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Laboratory study of LiOH in inhibiting alkali–silica reaction at 20 °C: a contribution

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Abstract

At 20 °C, alkali–aggregate reaction (AAR) expansion of mortar incorporated zeolitization perlite could be long-term effectively inhibited by LiOH and the effect increased with the augment of Li/(Na + K) molar ratio. Mortar strength would decrease when LiOH was added. The more LiOH was added, the more the strength would decrease. In addition, there was more effect on 28 days' strength than 3 days', and the influence degree of LiOH to compressive strength was higher than that to flexural one. The initial and final setting times of cement were shortened when LiOH was added, and the more Li/(Na + K) molar ratio of LiOH was added, the more the setting time was cut down. Not only mortar bar expansion, the change in 20 °C, but also, the evidence of reaction and the composition of reaction products after 4-year curing was studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). It was found that when both Li^+ and K^+ (Na^+) were added, more Li^+ reacted to form some matter that not as the same as normal alkali–silica reaction (ASR) gel, especially for its nonexpansive property. Such might be the main reason of the phenomenon that ASR expansion could be inhibited by adding lithium compounds.

Keywords: Alkali–aggregate reaction; Mechanism; Compressive strength; Flexural strength; Setting time; SEM

1. Introduction

Alkali–aggregate reaction (AAR), whose main type is alkali–silica reaction (ASR), is one of the important factors that cause concrete to lose its durability efficacy, lose its usable value too early and cut its life. Enormous expense has happened all over the world during the past years, and it is difficult for the mending of ASR, so the prevention of ASR has been one of the key researches. Traditional possible measures to solve this problem are such as follows. That is, the use of low-alkali cement, the use of nonreactive aggregate, the use of certain mineral admixtures, such as silica fume, fly ash and pozzolana, and the use of chemical admixtures [1–4].

Since McCoy and Caldwell [5] first reported that ASR expansion could be inhibited by adding some organic and inorganic admixtures in 1951, the measure using chemical admixtures to inhibit ASR has gotten more and more attention. Of all these admixtures, much more investigations have been carried out on the lithium compounds due to their special efficiency. Up until now, influence of lithium compounds on ASR has been investigated not only in laboratory but also in practical engineering [6–11]. These admixtures included LiOH, Li_2CO_3, LiF, $LiNO_3$, $LiNO_2$, Li_2SO_4, as well as $LiCH_3COO$. It was found that the effectiveness of admixtures in reducing ASR depends largely on some chemical composition of the admixtures. Compared with LiOH and Li_2CO_3, the unique response of $LiNO_3$ has been proved [12]. The use of $LiNO_3$, a fully soluble neutral salt, does not generate significant increases in OH^- concentration and thus does not undergo the risk of accelerating ASR at the same time that it is attempting to ameliorate its effects. In other words, if LiOH were proved to be able to inhibit ASR thoroughly, any worries would be eliminated to other lithium compounds. Hence, it is meaningful undertaking more researches on LiOH.

It is generally considered that with lithium-based admixtures, partial substitution of Li^+ for K^+ or Na^+ occurs in the ASR gel. The ratio of Li^+ ions to ordinary alkali ($Na^+ + K^+$) ions incorporated within the gel is a function of their relative proportions in solution. Thus, the effectiveness of lithium treatments depends on maintaining a high

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relative proportion of lithium to the other cations in solution. It was found that molar ratios of Li/(Na + K) in excess of 0.6–0.9 were required to completely eliminate expansion due to ASR. There are also some test results indicating that inadequate dosages of LiOH produce greater ASR expansion than that generated in the control mortars, in which ASR took place unchecked. There, ion concentration has the effect of substantially increasing the already high OH^- ion concentration as the result of LiOH treatment. Hence, more attention should be paid the case less lithium compounds was used. Although substantial work has been carried out on the effect of chemicals on the expansion reactions, relatively less attention has been directed to their effect on long-term and other properties of concrete. Currently, there is still a lack of understanding not only on the cause explaining the effectiveness of lithium compounds in inhibiting ASR, but also the effect of such compounds on the other properties of cement, such as the strength and setting time. Most of the previous researches were done at 38–40 and 80 °C or even autoclaved conditions. Those of long-term effect of lithium compounds at 20 °C were even in vacancy. More direct proofs helpful for the mechanism of lithium compounds in inhibiting ASR were needed. In this paper, much more detailed works and discussions on these aspects of LiOH have been carried out.

