Reaction between Alkaline Metal Ions and ASR Reactive Aggregate and Behavior of Na^+ and K^+ in Cement Paste Replaced by Li^+

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Abstract: This paper studies the reaction between alkaline metal ions Li^+ , Na^+ and K^+ and ASR (alkali-silica reaction) reactive aggregates to determine whether Li^+ can substitute Na^+ and K^+ that are unified in cement paste. Reactive aggregates use meta-sandstone from eastern Taiwan and Pyrex glass. Non-reactive aggregates use siliceous sand. The results show that the dissolved amount of SiO_2 is lower when the reactive aggregates are immersed in an 80 °C 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$ solution than in NaOH and KOH solutions. The reduced amounts of OH^- and Li^+ in the solution are also higher than those in the NaOH and KOH solutions. These results reveal that reactive SiO_2 can react with LiOH to form a reactant with low water solubility. When the powder of the cement paste is immersed in an 80 °C 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$ solution, the amounts of free Na^+ and K^+ in the solution are higher than those in water. The increased amount increases with the duration of immersion. The amount of Li^+ in the solution also decreases with the duration of immersion. These results reveal that Li^+ can substitute Na^+ and K^+ that are unified in cement paste, which indicates that ASR can be prevented with the existence of Li^+ .

Key words: Alkali-silica reaction, lithium, reactive aggregate, paste.

1. Introduction

An aggregate containing reactive silica combines with Na^+ (K^+) to form an alkali-silica colloid when the silica is decomposed by OH^- in a pore solution. This combination causes the occurrence of the ASR (alkali-silica reaction) in concrete. Concrete structures may collapse because the colloid expands as it absorbs water.

The reactive aggregate forms an acidic silanol ($\equiv\text{Si}\text{-OH}$) group with water because the aggregate has an irregular crystal internal structure and crystalloid quartz with an unstable O^- surface charge. However, this reaction is very slow for dense and impermeable aggregates. An aggregate that contains noncrystalline

or imperfect crystal SiO_2 is porous and permeable, and a small part of its Si atoms have silanol groups. SiO_2 absorbs some moisture without the extra OH^- , but no obvious dilation occurs because most of the Si-O-Si (siloxane, dimethyl polysiloxane, also known as silica gel) cross bands with SiO_2 . When a solution contains considerable alkali (potassium and sodium) hydroxide, the reactive SiO_2 colloid is inclined to dissolve in two stages. The acidic silanol is neutralized by OH^- in the first stage of reaction. Then, the charged O^- attracts the positively charged alkali metal ions [1]:

when the alkali solution contains a high degree of OH^- that breaks Si-O bonding, additional negatively charged O^- reaction areas appear, which combine with the alkali metals and cause the second reaction stage. When Si-O bonding is unbroken, the structure of SiO_2

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gradually loosens. This new oxygen-alkali part becomes reactive, absorbs extra moisture and expands. This structure then changes to an alkali silicate solution or an alkali-silica hydrated colloid (N + K – S – H) because of the difference in water content. When silicon dioxide dissolves, the OH⁻ concentration and the pH value decrease, whereas the concentration of the silicate ions increases. This reaction can be reduced to the following equation [1]:

Effective preventive measures for the concrete ASR problem generally use non-reactive aggregates to restrict the alkali content in the concrete or to add mineral admixtures (e.g., fly ash, silica fume and furnace slag) or chemical admixtures (e.g., Li compound) [2]. The Li compound is the admixture used in fresh concrete to inhibit the ASR problem. A related study can be traced back to 1951 when McCoy and Caldwell [3] introduced the use of the Li compound as an ASR inhibitor to effectively inhibit the ASR swelling capacity. When the Li compound is added in concrete, a part of the alkali metals combines with the cement hydration product. The remaining alkali metals exist in the pore solution in free form and successively combine with the colloid when reacting with the reactive aggregates to form an alkali-silica colloid [4].

Diamond and Ong's study [5] on the reaction between alkali metals and hydration products revealed that the alkali metals are joined in the cement hydration before the alkali-silica colloid is formed, and that Li⁺ is more rapidly consolidated in hydration products at a higher degree compared with Na⁺ and K⁺ if the specimen simultaneously contains Li⁺, Na⁺ and K⁺. Stade [6] indicated that the cause of such result is the smaller size of Li⁺ compared with Na⁺ and K⁺. Therefore, most of the Li⁺ are consolidated in the hydration products if insufficient Li compound is added in the specimen. The pore solution only contains very small amounts of free Li⁺ to change the alkali-silica colloid properties. The ratios of the free

Na⁺ and K⁺ consolidated in the hydration products are reduced when the specimen is added with the Li compound. Therefore, the quantity in the pore solution is larger than that without the Li compound, which generates the ASR problem.

