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PRELIMINARY STUDY OF EFFECT OF $LiNO_2$ ON EXPANSION OF MORTARS SUBJECTED TO ALKALI-SILICA REACTION

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ABSTRACT

The effect of $LiNO_2$ on the expansion of mortars made completely of reactive aggregate with five particle size fractions was investigated by means of an autoclave test. The results show that the effect of $LiNO_2$ varies with its content and Na_2O level, or more specifically, with the molar ratio of Li/Na in mortars. When the ratio reaches 0.8 at higher Na_2O level (greater than 2% in this study), ASR expansion is substantially suppressed and the ratio below or beyond this value will give different results. For the other cases of lower Na_2O levels the results are distinguished from this and the best Li/Na molar ratios of 0.1, 0.3 and 0.5 corresponding to the Na_2O levels of 0.5, 1.0 and 1.5%, respectively, are recommended.

Introduction

As is well known, alkali-silica reaction (ASR) has resulted in serious deterioration and damage of concrete constructions, which have to be repaired and maintained over their long service life at the cost of a great deal of money and by many different measures. It is very remarkable that the use of blending materials such as blast furnace slags, silica fumes and pozzolanas could suppress the expansion caused by ASR occurring in mortars and concretes, but they could not inhibit the deleterious reaction completely.

On the other hand, the effect of various chemicals has attracted researchers' attention, and numerous results have been published, although there are some differences among them since different conditions were used. Among them, the constructive work by McCoy and Caldwell in which lithium salts were used to suppress such detrimental expansion have been most widely recommended. McCoy and Caldwell (1) incorporated into mortars 1% of lithium chloride, 1% lithium carbonate and 1% lithium fluoride by weight of cement in which the equivalent Na_2O content was 1.15%. By comparing to the expansion values from 0.30% at 14 days to 0.54% at 56 days for reference samples such an experiment caused a reduction of expansion within 90–97%. It is noted that the corresponding molar ratios of Li/Na are 0.73, 0.73 and 1.20, respectively, for the three salts in their case.

Stark (2) confirmed the functions in inhibiting the abnormal expansion of lithium fluoride and lithium carbonate by following the guideline of ASTM C227, and that of lithium hydroxide by following ASTM P214. In the former test, the admixtures were added with dosages of 0.25, 0.50 and 1.0% against the weight of cement (Na_2O equi. of 0.92% in the cement), and thus that gave the corresponding ratios of Li/Na of 0.30, 0.60 and 1.20 for the case of LiF , of 0.23, 0.46 and 0.91 for Li_2CO_3. In comparison with the low dosage of 0.25% for LiF, the addition of 0.5 and 1.0% could decrease the expansion to 0.06% and 0.02%, which implied 10–fold and 30–fold reductions of expansion. As for Li_2CO_3, it seemed to need a higher dosage, for instance, when dosage was 0.5%, it only caused a minor reduction of expansion, but when the dosage was raised to 1.0%, a distinct reduction would be obtained. Moreover, Stark's results suggest that the threshold dosages of additives be 0.5% for LiF and 1.0% for Li_2CO_3 against the cement mass, and thus the corresponding Li/Na ratios be 0.60 and 0.91, respectively. For the P214 test, Stark also claimed that a minimum value of Li/Na molar ratio of 0.67 is desirable.

Analyses of the results of Sakaguchi et al (3) reveal also that the effect of lithium salts depends significantly on Li/Na molar ratios and alkali contents, and their test on mortars with Li/Na molar ratios of 0.9–1.2 gives the best results when added as lithium hydroxide.

However, it seems that the values of adequate Li/Na molar ratios depend on the kinds of admixtures, the alkali levels and the ratio of Na_2O to available SiO_2 as well as the other specific conditions. Generally, it could be concluded that a Li/Na molar ratio larger than 0.50 could result in a measurable reduction of expansion. In Japan, lithium nitrite was tried in the maintenance of concrete constructions subjected to ASR (4), but until now no advanced results are available. For more information on the effects of lithium salts one could consult Ref. 5, 6 and 7.

