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THE INHIBITING EFFECT OF LITHIUM COMPOUNDS ON ALKALI-SILICA REACTION

Yuriko Sakaguchi* , Makoto Takakura * , Akio Kitagawa* ,
Takahiro Hori * , Fuminori Tomosawa ** and Michihiko Abe ***

* Central Research Institute, Nissan Chemical Industries, Ltd.
Tsuboi-cho, Funabashi-shi, Chiba 274, Japan
** Dept. of Architecture, University of Tokyo,
Bunkyo-ku, Tokyo 113, Japan
*** Building Reserach Institute, Ministry of Construction
Tsukuba-shi, Ibaraki 305, Japan

1. ABSTRACT

Expansion of mortar bars, which contained Pyrex glass, due to alkali-silica reaction(ASR) was inhibited by addition of lithium compounds (lithium carbonate, lithium nitrite and lithium hydroxide). Lithium hydroxide was found also effective in inhibiting the expansion of mortar bars containing reactive aggregates. The inhibiting effect increased in proportion to the amount of its addition.Expansion was inhibited by impregnating the solution of lithium nitrite to both of mortar bars and concrete prisms which had been subjected to accelerated expansion. The effects of lithium compounds were examined by observing the boundary face between Pyrex glass and hardened cement paste by means of energy dispersive X-ray spectrometer and by analyzing the extracted pore solution from the mortars. It was confirmed that the alkali-silica gel, the reaction product of Pyrex glass and hardened cement paste, was not observed at the boundary face, and that the concentration of lithium ion in pore solution decreased and that of sodium and potassium ion in it was nearly constant with the passage of time.

In conclusion, these results suggest that the inhibiting effect of lithium compounds is attributed to the production of a kind of lithium silicate, which hardly swells and dissolves, at the surface of aggregate.

2. INTRODUCTION

The common approaches to prevent the expansion of concrete due to ASR are the selection of non-reactive aggregate, the use of low-alkali cement, and the use of certain proved pozzolanic admixtures. Except three main preventive approaches, the inhibiting effect of lithium compounds on ASR has been studied.[1] [2] The lower reactivity of lithium ion with amorphous-silica in comparison to sodium ion was identified by testing in accordance with the modified ASTM Methods C 289.[3] Recently it is generally said in Japan that the approaches of repairing concrete construction, which has been damaged by ASR, are grouting of an epoxy resin and coating of a waterproof paint and a silane agent. These repairing approaches, which are physical repairing approaches, are intended for shutting off the surface of concrete construction from water in order not to swell the alkali-silica gel.

This paper discribes a series of experiments to ascertain the effects of lithium compounds, which are concerned in the chemical reaction of ASR and thereby inhibit its expansion, and to study the possibility of employing the solution of lithium nitrite for impregnating and repairing concrete construction damaged by ASR. At the same time, the inhibiting mechanism of lithium compound on ASR was studied.

3. INHIBITING EFEECT OF LITHIUM COMPOUNDS ON EXPANSION OF MORTAR CONTAINING PYREX GLASS

3.1 Materials and Method

Mortar of the composition indicated in Table 1 was prepared. The solution of NaOH was added to adjust the Na_2O equivalent of the cement to 0.8% or 1.0%. Three lithium compounds, they are $LiOH \cdot H_2O$, $LiNO_2$ and Li_2CO_3, were added to mortar at the mixing stage and the amounts of three compounds were 0.65%, 0.95%, and 0.72% of cement, respectively.

Bars of 4 × 4×16cm were cast and cured under saturated water vapor for 24hours and then removed from the mold. The bars were stored in the saturated water vapor box which was placed in the room with a constant temperature of 40 ℃ after the measurement of their initial length. The bar length was measured by contact gage in the room with a constant temperature of 23℃.

Table 1 Composition of mortar

C :Cement	portland cement Na_2O equivalent 0.57%
S :Fine aggregate	S_s :standard Toyoura sand S_{pg}:Pyrex glass #7740 (100 ～28 : 28～8 : 8～4 =2 :5 :3)
W :Water	added so as to provide a flow value of 201～216 mm*)
R :Alkali	NaOH solution

C :S (S_s : S_{pg}) :W =1 :2 .25(1.35:0.9) :X

*) The water/cement ratio of 0.55 gave an appropriate flow value irrespective of lithium compounds.

