

## DEVELOPMENT OF A LITHIUM-BASED MATERIAL FOR DECREASING ASR-INDUCED EXPANSION IN HARDENED CONCRETE

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### ABSTRACT

This paper discusses work performed in the development of an aqueous lithium-based solution for use on hardened concrete to minimize ongoing alkali-silica induced expansions. The material is based on lithium nitrate and includes a proprietary blend of surfactants for aiding in penetration of hardened concrete. Penetration tests are described showing its advantages over other lithium-based solutions. For example, a lithium nitrate solution penetrated twice as well as a lithium hydroxide solution, and a lithium nitrate solution with the proper choice of surfactants penetrated 50% better than the lithium nitrate solution alone, and three times as well as the lithium hydroxide solution. Mortar bar testing with high alkali cement and a highly reactive rhyolite with the lithium nitrate and surfactants shows twice the reduction in post-treatment expansion over treatments with lithium hydroxide solutions when the same amount of lithium is used in both. Soaking bars with the solution has shown better than 75% reduction in post treatment expansion compared to control. Finally, reduction in alkali-silica induced expansion following treatment on concrete prisms made with high alkali cement and the same reactive aggregate is shown and discussed. In both the mortar bars and the concrete prisms, the level of expansion (and hence, the cracking) influenced the effectiveness of the treatments.

Keywords: Alkali-silica reaction, lithium, lithium hydroxide, lithium nitrate

## INTRODUCTION

While many options are available to a concrete supplier to control expansions from alkali-silica reaction (ASR) in the selection of materials, options for controlling the expansions after the condition is discovered in hardened concrete are severely limited. Three things are necessary for ASR expansions to occur:

- A reactive form of silica in the aggregate
- Sufficient alkali in the system
- Sufficient moisture

Once the concrete has hardened, nothing can be done to change the first two conditions, and the third is usually also difficult, if not practically impossible, to change in the majority of outdoor exposures. In cases of limited cross section and appropriate geometry, materials that prevent the ingress of liquids can be used to good effect. Not only will they minimize moisture in the outer layer to which they are applied, they will minimize any wetting and drying cycles that can exacerbate the reaction.

Another approach is to attempt to chemically inhibit ongoing expansion. Various lithium salts have been shown by many researchers to be extremely effective in inhibiting ASR-induced expansions in concrete and mortar, even after the reaction has begun in hardened laboratory specimens (Blackwell et al. 1997, Lumley 1997, Sakaguchi et al. 1989, Stark et al. 1993). Unfortunately, one of portland cement concrete's most important fundamental properties is its relative impermeability to fluids. And there is no fluid that can readily pass through thick layers of concrete in a time frame suitable to be of any utility in the lifetime of the structure.

However, one of the effects of ASR-induced distress in concrete which compromises the permeability of the material, namely cracking, can also allow for ingress of materials that may be used to minimize the continued expansion. If the continued expansion caused by a continuation of the reaction can be minimized, then any other repairs necessary to the concrete should benefit in longevity. Solutions of lithium hydroxide have been suggested as a possibility for this task, as well as others (Stark et al. 1993). One of the drawbacks to lithium hydroxide solutions however is their caustic nature.

Another important area of concrete rehabilitation where ASR and lithium-based materials is concerned involves the use of repair materials that develop basic (high pH) pore solutions when they are used in direct contact with ASR-affected concrete. The introduction of alkalis at the interface of the repair can exacerbate the reaction and lead to early failure. In an application such as this, it should be expected that lithium-based materials should be very effective in preventing this aggravation at the interface.

This paper describes the development of a lithium-based solution that is safe to handle, and penetrates better than any other lithium-based solution in the literature at the time of this writing. First, tests are described showing comparisons among a variety of lithium solutions. Secondly, tests are described showing the efficacy of the application of that

solution in reducing ASR-induced expansions in mortar bars. Finally, work done with concrete prisms gives the same indications of efficacy. One of the points also discussed is the importance of the cracking caused by the expansion in the performance of this type of material. The more extensive and interconnected the cracking is, the better are the avenues for penetration by solutions to chemically inhibit the reaction. At the same time, the greater the cracking, then obviously the degree of compromise to the structure is greater. Non-reactive rubble does not have a particularly high intrinsic economic value, and so there is likely an optimum time frame to consider the use of a material to chemically inhibit ongoing ASR-induced expansion. However, if its worth repairing, and expansion from an ongoing ASR reaction is occurring, then treatment with this type of material should be considered.

