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Long-term effectiveness and mechanism of LiOH in inhibiting alkali–silica reaction

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Abstract

A practical alkali reactive aggregate–Beijing aggregate was used to test the long-term effectiveness of LiOH in inhibiting alkali–aggregate reaction (AAR) expansion. In this paper, the most rigorous conditions were so designed that the mortar bars had been cured at 80 °C for 3 years after being autoclaved for 24 h at 150 °C. At this condition, LiOH was able to inhibit long-term alkali–silica reaction (ASR) expansion effectively. Not only was the relationship between molar ratio of $n(\mathrm{Li})/n(\mathrm{Na})$ and the alkali contents in systems established, but also the governing mechanism of such effects was studied by SEM.

Keywords: Lithium compounds; Alkali–aggregate reaction; Expansion; Long-term performance; SEM

1. Introduction

Alkali–silica reaction (ASR) is the most important type of alkali–aggregate reaction (AAR). Excess expansion and cracking of concrete occurs when some of the alkali reactive rocks were used as coarse aggregate in concrete made with high-alkali cement. Papers on this subject indicate a consensus that there are three possible measures to solve this problem [1]: the use of low-alkali cement, the use of nonreactive aggregate, and the incorporation of certain mineral admixtures such as silica fume, fly ash, and pozzolan into the concrete. However, each has its own limitations. For example, in using low-alkali cement, the level to which the alkali content must be reduced to prevent abnormal expansion of ASR has not been yet ascertained. Usually, a low-alkali cement means an alkali content of no more than 0.6% as equivalent sodium oxide ($Na_2O_{eq.} = Na_2O + 0.658K_2O$). However, as the cement content of a concrete mix increases, and as more and more admixture is used in the concrete, this seems to be an inadequate requirement.

Since McCoy and Caldwell first reported the use of chemical admixtures (as distinct from mineral admixture) to prevent expansion due to ASR in 1950 [2], considerable interest has been aroused among users and producers of Portland cement and aggregate, and other laboratories have investigated such chemical inhibitors. The latter might also have appreciable effect on other properties of concrete as reported by Mo [3]. In these research, much work was done concerning the effect of lithium compounds. Up until now, some progresses have been made of the mechanisms, the added amount of lithium compounds in inhibiting ASR. Also, some experiments have been making of the applications of lithium admixtures in practical engineering [4–7]. However, there are still some key problems to be solved. Although lithium compounds have been known for many years to ameliorate the effects of ASR, the long-term effectiveness has not been tested thoroughly and the evidence to prove such effects is also lacking. In this paper, not only was the long-term performance of lithium

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in inhibiting ASR tested by expansion work, but also corroborating evidence from scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) was obtained.

2. Materials and experimental methods

2.1. Experimental materials

2.1.1. Cement

To avoid the effect of paste expansion on the results, the low-alkali cement produced by Jiangnan Xiaoyetian, China was used. Its chemical composition is given in Table 1. Other properties include: initial setting time of 134 min, final setting time of 201 min, and Blaine specific surface of 360 m^2/kg. After being autoclaved at 150 °C, the paste expansion was 0.01%.

2.1.2. Aggregates

A practical alkali reactive aggregate–Beijing aggregate of particle size 3–5 cm and supplied by Beijing No. 12 Granite Factory was used. XRD showed that the main minerals present in the rock were plagioclase and quartz, while the alkali reactive component was microcrystalline quartz as shown in Fig. 1.

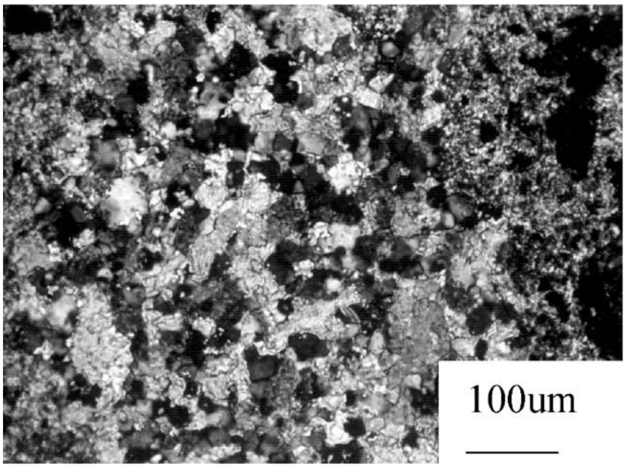


Fig. 1. Microcrystalline quartz in rocks by crossed Nicols.