3.2 Results and Discussion

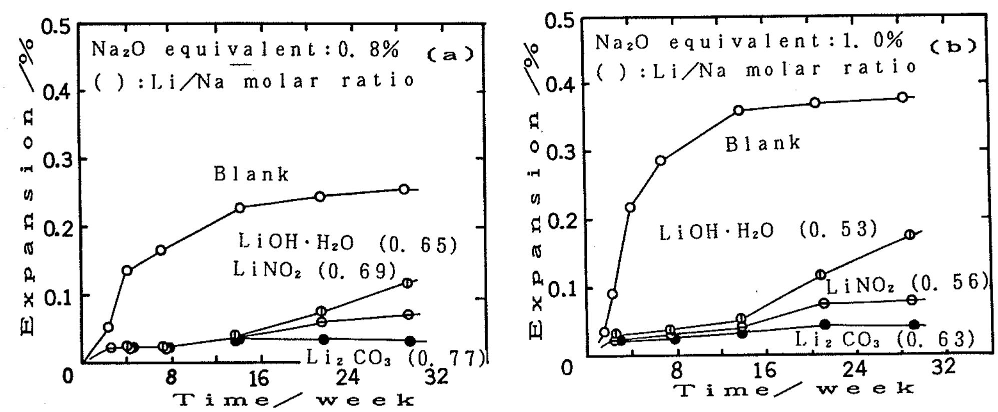

Fig.1(a)(b) inhibiting effect of lithium compounds on expansion of mortar

All of the three lithium compounds were useful for inhibiting the expansion of mortar whether alkali content of cement was 0.8% or 1.0% Na_2O equivalent, which are shown in Fig.1(a) and (b). Fine cracks were found on the 100th day (after about 14 weeks) on the bars having 1.0% of alkali and found on the 150th day (after about 21 weeks) on the bars having 0.8% alkali, and both of them did not contain any lithium compound. The cracks were seen on three surfaces other than mold bottom surface. No crack was, however, found in any bars with the addition of the lithium compounds.

These results confirm the findings that all of three lithium componds had an appreciable inhibiting effect on ASR, but the inhibiting effects differed from one compond to another. Also they suggest that the inhibiting effect of a particular lithium compound depends mainly upon Li/Na molar ratio under the same condition.

4. INHIBITING EFFECT OF $LiOH \cdot H_2O$ ON EXPANSION OF MORTAR CONTAINING A REACTIVE AGGREGATE

4.1 Materials and Method

Mortar was prepared by using portland cement, which had alkali content of 0.48% Na_2O equivalent, and reactive aggregate X. Lithium hydroxide was used to be dissolved and to be mixed the mortar. The addition amounts were 0.27%, 0.55%, 0.83% and 1.11% of the cement giving different Li/Na molar ratios of 0.3, 0.6, 0.9, and 1.2, respectively. The experiment was carried out in accordance with the Method for Alkali-Silica Reaction Tests for Aggregate (Mortar Bar Method) as specified provisionally by the Ministry of Construction. The reactive aggregate X was a pyroxene andesite from Hokuriku district in Japan and it was considered a potentially delterious degree in the test of ASTM Method C 289.

4.2 Results and Discussion

As shown in Fig.2, the inhibiting effect of $LiOH \cdot H_2O$ was appreciated on the mortar bars by use of the aggregate X, and the expansion was almost stopped to 52 weeks by adding $LiOH \cdot H_2O$, Li/Na molar ratio 0.9 at least. The weight of bars increased in proportion as the length of bars increased. This correlation apparently due to the absorption of water by gel which had been formed by alkali-silica reaction. A fluid, which appeared to be a sol, was observed on the surface of each bars in the absence of $LiOH \cdot H_2O$ at 4 weeks. On the bars with the addition of $LiOH \cdot H_2O$, however, the appearance of the sol occurred later than ones without $LiOH \cdot H_2O$. Referring to crack on the bars, fine cracks were found on them without $LiOH \cdot H_2O$ and with small amounts addition of $LiOH \cdot H_2O$ (Li/ Na molar ratio was 0.3 and 0.6) at 39 weeks.

Although the experiment was carried out by use of mortar bars as the samples, the lithium compound is assumed to exhibit a similar inhibiting effect for concrete prisms, too.

