Other

Preventive Measures

For

Alkali-Aggregate Reaction

USE OF LITHIUM TO COMBAT ALKALI SILICA REACTIVITY

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ABSTRACT

Various lithium compounds have been investigated over the years for their effectiveness in mitigating alkali silica reactivity. Although lithium has been shown to be effective by many researchers, only recently has it been marketed on a commercial basis. Difficulties with accelerated testing are discussed. Finally, some promising field trials that were begun under the National Research Council's Strategic Highway Research Program are discussed.

Keywords: Accelerated testing, admixtures, alkali-silica reaction, concrete, lithium, reactive aggregates.

A brief overview of lithium research

Within approximately ten years of Stanton's original description of alkali-silica reactivity in concrete (Stanton. 1940), McCoy and Caldwell demonstrated the effectiveness of some simple lithium salts to mitigate the reaction in mortars containing high alkali cement and Pyrex glass as the aggregate (McCoy & Caldwell. 1951). This was the first reference to the ability of the lithium ion to mitigate the reaction. These results basically stayed in an anecdotal state until about the nineteen eighties, when research efforts again began to be directed to these materials.

Among the notable efforts were the work of Y. Sakaguchi, et al. (Sakaguchi *et al.* 1989), S. Ong, while at Purdue University in Indiana under S. Diamond (Ong. 1993), H. Wang, et al. (Wang *et al.* 1994), and D. Stark's efforts under the Strategic Highway Research Program (Stark *et al.* 1993).

In Y. Sakaguchi's work, lithium nitrite, lithium carbonate, and lithium hydroxide monohydrate were all used to effectively arrest the expansion of mortars made with a blend of Pyrex glass and sand. Sodium hydroxide was added to adjust the sodium equivalent to relatively high values (0.8% to 1.0%). Y. Sakaguchi used varying dosages of the salts and found that molar ratios of Li : Na of about 0.6 to 0.7 was generally effective (Sakaguchi *et al.* 1989).

Data was presented with different dosages of lithium hydroxide monohydrate in mortars that were made with a naturally occurring reactive aggregate. In those results, the ratio was somewhere between 0.6 and 0.9, but sufficient mixes were not presented to allow further refinement of the dosage level (Sakaguchi *et al.* 1989).

Another important piece of Y. Sakaguchi's work had important implications in the area of concrete rehabilitation for concrete subject to alkali-silica reaction. Concrete prisms made with reactive materials were allowed to expand and were then soaked in a lithium nitrite solution. The result was a significant drop in the expansion of the prisms relative to the control (Sakaguchi *et al.* 1989).

Among the conclusions was the concept that the reason that lithium was effective in suppressing the alkali silica reaction was because it forms an insoluble product, namely, lithium silicate (Sakaguchi *et al.* 1989). Although it is in the same chemical family as sodium and potassium, which cause the problem, lithium silicates are far less soluble and do not absorb water, and so the conclusion is reasonable and has been reached by other workers in the field.

S. Ong's work included pore solution analysis with both pastes and mortars, and mortar bar expansions. The mortars were made with either a non-reactive limestone, or the limestone with 4.5% Beltane opal, or the limestone with 30% cristabolite. The alkali content of the mortars was increased by adding sodium hydroxide and potassium hydroxide in equal amounts, each equal to 0.5% sodium equivalent of the cement (Ong. 1993).

One of the important conclusions from S. Ong's work is that adding lithium carbonate or lithium fluoride has a very similar effect on the pore solution as adding lithium hydroxide monohydrate (Ong. 1993). Specifically, the changes in the all of the ions except for the fluoride and carbonate are about the same. Basically, the fluoride and carbonate ions never show up in solution to any degree compared with the actual dose (Ong. 1993).

Another vital piece of information from S. Ong's work is that a certain threshold of lithium is needed to control the expansion. Below this threshold, the expansion can actually increase, at least for the salts that were tested (Ong. 1993).

H. Wang showed, among other things, that a chemical admixture based on lithium could effectively control alkali-silica reaction (Wang *et al.* 1994). It was shown that a lithium-based admixture could be formulated that met the requirements of ASTM C-494 as a type A admixture. Its effectiveness in controlling alkali-silica reaction was demonstrated both in the CSA A23.2-14A concrete prism test and in ASTM C-441 testing with Pyrex glass (Wang *et al.* 1994).

D. Stark, et al., made a significant contribution in the National Research Council's Strategic Highway Research Program (Stark *et al.* 1993). S. Ong's conclusion about the equivalence of lithium carbonate, lithium fluoride, and lithium hydroxide monohydrate's effects on the pore solutions was reiterated in the work, as was the concept that too small an amount of those salts would be detrimental.

