

USE OF AN APPLIED ELECTRIC FIELD TO DRIVE LITHIUM IONS INTO ALKALI-SILICA REACTIVE STRUCTURES

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ABSTRACT

One of the most daunting issues related to alkali-silica reactivity, is determining what can be done to maintain hardened structures that are suffering from the deleterious effects. Some of the earliest research demonstrated that lithium could slow, or halt altogether, the expansion of the ASR gel. Experimentation and field installation have proven that an applied electric field can be utilized to migrate lithium ions into a concrete structure.

Keywords: Alkali-Silica Reactivity, Rehabilitation, Electrochemical, Lithium, Ion Migration

INTRODUCTION

Many methods have been explored over the years to halt the damaging effects of alkali-silica reactions. While much knowledge has been gained in recent years towards understanding the reaction mechanisms, one of the greatest problems remains largely unsolved. More precisely, that problem concerns the rehabilitation or repair of the many structures that are already suffering from the effects of alkali-silica reactivity.

During planning and construction of new structures, a number of strategies have been developed to avoid, or at least minimize the risk of developing ASR. Some of these methods may be simple enough to employ during new construction, but are impossible or impractical to implement on existing structures. There are a great number of structures in North America experiencing the damaging expansive forces that result from ASR. For some of these structures the expansion and cracking will not present immediate consequences, but it will lead to a long-term problem, with long-term repair concerns. The monetary value of these structures is immense, and it is therefore worthwhile to evaluate possible methods of preserving these structures. Many of the affected structures are quite old and therefore heritage structures, making replacement or repair an even more delicate issue.

Application of chemicals containing lithium has demonstrated an ability to mitigate the expansive nature of the ASR gel. It is relatively simple to incorporate lithium into a fresh concrete mix, however application to a hardened structure is more difficult. A variety of lithium bearing solutions are available on the commercial market, and these solutions have been used as a topical treatment on affected concrete. These solutions work by penetrating into the pores and cracks of exposed concrete surfaces, and can be effective for structures with a large surface to volume ratio. However, because the ASR reactants generally occur throughout the volume of an affected structure, for many massive structural members a topical treatment may not be effective enough.

A technology currently being used in industry for another purpose, namely removal of chloride ions from concrete structures has been adapted for the purpose of treating ASR. By using an applied electric field, lithium ions (which carry a positive charge) can be migrated into a concrete structure. This new approach for treatment of structures suffering from ASR shall be discussed further in this paper. Additionally, information and discussion will follow regarding three such projects.

FIELD TREATMENT

Using Lithium to Mitigate Abnormal Expansion

Early in the 1950's the first research was released demonstrating the beneficial effects of using lithium salts to slow or halt the expansion due to Alkali-Silica Reactions. Researchers have proven that the lithium ion specifically is the beneficial component in this relationship. In recent years a variety of lithium bearing solutions have come onto the market for the express purpose of combating ASR. In situations where Alkali-Silica Reactive aggregate is a concern, lithium admixtures can be used during construction to neutralize the risk of deleterious expansion.

By using lithium in conjunction with other preventative measures during construction, the risk of suffering the damaging effects of ASR can be minimized. ASR is however a complicated problem in existing hardened structures, requiring a unique effort. Laboratory studies had shown early on that lithium could be successfully utilized to treat ASR in mortar bars and test slabs. The majority of this testing involved either ponding a solution containing lithium on the surface of the test piece, or immersing the test piece in such a solution. While this supplies valuable data for research purposes, it does not necessarily yield practical methods for application to full-scale field projects.

Much of the fieldwork has involved spray application of lithium bearing solutions onto the affected structure (i.e. pavements, etc). In these cases, the primary routes of entry for the lithium are through cracks, and the pore structure within the concrete. This form of treatment is able to impregnate the concrete with lithium, which in turn will slow the damage caused by ASR. Its effectiveness however, will be limited to the extent that the lithium can penetrate into the concrete member. Permeability and access of the lithium into the concrete varies from structure to structure. Factors such as the number and depth of cracks, as well as concrete porosity will determine how quickly the lithium penetrates, and to what depth it will reach.