The reactivity of the test aggregate was assessed by "The Chinese Method for ASR", which is the same as "A Rapid Test Method for Determining the Alkali Reactivity of Sands and Rocks" [8]. The major factors of the procedure include a test temperature of 150 °C, aggregate size of 0.15–0.80 mm, 10% KOH alkali solution, cement alkali content of 1.5% $Na_2O_{eq.}$, and a 6 h test period. The results are shown in Table 2.

2.1.3. Chemical reagents

Both KOH and water were used to adjust the alkali content of the mortar. The added amount of admixtures implied by an $n(\mathrm{Li})/n(\mathrm{Na})$ molar ratio was calculated according to the following equation:

$$m_x = 2m(A)w_m x_m M_0/[n_0 N_0 M(\mathrm{Na_2O})] \qquad (1)$$

where m_x implies the amount of admixtures added in mortars (g), $m(A)$ is the cement amount in mortars, w_m is the $Na_2O_{eq.}$ content in the cement (%), X_m is the molar ratio of $n(\mathrm{Li})/n(\mathrm{Na})$, M_0 is the formula weight of the admixture (g/mol), n_0 is the molar amount of Li per molar admixture, N_0 is the pure content percent of the admixture, and $M(\mathrm{Na_2O})$ is the formula weight of Na_2O.

Table 1
Chemical composition of cement (wt., %)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	LOI
64.6	22.1	4.76	3.28	0.82	2.60	0.07	0.59	0.91

2.2. Experimental methods

This method is quite similar to "The Chinese Method for ASR" [8], but some changes were also made [9]. When curing, the mortars were not steeped in either water or alkali solution, but in steam or moisture in order to keep the $n(\mathrm{Li})/n(\mathrm{Na})$ molar ratio in the system.

Curing of the test specimens in the present paper consisted of two stages—autoclaving followed by a long-term moist storage at 80 °C. Prisms (1 × 1 × 4 cm) were moulded from mortars of water/cement ratio of 0.40:1.00. These were demoulded at the age of 24 h, and initial length readings were obtained by means of a dial micrometer. The prisms were then autoclaved at 150 °C for 24 h in water vapour saturated air. After cooling to room temperature, the second length readings were taken on the prisms, which were then transferred to the long-term storage environment of an atmosphere of air at 80 °C and a relative humidity of 95%. To minimize leaching, the prisms were never in contact with liquid water. The final length readings were taken at the age of 3 years. Taking the autoclaving into account, curing of the mortars might produce the greatest maturity or effective long-term curing of all the world's lithium work.

Table 2
The results of alkali activity of Beijing aggregate

Weight (cement)/ weight (sand)	Expansive rate (%)		
	6 h	12 h	18 h
10:1	0.046	0.075	0.082
2:1	0.168	0.244	0.295

3. Results and discussion

According to the various published papers, ASR expansion occurs only when a certain minimum alkali content of the concrete is exceeded. This minimum value depends upon various factors. The addition of lithium to the concrete results in partial replacement of the potassium gel by a lithium gel, which is much less expansive [10–12]. Thus, the amount of lithium compound to be added varies from one concrete to another.

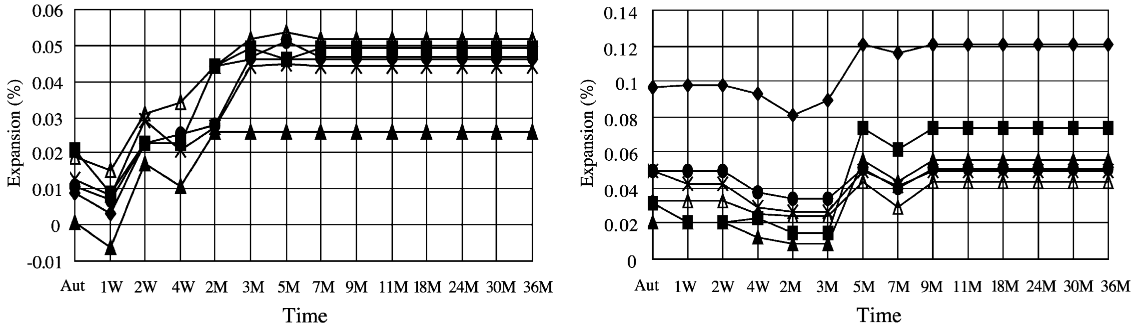
In the present work, mortars were prepared having their equivalent soda contents adjusted to four levels, viz. 1.5%, 2.0%, 2.5%, and 3.0% on the cement. Six of each of these mortars were made, one as a control containing no lithium, and the other five were doped with lithium hydroxide at the n(Li)/n(Na) molar ratios of 0.3, 0.6, 0.9, 1.2, and 1.5. These ranges of equivalent soda content and n(Li)/n(Na) ratios should cover most practical engineering cases.

