Pergamon

Cement and Concrete Research 29 (1999) 1271–1275

CEMENT AND CONCRETE RESEARCH

Unique response of $LiNO_3$ as an alkali silica reaction-preventive admixture

Sidney Diamond*

Purdue University, School of Civil Engineering, 1284 Civil Engineering Bldg., West Lafayette, IN 47907, USA

Received 6 August 1998; accepted 27 May 1999

Abstract

Lithium hydroxide and various lithium salts have been known to ameliorate the effects of alkali silica reaction for many years. The use of lithium hydroxide is not without risk. A significant increase in the pore solution OH^- ion concentration (and pH) by lithium hydroxide and inadequate dosages are known to result in increased, rather than decreased expansion. Almost insoluble lithium salts (such as lithium fluoride and lithium carbonate) are effective at large dose levels, but generate lithium hydroxide in solution, and are thus subject to the same difficulty as LiOH. It is shown that lithium nitrate, a fully soluble neutral salt, does not generate significant increases in hydroxide ion concentration, and thus does not undergo the risk of accelerating the alkali silica reaction at the same time that it is attempting to ameliorate its effects. Lithium nitrate is, however, subject to the same extensive sorption by newly forming cement hydration products as other forms of lithium treatment, and a high dosage level is needed to indefinitely maintain the requisite concentration in solution.

Keywords: Alkali aggregate reaction; Pore solution; Admixture; Lithium compounds; pH

1. Introduction

Alkali silica reactions (ASR) in concrete have been the subject of much concern since the 1940s. Serious deterioration of a number of major structures has been recorded over the intervening years. More recently special concern with respect to ASR in highway pavements in the United States has been evidenced by the Federal Highway Administration and various State Departments of Transportation. The prospective use of lithium compounds as ASR-ameliorating admixtures has received much attention and both laboratory studies and field trials are underway in various parts of the world.

ASR reactions are generally considered to produce expansion, cracking, and other deterioration in concrete as the eventual result of reactions between hydroxide ions in concrete pore solutions and susceptible siliceous aggregate components. The response normally involves formation of a hydrous alkali silica gel that incorporates both the hydroxide ions and the alkali cations accompanying them from the pore solution. With modern cements the alkali cations are primarily potassium ions, although occasionally sodium may predominate. The reaction itself is induced by the attack of hydroxide ions on the silica structure of the susceptible aggregate; the accompanying alkali cation plays little part in the reaction per se. However, the accompanying cation does have some influence on the properties of the gel produced. Gels incorporating either sodium and potassium ions show similar properties, but the behavior of the gel will vary to the extent that other cations, especially calcium cations, are incorporated into it.

It is generally considered that with lithium-based admixtures, partial substitution of lithium ions for potassium or sodium ions 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 relative proportion of lithium to the other cations in solution. Sakaguchi et al. [1] found that mole ratios of Li^+ to $Na^+ + K^+$ in excess of about 0.9 were required to completely eliminate expansion due to ASR in their test conditions. Stark et al. [2] studied the effect of adding various amounts of LiOH to the 1 N NaOH solutions specified in the ASTM C 1260 test conditions (mortar bars immersed in 1 N NaOH solutions at 80°C for 14 days). Using a highly reactive aggregate, they found that LiOH addition to reach a Li^+:Na^+ mole ratio of 0.85 in the exposure solution was required to prevent the expansion. In general it is evident that high proportions of lithium need to be incorporated into the

---

* Corresponding author. Tel.: 765-494-5016; fax: 765-496-1364.

E-mail address: diamond@ecn.purdue.edu (S. Diamond)

0008-8846/99/$ – see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0008-8846(99)00115-5

gel for its expansive character to be sufficiently mitigated to render it innocuous.

In their classical paper reporting trials of various substances as possible admixtures to ameliorate the expansive effects of ASR, McCoy and Caldwell [3] noted that various lithium-containing compounds provided significant benefit. However, until very recently most trials of lithium-based admixtures concentrated on two almost insoluble salts, lithium fluoride and lithium carbonate, or on lithium hydroxide; all of these were found to be effective at sufficiently high dosage levels by Sakaguchi et al. [1].