In the present study, the relations between Li/Na molar ratios and the expansions of mortars made completely of reactive aggregate sand at different alkali levels were investigated by using $LiNO_2$ as an admixture.

Starting Materials and Procedure

1. Starting Materials

An ordinary portland cement with low alkali content (0.46% Na_2O equivalent) was used as a cementitious material, and an andesite (designated as O) from East Seitouchi (Japan) was crushed and sieved into 5 fractions as a fine aggregate shown in Table 1. It is identified by ASTM C289 as potentially reactive, and its Sc=732, Rc=177 mmol/l (Sc/Rc=4.14) with the specific gravity of 2.25 and water adsorption capacity of 1.81%.

A commercial $LiNO_2$ solution with a mass concentration of 40% and a solid NaOH were used as additives to give adequate molar ratios of Li/Na in mortars by taking into account the primary Na_2O content in the cement.

TABLE 1 Fractions and Proportions of Aggregate

Sieve size, mm	Weight, %
4.76–2.38	10
2.38–1.19	25
1.19–0.60	25
0.60–0.30	25
0.30–0.15	15

The added $LiNO_2$ amount was calculated according to the following equation:

$$W = \frac{2GM_{LiNO2}}{GM_{Na2O}} \cdot A \cdot a_m \cdot b_m = 1.71 \cdot A \cdot a_m \cdot b_m \qquad (1)$$

and the weight percentage of $LiNO_2$ against cement was determined by:

$$LiNO_2\ (\%) = 1.71 \cdot a_m \cdot b_m \qquad (2)$$

where, W implies the amount of $LiNO_2$ added in mortars, GM_{LiNO2} the formula weight of $LiNO_2$, GM_{Na2O} the formula weight of Na_2O, A the cement amount in mortars (here A=600g), a_m the required Li/Na molar ratio and b_m the Na_2O content in cement.

The proportions of NaOH and $LiNO_2$ in mortars are shown in Table 2.

2. Procedures

Mortar bars (4 × 4 × 16 cm) equipped with gauge studs at two ends were cast with 600g cement, 1350g aggregate (C/A=1: 2.25) and 300g water (W/C=0.50) according to JIS A 1129. Stripping them from molds by the end of 24-hour-curing interval in a fog room at 20 ℃, the mortars were then put in an autoclave under the condition of a gauge pressure of 0.28 MPa for a period of 4 hours immediately following their initial lengths (L_0, μm) measurements. After the treatment, the specimens were moved into the same fog room for curing 16-24 hours, and then the augmented lengths (L, μm) were measured. Next they were removed into a curing container at 20 ℃ for 4 months and then elevated to 40 ℃ constantly for long term measurements.

The expansion rates are calculated by the equation:

$$\text{exp.}\ (\%) = \frac{L - L_0 - \varepsilon_0}{1600} \qquad (3)$$

where ε_0 means the induced length change of specimens due to the change in temperature during the interval of measurements.

TABLE 2 The Proportions of Na_2O and $LiNO_2$ in Mortars *

a_m Li/Na molar ratio	b_m, Na_2O(%)/ NaOH(g)**						
	0.5 / 0.32	1.0 / 4.27	1.5 / 8.22	2.0 / 12.17	2.5 / 16.12	3.0 / 20.17	3.5 / 24.02
	NaOH (g)						
0.00 (Na_2O)	0.32	4.27	8.22	12.17	16.12	20.17	24.02
	Li_2O (%)/$LiNO_2$ (g)						
0.10	0.08 / 0.51	0.17 / 1.03					
0.30	0.26 / 1.53	0.51 / 3.08					
0.50	0.43 / 2.57	0.86 / 5.13	1.28 / 7.70	1.71 / 10.26	2.14 / 12.83	2.57 / 15.39	2.99 / 7.96
0.80	0.68 / 4.10	1.37 / 8.21	2.05 / 12.31	2.74 / 16.42	3.42 / 20.52	4.10 / 24.62	4.79 / 28.73
1.01	0.86 / 5.18	1.73 / 10.36	2.59 / 15.54	3.45 / 20.73	4.32 / 25.91	5.18 / 31.10	6.05 / 36.28
1.26	1.08 / 6.46	2.15 / 12.93	3.23 / 19.39	4.31 / 25.86	5.40 / 32.40	6.48 / 38.88	7.56 / 45.36
1.52	1.30 / 7.80	2.60 / 15.60	3.90 / 23.39	5.18 / 31.10	6.48 / 38.88	7.78 / 46.66	9.07 / 54.43
1.90	1.62 / 9.75	3.25 / 19.49	4.86 / 29.16	6.48 / 38.88	8.10 / 48.60	9.72 / 58.32	11.34 / 68.04