3.1. Effect of LiOH in inhibiting ASR expansion

The long-term effects of LiOH of various n(Li)/n(Na) molar ratios in inhibiting ASR expansion of Beijing aggregate mortar are depicted in Fig. 2. These show that the expansions of the control mortars (no added lithium compounds) increased as the alkali content increased through KOH addition; all specimens identically cured. The LiOH additions clearly had long-term effectiveness in inhibiting ASR expansion. When the equivalent soda content was effectively raised to 1.5% by KOH addition, the control mortar expansion was 0.046%. As this value is rather small, the inhibiting effect of LiOH was not significantly apparent. At 2.0% $Na_2O_{eq.}$, the control expansion increased to 0.121%, while the lithium-doped mortars expanded no more than 0.074%. At 2.5% $Na_2O_{eq.}$, the respective expansions rose to 0.144% and 0.090%. For 3.0% $Na_2O_{eq.}$, control prisms expanded 0.210%, with a maximum of 0.095% for the lithium-doped prisms with the n(Li)/n(Na) ratio of 0.6, 0.9, 1.2, or 1.5. With the ratio at 0.3, the expansion was 0.562%. The final expansions of the mortars after 3 years curing are shown in Table 3.

Not only could the ASR expansion be inhibited by LiOH addition, but also the inhibiting effect had long-term stability with significant expansions occurring after 9 months curing. The lithium hydroxide monohydrate used in this work is fully soluble in the mortar's mixing water in the amounts added for these tests. The Beijing aggregate is a practical aggregate used in building work. It is typical of the aggregates in Beijing, China can be used a reference reactive aggregate against which other reactive aggregates can be compared.

Usually, effective inhibition of ASR means that the expansion is limited to no more than 0.10% according to Ref. [8]. The following conclusions can be drawn from the present research. When the alkali content was no more than 2.5%, the ASR expansion of Beijing aggregate mortars



(a) $Na_2O_{eq.}$=1.5%

(b) $Na_2O_{eq.}$=2.0%

(c) $Na_2O_{eq.}$=2.5%

(d) $Na_2O_{eq.}$=3.0%

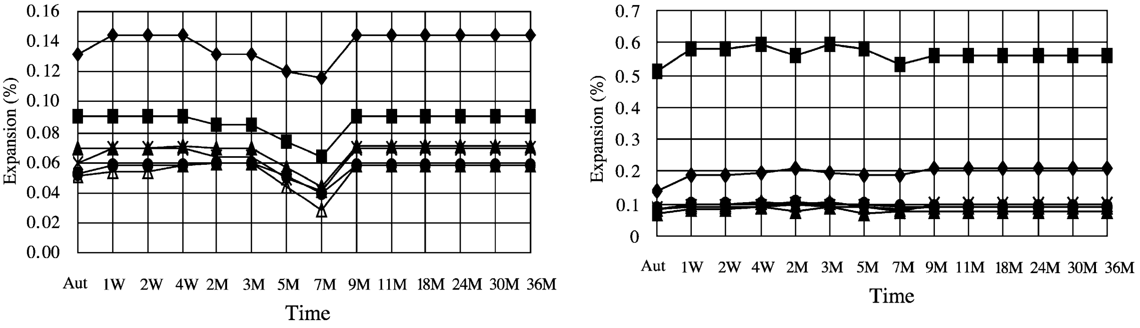


Fig. 2. Long-term effect of LiOH on ASR expansion of Beijing Aggregate mortar n(Li)/n(Na): (◆) 0; (■) 0.3; (▲) 0.6; (×) 0.9; (△) 1.2; (●) 1.5.

Table 3
Comparison of mortar expansive length after long-term curing (36 months)

$Na_2O_{eq.}$ (%)	Li/Na molar ratio					
	0	0.3	0.6	0.9	1.2	1.5
1.5	0.046	0.049	0.026	0.044	0.052	0.047
2.0	0.121	0.074	0.056	0.049	0.044	0.051
2.5	0.144	0.090	0.071	0.069	0.058	0.058
3.0	0.210	0.562	0.079	0.095	0.088	0.094

could be effectively inhibited long term by adding LiOH with n(Li)/n(Na) molar ratio of 0.3 or above. When the alkali content was 3.0%, the ASR expansion could be effectively inhibited long term by adding LiOH with an n(Li)/n(Na) molar ratio of 0.6 or above.