LiOH at first glance seems an unusual choice of reagent for the amelioration of ASR effects. LiOH is a strong alkali hydroxide that dissolves completely in water and is fully ionized in solution; it is thus similar in its basic properties to NaOH and KOH. Accordingly, its use in concrete that is potentially subject to ASR because of its already high OH^- ion concentration has the effect of substantially increasing the already high OH^- ion concentration as the result of LiOH treatment. Thus the admixture substantially increases the "challenge" presented to the stability of any potentially reactive siliceous component present in the concrete. For the ameliorative effect to take place, the effect of incorporating Li^+ cations into the ASR gel that is formed must overcome the potential for increased reaction associated with the higher pH produced in the pore solution.

Lithium carbonate and lithium fluoride are also unusual choices for chemical admixtures. Lithium fluoride is almost insoluble in water; lithium carbonate is only slightly soluble. Accordingly these reagents cannot be predissolved in the mix water, as is customary for most chemical admixtures, but must be added in powder form. These leads to some practical difficulty in obtaining uniform distribution of the admixture in the concrete.

Nevertheless, these admixtures, added in powder form in sufficiently large dosages, do indeed display efficacy in ameliorating ASR effects. To produce this response they must in some way have dissolved in fresh concrete water solution to a much greater extent than they do in ordinary water. As will be illustrated later, it turns out that the dissolution of these compounds in the concrete water solution results in the formation of lithium hydroxide. In effect, the use of either LiF or Li_2CO_3 as a concrete admixture generates an enhanced pH that results in the same potential for increased ASR that is induced by the use of LiOH directly.

Thus attention has been turned to the potential use of other lithium-bearing compounds that may not suffer from this difficulty. In this paper it is shown that $LiNO_3$ is indeed such a compound, and one that does not suffer from various possible complications that might limit its use in concrete. Admixtures based on $LiNO_3$ are currently being marketed by at least one producer.

1.1. Effect of inadequate dosage of LiOH

The successful use of LiOH requires a dose level sufficiently high that the pH augmentation produced is at least counterbalanced by the ameliorating effect of the lithium on the ASR gel produced. The dosage required is higher than it might be due to the fact that lithium (and its accompanying anion) tends to be sorbed into the developing cement hydration product in the early stages of cement hydration. For example, Ong [4] found that by the end of the first day approximately 40% of the Li^+ added as predissolved LiOH in a water:cement 0.49 cement paste had been removed from the pore solution by sorption into the hydrating cement. By 28 days more than half had been removed. Presumably lithium so removed from solution is not available for subsequent incorporation into ASR gel.

The practical consequence of the prior removal of much of the lithium from solution before ASR takes place is that a substantial excess dosage must be supplied to achieve the desired effect of lithium on the expansive character of the gel.

Not only do inadequate dosages not provide the expected amelioration of ASR, but indeed, inadequate dosages of LiOH may be worse than no admixture at all. A number of test results indicate that inadequate dosages of lithium hydroxide produce greater ASR expansion then that generated in the control mortars in which ASR took place unchecked. For example, data of Ong [5] are plotted in Fig. 1, showing the expansion at 9 months of ASTM C 227 mortar bars containing 4.5% Beltane opal, and incorporating respectively no lithium hydroxide or the molar equivalents of 0, 0.4, 0.8, and 1.2 equivalent %Na_2O in the cement, in the form of predissolved LiOH. The mortar bars were encapsulated in heat-sealed plastic sleeves to prevent leaching, with enough water sealed with each bar to insure 100% relative humidity. As seen in Fig. 1, LiOH treatment levels corresponding to 0.4 and 0.8% both substantially increased expansion, rather than reducing or preventing it. An LiOH treatment corresponding to at least 1.2% Na_2O equivalent in the cement was required to demonstrate effectiveness, that is, to reduce expansion below that of the control mortar. Similar results

