 appeared to be effective in minimizing expansion over the time period tested and even made the samples micro-shrink so the expansion value of samples decreased from about 0.049% at 63 days to about 0.017% at 210 days, whereas at a dose of 0.83, expansion significantly increased after 60 days, and samples were damaged at 120 days. It was hard to make such a huge expansion with ASR gel, and we did not find ASR gel in the samples with LiNO$_3$. So, the reason for expansion must be a different reaction from that of the general ASR.

![Expansion curves of concrete microbars cured in different alkaline solutions at 80 °C.](image)

**Figure 5.** Expansion curves of concrete microbars cured in different alkaline solutions at 80 °C.

At a dosage of 0.41, expansion showed an increasing trend with respect to the reference sample during the first 28d which indicated that the lower the concentration of Li$^+$, the faster the reaction in the early stage. However, dose of 0.83 exhibited the larger expansion compared to dose of 0.41 after 47 days because large number of formed cracks increased the reaction area and dose of 0.83 provided more Li$^+$. The concentration of Li$^+$ can be considered constant as the fresh solutions were replaced every 28 days. The dose of 1.24 appeared to be effective in reducing expansion during the first 80d, but the expansion increased rapidly after 80d and even was greater than the reference samples at 120d. This phenomenon may result from that the dose of 1.24 was so near the critical concentration that the reactions of increasing expansion occurred so slowly that cracks cannot be observed until samples were cured after several weeks. And with the constantly increasing of cracks, the increasing expansion reaction was more and more intense which led to the accelerated expansion in the later stage. So high concentration of Li$^+$ cannot inhibit the expansion of mortar microbars after many years. And this phenomenon also proved that protective layer may not really exist, that is to say, the production layer may not be the real reason for decreasing the expansion of ASR.

By studying the images displayed by the polarizing microscope, we found that the cracks were mainly formed inside the aggregate of the concrete microbars. To study the reaction products in concrete microbars cured in different alkaline solutions, we analyzed the internal aggregate after the reaction at 120 days using XRD. Figure 6 showed the effects of the LiNO$_3$ concentration on the mineralogical composition of crystalline reaction products in concrete microbars cured in 1 mol/L NaOH solution. Li$_2$SiO$_3$ was the only crystalline compound when the LiNO$_3$ concentration was 0.83 mol/L. But we did not find any products from XRD when the LiNO$_3$ concentrations were 0 and 2 mol/L.
This phenomenon was consistent with the results of the macroscopic expansion experiments which showed that the expansion of samples with 0.83 mol/L LiNO$_3$ was greater than that of samples with 0 and 2 mol/L LiNO$_3$. So, the formation of Li$_2$SiO$_3$ appeared to be the reason for the expansion. When the LiNO$_3$ concentration was higher than a certain concentration, the product of Li$_2$SiO$_3$ was greatly reduced but not prohibited, resulting in a sudden increase in expansion at a later stage. When the concentration of LiNO$_3$ was particularly high, the later time might be very long and the products of Li$_2$SiO$_3$ were very small and difficult to find.

Therefore, we consider Li$_2$SiO$_3$ to be a deleterious product of the alkali–silica reaction. LiNO$_3$ behaves similarly to other lithium compounds, such as hydroxide or carbonate and gives a pessimum effect.

3.2. Expansion Stress

Figure 7 showed that the expansion stress curve of a compacted body which made of SiO$_2$ powder and placed in a self-made stress device. It proved that Li$_2$SiO$_3$ was obviously expansive. The curing solution included 0.83 mol/L LiNO$_3$ and 1 mol/L NaOH, and the main reactions occurred as followed:

\[
\text{SiO}_2 + 2\text{OH}^- = \text{H}_2\text{O} + \text{SiO}_3^{2-} \tag{2}
\]

\[
2\text{Li}^+ + \text{SiO}_3^{2-} = \text{Li}_2\text{SiO}_3. \tag{3}
\]
The expansion stress was continuously reduced until 27 days, and then it increased until 58 days due to the pre-stressing of the compacted body and the slow penetration of the solution. Finally, the stress broke out, resulting in damage to the device, and stress value was more than 195 MPa. The dissolution of SiO$_2$ on the surface of compacted body caused formation of Li$_2$SiO$_3$, which was difficult for the surface of compacted body to absorb, resulted in a decrease in the expansion stress during the early days. Then, Li$_2$SiO$_3$ was formed inside, causing a rise in expansion stress as the solution continuously penetrated into the compacted body. The sudden rapid increase in stress on the last day may have been due to the filling of the internal voids of the compacted body and an order of magnitude change in the rate of reaction, which was similar to the rapid expansion of rock prisms and concrete microbars.