2. Materials and experimental methods

2.1. Experimental materials

2.1.1. Cement

To prevent the effect of paste expansion on the results, this investigation was carried out on the use of a Portland cement of a relatively low alkali content (0.458% $Na_2O_{eq.}$), mostly as potassium. Its chemical composition is given in Table 1. Other properties of the cement were a Blaine fineness of 360 m^2/kg and an autoclave expansion (at 150 °C) of 0.01%.

2.1.2. Aggregates

An alkali-reactive aggregate–zeolitization perlite from the Shandong Province, China, was used. The main minerals identified by XRD were quartz, plagioclase and mica. According to lithofacies analysis, a large amount of chalcedony, some silk zeolitization, pinholes and cracks in quartz are all the main causes of the high alkali reactivity.

Zhen and Tang [13] tested the alkali reactivity of the aggregate by rapid chemical method according to ASTM C 289-71, and the results are shown in Table 2. From the results, it could be seen that zeolitization perlite was in the area of potential alkali reactivity.

Table 1
Chemical composition of cement w/%

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	LOI	Total
64.6	22.1	4.76	3.28	0.82	2.60	0.07	0.59	0.91	99.73

Table 2
Alkali reactivity of the aggregates: results of rapid chemical method

	Rc (mM/l)	Sc (mM/l)	Sc/Rc
Standard sand	19.6	23.4	1.19
Zeolitization perlite	370.8	510.5	1.38
Quartz glass	76.4	874.1	11.44

2.1.3. Chemical reagents

As the fact that the content of K_2O in the aggregate is less than that of Na_2O, KOH was used to adjust the alkali content of the mortar to study the ASR gel more easily. The total alkali content of the mortar is 2.5% $Na_2O_{eq.}$. The added amount of LiOH was implied by molar ratio of Li/(Na + K).

2.2. Experimental methods

The method of testing the effect of LiOH in inhibiting ASR is described hereafter. The mortars were manufactured with a water-to-cement ratio of 0.40. The initial length of the mortar bars, 1 × 1 × 4 cm in size, was measured by gyroidal micrometer at the age of 24 h. Then, the long-term curing process started. The mortar bars were cured at 20 °C and 95% humidity, and length change was monitored over a 4-year period. The effect of LiOH on mortar strength and cement curing time was tested according to GB 177-8 and GB 1346-77, respectively.

The mechanism of LiOH in inhibiting ASR was studied by the method of scanning electron microscopy (SEM), energy disperse spectroscopy (EDS) and inductively coupled plasma atomic emission spectra (ICP-AES). During the study of ICP-AES, 5 g of quartz glass ranging from 0.15 to 0.80 mm in size was immersed in some of the following solutions: LiOH, KOH, LiOH and KOH. The solutions were maintained at 80 °C, and the ionic concentration was tested as a function of time.

3. Results and discussions

3.1. Effect of LiOH in inhibiting ASR

Although the long-term effectiveness of LiOH in inhibiting ASR in either autoclaved or 80 °C curing condition has been tested, experiments of testing performance of LiOH at 20 °C seems to be more representative of practical engineering condition.