### PENETRATION TESTS

ASTM C109 mortar made with a non-reactive quartz sand were cast into 150mm by 300mm cylinders, with a 75mm by 25mm plug inserted at the top. The cylinders were kept moist cured for 28 days, and the plugs were removed. Plastic nipples were epoxied to the top of the cavities, and flexible plastic hose was attached to the nipples for loading with various solutions of lithium salts. Besides varying the types of lithium salts used, different concentrations of solutions were used, and various surfactants were also used in combination with these solutions. The volume of liquid entering the cylinders was recorded over time for a minimum of 16 hours for all tests. An selected highlight of the results are shown in Fig. 1.

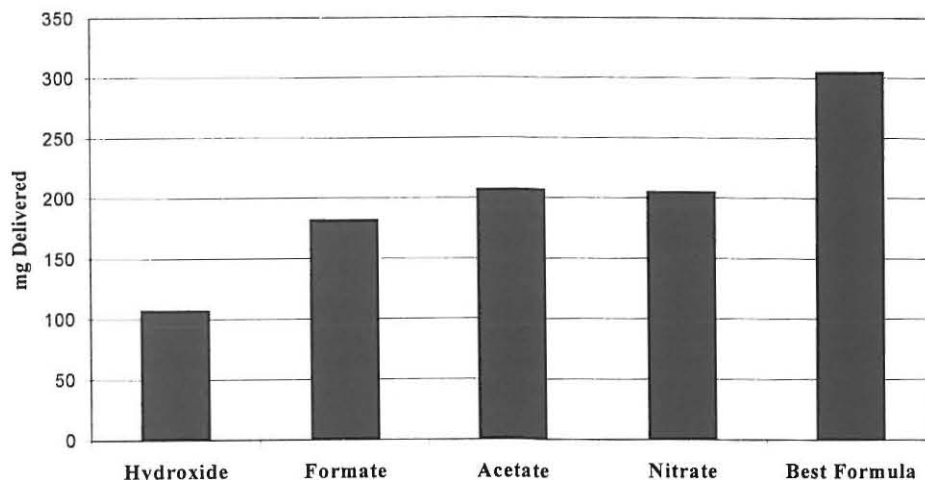


Fig. 1: Relative penetrating abilities of various aqueous Li salt solutions. The anion is listed on the lower axis. "Best formula" is 30% lithium nitrate with proprietary blend of surfactants.

Fig. 1 shows the mg of lithium "delivered" in the penetration tests. This was calculated from the concentration of the volume that entered the cylinder through the plastic hose.

After testing the various solutions as mentioned above, the question remained as to whether the lithium ion itself had penetrated the mortar, or was it left behind near the interior surface as the solvent continued into the matrix. To answer the question, a specimen representing the solution called "best formula" above was drained after 16 hours of this test, and sliced vertically in the middle. Then small powder samples were collected in a grid pattern radiating from the cavity where the solution was introduced. A contour map showing the results of this analysis are shown in Fig. 2.

