

EFFECTS OF LITHIUM HYDROXIDE ON ALKALI SILICA REACTION GELS

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ABSTRACT

The reaction of opal with a combined solution of sodium hydroxide and lithium hydroxide was investigated. Sol-Gel Expansion Method has been carried to test the expansion capability of ASR gels. To make clear the effect of lithium hydroxide on SiO_2 dissolution from opal particles, SiO_2 concentration in final solution was determined by kalium fluosilicate method.

The results of Sol-Gel Expansion Method suggested that a high dosage level is required to alleviate ASR in a given mix, which is broadly in agreement with those published by other laboratories using other reactive aggregates and tests. The concentration of SiO_2 in the final solution indicated that the reaction of the alkali with the opal starting material is inhibited in the presence of lithium hydroxide. SEM revealed that the morphology of the reaction products is markedly different from those of opal with sodium hydroxide and there is a protective layer on the surface of the reacted opal grains.

Key words: ASR; lithium hydroxide; opal

1 INTRODUCTION

The application of lithium compounds as ASR ameliorating admixtures has been studied in many countries of the world. McCoy and Caldwell [1] found that lithium compounds were effective to reduce the expansion of concrete caused by ASR and a mixture of lithium carbonate and fluoride at a combined ratio of 0.31 reduced expansion by three quarters. In a classical work of measuring osmotic pressures developed during alkali-aggregate reaction, Verbeck and Gramlich [2] showed that aggregates exposed to LiOH generated lowed osmotic pressure than exposed to NaOH and KOH. Hudec and Banahene [3] investigated the ability of several lithium compounds to interfere with the alkali-silica reaction and found that LiOH was able to practically eliminate the expansion due to ASR, whereas the other lithium compounds (LiCl , LiF , Li_2CO_3 , etc.) were not as effective. In 1996, Lawrence and Vivian [4] reported that LiOH, 0.5, 1.0 and 1.5 percent by mass of cement, could control the expansion due to ASR.

While various reports have confirmed the effectiveness of lithium treatments in preventing ASR damage, there have been comparatively few studies aiming at elucidating the involving mechanisms [5]. In the above-mentioned papers much of the authors

selected ASTM C 1260 to evaluate the chemical treatments. Unfortunately, ASTM C 1260 seems to be inappropriate for the task. Firstly, the correlation between the experiment results of ASTM C 1260 in high alkali concentration at high temperature and field concrete need to be investigated. Secondly, in order to know how much of each chemical remains in solution available for interaction with the aggregate, it would be necessary to extract the pore solution and to determine its ionic concentration several times during testing and such concentration can only represent bulk concentration of the mortar other than in certain pore solution. Thirdly, because ASTM C 1260 testing procedures require the immersion of the mortar bars in an 1 M NaOH solution maintained at 80 deg C, the concentration gradient between the solution in the mortar pores and the external solution causes the diffusion of ions in and out of the specimens, which will effect the expansion result[6]. In fact, we can only get results using mortar bars or concrete prisms to study inhibition effect of lithium compounds on ASR. It is very hard to analysis the mechanism from them. Besides these, specimen preparation and microscopic examination are very time-consuming. In view of those disadvantages, a new test method, Sol-Gel Expansion Method (A method which was thought to reflect essence of ASR.), was used to study the

inhibition mechanism of lithium compounds on ASR in this paper.

2 MATERIALS AND EXPERIMENTAL METHOD

The influence of several lithium compounds on ASR and the resulting expansion in mortar bars have been investigated, including LiSO_4 , LiCO_3 , LiF , LiCl , LiOH and LiNO_3 . It is obviously unfeasible to adding LiCl or LiSO_4 in concrete for chlorine ions might cause steel corrosion, and sulfuric acid might result in concrete internal sulfate attack.

As for other lithium compounds, lithium fluoride is almost insoluble in water while lithium carbonate is only slightly soluble and both compounds in concrete pore solution will result in the formation of lithium hydroxide. So in this paper, effect of lithium hydroxide on ASR was investigated under Sol-Gel Expansion Method. Lithium hydroxide was added into 50 ml 0.7 mol/L NaOH solution with 7 grams opal

powder at various Li/ Na mole ratios of 0.1, 0.2, 0.3, 0.5, 0.8 and 1.2 respectively. The aim was to cover a range of lithium additions from largely ineffective to complete ASR suppression, so as to determine the most economic dosage in the given mix. The expansion of ASR gels was measured according to Sol-gel expansion method [7].