At 20 °C, the long-term effect of LiOH with different Li/(Na + K) molar ratio in inhibiting ASR expansion when the alkali content of the mortars was raised to 2.5% is shown in Fig. 1. It could be seen that ASR is a slow process, and the expansion of the control mortar specimen was increased gradually with time. The 4-year expansion of the control mortar specimen was 0.106%, while the expansion of those

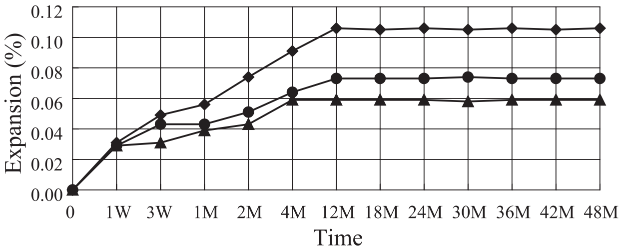

Fig. 1. Long-term effect of LiOH on ASR expansion of zeolitization perlite mortar Li/(Na + K): ◆0; ●0.3; ▲0.6.

with Li/(Na + K) molar ratio 0.3 and 0.6 was 0.073% and 0.059%, respectively; this corresponds to expansion reductions of 31% and 44%. It seemed that there was some relationship between the ASR inhibition ratio and the Li/(Na + K) molar ratio. At the experimental conditions, ASR could be inhibited more effectively with more LiOH added. Papers on the subject of chemical admixtures in inhibiting ASR indicated that partial Li^+ would be absorbed by the cement hydration products at the early ages, and this part of Li^+ seemed more difficult to play any function in inhibiting ASR [12–18]. In addition, the solubility of LiOH in water solution decreased with decreasing temperature, and there seemed to be a low solubility degree of LiOH at 20 °C. All these indicated that the concentration of Li^+ in the mortar pore solution was low. When more Li^+ was dissolved with an increase in the Li/(Na + K) molar ratio, the competition ability of Li^+ compared with K^+ or Na^+ would be thus improved, thus, the ASR expansion was more inhibited by further LiOH added.

It could be concluded that at 20 °C, the expansion of mortar bars incorporating zeolitization perlite aggregate would be long-term effectively inhibited by LiOH, and the inhibition effect would be improved when the Li/(Na + K) molar ratio increased.

3.2. *Effect of LiOH on other performance of cement materials*

As LiOH has shown some effect in inhibiting ASR expansion and mortar strength is an important parameter to practical concrete engineering, it would be meaningful to investigate the effect of LiOH on mortar strength. The effect of LiOH on mortar strength is shown in Table 3. In general, mortar strength would decrease when LiOH was added. The higher the LiOH added, the higher strength reduction

Table 3
Alkali reactivity of the aggregates: results of rapid chemical method

Admixture	Curing time (*d*)	Compressive strength (MPa)			Flexural strength (MPa)		
		0	0.5 Added	1.0 Added	0	0.5 Added	1.0 Added
LiOH	3	34.8	30.0	26.6	6.5	6.4	6.5
	28	53.1	46.3	32.8	8.6	8.1	7.6

Table 4
Effect of LiOH on setting time

	Without added alkali	With alkali raised to 3% Na_2O_{eq}			
Li/(Na + K) molar ratio	0	0	0.3	0.6	0.9
Initial setting time (min)	134	25	18	17	15
Final setting time (min)	201	188	129	113	77