Besides showing the effectiveness of lithium with ASTM C-227, D. Stark used a modified version of ASTM C-1260 to arrive at very similar ratios of Li: Na (on a molar basis) to those shown in Y. Sakaguchi's work. Namely, for hydroxide ion concentrations up to 1 molar, a Li : Na ratio of 0.67 would handle the most reactive aggregate in the suite of 12 aggregates used in the program (Stark *et al.* 1993). This is equivalent to using a cement with a sodium equivalent of 1.4%, assuming a water to cement ratio of 0.5. For hydroxide ion concentrations of 2 molar and above, Li : Na ratios of 1 could be necessary.

Difficulties with ASTM C-1260 and lithium

ASTM C-1260 evolved from R.E. Oberholster and G. Davies' method (Oberholster & Davies. 1986) as a method to evaluate the potential reactivity of aggregates. It fills a great need of specifying agencies everywhere to make an assessment of an aggregate in a reasonable period of time.

Its use has sometimes been extended to assessing the capability of various substances to mitigate alkali-silica reactivity. The way in which this is generally done is to dose the mortar bars at whatever rate is proposed to be used in the concrete mix to be evaluated, as a function of the cement. For example, if one wished to evaluate the effectiveness of a 35% loading of ground granulated blast furnace slag, then you simply substitute 35% of the cement to be used in the mortar bar with the ground granulated blast furnace slag and otherwise perform the test as normal.

This is also a proposal of D. Stark's, made in the Strategic Highway Research Program. However, D. Stark recognized two important facts about using lithium in ASTM C-1260. First is the all important Li : Na ratio discussed earlier. The second is the fact that lithium will leach out of the bar into the soak solution during the test. What was done in the Strategic Highway Research Program to get around these difficulties was to add the lithium to the soak solution in the appropriate ratios. It should be remembered that the doses predicted by this methodology have been verified by independent methodology, e.g., ASTM C-227.

In order to illustrate this difficulty, and to assess the magnitude of the errors made by not following this modification (if one wishes to see the effect of lithium in the ASTM C-1260 test), the Federal Highway Administration is sponsoring a round robin of tests where lithium is in one case placed in the bar at the "recommended" dose and compared with the other case of having the lithium in the soaking solution at the right concentration.

Also of interest in the round robin testing will be mixes that include combinations of lithium and fly ash (both C and F ashes were used). It was shown in the Strategic Highway Research Program that such combinations worked even better than either one alone, particularly if the material being tested is subject to deicer salts (Stark *et al.* 1993).

Field tests of lithium to combat alkali-silica reaction

In the Strategic Highway Research Program, a field test was devised to evaluate lithium hydroxide monohydrate in some pavement sections in Albuquerque, NM (Stark *et al.* 1993). Two very reactive aggregates were used, and various combinations of lithium or fly ashes were used. The cement was a low alkali cement, with a sodium equivalent of about 0.55%. After two years, the site was visited and some sampling and testing was done on part of the site. Results of static modulus of elasticity testing are given in Figure 1. The site has now been added to the Long Term Pavement Performance program being administered by the Federal Highway Administration, and will be followed up for at least five years.

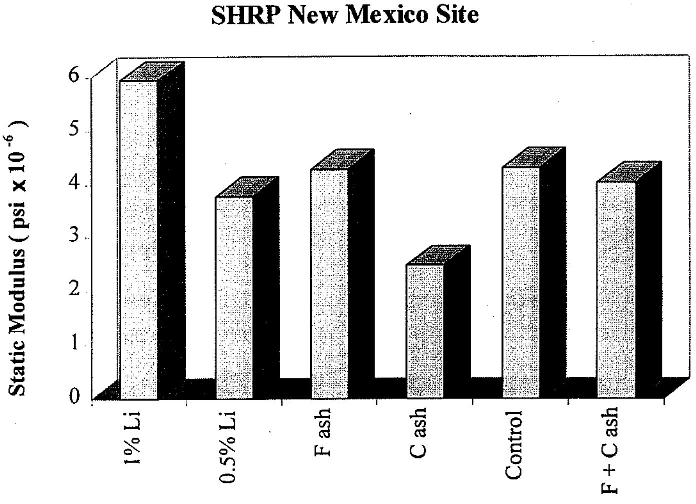

Fig. 1 New Mexico field test

So far, the control section (reactive aggregate and low alkali cement) and the section with the Class C fly ash are showing signs of cracking, while the other sections generally look normal. The modulus values seem to reflect the general condition of the pavement, but since these are the first values taken, the real test will be in seeing how the values change in time.