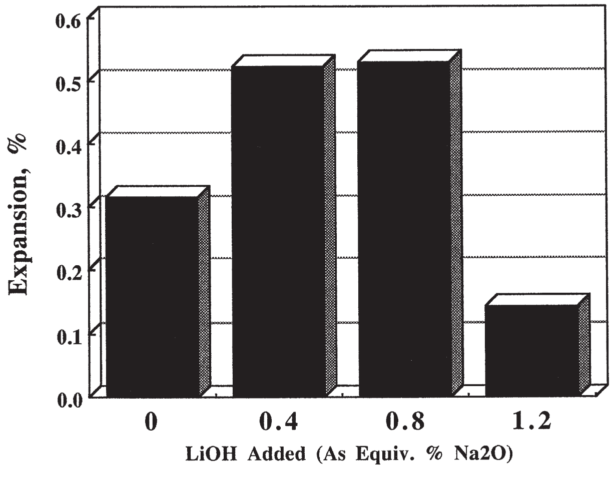

Fig. 1. Expansion at 9 months of ASTM C 227 mortar bars containing Beltane opal as a function of dosage of LiOH concentration dissolved in the mix water. Concentration is expressed as equivalent %Na_2O in cement.

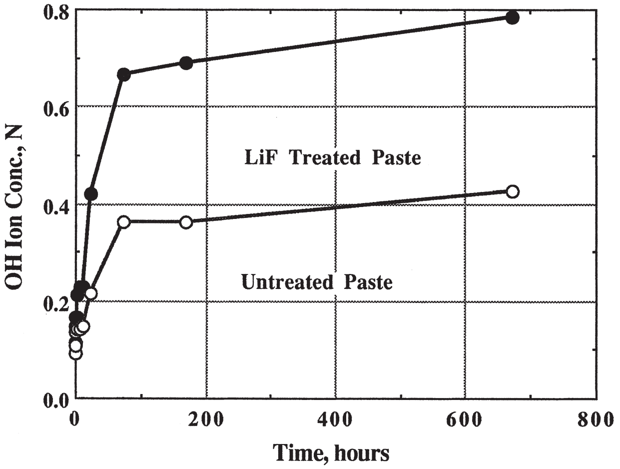

Fig. 2. OH^- ion concentrations as functions of time for control pastes and pastes with 1% LiF intermixed in powder form with the Portland cement.

were recorded for ASR-reactive mortars containing cristobalite rather than Beltane opal.

1.2. Effects of Li_2CO_3 and LiF treatments: generation of LiOH

Several years ago Ong [5] carefully investigated the seeming paradox that far greater LiF and Li_2CO_3 dosages than could be dissolved in water were effective in ameliorating the expansive effects of ASR. Ong showed that these almost water-insoluble lithium salts dissolved in concrete water solutions as the consequence of the precipitation of the corresponding even more insoluble calcium salts, calcium fluoride and calcium carbonate. The precipitation of these calcium salts left the lithium ions in solution, but were now balanced by newly generated OH^- ions.

Thus, in effect the lithium fluoride or lithium carbonate supplied in solid form was replaced by an equivalent amount of dissolved lithium hydroxide.

In Fig. 2, plotted from the data of Ong [5], the OH^- ion concentrations measured for pore solutions expressed from a water:cement 0.49 cement paste without added lithium salt are compared with those for an otherwise identical paste incorporating 1% LiF as a powder intermixed with the Portland cement. It is seen that the 1% LiF treatment virtually doubled the measured OH^- ion concentration. It was found that the excess OH^- ion concentration measured was equivalent, within reasonable experimental error, to the concentration of Li^+ ions found to be retained in the pore solution.

Thus, it is seen that incorporating almost insoluble lithium salts is essentially equivalent to incorporating LiOH directly. The same concern with respect to the potentially harmful effects of inadequate dosage levels apply here as well.

1.3. The potential benefit of use of neutral soluble lithium salts

The generation of LiOH and its unfavorable consequences at low dosage levels would not be expected if the lithium was supplied as a neutral salt (i.e., a highly ionizable salt representing the neutralization of LiOH with a strong acid). The lithium-bearing substances tested by McCoy and Caldwell [3] included LiCl, Li_2SO_4, and $LiNO_3$, all of which fit this description. Presumably lithium added in any of these forms would not generate LiOH in solution and experience the consequent pH increase.