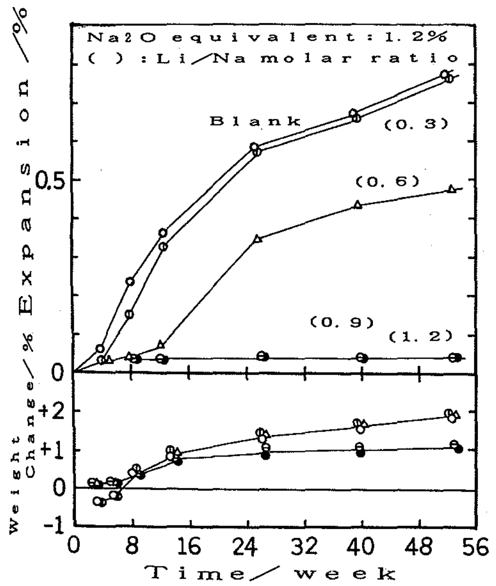

Fig.2 Inhibiting effect of lithium hydroxide on expansion of mortar

5. INHIBITING EFFECT OF IMPREGNATING $LiNO_2$ AQUEOUS SOLUTION TO MORTAR

5.1 Materials and Method

The same cement, fine aggregates and alkali as those used in the experiment described in 3. were used. The water/cement ratio was 50% and the aggregate/cement ratio was 2. Fine aggregates consisted of 40% Pyrex glass and 60% standard Toyoura sand. The alkali content was 2.0% Na_2O equivalent of cement by adding NaOH solution. After the bars were under standard curing, they were previously subjected to expansion of about 0.2% of the initial length in a saturated water vapor box at 40℃ and then dried in the room at 23℃ 55%R.H. in the purpose of impregnation with $LiNO_2$ solution by 4% decrease of the intial weight. The bars were dipped in $LiNO_2$ solution for the different period of time.

The solution of $LiNO_2$ was prepared from the slurry of LiOH and NO_x gas at Nissan Chemical Ind., LTD. and it has 25% concentration, pH of 11.5, specific gravity of 1.16 and viscosity of below 10cps.

5.2 Results and Discussion

Fig.3 shows the changes of length and the changes of weight with the passage of time. Insofar as the bars did not show any appreciable increase in weight when they had been caused to expand by about 0.2% in a saturated water vapor box, it is apparent that even only the mortar containing water contributed to its expansion by ASR. The bars showed a shrinkage of about 0.1% and a weight loss of about 5% while they had been dried at 23°C 55%R.H..

Some inhibiting effect on expansion was found even in the bars having an impregnant depth of only 3 mm. The bars having impregnated depth of 7 mm and 9mm expanded their length by the amount of shrinkage which had resulted from drying at 23°C, and hardly showed any further expansion. Fine cracks were found on the bars which had not been impregnated with $LiNO_2$ solution and on the bars having an impregnated depth of 3 mm, when they reached the age of 4weeks.

It will hereafter be necessary to study the water content which mortar has prior to impregnation, the degree of its expansion prior to impregnation, etc.

