Alkali - Silica Reaction Inhibited by LiOH and Its Mechanism *

MO Xiang-yin[1,2] XU Zhong-zi[3] WU Ke-ru[2] TANG Ming-shu[3]
[1] *Nanjing Normal University* [2] *Tongji University* [3] *Nanjing University of Technology*
(Received: Apr. 8, 2002)

Abstract: *A high alkali reactive aggregate-zeolitization perlite was used to test the long-term effectiveness of LiOH in inhibiting alkali-silica reaction. In this paper, the rigorous conditions were designed that the mortar bars had been cured at 80℃ for 3 years after autoclaved 24 hours at 150℃. Under this condition, LiOH was able to inhibit the alkali-silica reaction long-term effectiveness. Not only the relationship between the molar ratio of n (Li)/(Na) and the alkali contents in systems was established, but also the governing mechanism of such effects was also studied by SEM.*

Key words: *lithium compounds; alkali-silica reaction; long-term performance; mechanism*

1 Introduction

Much work has been done to prevent destroy of alkali-silica reaction(ASR) of concrete since it was first found in America in 1940[1]. Since McCoy and Caldwell first investigated the use of chemical salts and organic compounds to inhibit expansion caused by ASR, researches on reducing expansion in existing structures have been focused on the use of chemical additives. Some lithium salts, including LiOH, have been shown to be particularly effective and have been the focus of many ongoing researches. It is well known that the normal properties of Li are parallel to K and Na as they are in the same alkali - metal group while special ones may also behave as the cation radius of Li^+ is more small and the electric charge density is bigger compared to that of K^+ and Na^+. So, action of lithium compounds may also be different with that of potassium and sodium salts in ASR of concrete[2,3]. Some key problems to be solved in these researches are as follows. Although ASR expansion was able to be reduced by lithium compounds, the long-term effectiveness of such effect has not been tested thoroughly. Also, the mechanism of lithium compounds in inhibiting ASR has not been made clear thoroughly while some hypothesis have been put up.

In this paper, the results of extensive laboratory investigations to evaluate the effectiveness of LiOH in inhibiting ASR expansion are presented. Not only the rigorous conditions were designed to test long-term effectiveness of LiOH in inhibiting ASR but also the direct and convictive evidences to prove such effect could be found by SEM and EDS.

MO Xiang-yin (莫祥银): Born in 1974; Post PhD; Analysis and Test Central, Nanjing Normal Univ., Nanjing 210097, China. xiangyinmo@163.com

* Funded by the State"Tenth-Five Years Plan"Project of China(2001BA307B01-1)

2 Experimental

2.1 Materials

2.1.1 Cement

To prevent the effect of paste expansion on the results, the low-alkali cement produced by Jiangnan Xiaoyetian Corp. (China) was used. Its chemical composition is shown in Table 1. Other properties of the cement were that: initial setting time was 134 min, final setting time was 201 min. The Blaine of the cement is 360 m^2/kg. After being autoclaved at 150℃, the expansion ratio of paste is 0.01%.

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

LOI * ——Loss on ignition

2.1.2 Aggregates

A highly alkali-reactive aggregate-zeolitization perlite from the Shandong Province (China) was used. The rock is yellow alternate with green. The main minerals identified by XRD in the aggregate were plagioclase, quartz and mica. According to optical microscopy analysis, the alkali-reactive material present is chalcedony and some other-crystalline quartz, which is shown in Fig. 1.

On the other hand, SEM observations reveal several pinholes and some cracks in quartz, as shown in Fig. 2. These could be the inartificial channels for OH^-, Na^+ and K^+ to penetrate into the aggregates during the process of ASR in either concrete or mortars.