Of these salts, LiCl is clearly unsuitable for use in concrete because of the potential for steel corrosion, and Li_2SO_4 is suspect because of possible contributions of the extra sulfate to internal sulfate attack. Thus in the last few years attention has been focused on $LiNO_3$ as a suitable form of lithium for incorporation in concrete. This salt is relatively inexpensive and can be made widely available.

The remainder of this paper reports the results of experimental determinations of the pore solution effects of incorporating $LiNO_3$ as a predissolved admixture in cement paste mix water.

2. Materials and experimental methods

This investigation was carried out on pastes prepared from an ASTM Type I Portland cement of relatively low alkali content (0.46% equivalent Na_2O, mostly as potassium). The mill analysis showed a calculated Bogue composition of 60.9% C_3S, 13.5% C_2S, 10.9% C_3A, and 6.3% C_4AF. Pastes with and without $LiNO_3$ were prepared at a water:cement ratio of 0.49 by mixing in a standard Hobart mixer in conformance with ASTM C 305. Where used, reagent grade lithium nitrate was predissolved in the mix water at a dose rate equivalent to 1% $LiNO_3$ by weight of cement, providing a calculated initial concentration of 0.30 N in the water to be used in mixing the paste.

The paste samples were hydrated in sealed containers at 23°C for various periods ranging from 0.2 h to 28 days. Pore solutions were removed either by pressure-assisted filtration or, after setting, by the usual pore solution expression procedure described by Barneyback and Diamond [6]. The pore solutions were analyzed by normal chemical methods and the nonevaporable water contents determined at ages beyond 6 h by oven drying and subsequent ignition. This determination provided data for the estimation of bound water in order to adjust the measured concentrations of the various ions for the effect of progressive reduction in the amount of solvent water as a consequence of ongoing cement hydration in the sealed pastes.

3. Results

3.1. Effect of $LiNO_3$ treatment on OH^- ion concentrations

Pore solution OH^- ion concentrations were determined by direct titration with standardized HCl to the methyl red end point (after boiling to expel any dissolved CO_2). The results are plotted in Fig. 3.

In contrast with previous findings for LiOH, LiF, and Li_2CO_3, introduction of $LiNO_3$ into the cement paste does

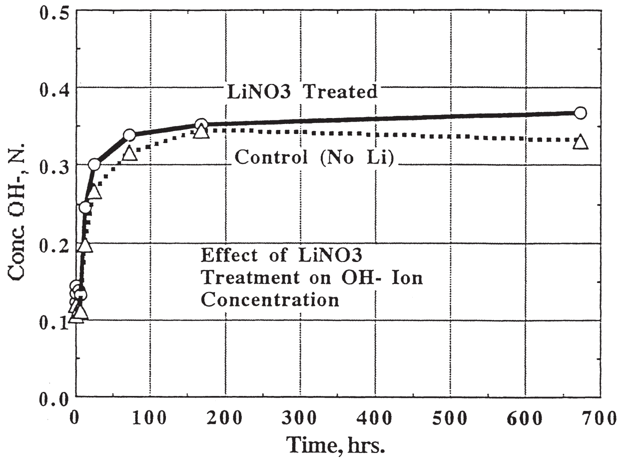

Fig. 3. OH^- ion concentrations as functions of time for control pastes and pastes prepared with mix water containing 0.3 N dissolved $LiNO_3$.