3.2. Discussions of the mechanism of LiOH in inhibiting ASR expansion

The nature of ASR product from Beijing aggregate mortars of 3.0% $Na_2O_{eq.}$ content and 3 years of curing was examined by SEM. Relevant photomicrographs are presented in Fig. 3. It can be seen that the aggregate particles have been eroded in the control mortar and that the cracks run through both the aggregate and the paste. In the mortars with added LiOH at an n(Li)/n(Na) ratio of 0.3, the aggregate particles both eroded and unblemished are in evidence. A great deal of ASR gel was found around the particles not attacked by ASR, and many cracks formed in the paste nearby. Also, much ASR gel and many cracks formed around the particles badly eroded.

In the case of the LiOH mortars at an n(Li)/n(Na) ratio of 1.5, a great deal of crystalline products formed as the Li^+ entered the alkali silica reaction. EDS showed large amounts of Ca and Si in the crystalline product but less K than that in a typical ASR gel. A speculative explanation of this phenomenon is that, because Li^+ has both a smaller ionic radius and a higher ionic surface charge density than either Na^+ or K^+, when enough lithium compounds are added, Li^+ is able to enter the reaction with the reactive aggregates more easily. The results show that in none of the mortars with LiOH addition at an n(Li)/n(Na) of 0.3 has the expansive property of the ASR product been substantially changed. The expansion was even increased in the 3.0% $Na_2O_{eq.}$ mortar presumably because of a significant increase in the pore solution OH^- ion concentration (and thus pH) by LiOH as indicated by Diamond [13]. When a sufficiently high dosage of lithium is added to a reactive mortar, some lithium will enter the C-S-H, but sufficient

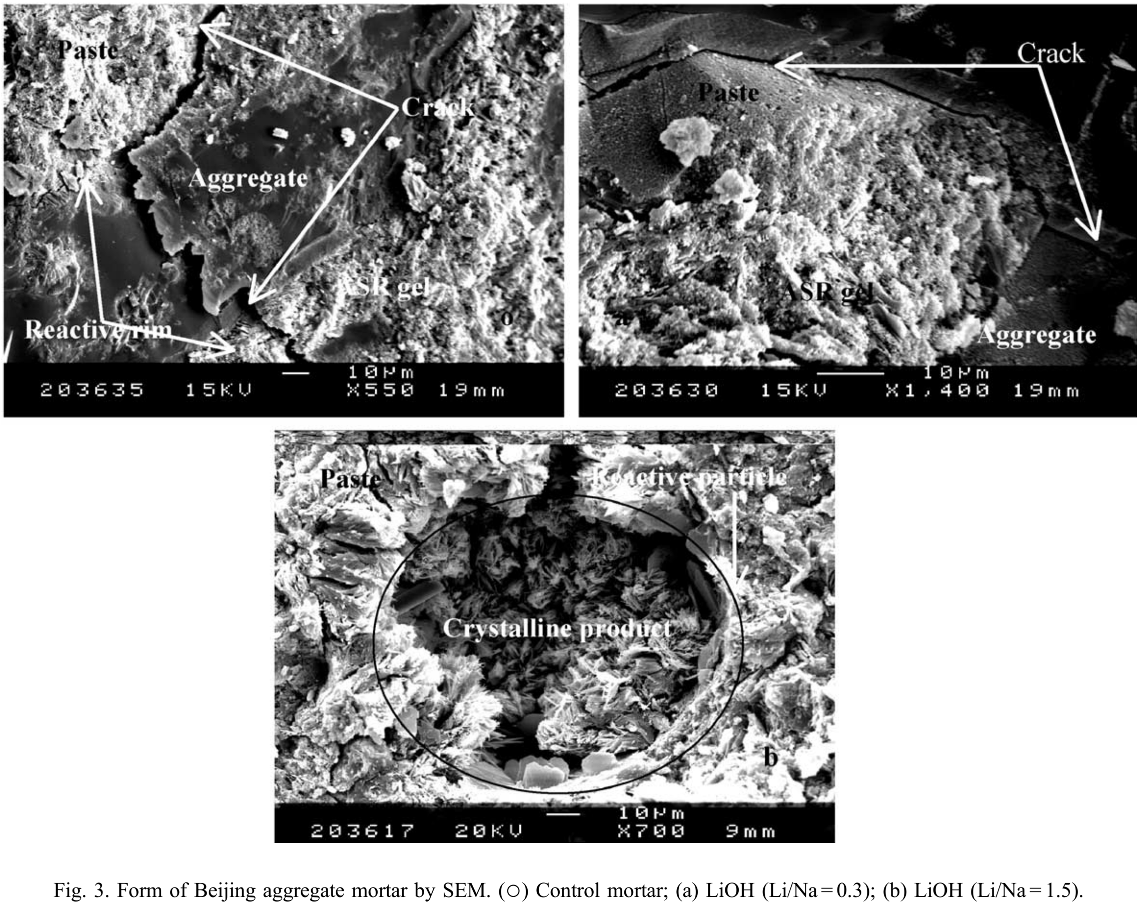


Fig. 3. Form of Beijing aggregate mortar by SEM. (○) Control mortar; (a) LiOH (Li/Na = 0.3); (b) LiOH (Li/Na = 1.5).

will remain to enter the ASR gel at a later stage and render it nonexpansive.