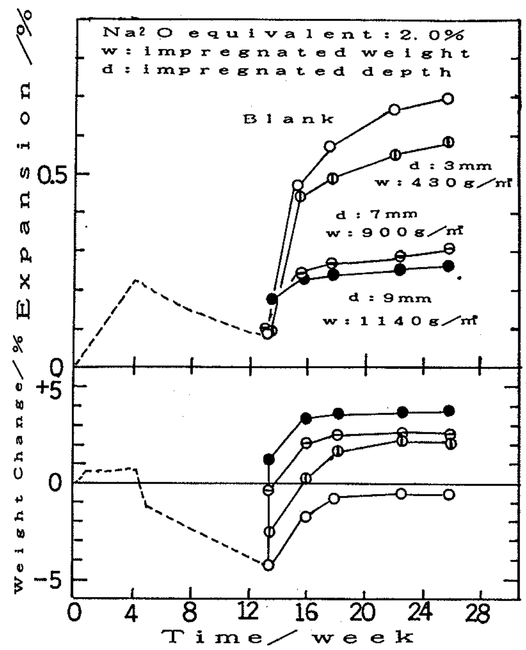

Fig.3 Inhibiting effect of impregnating $LiNO_2$ solution to mortar

6. INHIBITING EFFECT OF IMPREGNATING $LiNO_2$ AQUEOUS SOLUTION TO CONCRETE

6.1 Materials and Method

Concrete prism (10×10×40cm) were prepared by using cement having 0.48% Na_2O equivalent, silicasand and the reactive aggregate X. The placing of concrete was carried out according to the procedure of JIS A 1132. The water/cement ratio was 55.7% and sand percentage was 43.6%. Cement content, water content and alkali content per unit volume of concrete was 350kg/m³, 195kg/m³ and 6.75 kg/m³, respectively. The prisms were previously subjected to expansion of about 0.1% of the initial length at 40°C 100%R.H. and then dried under the condition of 20°C 60% R.H. by 1% decrease of the initial weight. After that they were dried further at 50°C by 4% decrease of it. The prisms were dipped in $LiNO_2$ solution for 24hours.

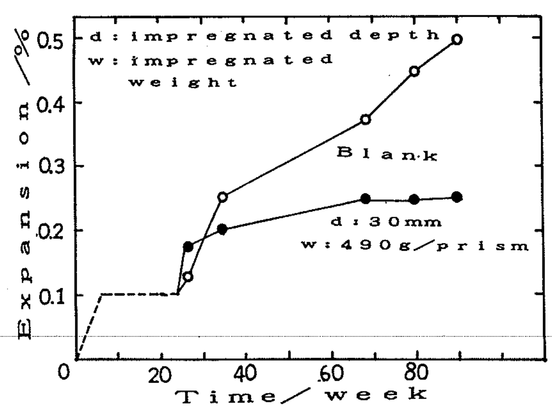

Fig.4 Inhibiting effect of impregnating $LiNO_2$ solution to concrete

6.2 Results and Discussion

The inhibiting effect of impregnating $LiNO_2$ solution to concrete prisms, which had been subjected to be expand previously by about 0.1%, on expansion is shown in Fig.4. Some inhibiting effect on expansion was found in the prisms impregnated with $LiNO_2$ solution as compared with the prisms without it.

7. INHIBITING EFFECT OF LITHIUM COMPOUND AS ASCERTAINED BY ENERGY DISPERSIVE X-RAY SPECTROMETER

7.1 Materials and Method

The portland cement having 0.59% Na_2O equivalent and water were mixed in a ratio of 1:0.35. The solution of NaOH was added to adjust Na_2O equivalent to 1.2%. The solution of $LiNO_2$ was added in an amount giving Li/Na molar ratio of 1 at mixing stage.

A bar of Pyrex glass measuring 25mm in diameter and 10 cm in length and having a surface polished by sand blasting was placed in the center of a mold, which is 5cm in diameter and 10 cm in length. And then cement paste was poured into the mold to prepare a solid cylindrical sample while a similar sample to which no $LiNO_2$ solution had been added was also prepared. Each sample cured with wet air at 20 ℃ for 24hours. It was stored in a wet air box at 40 ℃ for 4 months, and it was removed from the box. A circular specimen of about 5 mm in thickness was cut from the sample and 15mm square specimen was further cut from it by means of diamond cutter. The boundary face between Pyrex glass and hardened cement paste in square specimen was examined by energy dispersive X-ray(EDX) spectrometer.