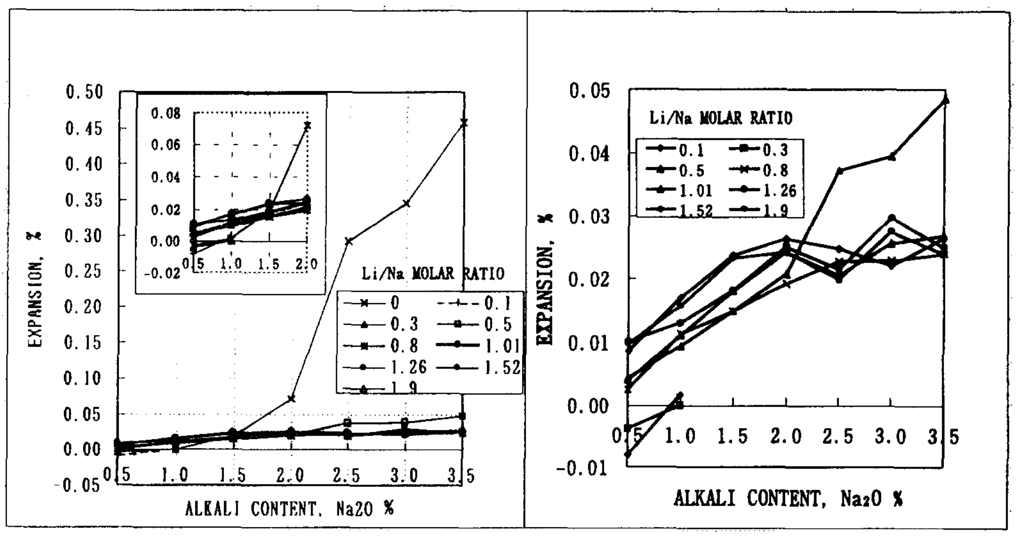
*: The top number signifies the amount of chemical(s) added in mortars, and the bottom number means the weight percentage with respect to cement mass.
**: The purity of NaOH is regarded as 98%.

Results and Discussions

The results on expansions of mortars subjected to ASR are shown in Figs.1 & 2. Obviously, the expansions of mortars increase with increasing Na_2O content in all the above cases. For specimens containing no $LiNO_2$, the expansions reach 0.072, 0.292, 0.345 and 0.459% when the corresponding Na_2O contents are 2.0, 2.5, 3.0 and 3.5%, respectively.

It can be seen that the addition of $LiNO_2$ could greatly suppress the expansions of mortars (Fig.1). For example, even when the Na_2O contents in mortars are as high as 3.0 and 3.5%, the addition of $LiNO_2$ could decrease the expansions by 88.7% and 89.5%, and thus the expansions became 0.039 and 0.048%, respectively, as the ratio of Li/Na is 0.5. This is in good accordance with the results of Y. Nakamura et al (6).