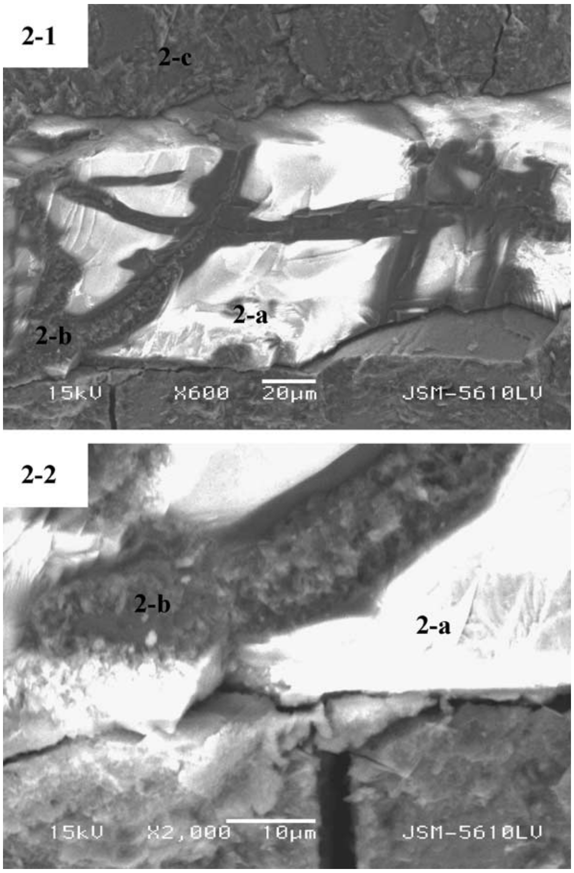

Fig. 2. Results of zeolitization perlite mortar by SEM and EDS (without lithium compounds).

Table 5
Chemical composition of mortar products w/%

No.	K_2O	Na_2O	SiO_2	CaO	Al_2O_3	CO_2	Total
2-a	1.10	9.61	45.65	1.07	13.19	29.38	100.00
2-b	15.22	0	68.03	0	16.75	0	100.00
2-c	0	0	15.75	63.53	2.64	18.07	100.00
3-d	5.27	4.11	47.10	0	12.52	31.00	100.00

observed. In addition, the effect was more pronounced on the 28-days strength than on 3 days. The effect of LiOH was more important on compressive than on flexural strength. In addition, there seemed to be an exception to 3 days' flexural strength. When 0.5% LiOH was added, 3 days' flexural strength would decrease in some degree, while when 1.0% LiOH was added, there seemed to be no obvious effect on 28 days' flexural strength. Reasons of such effect are to be researched more deeply.

The effect of LiOH with different Li/(Na + K) molar ratios on the setting time of cement is shown in Table 4. The initial setting time of the cement used was 134 min, and final setting time was 201 min. The alkali content of the cement was adjusted to 3.0% $Na_2O_{eq.}$, by adding KOH to the mixture. It can be seen that the initial and final setting times of the cement with 3.0% $Na_2O_{eq.}$ were significantly less than that of the original cement. The possible reason might be that when KOH was added, additional OH^- was introduced into the hydrating cementitious system that would react with the cations, such as Ca^{2+}, to precipitate hydrates. A "solid network" would then form, which would have some effect on cement hardening and thus reduce the setting time. The addition of LiOH also increases the