3 RESULTS AND DISCUSSION

It is generally considered that with lithium-based admixtures, partial substitution of lithium ions for potassium or sodium ions occurs in the ASR gel. Diamond [8] suggested that the ameliorative effect produced by lithium appeared to involve the effect that lithium reduced the tendency of the ASR gel to imbibe water and swell. There is presently no supporting evidence for this hypothesis. Using Sol-Gel Expansion Method, the expansion of ASR gels with lithium was measured. The results are illustrated in table 1.

Table 1 Effects of lithium hydroxide on alkali-silica reaction

| Li/Na mole ratios | 0 | 0.1 | 0.2 | 0.3 | 0.5 | 0.8 | 1.2 |
|---|------|------|------|------|------|------|-----|
| free expansion of ASR gels (%) | 98 | 75.1 | 47.3 | 35.7 | 32.1 | 10.1 | 8.2 |
| SiO_2 concentration in final solution (mmol/L) | 1766 | 1048 | 924 | 790 | 699 | 669 | 638 |

Table 1 shows that LiOH addition do provide the expecting amelioration of ASR gels. The reduction in expansion appears to be related to an increase of Li/Na mole ratio in solution. When the mole ratio of Li to Na is more than 0.8, free expansion of ASR gels is below 11% (Division between innocuous and potentially reactive aggregate made for Sol-Gel Expansion Method is at an free expansion of 11%). Sakaguchi [9] also found that mole ratios of Li^+ to $\text{Na}^+ + \text{K}^+$ in excess of 0.9 were required to completely eliminate expansion due to ASR in their test conditions. Stark [10] studied the effect of adding various amounts of LiOH to the 1N NaOH solutions specified in the ASTM C 1260 test conditions and found that LiOH addition reaching a $\text{Li}^+ : \text{Na}^+$ mole ratio of 0.85 in the exposure solution was required to prevent the expansion. Those tests results indicate that the successful use of LiOH requires a dose level sufficiently high.

In the final analysis, expansion of ASR lies on alkali-silica-gel, which mainly depend on how many SiO_2 dissolved from reactive aggregate in solution. To make clear the effect of lithium hydroxide on dissolution of SiO_2 from opal particles, final concentration of SiO_2 in mixture solution was

determined by kalium fluosilicate method. In table 1, it demonstrates clearly that the SiO_2 concentration in the solution decreased with increasing addition of lithium hydroxide, which is consistent with the same rule as above expansion of ASR gels measured by Sol-Gel Expansion Method. It seems that adding lithium hydroxide could restrain diffusion of SiO_2 from opal.

Prezzi[6] selected ASTM C1260 to evaluate the influence of several chloride salts on ASR and found that SiO_2 content in the gels composition increased with the type of cation in the order: $\text{Li} < \text{K} < \text{Na}$. This is essentially identical to the results obtained in our investigation.

The SEM pictures depict an interesting body of evidence. Fig. 1 shows the dried ASR gels with lithium. Plenty of circle particles can be observed spreading around in the gels. The particle size is below $1\mu\text{m}$. There are no such products in alkali-silica gel without LiOH addition.

Fig. 2 shows a compact layered materials covering on the opal grains. The morphology of the reaction products is markedly different from those of opal with sodium hydroxide in Fig. 3 in which noticeable changes is loss of surface relief and have an almost honeycomb pattern, indicating a dissolution

or erosion of the constituent grains. In addition to this, there are amorphism gel products and a reduction in the particle size.

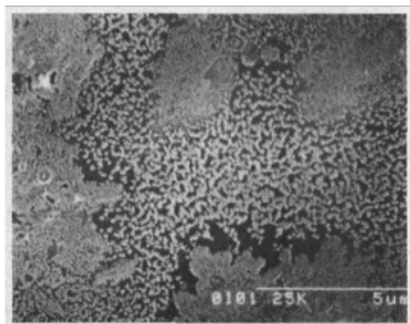


Fig.1 SEM micrographs of products in dried gel (opal+sodium hydroxide+lithium hydroxide)