In a 1961 study on the reactions between alkali metals and reactive aggregates, Lawrence and Vivian [7] found the formation of indiffusible agglutinates that could protect SiO₂ from further dissolution around SiO₂ in LiOH, NaOH and KOH solutions because of the existence of Li. In 1989, Sakaguchi et al. [8] first mentioned that the effectiveness of the Li compound in inhibiting ASR dilation is related to the non-water soluble lithium silicate reaction product, which is different from the effects of the Na⁺ and K⁺ formed from the reaction between the reactive aggregates and Li⁺. In 2000, Thomas et al. [9] revealed that the Li⁺ in the pore solution does not prevent Na⁺ and K⁺ from reacting with SiO₂ because all the ions join in the reaction to form hard water swelling in the alkali-silica colloid that contains Li.

This study has two fundamental purposes: (1) to determine the differences in the reactions of Li⁺, Na⁺, and K⁺ with ASR reactive powder; (2) to ascertain whether additional Li⁺ can substitute Na⁺ and K⁺ combined in cement hydration products.

2. Methodology

2.1 Analysis of Reactions of Li⁺, Na⁺ and K⁺ with Reactive Powder

A 25 g Pyrex glass, non-reactive silica sand, and eastern Taiwan metasandstone reactive aggregate powder containing SiO₂ with a particle size from 50 mesh to 100 mesh was soaked in 25 mL of 80 °C 1 N NaOH, KOH and LiOH·H₂O solutions for 1, 7 and 14 days, respectively, based on the ASTM C289 method. The reaction behaviors of Li⁺, Na⁺ and K⁺ with the reactive aggregate powder were analyzed based on the dissolved amount of Si from the solution, the consumption of alkali (OH⁻), and the decrement of the alkali metal ions Li⁺, Na⁺ and K⁺. The dissolved

amount of Si was measured using a spectrophotometer (capable of measuring the transmission of light at a constant wavelength of approximately 410 nm). The consumption of alkali (OH^-) was measured using a pH meter. The decrements of the alkali metal ions Li^+ , Na^+ and K^+ were measured using an IC (ion chromatograph, brand model Dionex ICS-1000).

2.2 Behavior Analysis of Li^+ Substituting Na^+ and K^+ in Cement Hydration Products

A $5\text{ cm} \times 5\text{ cm} \times 5\text{ cm}$ cement paste specimen in a water cement ratio of 0.5 was prepared. The cement composition is shown in Table 1. Reagent-grade NaOH was used to adjust the alkali equivalent to 2.0%. The produced specimen was maintained in a 100% R.H. environment at 23°C for one day before the form removal. The specimen was then maintained at 38°C in a 100% R.H. environment for 56 days and was dried to a constant weight at 60°C . A total of 25 g of 50-mesh powder was placed in a reaction vessel with clear water and 1 N $\text{LiOH} \cdot \text{H}_2\text{O}$ solution. The vessel was sealed and placed in an oven at 80°C . IC was used to measure the Li^+ , Na^+ and K^+ contents in the solution on the 7th, 14th and 28th days to analyze the ability of Li^+ to substitute Na^+ and K^+ combined in cement hydration products.

3. Results and Discussion

3.1 Analysis of Reactions of Li^+ , Na^+ and K^+ with Reactive Powder

Fig. 1 shows the silica dissolved amount and the OH^- and alkali metal ion decrements from the Pyrex glass soaked in 80°C 1 N NaOH, KOH and $\text{LiOH} \cdot \text{H}_2\text{O}$ solutions, Pyrex is an aggregate that is highly ASR reactive. Figs. 1a and 1b show that the

silica dissolved amount from the Pyrex glass in 1 N NaOH and KOH solution is very large, whereas the decrements of OH^- , Na^+ and K^+ are small. This finding indicates the formation of a large amount of dissociable sodium silicate and potassium silicate. When the Pyrex glass is soaked in the 1 N $\text{LiOH} \cdot \text{H}_2\text{O}$ solution, the silica dissolved amount is smaller than that soaked in the NaOH or KOH solution. However, the decrements of OH^- and Li^+ are larger, which proves that the reactive SiO_2 and $\text{LiOH} \cdot \text{H}_2\text{O}$ form a Li-S-H colloid that has low water solubility.