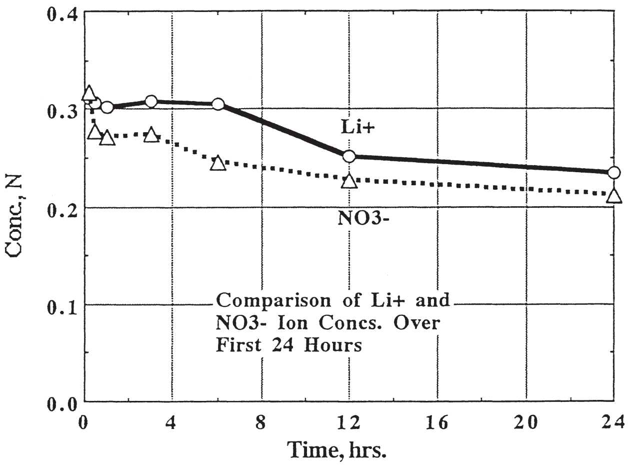

Fig. 4. Results of analyses of Li^+ and NO_3^- as functions of time for pastes prepared with mix water containing 0.3 N dissolved $LiNO_3$.

not result in significant increase in the OH^- ion concentration developed in the paste. The 28-d concentrations plotted in Fig. 3, which represent more or less the steady state conditions, are of the order of 0.35 N, with that of the $LiNO_3$-treated paste slightly above this value and that of the untreated paste slightly below.

Some years ago the writer published a compilation of data showing that a linear relationship existed between the steady state pore solution OH^- ion concentration found in sealed mortars made with Portland cements and the equivalent Na_2O contents of the cement used [7]. It was found that for sealed mortars of water:cement ratio 0.50, the OH^- ion concentration levels were approximately 0.7 times the equivalent Na_2O content of the cement. For the present cement this would correspond to an expected OH^- concentration of approximately 0.32 N, in quite satisfactory agreement with the results obtained for the untreated paste, and only slightly less than that found in the $LiNO_3$-treated paste.

Thus it is evident that use of $LiNO_3$ does not entail any substantial increase in the pH of the pore solutions in concrete, and thus does not increase the potential for ASR due to this factor.

3.2. What anion balances the Li^+ cations in $LiNO_3$-treated pore solutions?

Since with $LiNO_3$ treatment the added Li^+ ions are not balanced by OH^- ions, the obvious question arises as to what anion or anions provide this function.

The obvious presumption that the pore solution simply retains the original nitrate as NO_3^- ions balancing the Li^+ turns out to be almost correct. Fig. 4 provides the results of separate analyses for Li^+ ions (by flame emission spectrometry) and NO_3^- ions (by ion chromatography) as a function of time over the first 24 h in the pastes shown in Fig. 3. It is seen that the Li^+ is in fact almost, but not entirely, balanced by NO_3^- ions (i.e., there is a slight excess of Li^+ over NO_3^- at any given age). Part of the difference is made up of the small content of extra OH^- ions as seen in Fig. 3, and the remainder involves a slight excess of SO_4^2 ions over that found in the corresponding untreated paste.

3.3. Sorption of $LiNO_3$ by hydrating cement

As indicated earlier, much of the lithium incorporated into concrete as LiOH, or converted to LiOH in the course of its dissolution in concrete water solution, may subsequently be lost to the pore solution by early incorporation into cement hydration products. This tendency provides an obvious limitation on the effectiveness of such treatments, since presumably to be effective the Li^+ ions must remain in solution until incorporated into ASR gel. The question naturally arises as to the extent to which lithium added as $LiNO_3$ is similarly sorbed by the hydrating cement paste.

Fig. 5 provides data relevant to this point from the experiment described above. The upper curve in Fig. 5 is a plot of

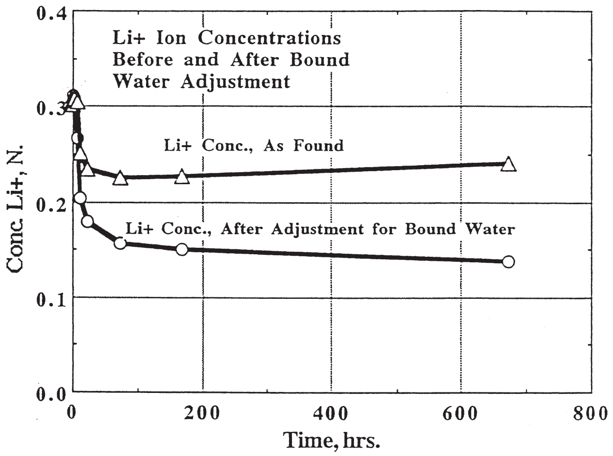

Fig. 5. Measured Li^+ concentrations and Li^+ concentrations adjusted for bound water as functions of time for pastes prepared with mix water containing 0.3 N dissolved $LiNO_3$.