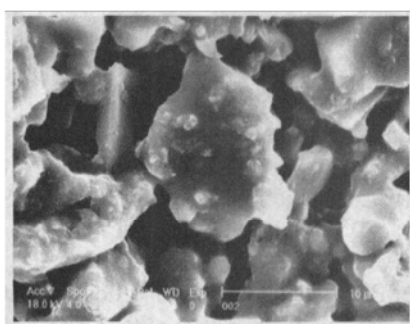


Fig.2 SEM micrographs of products covering on the opal particles (opal+sodium hydroxide+lithium hydroxide)

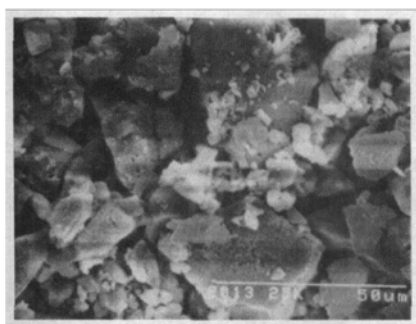


Fig. 3 SEM micrographs of opal reacted with NaOH solution

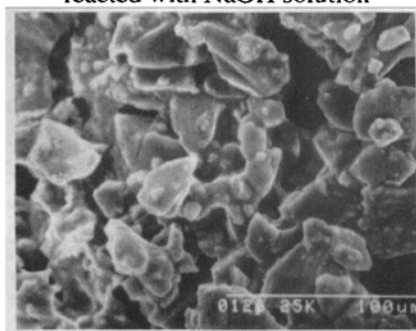


Fig.4 SEM micrographs of Products covering on the opal (opal+sodium hydroxide+lithium hydroxide)

Fig. 4 shows the layered materials covering on the opal grains after imbibing water. The figure clearly reveals that the layered foil is still on the surface of the opal grains, indicating low levels of their dissolution.

Liu[11]observed that Li-Si-H can polymerize and form solid lithium silicate by further being evaporated. Lithium silicate is insoluble compound neither in water nor in organic solvent. Both sodium silicate and potassium silicate are compounds with high solubility. This difference seems to be the main reason why lithium compounds can restrain the silica ion diffusion. That is, if lithium silicate could form compact layer on the surface of the susceptible aggregate, the dissolution of SiO_2 will be limited. So the reaction between lithium hydroxide and SiO_2 could not proceed and ASR expansion would be ameliorated. Length change measurements on mortar bars confirmed that lithium gel did not induce expansion [12]. For the reaction system in this study only include opal, sodium hydroxide and lithium hydroxide, the circle particles and layered materials in above SEM pictures could possibly be lithium silicate or lithium- sodium -silicate-gel.

Why is the behavior of lithium ion so different from sodium ion or potassium ion in the silica systems? An understanding of the effects of different alkali metal cations on structure of silica gels can shed some light on this question. In the presence of metal cations, silica sols tend to form a gel. Iler [13]discussed the mechanism in detail and pointed out that coordinate bond was the main force which connect silica to alkali metal cations. It is generally believed that in the structure of silicate, oxygen ion, which has a 1.4 \AA radius, usually form compact cube stack, silica ions stuff the tetrahedron interspaces of oxygen ions and results in the formation of silicon-oxygen tetrahedron. If metal ion is small, it can easily inset the tetrahedron or octahedron interspaces of oxygen ions without distortion of the structure of silicate. If metal ion is large, the compact stack of oxygen ions will twist and be unstable. It is known that lithium ion has a 0.6 \AA radius, potassium ion has a 1.4 \AA radius and sodium ion 1.0 \AA radius respectively. Obviously, lithium ion is the smallest and least affect the compact stack structure of oxygen ions. The structure of lithium-silicate-gel is closer than potassium (sodium) silicate-gel. It becomes difficult for water molecule to ingress into lithium-silicate-gel. So lithium-silica-gel is less soluble and expansive than the pure potassium (sodium) silicate-gel. When lithium-silica-gel form compact layer on the surface of the opal grains, the dissolution of SiO_2 will be limited.

Moreover, the sodium-silica gel dried in the vacuum desiccator cabinet was found to be brittle, while the lithium-Sodium-silica gel was glutinous. This may also indicate the force between lithium

-sodium – silica molecules is stronger.

4 CONCLUDING MARK

(1)The addition of lithium hydroxide could ameliorate ASR expansion. It appears that the greater the proportion of lithium (as against sodium) the less the expansion taking place.

(2)The diffusion of SiO_2 from opal grains was limited in the presence of lithium hydroxide, as lithium-silica-gel formed compact protective layer on the surface of the opal grains.

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