4. Conclusions

1. The expansion of Beijing aggregate mortars increased as the alkali content was raised, but curing time remained the same for all specimens. With the cement's equivalent soda content raised to 3.0% by KOH addition, the expansion was 0.21% after curing for 3 years at 80 °C.

2. When the cement's effective alkali content was no more than 2.5%, the ASR expansion of Beijing aggregate mortars could be inhibited long term by adding LiOH at an $n(\mathrm{Li})/n(\mathrm{Na})$ molar ratio of 0.3 or above.

3. At an alkali content of 3.0%, LiOH at an $n(\mathrm{Li})/n(\mathrm{Na})$ ratio of 0.6 or above will inhibit the ASR expansion long term.

4. It is suggested that the key factors that enable lithium to inhibit ASR expansion long term are that the lithium ion Li^+ having both a smaller ionic radius and a higher surface charge density than Na^+ or K^+ enables it to enter the ASR product more readily than Na^+ or K^+, and that the lithium ASR product is crystalline and nonexpansive.

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References

[1] X.Y. Mo, D.Y. Lu, Z.Z. Xu, Mechanism of chemical admixtures in inhibiting alkali–silica reaction and its research progress, J. Nanjing Univ. Chem. Technol. 22 (3) (2000) 72.

[2] W.J. McCoy, A.G. Caldwell, New approach to inhibiting alkali–aggregate expansion, J. Am. Concr. Inst. Proc. 22 (9) (1951) 693.

[3] X.Y. Mo, Long-term effectiveness and mechanisms of chemical admixtures in inhibiting alkali–silica reaction, PhD thesis, College of Materials Science and Engineering, Nanjing University of Chemical Technology, 2001.

[4] D.B. Stokes, C.E. Manissero, D.M. Roy, R.I. Malek, J.C. Roumain, Portland cement manufacture containing lithium for ASR control, in: M.A. Berube, et al. (Eds.), Proceedings of the 11th International Conference on AAR in Concrete, Quebec, Canada, 2000, pp. 773–781.

[5] S.Z. Baxter, D.B. Stokes, C.E. Manissero, A lithium-based pozzolan for ASR control, in: M.A. Berube, et al. (Eds.), Proceedings of the 11th International Conference on AAR in Concrete, Quebec, Canada, 2000, pp. 573–582.

[6] D. Whitmore, S. Abbott, Use of an applied electric field to drive lithium ions into alkali–silica reactive structures, in: M.A. Berube, et al. (Eds.), Proceedings of the 11th International Conference on AAR in Concrete, Quebec, Canada, 2000, pp. 1089–1098.

[7] D.P. Johnston, R. Surdahl, D.B. Stokes, A case study of a thium-based treatment of an ASR-affected pavement, in: M.A. Berube, et al. (Eds.), Proceedings of the 11th International Conference on AAR in Concrete, Quebec, Canada, 2000, pp. 1149–11581.

[8] H. Sufen, X. Zhongzi, T. Mingshu, The Standard of the Association of Chinese Construction Standardization, A Rapid Test Method for Determining the Alkali Reactivity of Sands and Rocks, Association of Chinese Construction Standardization, Beijing, China, 1995.

[9] X.Y. Mo, Z.Z. Xu, Studies on the long-term effect of lithium compounds on alkali–silica reaction, J. Chin. Ceram. Soc. 28 (2) (2000) 123.

[10] J.S. Lumley, ASR suppression by lithium compounds, Cem. Concr. Res. 27 (2) (1997) 235.

[11] V.S. Ramachandran, Alkali–aggregate expansion inhibiting admixtures, Cem. Concr. Compos. 20 (1998) 149.

[12] X.Y. Mo, Z.Z. Xu, Investigations of lithium compounds in inhibiting alkali–silica reaction at high temperature, J. Chin. Ceram. Soc. 28 (6) (2000) 578.

[13] S. Diamond, Unique response of $\mathrm{LiNO_3}$ as an alkali silica reaction-preventive admixture, Cem. Concr. Res. 29 (1999) 1271.