the actual Li^+ concentration found in the expressed pore solution vs. time. The initial Li^+ concentration of 0.3 N reflects the fact that all of the lithium nitrate added is in solution. The measured Li^+ concentration drops to about 0.23 N over the first 12 h and then stabilizes at approximately this level.

During cement hydration, the solution concentration level of Li^+ ions maintained in this sealed system is in a sense artificially supported by the fact that while Li^+ is being sorbed from the water, the water content itself is being progressively reduced by the ongoing cement hydration. This reduction in liquid water content can be monitored by determination of the content of bound water at each stage. The lower curve of Fig. 5 shows the concentration data of the upper curve corrected for this water-binding effect. It thus provides a more appropriate estimate of the mass of Li^+ ions still present in solution within the paste at any stage.

It appears that only about half of the added lithium remains in solution indefinitely and would thus be available to ameliorate the effects of ASR. This is essentially identical to what has been previously found with LiOH and with LiF and Li_2CO_3 addition. The uptake of Li^+ ions by hydrating cement components is thus apparently independent of the balancing anion in the pore solution.

4. Conclusions

1. Lithium incorporated into cement paste in the form of dissolved lithium nitrate remains in solution primarily as lithium nitrate and does not appreciably increase the OH^- ion concentration or pH of the pore solution. This is in contrast to the behavior of lithium added as LiOH or as nearly insoluble lithium salts (LiF and Li_2CO_3), which appear in solution as LiOH. The $LiNO_3$ treatment thus avoids the potential for inducing an extra challenge to the stability of potentially reactive aggregates associated with increased pore solution pH. This is a factor that may be the cause of augmented (rather than reduced) expansions that are observed when inadequate dosages of these forms of lithium treatment are supplied.
2. Lithium incorporated as lithium nitrate is subject to the same tendency of premature removal from solution by the products of cement hydration as are other forms of lithium treatment. As much as half the added lithium is sorbed by newly formed cement hydration products during the period of active hydration. This factor needs to be taken into account in setting practical dosage levels for ASR amelioration.

Acknowledgments

The writer thanks Claudio Manissero and David Stokes of the Lithium Division, FMC Corporation, for authorization to publish these results, which were originally obtained on behalf of that corporation. The pore solution expressions were conducted by Daniel Constantiner and the chemical analyses were carried out by Janet Lovell. Thanks are also due to Shaode Ong for his many contributions toward the understanding of lithium effects in concrete.

References

[1] Y.M. Sakaguchi, M. Takamura, A. Kitagawa, T. Hori, F. Tomosawa, M. Abe, Proc. 8th Intl. Conf on Alkali Aggregate Reactions, Kyoto, Japan, 1989, p. 229.

[2] D. Stark, B. Morgan, P. Okamoto, S. Diamond, SHRP C-343, Eliminating or minimizing alkali-silica reactivity, Strategic Highway Research program, National Research Council, Washington, D.C., 1993.

[3] W.J. McCoy, A.G. Caldwell, J Amer Concr Inst Proc 22 (9) (1951) 693.

[4] S. Ong, Study of effects of LiOH, NaOH, and KOH on alkali silica reaction, M.S.C.E. thesis, School of Civil Engineering, Purdue University, 1990.

[5] S. Ong, Studies on effects of stream curing and alkali hydroxide additions on pore solution chemistry, microstructure, and alkali silica reactions, Ph.D. thesis, School of Civil Engineering, Purdue University, 1993.

[6] R.S. Barneyback, Jr., S. Diamond, Cem Concr Res 11 (1981) 279.

[7] S. Diamond, Proc. 8th Intl. Conf on Alkali Aggregate Reactions, Kyoto, Japan, 1989, p. 149.