7.2 Results and Discussion

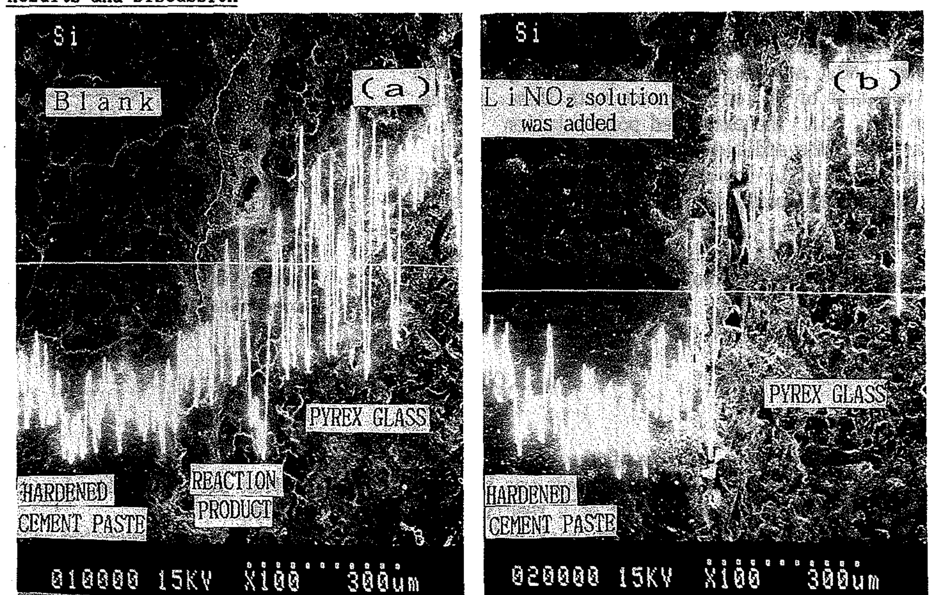

Fig.5(a)(b) The boundary faces between Pyrex glass and hardened cement paste

Fig.5(a)(b) show the boundary faces between Pyrex glass and hardened cement paste in the sample with no addition of $LiNO_2$ solution, and in the sample with addition of $LiNO_2$ solution, respectively, as they were analyzed for silicon by EDX spectrometer. The reaction product, which had about 300μm width, was found between Pyrex glass and paste in the sample in which no $LiNO_2$ solution had been added.(Fig.5(a)) On the other hand, it was obvious from the intensity of silicon as shown in Fig.5(b) that the addition of $LiNO_2$ solution made so clear the boundary face between Pyrex glass and paste and that any such product hardly was formed therebetween. This is apparently due to the fact that Li ion is concerned in the chemical reaction of ASR to inhibit the formation of alkali-silica gel.

8. INHIBITING EFFECT OF LITHIUM COMPOUND AS ASCERTAINED BY ANALYZING THE EXTRACTED PORE SOLUTION FROM MORTAR

8.1 Materials and Discussion

The same cement as used in the experiment described in 7. The content of alkali and the addition amount of $LiNO_2$ solution were adjusted to the same as the procedure described in 7. Fine aggregates consisted of 40% the crushed Pyrex glass and 60% standard Toyoura sand. The water/cement ratio was 50% and the aggregate/cement ratio was 2.25.

The experiment was carried out according to the procedure of R.S.Barnneyback,Jr.et al.[4] The mortars of 5cm in diameter and 10 cm in length were stored in the saturated water vapor box at 40℃ wrapped with vinyl bags.

The concentration of OH ion was determined by direct titration against standard HCl and that of Na, K and Li ion was determined by means of ionchromatography. The concentration of Ca ion was measured by use of inductively coupled plasma atomic emission(ICP) spectroscopy.

8.2 Results and Discussion

As shown in Fig.6(a), the concentration of Na and K ion in the extracted pore solution from mortars without $LiNO_2$ solution decreased with the passage of time and that of OH ion kept pace with them. On the other hand, in the extracted pore solution from the mortars with the addition of $LiNO_2$ solution, the concentration of Li ion decreased and that of Na and K ion was nearly constant with the passage of time. (Fig.6(b))

The results confirm the fact that Li ion is concerned in the product of alkali-silica gel.

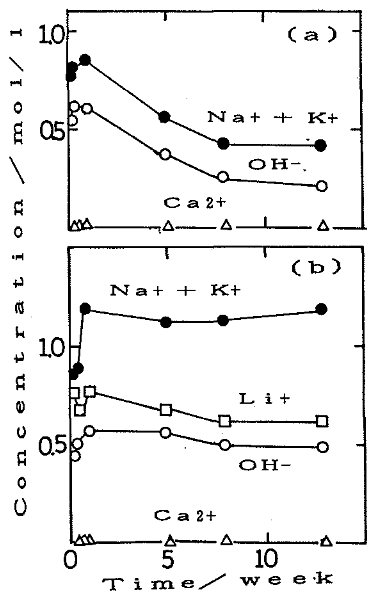

Fig.6(a)(b) The relation between concentration of ions and time

9. CONCLUSION

The following is a summary of the results of this paper:

(1) The addition of the Lithium compounds was effective for inhibiting the expansion of mortar due to ASR, whether Pyrex glass or a reactive aggregate were used.

(2) When both of mortar and concrete which had been expanded due to ASR was impregnated with $LiNO_2$ solution, any further expansion thereof could be retarded or inhibited.

(3) It was confirmed that lithium compound was concerned in the chemical reaction of ASR and inhibited the formation of alkali-silica gel.

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