Fig. 2 shows the silica dissolved amount and the OH^- and alkali metal ion decrements from the non-reactive silica sand soaked in 80°C 1 N NaOH, KOH and $\text{LiOH} \cdot \text{H}_2\text{O}$ solutions. Figs. 2a and 2b show that the dissolved amount of silica is much smaller than that from the Pyrex glass and that the decrements of OH^- , Na^+ and K^+ are smaller although the silica sand is soaked in a 1 N NaOH and KOH highly basic solution. This result indicates that the silica sand is a non-ASR-reactive aggregate. When the non-reactive silica sand is soaked in a 1 N $\text{LiOH} \cdot \text{H}_2\text{O}$ solution, the silica dissolved amount is much smaller than that soaked in NaOH or KOH solution. However, the decrement of OH^- and Li^+ is larger, which proves that the non-reactive aggregate will still react with LiOH and that the reactant has low water solubility.

Fig. 3 shows the silica dissolved amount and the OH^- and alkali metal ion decrements from a metasandstone aggregate soaked in 80°C 1 N NaOH, KOH and $\text{LiOH} \cdot \text{H}_2\text{O}$ solutions. Metasandstone is a highly ASR-reactive aggregate. Figs. 3a and 3b show that the amount of dissolved silica from the metasandstone aggregate soaked in 1 N NaOH and KOH highly basic solution is very large, whereas the

Table 1 Oxide composition in cement, Pyrex glass and metasandstone (unit: %).

Oxide material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	$\text{Na}_2\text{O}_{\text{eq}}$
Cement	21.8	5.13	4.40	63.33	2.38	2.05	0.59	0.11	0.50
Pyrex glass	87.27	-	0.35	0.44	0.35	1.23	0.11	3.84	-
Metasandstone	76.29	6.45	3.22	1.28	0.80	1.07	1.24	2.17	-

Fig. 1 Silica dissolved amount and OH^- and alkali metal ion decrements from Pyrex glass soaked in 80 °C 1 N: (a) NaOH; (b) KOH; (c) $\text{LiOH} \cdot \text{H}_2\text{O}$ solutions.

Fig. 2 Silica dissolved amount and OH^- and alkali metal ion decrements from non-reactive silica sand soaked in 80 °C 1 N: (a) NaOH; (b) KOH; (c) $\text{LiOH} \cdot \text{H}_2\text{O}$ solutions.

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Fig. 3 Silica dissolved amount and OH^- and alkali metal ion decrements from metasandstone soaked in 80 °C 1 N: (a) NaOH; (b) KOH; (c) $\text{LiOH} \cdot \text{H}_2\text{O}$ solutions.

decrements of OH^- , Na^+ and K^+ are small, which is similar to the test result of the Pyrex glass and indicates the formation of a large amount of dissociable sodium silicate and potassium silicate solutions. When the metasandstone aggregate is soaked in a 1 N $\text{LiOH} \cdot \text{H}_2\text{O}$ solution, the amount of dissolved silica is smaller than that soaked in either NaOH or KOH solutions. However, the decrement of OH^- and Li^+ is larger, which is similar to the test result of the Pyrex glass and proves that the reactive SiO_2 and the LiOH will form a soluble Li-S-H colloid that has low water solubility.

Thus, the high concentration NaOH and KOH solutions causes a reactive aggregate with ASR to generate an easily absorbed swelling alkali-silica colloid, whereas a reactive aggregate in the LiOH solution leads to the absorption of a swelling lithium-silica colloid to protect the aggregate and to greatly reduce the amount of dissolved silica.

3.2 Behavior Analysis of Li^+ Substituting Na^+ and K^+ in Cement Hydration Products

The total Na^+ and K^+ contents in the 1 g cement of the grout are 0.0355 mmol and 0.6093 mmol, respectively. The paste is maintained for 56 days before drying and is soaked in an 80 °C clear water and 1 N $\text{LiOH} \cdot \text{H}_2\text{O}$ solution for 7, 14 and 28 days. The results are shown in Fig. 4.

The Na^+ and K^+ contents dissolved from every 1 g of dried paste powder soaked in the solution can be calculated based on the Na^+ and K^+ contents in the solution. Fig. 4 shows that the Na^+ and K^+ contents dissolved from the paste soaked in a 1 N $\text{LiOH} \cdot \text{H}_2\text{O}$ solution are higher than those soaked in clear water. This phenomenon may be caused by the consolidation of the Li^+ in the solution into paste powder. The Na^+ and K^+ that originally consolidated in the paste powder were replaced by Li^+ . Therefore, the Na^+ and K^+ contents dissolved from the paste soaked in a 1 N

Fig. 4 Dissolved from every 1 g of dried paste powder in 80 °C clear water and 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$ solution: (a) Na^+ and (b) K^+ content.