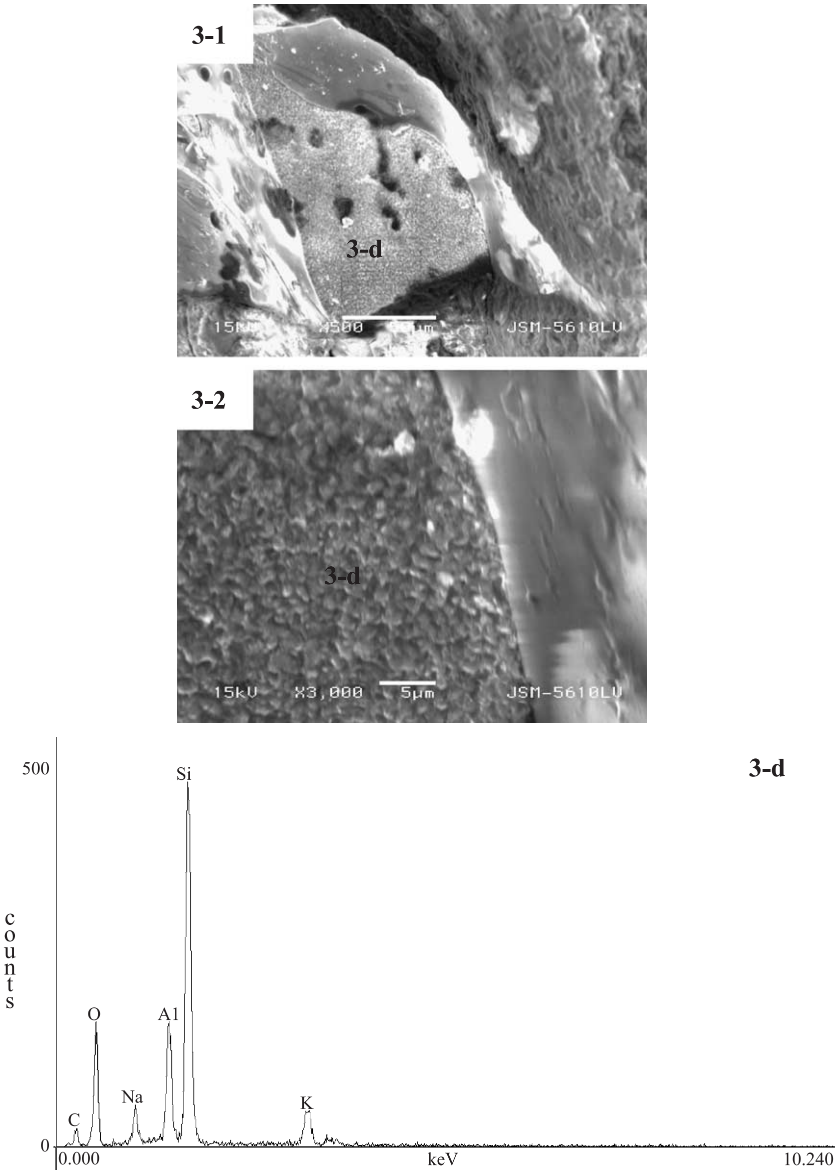

Fig. 3. Results of zeolitization perlite mortar by SEM and EDS (with lithium compounds).

content of OH^- in the hydrating cementious system, so that LiOH may affect the hydration process similar to KOH. That was to say that the initial and final setting time was shortened when LiOH was added, and the higher the Li/(Na + K) molar ratio of LiOH, the shorter the setting time.

3.3. Mechanism of LiOH in inhibiting ASR

The nature of ASR product from mortars incorporating zeolitization perlite of 2.5% $Na_2O_{eq.}$ content after 4-year curing was examined by SEM and EDS. Relevant photomicrographs of control mortars, without LiOH, are presented in Fig. 2, and the detailed chemical composition of mortar products is shown in Table 5. 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 (Fig. 2-1 and 2-2). In addition, a large amount of gel product has been shown in the mortar (2-b in Fig. 2-2). The dot map display shows that such product is a typical ASR gel, as that it contents obvious amount of K, which may come from the added KOH admixture. In details, the unreacted aggregate was composed of SiO_2, Al_2O_3, Na_2O, K_2O, CaO, etc., and the amount of K_2O is higher than that of Na_2O (2-a in Fig. 2-2). In the mortar, typical C-S-H product, which is mostly made up of CaO, SiO_2 and Al_2O_3, has been formed.

Relevant photomicrographs of mortars with LiOH added are presented in Fig. 3, and the detailed chemical composition of mortar products is also shown in Table 5. In the mortars with added LiOH at a Li/(Na + K) molar ratio of 0.3, the aggregate particles, both eroded and unblemished, are in evidence. A great deal of reaction products were found around the particles, and these seemed to be crystalline as the Li^+ entered the alkali silica reaction (Fig. 3-1 and 3-2). Energy dispersive spectroscopy (EDS) showed that there was a large amount of both K and Na in the crystalline product (Fig. 3-d) but less K than that in a typical ASR gel, according to Table 5. A speculative explanation of this phenomenon is that since Li^+ has both a smaller ionic radius and a higher ionic surface charge density than either Na^+ or K^+ does, when enough lithium compounds are added, Li^+ is able to enter the reaction with the reactive aggregates more easily. The results also show that in the mortars with LiOH addition at (Li)/(Na + K) of 0.3, the expansive property of the ASR product has been substantially changed. The expansion was inhibited even in the 2.5% $Na_2O_{eq.}$ mortar presumably because of a significant increase of Li^+ in the products by LiOH. That is, when a sufficiently high dosage of lithium is added to a reactive mortar, some lithium will enter the C-S-H, but sufficient will remain to enter the ASR gel at a later stage and render it nonexpansive.