3.3. Microstructure

Figure 8 presents the findings from the observations of the microstructure of mortar microbars cured in 1 mol/L NaOH with 0.83 mol/L LiNO$_3$ at 80 °C. Figure 8a presented products formed at 42 days. Needle-like and filamentous crystals containing only Si and O represent Li$_2$SiO$_3$ formed on the surface of SiO$_2$ around the cracks, because Li cannot be detected by energy dispersive spectrometer (EDS). Figure 8b presented products at 120 days. The many spindle-like crystals containing only Si and O represent Li$_2$SiO$_3$ which formed by the growth of needle-like and filamentous crystals. There were some SiO$_2$ residues at position 1, 2, and 3, and cracks were mostly filled with products.

![SEM images of aggregate in concrete microbars](image_url)

**Figure 8.** The SEM images of aggregate in concrete microbars cured in 1 mol/L NaOH with 0.83 mol/L LiNO$_3$ at 80 °C: (a) at 42 days; (b) at 120 days.

As mentioned before, LiNO$_3$ did not decrease the expansion of samples until its concentration exceeded 1.66 mol/L. The expansion of samples when LiNO$_3$ was present in concentrations below the critical concentration increased more quickly than in the reference sample. There must have been lots of formed products, namely, Li$_2$SiO$_3$ and ASR gel, leading to significant expansion of mortar microbars. However, it was hard to produce such a huge expansion with ASR gel, and we did not find ASR gel in the samples with LiNO$_3$. It was indicated that Li$^+$ reacted with the microcrystalline quartz inside the aggregate causing most of the expansion and this reaction consumed the reactants belonging to the ASR and inhibited the formation of ASR gel. Formed Li$_2$SiO$_3$ resulted in expansion increasing the reaction area, accelerated the reaction rate and finally formed larger cracks.

Figure 9 presented the findings from the observations of the microstructure of mortar microbars cured in 1 mol/L NaOH with or without 2 mol/L LiNO$_3$ at 120 days. Compared with Figure 8, there were little reaction product and cracks in Figure 9a, which shows the sample in solution without LiNO$_3$. The surface shown in Figure 9b with 2 mol/L LiNO$_3$ was so smooth that there were almost no product formation and no cracks. Excess lithium nitrate made the sandstone denser, which corresponded to the minimal expansion and even micro-shrinkage of concrete microbars.
The expansion stress test proved that LiNO3 did not decrease the expansion of rock prisms and concrete microbars with sandstone until the molar ratio of [Li]/[Na + K] exceeded 1.66, and expansion increased when the LiNO3 concentration was below the critical concentration.

2. The expansion stress test proved that Li2SiO3 is obviously expansive and the expansion stress was more than 195 MPa at the end of the test.

3. The XRD and SEM analyses indicated that product of Li2SiO3 caused greater expansion of samples, and reaction consumed the reactants belonging to ASR and inhibited the formation of ASR gel. LiNO3 reacted with the microcrystalline quartz inside the aggregate of sandstone and formed Li2SiO3; the expansion increased the reaction area, accelerated the reaction rate and finally, caused more and larger cracks.

4. The long-term effectiveness of excessive LiNO3 at inhibiting ASR was questionable. The high concentration of LiNO3 only inhibited the ASR reaction in the early stages and the formation of Li2SiO3 caused expansion and cracks in the concrete after a long period of time.

According to the results, the formation of Li2SiO3 caused greater expansion of sandstone when in the molar ratio of [Li]/[Na + K] was less than 1.66. LiSiO3 did not form or minimally formed in concrete microbars with higher concentrations of LiNO3, which should be studied further in the future.

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