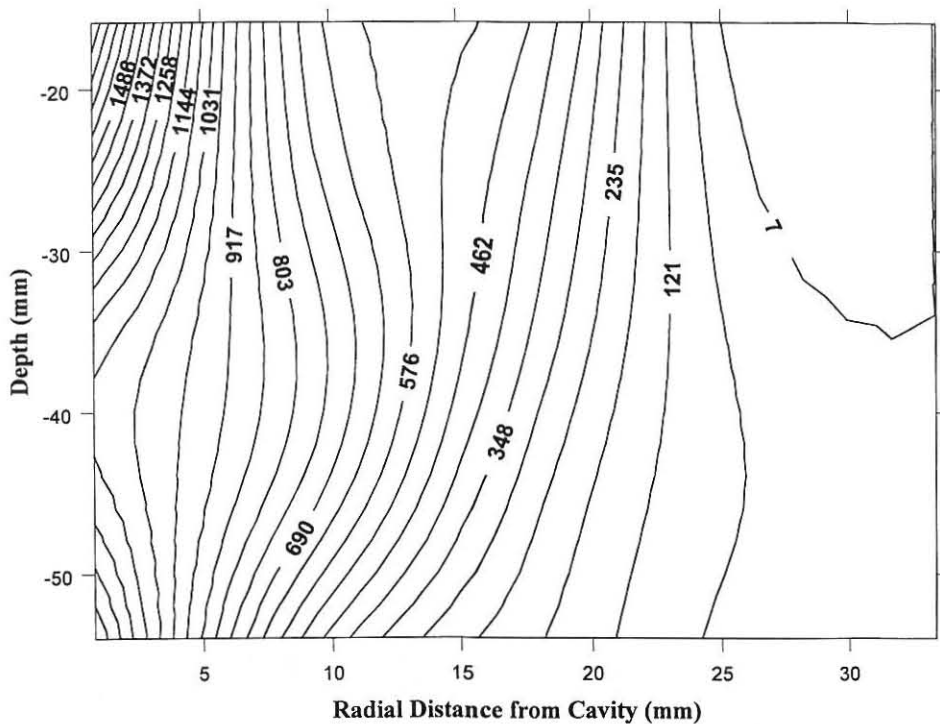


Fig. 2: Contour map showing penetration of lithium ion (in ppm) radially outward from the cavity where the solution was introduced.

To help visualize the data shown in Fig. 2, the left axis can be viewed as the wall of the cavity through which the solution was introduced into the cylinder. This analysis showed that after 16 hours of exposure to the solution, the lithium ion concentration had exceeded 100 ppm beyond 20mm (nearly 25mm) from the surface. This was, again, in uncracked, non-reactive mortar, that had been maintained in a moist condition up to and through the

testing period. A level of 100 ppm lithium is the right order of magnitude to significantly repress ASR expansion in normal concrete mixes (discussed below).

### TESTING THE SOLUTION ON ASR-AFFECTED MORTAR BARS

ASTM C227 mortar bars were cast using a high alkali (1% sodium equivalent) cement and a highly-reactive rhyolite from the southwestern U.S. This aggregate typically gives expansions in ASTM C1260 in excess of 0.7 to 0.8% at 14 days. It is known to be reactive even with low alkali (less than 0.6% sodium equivalent) cements in actual usage.

Two types of application of the lithium solution were made to the mortar bars. On some, the solution was applied to one side only of the mortar bar. Others were placed entirely in the solution for one day. The bars were returned to ASTM C227 storage conditions for many months to compare the expansions after treatment with controls untreated. Also, treatments were done at different expansion levels to evaluate that factor as well. Fig 3 shows results of this testing.

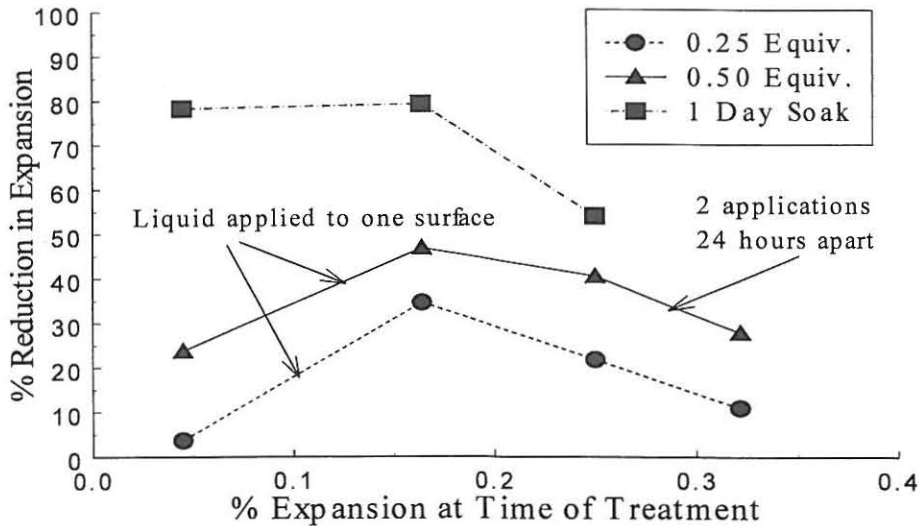


Fig.3: %Reduction in expansion for mortar bars after various treatments. 0.25 and 0.50 equiv refer to standard admixture doses. That is, 0.50 equiv means one half of the amount of this lithium solution that would have been needed to control the reaction as an admixture was applied to the surface of the bar. These results are from 3 to 4 months after treatment.

In Fig.3 it is shown that soaking is of course the most effective means of reducing the expansion, but this may not always be a possible situation in the field. Also note that the timing of the application in relation to its subsequent effectiveness is a strong variable affecting the performance of this type of treatment. For the "one side only" treatment, early on there is not enough cracking of the specimen for effective penetration; much later most of the expansion has happened and again there is less effectiveness. While these expansion levels do not generally have an exact correspondence to field situations, it strongly highlights the importance of the proper timing during the life cycle of the distress for this type of treatment. In Fig.4 the comparison between the "best formula" shown above and an equivalent amount of lithium when used in the form of lithium hydroxide is shown.