The concentration of Li^+ and K^+ at different ages was measured by the method of ICP-AES; the results are shown in Fig. 4. It can be seen that the concentration of both Li^+ and K^+ decrease through the reaction with SiO_2 either as the form of pure (A and B) or mix solution (C), and the quantity of Li^+ that reacted was more than that of K^+ at least at early ages. This might mean that Li^+ had more competition than K^+ during ASR at the same condition. Sakaguchi et al. [14] reported from a series of tests performed on mortars with alkali reactive aggregates, that the concentration of Li^+ would decrease and the concentration of K^+ (Na^+) would almost keep unchanged as time went on when both Li^+ and K^+ (Na^+) were added. However, the concentration of K^+ (Na^+) would also decrease when only K^+ (Na^+) was added. This was another evidence for the above explanation. All these mean that the competition

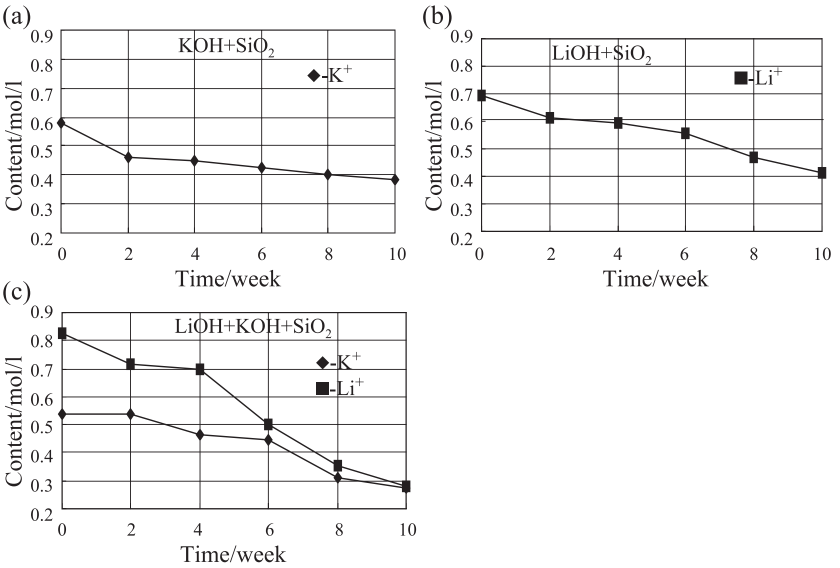

Fig. 4. Change of alkaline cation concentration with the time.

between Li^+ and K^+ (Na^+) occurred in the alkali silica reaction and Li^+ had some superiority relatively. Much Li^+ reacted to form some products that are different from typical ASR gel, and that possess a nonexpansive property. This may explain why lithium compounds inhibit expansion due to ASR [15–18].

It is suggested that the key factors that enable lithium to inhibit ASR expansion long term are that 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, and that the lithium ASR product is crystalline and nonexpansive.

4. Conclusions

1. ASR expansion could be long-term effectively inhibited by LiOH at 20 °C, and the more the Li/(Na + K) molar ratio of LiOH was, the better the inhibition effect was.
2. When LiOH was added, both the compressive and flexural strengths of the mortar would decrease. Generally, the degree would be more obvious as the added quantity increased. In addition, there was more effect on 28 days' strength than on 3 days', and the influence degree of LiOH on compressive strength was higher than that on flexural one.
3. Both the initial and final setting times of cement were shortened by adding LiOH, and the more Li/(Na + K) molar ratio of LiOH was added, the more the setting time was cut down.
4. Both Li^+ and K^+ (Na+) would react in the ASR procession, and Li^+ had more competition than K^+ (Na^+) does. Meanwhile, the reason of the phenomenon that ASR expansion could be inhibited by adding lithium compounds might be connected with this. More Li^+ than K^+ (Na^+) reacted to form some matter that not as the same as normal ASR gel, especially for its nonexpansive property, which might be the main reason of the phenomenon that ASR expansion could be inhibited by adding lithium compounds.

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