Based on Fig.1, however, when the Na_2O content is beyond 2.0%, the Li/Na ratio of 0.5 has a relatively smaller effect on the suppression of expansion. While increasing the Li/Na ratio from 0.5 to 0.8 decrease the expansion further, and the further reduction of expansion would be 7.2, 38.8, 41.3 and 50.1% when the corresponding Na_2O contents are 2.0, 2.5, 3.0 and 3.5% respectively. It is, therefore, regarded that the concentration of $LiNO_2$ is not enough in the situation of the low Li/Na ratio of 0.5, when Na_2O content is greater than 2.0%. But otherwise, the ratios of Li/Na higher than 0.8 do not always benefit the suppressive effect.

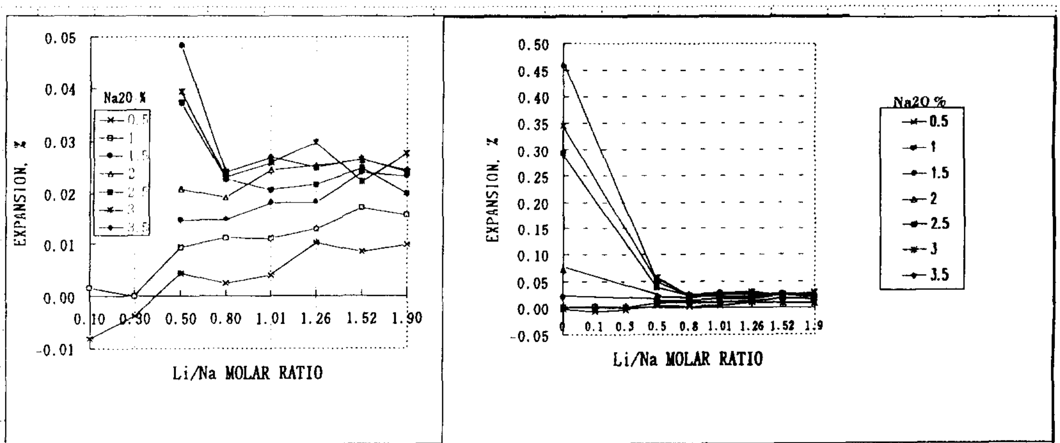


(a) (b)

FIG.1 The relation between expansion and Na_2O content in mortars:
(a) overall results;
(b) an enlarged Y−axis to show the effect of increasing Li/Na ratio on expansion

On the other hand, when Na_2O content is 1.5%, the mortars with ratios of Li/Na of 0.5 and 0.8 behave similarly, and increasing the Li/Na ratio more will add slightly to the expansion. Further reducing the Na_2O content to 1.0 and 0.5% will require a much smaller Li/Na ratio, e.g. 0.3 and 0.1, respectively, and subsequently increasing the Li/Na ratio beyond these values will also adversely result in minor increase in expansion (Fig.1b and Fig.2a). Thus, in conclusion, when Na_2O content is equal to or less than 1.5% the expansion tends to increase slightly with increasing the Li/Na ratio larger than the value at which $LiNO_2$ effectively suppress the deleterious expansion, even though the expansion is still regarded as being innocuous in this event.

Thus we conclude that the effect of Li/Na molar ratios on expansion depends on the Na_2O contents in mortars, generally when Na_2O content in mortars is greater than 2.0%, a 0.8 Li/Na molar ratio might be most effective for inhibiting the serious expansion caused by



(a) (b)

FIG. 2 The relation between expansion and the ratio of Li/Na in mortars
(a) an enlarged Y-axis to show the effect of increasing Na_2O contents on expansion; (b) overall results of the effect of Li/Na ratios on expansion