Fig. 5 Percentage composition of consolidated: (a) Na^+ ; (b) K^+ in paste powder soaked in 80 °C clear water and 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$ solution.

Fig. 6 Increase in the amount of Na^+ and K^+ contents dissolved from every 1 g of dried paste powder soaked in 80 °C 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$ solution compared with clear water.

$\text{LiOH}\cdot\text{H}_2\text{O}$ solution are higher than those soaked in clear water.

Fig. 5 shows that the Na^+ and K^+ contents consolidated in paste soaked in a 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$

Fig. 7 Li^+ content combined in every 1 g of dried paste powder soaked in 80 °C 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$ solution.

solution are lower than those soaked in clear water. Fig. 6 shows that the Na^+ and K^+ contents dissolved from paste soaked in a solution that contains Li increase as the soak time is extended, compared with that soaked in clear water. Fig. 7 shows that the Li^+

content combined in every 1 g of dried paste powder increases as the soak time in 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$ extends.

The free and consolidated Na^+ and K^+ contents in the paste powder soaked in clear water and 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$ solution and the result of the Li^+ combined in paste powder prove that Li^+ can actually substitute the partial Na^+ and K^+ consolidated in paste.

4. Conclusions

(1) When a Pyrex glass or metasandstone aggregate with high ASR reactivity is soaked in 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$ solution, the dissolved amount of silica is lower than that obtained when soaked in 1 N NaOH or KOH solution. However, the decrement of OH^- and Li^+ is high. This result proves that the reactive SiO_2 and LiOH form a reactant that has low water solubility;

(2) When the paste powder is soaked in 1 N $\text{LiOH}\cdot\text{H}_2\text{O}$ solution, the dissolved Na^+ and K^+ contents are higher than that soaked in clear water. The amount of dissolved Na^+ and K^+ increases as the soak time is extended. The combination of Li^+ with paste powder also increases as the soak time in a solution containing Li is extended. This result proves that Li^+ can substitute the partial Na^+ and K^+ consolidated in the paste, which indicates that the alkali silica reaction can be prevented by the presence of Li^+ .

Acknowledgments

The authors would like to thank the National Science Council of Taiwan for their financial support

of this research under Contract No. NSC 101-2221-E-033-056-MY3.

References

- [1] R. Helmuth, Eliminating or Minimizing Alkali-Silica Reactivity, SHRP-C-342, Strategic Highway Research Program, National Research Council, Washington, DC, 1993.
- [2] W.E. Touma, D.W. Fowler, R.L. Carrasquillo, Alkali-Silica Reaction in Portland Cement Concrete: Testing Methods and Mitigation Alternatives, Research report ICAR 301-1F, 2001.
- [3] W.J. McCoy, A.G. Caldwell, New approach to inhibiting alkali-aggregate expansion, *Journal of the American Concrete Institute* 22 (9) (1951) 693-706.
- [4] M.A. Bérubé, J. Frenette, M. Rivest, D. Vézina, Measurement of the alkali content of concrete using hot-water extraction, in: *Proceeding of the 11th International Conference on Alkali-Aggregate Reaction*, Quebec, Canada, 2000, pp. 159-168.
- [5] S. Diamond, S. Ong, The mechanisms of lithium effects on ASR, in: *Proceeding of the 9th International Conference on Alkali-Aggregate Reaction*, London, 1992, pp. 269-278.
- [6] H. Stade, On the reaction of C-S-H (Di, Poly) with alkali hydroxides, *Cement and Concrete Research* 19 (1989) 802-810.
- [7] M. Lawrence, H.E. Vivian, The reactions of various alkalis with silica, *Australian Journal of Applied Science* 12 (1961) 96-103.
- [8] Y. Sakaguchi, M. Takakura, A. Kitagawa, The inhibiting effect of lithium compounds on alkali-silica reaction, in: *Proceeding of the 8th International Conference on Alkali-Aggregate Reaction*, Kyoto, 1989, pp. 229-234.
- [9] M.D.A. Thomas, R. Hooper, D. Stokes, Use of lithium-containing compounds to control expansion in concrete due to alkali-silica reaction, in: *Proceeding of the 11th International Conference on Alkali-Aggregate Reaction*, Quebec, Canada, 2000, pp. 783-792.