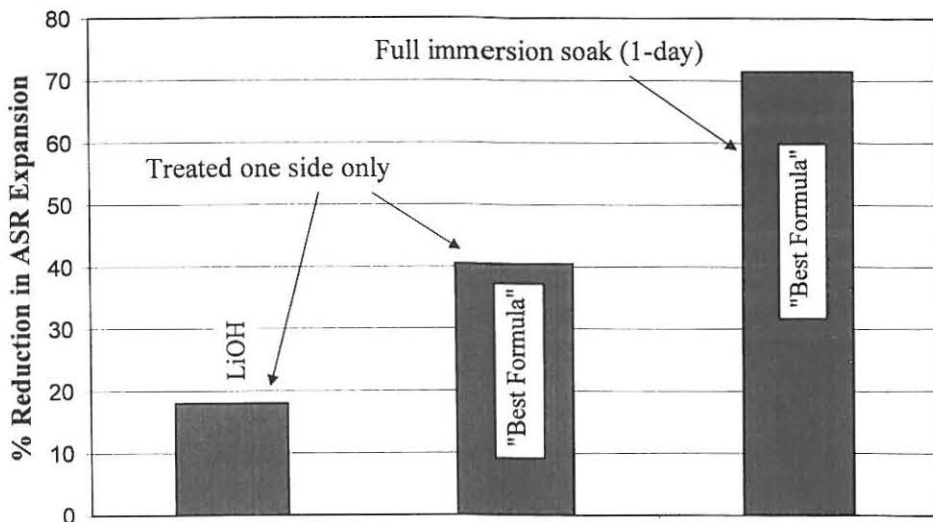


Fig. 4: Reduction in expansion compared to controls after treatment.

Fig. 4 represents the average of treatments that occurred over different times, and is based on the results after 9 to 10 months since the treatment. Fig. 3 had shown the post-treatment expansions at different expansion times, as opposed to the averages over all times, as shown in Fig. 4. After nine months, the reduction in expansion was slightly greater than at 3 months, suggesting a long-term reduction in expansion from this treatment.

#### TESTING THE SOLUTION ON ASR-AFFECTED CONCRETE PRISMS

Eighteen ASTM C1293 concrete prisms were cast using a high-alkali (1% sodium equivalent) cement and the same highly-reactive rhyolite from the southwestern U.S. used in the mortar bar work described above. They were stored as per C1293 and 2 prisms were

used as a control. When the average expansion had reached 0.061% at 10 weeks, 8 prisms were removed and treated with water or the "best formula" in the following way. Two prisms each were subjected to each treatment. The prisms were air dried for 3 days, and then soaked in either water or the "best formula" for 1 day. Then for 2 of the sets, this cycle was repeated 5 times, whereas the first 2 sets only received one cycle. At 16 weeks, when the average of the control prisms had reached 0.107% expansion, this same treatment sequence was repeated on 8 remaining untreated prisms. The prisms were all returned to the C1293 storage conditions at the conclusion of their treatment. Fig. 5 shows the resulting expansions after the treatments.