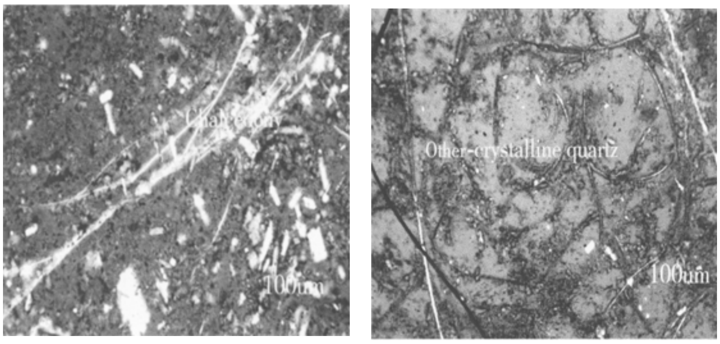

Fig.1 Alkali reactive minerals in rocks by crossed Nicols

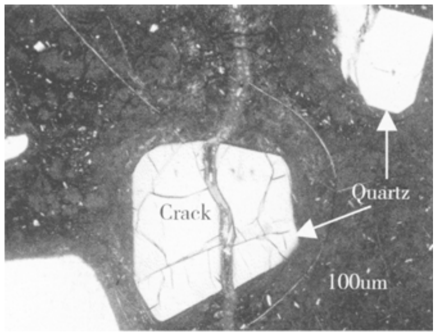

Fig.2 Cracks in quartz

The results of the alkali activity testing of the aggregate are shown in Table 2 according to "A Rapid Test Method for Determining the Alkali Reactivity of Sands and Rocks", which is also named "The Chinese Method for ASR"[4]. The major factors of the procedure include 150℃ of test temperature, 0.15 – 0.80mm size of aggregates, 10% KOH of alkali solution, 1.5% Na_2O_{eq} of alkali content in cement and 6 hours of test period.

Table 2 The Results of Alkali Activity of Beijing Aggregate sand

Cement-to-sand ratio	Expansive rate/%		
	6h	12h	18h
10:1	0.313	0.427	0.437
2:1	0.651	1.045	1.315

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 molar ratio of $n(\mathrm{Li})/n(\mathrm{Na})$ was calculated according to the following equation:

$$m_x = 2 \cdot m(A) \cdot w_m \cdot x_m \cdot M_0 / [n_0 \cdot N_0 \cdot M_{Na_2O}] \quad (1)$$

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

2.2 Methods

This method is quite similar to "The Chinese Method for ASR"[4], but some changes were also made. When curing, the mortars were not immersed in either water or alkali solution, but in steam or moisture in order to keep the molar ratio of $n(\mathrm{Li})/n(\mathrm{Na})$ in the system.

The autoclaved process in the present paper was made up of two stages: the autoclave process and the long-term curing process. The whole process is such as follows. The mortars of 1cm × 1cm × 4cm were molded with the water to cemen weight ratio of 0.40. The initial length of the mortars was measured by a gyroidal micrometer after the moulds were stripped 24 hours later. Then the autoclaved process was performed. The mortars were cured at 150℃ for 24 hours in a sealed container filled with water and the mortars above the water without touching it. When cooled to the temperature that the initial length was measured, the first final length was measured. Then the stage of long-term curing process was entered. The mortars were cured at 80℃ in a constant temperature container with 95% humidity. The mortars were also not placed in contact with the water and the other final length was measured according to the curing time. In this paper, the whole curing time was 3 years. If the autoclaved process of 24 hours was also considered, this research might have the most long-term cycle under the most rigorous condition.

3 Results and Discussion

ASR expansion occurs only when some alkali content in the concrete reaches and the difference between Li^+ and Na^+ is the main reason of lithium compounds in inhibiting ASR[5-8]. So the added amount of lithium compound would be different according to the alkali content. In this paper, 4 conditions were designed and the alkali content of the practical engineering was represented approximately.

3.1 Effect of LiOH on inhibiting ASR expansion

The long-term effect of LiOH with different $n(\mathrm{Li})/n(\mathrm{Na})$ molar ratios in inhibiting ASR expansion of zeolitization perlite mortar is shown in Fig.3. As a result, the expansion ratio of the control mortar, where no lithium compound is added, increases at the same curing time as the alkali content increase, while LiOH has long-term effectiveness in inhibiting ASR expansion. When the alkali content is 1.5%, the expansive length of the control mortar is 0.075% and that of the mortars is no more than 0.039% when LiOH is added. When the alkali content is 2.0%, the expansive length of the control mortar is 0.903% and that of the mortars is no more than 0.070% when LiOH is added. When the alkali content is 2.5%, the expansive length of the control mortar is 1.329% and that