ASR, and thus, proportioning more $LiNO_2$ into the specimens than the allowed amount corresponding to the ratio of 0.8 would be meaningless technically and economically. It is also very interesting that the effectiveness of $LiNO_2$ in suppressing expansion became greater with increasing Na_2O contents. As compared the results from Li/Na ratio of zero with 0.8, the expansions are decreased by 73.3%, 92.2%, 93.3% and 94.7% relative to the values of control specimens (i.e. Li/Na=0.0) when the Na_2O content is raised continuously from 2.0% to 2.5, 3.0 and 3.5%, respectively. This could be observed from Fig.2b and be explained as follows: when the Na_2O content increases, the amounts of reaction products (sodium silicate gels) increase and, hence, the swelling also increases. After adding $LiNO_2$, Li^+ ions can get into the structures of the gels, and substitute for some Na^+ and K^+ ions owing to their smaller ionic radii. Further Li^+ ions form stabler 4-coordination linkages with hydroxyl groups in gels because of its lack of d orbits (8,9) relative to the 6-coordination ones of Na^+ and K^+ ions which have d orbits, as contracts the structural skeletons of the solid solution of the gels, consequently, the swelling becomes difficult through the adsorption of water. So it is speculated that based on the above results the level of Li/Na=0.8 might induce an almost complete substitution of Li^+ ions for Na^+ and K^+ ions in N(K)-C-S-H gels and make the gel structures densified when relatively high Na_2O content is available. Due to this fact, Li^+ ions could be considered as antiswelling stabilizers for gels. On the other hand, when the amount of $LiNO_2$ is beyond the amount corresponding to the ratio of 0.8, the remaining Li^+ ions might hold more hydroxyl groups in pore solutions for the aforesaid reason. Subsequently, they could directly break up, along with Na^+, K^+ and OH^- ions, the silicate structures of the reactive components in an aggregate and combine with the broken pieces, the species $\equiv Si-O-$. This could contribute to the more formation of gels with denser structure, in which Li^+ ions bind the silica pieces more intensely than Na^+ and K^+ ions because of their stronger chemical affinity and thus in which more Li than Na and K are contained, and also this would contribute to the slightly increased expansion.

Similar to the phenomena observed by Ohstuka et al (7), adding $LiNO_2$ into the mortars would reduce the dissolution of SiO_2 in a reactive aggregate. This is because enveloping the aggregate with the newly formed Li–bearing gels makes the diffusion of water molecules and ions through the gel layers more difficult, and therefore, inhibit the subsequent corrosion of aggregate by alkalies in pore solutions. As a result, the suppression of the detrimental expansion of mortars subjected to ASR is realized.

In addition, for the specimens with high Na_2O contents and $LiNO_2$ free, cracks could be apparently observed just through the autoclave treatment, but no cracks occurred on the surfaces of the specimens containing $LiNO_2$. Moreover, over a 16–month period of storage, gels exude out of the surfaces of specimens containing Li^+, even with the highest Na_2O content (e.g. 3.5%) but still no cracks appear. The exuded gels which are covered by a slightly loose white substance consolidated and strongly adhere to the surfaces of mortars. These also account for the effectiveness of $LiNO_2$ in suppressing the expansion induced by ASR. Unfortunately, until now there is no evidence to show if the anions of chemical admixtures such as NO_2^- directly take part in the reaction with reactive aggregate. So the relevant mechanisms should be researched further. Also, the continuous measurements of the long–term volumetric stability of the specimens are ongoing and the results will be reported.

Conclusions

1. Mortar specimens made completely of fine reactive andesite without $LiNO_2$ expand greatly with the increase in alkali content. The expansion of the specimens with 3.5% Na_2O subjected to a hydrothermal treatment reaches as high as 0.459%.

2. $LiNO_2$ can evidently suppress the expansion caused by ASR with appropriate incorporations and the effect increases with increasing alkali contents.

3. The effectiveness of $LiNO_2$ in suppressing expansion is related to the Li/Na molar ratio in mortars: its amount added relative to the alkali content.

4. The most effective Li/Na ratio is about 0.8 at higher alkali level (greater than 2.0%). Below this ratio, for example, 0.5, the effectiveness is less, although the expansion is still less than 0.05% within the range being considered innocuous. But at relatively low alkali

levels (e.g. less than 2.0%) smaller Li/Na ratios are desirable; Adding $LiNO_2$ above these ratios is meaningless technically and economically.

5. $LiNO_2$ in suppresses ASR expansion by its Li^+ ions acting as swelling stabilizers for sodium silicate gels; extra Li^+ ions in mortars could cause more formation of gels as well as expansion of mortars, however.

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