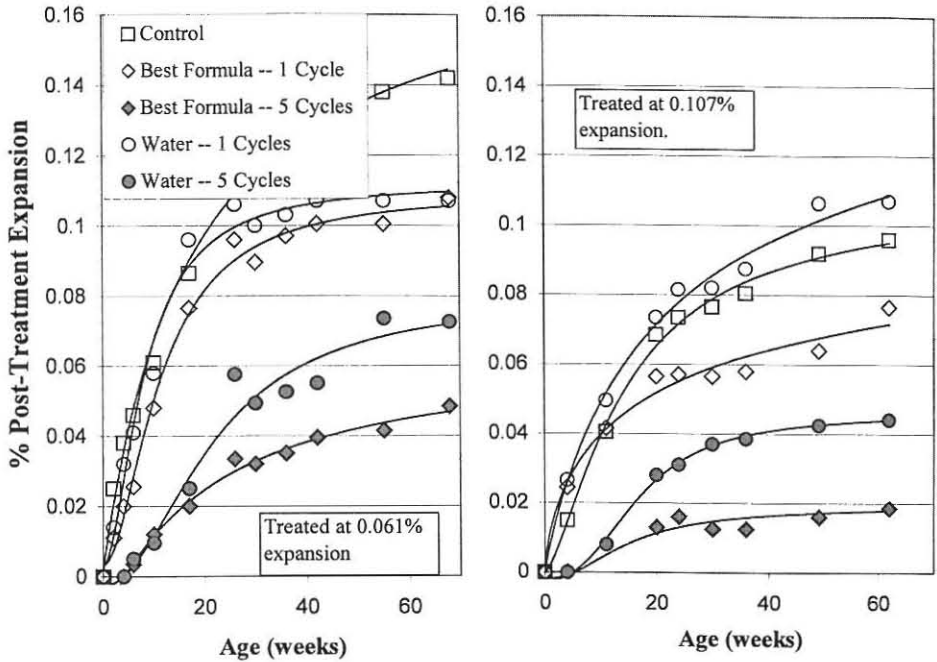


Fig. 5: The expansion of the concrete prisms after treatment is shown. The graph on the left shows the results for prisms treated at an expansion level of 0.061% and the other graph shows the results after treating the prisms at 0.107% expansion.

It is clear from Fig. 4 that repeated treatments of the lithium material is significantly more effective than the single treatment, and that the lithium treatment shows less post-treatment expansion than the water treatment. It seems likely that the water treatment has reduced expansion by leaching alkali from the prisms. Furthermore, the treatments at the 0.107% expansion level were more effective than the treatments at the 0.061% expansion level. This is consistent with the mortar bar results and is presumably related to the greater permeability of the higher expansion level.

## **DISCUSSION ON THE AMOUNT OF Li NEEDED FOR HARDENED CONCRETE TO SIGNIFICANTLY IMPACT THE EXPANSION FROM ASR**

While work has been done to estimate the amount of lithium needed to control expansions from ASR when the lithium is used as an admixture (Blackwell et al. 1997, Lumley 1997, Sakaguchi et al. 1989, Stark et al. 1993), it is very difficult to assess the amount needed to significantly impact ongoing expansions in concrete. It is reasonable to suppose that if the lithium could be placed only where it was needed, in the reaction site itself, much less would be needed than is shown when the material is used as an admixture. This is so because the lithium, at least early on, is more or less uniformly distributed throughout the concrete matrix in a similar way with the cement paste. Also, much of the lithium is presumably bound to the cement paste after the first day of hydration (Stark et al. 1993), as much as perhaps 50% when the lithium is supplied as a soluble salt.

So while we do not have methods of delivering the lithium exactly where it could best be utilized in the matrix, we can still use the fact that significant amounts of the lithium are presumably not available for helping with the reaction, when it is used as an admixture, to estimate an upper limit on the amount needed. This assumes that the same binding capacity of the calcium silica hydrate for the lithium is different when the lithium is introduced into the hardened concrete matrix long after the bulk of the cement has hydrated. This then would mean that perhaps only 50% of the demonstrated admixture level would be an upper limit for estimation purposes.

As an example of how we could calculate the amount of lithium ion necessary for remediation, if we take the Li:Na molar ratio from one of the references above (Blackwell et al. 1997) (they are all similar) of 0.74, and a hypothetical concrete made with 375 kg of cement per cubic meter with a sodium equivalent of 0.8%, this gives a total alkali loading of 3 kg/m<sup>3</sup>. Then we can calculate that we have approximately 96.8 moles of sodium in 3 kg of Na<sub>2</sub>O. Multiplying by the ratio of 0.74 gives 71.6 moles of lithium needed, and taking 50% of that yields 35.8 moles of lithium. This is approximately 0.25 kg of lithium. If we assume a cubic meter of this concrete weighs 2400 kg, this can be converted to mg/kg of concrete (mg/kg is ppm) which gives 104 ppm of lithium in the cubic meter of concrete just described as a hypothetical amount necessary to control ASR expansion, if the lithium could be supplied after the bulk of the cement hydration had occurred.

This type of calculation explains the statement above in the paper that 100 ppm lithium is the right order of magnitude for controlling expansions from ASR if the lithium can be introduced into the matrix after significant hydration has taken place.



## CONCLUSIONS

- The use of a proper selection of surfactants in concert with the lithium solution aids in the ability of the solution to penetrate the affected concrete or mortar.
- The level of expansion that exists at the time of treatment affects the ability of the solution to mitigate future expansions, presumably because of increased permeability of the affected specimen.
- The lithium nitrate formulation with surfactants is superior to lithium hydroxide solutions in both penetrating ability and reduction in post-treatment expansions.
- Unlike the use of lithium hydroxide solutions, the lithium nitrate formulation is non-hazardous to handle.

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