Meanwhile, another Strategic Highway Research Program that dealt with the electrochemical removal of chloride from concrete structures found a need for lithium, and field trials are currently underway (Bennett & Schue. 1993). Basically, the process involves setting up an electrochemical cell, using the reinforcing steel as the cathode, and immersing an anode in an electrolyte at the surface. A potential of 50 to 60 volts is applied over about 4 to 6 weeks, and chloride ions are removed from the vicinity of the reinforcing steel. As a consequence, the hydroxide ion concentration increases in the vicinity of the steel (Bennett & Schue. 1993). This is good for the steel, but bad for any aggregate with a potential for alkali-silica reactivity. If, therefore, the concrete has the potential for reactivity, then using lithium in the electrolyte will prevent any worsening or development of the expansion from the reaction.

In a trial underway in Virginia, sponsored by the Federal Highway Administration, two spans of a bridge deck were treated. Enough lithium was contained in the electrolyte to treat half the thickness of the deck. The reason for this amount was as follows: since the deck is about 200mm thick, and the depth of cover was about 50mm (one quarter of the thickness, also the depth to which the lines of electromotive force would reach, since that is the first layer of steel), it was considered reasonable to put in somewhat more than the minimum, but unrealistic to try to get enough in to treat the entire thickness.

To date, the electrolyte has been analyzed, and 95% of the dose of lithium has been removed from the solution (see Figure 2). Cores have been taken, and will be analyzed in the near future for a profile of the depth of penetration of the lithium. Besides removal of chloride then, this appears to be a very promising method for driving lithium into structures with reinforcing steel.

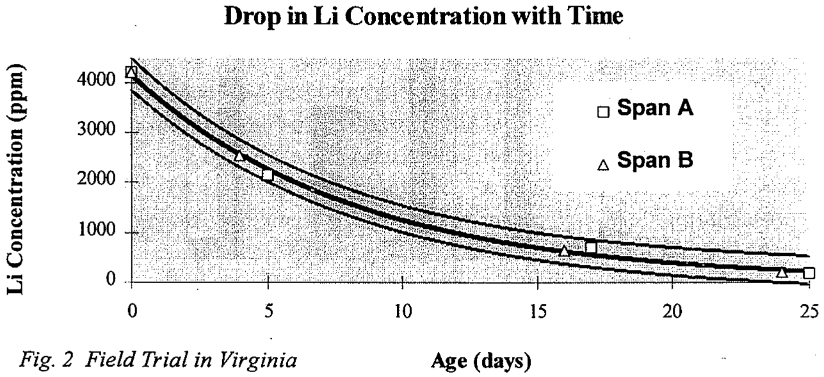

Fig. 2 Field Trial in Virginia

Some similar projects have been done in the United Kingdom and Canada, but the details were unavailable to this author at this time. In addition, another electrochemical trial is underway presently in South Dakota, but no results are yet available.

Conclusions

- There exists a large amount of convincing evidence that lithium mitigates alkali-silica reactivity in portland cement concrete.
- A field trial in New Mexico has demonstrated the feasibility of using lithium in actual installations.
- The electrochemical trial in Virginia shows that it is feasible to drive lithium into structures to remediate alkali-silica reactivity.

References

Bennett, J. and T. Schue. 1993. *Chloride removal and implementation guide*, Washington, D.C.: National Research Council, Strategic Highway Research Program, SHRP-C-347.

McCoy, W.J. and A.G. Caldwell. 1951. 'New approach to inhibiting alkali-aggregate expansion', *Journal of the American Concrete Institute*. Vol. 22: 693-706.

Oberholster, R.E. and G. Davies. 1986. 'An accelerated method for testing the potential alkali reactivity of siliceous aggregates', *Cement and Concrete Research*. Vol. 16: 181-186.

Ong, S. *Studies on effects of steam curing and alkali hydroxide additions on pore solution chemistry, microstructure, and alkali silica reactions*, PhD Thesis, Purdue University, 1993.

Sakaguchi, Y., M. Takamura, A. Kitagawa, T. Hori, F. Tomosawa, and M. Abe. 1989. 'The inhibiting effect of lithium compounds on alkali-silica reaction', *Proceedings, 8th international conference, alkali aggregate reaction.* Kyoto, Japan: 229-234.

Stanton, T.E. 1940. 'Expansion of concrete through reaction between cement and aggregate', *Proceedings of the American Society of Civil Engineers.* 66: 1781-1811.

Stark, D., B. Morgan, P. Okamoto, and S. Diamond. 1993. *Eliminating or minimizing alkali-silica reactivity*, Washington, D.C.: National Research Council, Strategic Highway Research Program, SHRP-C-343.

Wang, H., S. Tysl, and J.E. Gillot. 1994. 'Practical implications of lithium-based chemicals and admixtures in controlling alkali-aggregate reactions', *Proceedings, 4th international conference on superplasticizers and other chemical admixtures in concrete*. Montreal, Canada: 353-366.