Electrochemical Lithium Impregnation

In order to shorten treatment time, and increase the amount of lithium impregnation, new treatment methods have been studied by the Vector Construction Group, with assistance from the FMC Corporation. By adapting a previously available technology called Electrochemical Chloride Extraction, a method was devised to electrochemically drive lithium ions into the concrete.

Electrochemical Chloride Extraction (ECE) is a process specifically developed to rehabilitate salt (chloride) contaminated concrete structures. It is a temporary treatment process that involves the application of a low voltage DC electric potential to migrate chloride out of a concrete structure. By making a few modifications to this system, it can be used to impel lithium ions into a structure, rather than removing chloride ions.

Installation of this type of system requires several key components:

- 1) Anode
- 2) Cathode
- 3) Power source
- 4) Source of lithium ions

The anode of choice is typically a metallic mesh composed of specially coated titanium. This material is basically inert, and is the same type of mesh used in many cathodic protection and chloride extraction projects. Because the mesh is inert, it will not be consumed during treatment in the same manner that a steel anode would.

As in all electrochemical processes, a cathode of some form must be paired with the anode. For a lithium treatment, the network of reinforcing steel inside the structure normally plays the role of cathode. Prior to installation of such a system it is therefore imperative to check the electrical continuity of the reinforcement to determine if any areas are isolated electrically from the rest of the structure. In most cases, the grid nature of the rebar mat ensures more than adequate continuity throughout the structure. If a problem is located, continuity can be restored with a few simple connections.

The electricity for a treatment such as this comes from an AC/DC rectifier. These rectifiers can draw power from a local grid, or in remote locations from a generator. They convert high voltage AC power to the low voltage DC output required for treatment. Since this type of system operates at no more than 40 volts DC, it is considered low voltage, and is safe for utilization in public areas. Each rectifier is capable of treating up to approximately 100 m² (1000 ft²) of concrete surface area. Therefore the size of the treatment area will determine the number of rectifiers required.

A number of different lithium compounds are available on the commercial market. For ASR treatment, lithium in an aqueous form is the easiest to use. For this purpose the FMC Corporation has manufactured a couple of different solutions; Lifetime N which is a solution of lithium nitrite, and Renew ECE which is a lithium borate/lithium hydroxide mixture. Both are aqueous solutions, however they do have a few differences. The Lifetime mixture contains a higher concentration of lithium and has a neutral pH, whereas the Renew ECE is somewhat less concentrated but highly alkaline. Regardless of which solution is used, the function will be the same. Each solution will act as a reservoir of lithium ions, and shall function as the electrolyte for the system, providing electrical continuity between the anode mesh and the concrete surface.

Once electrical continuity of the reinforcing steel is verified, the components of the system can be laid on the structure. The negative terminal of the DC power source is first connected to the reinforcing steel via several points around the treatment area. Next a geo-textile felt or similar material is laid against the surface of the structure. The felt acts as a spacer between the anode mesh and the concrete surface. A titanium mesh anode is laid down in pieces of pre-determined size (normally about 10-25 m²) on top of the felt. Each individual piece of titanium must be electrically wired into a junction box, which is in turn connected to the positive terminal on the rectifier. A final layer of geo-textile is

then placed on top to cover the anode. The final steps of installation include addition of the lithium electrolyte, and covering with plastic sheeting to minimize evaporation.

Once energized, the rectifier sets up a low voltage DC potential between the anode and the cathode. In essence, a low voltage electric field has been created between the titanium mesh and the reinforcing steel. A lithium ion carries a net positive charge, and can therefore be moved under the influence of such an electric field. During treatment, the positively charged lithium ion is repelled away from the anode mesh, and simultaneously attracted toward the reinforcing steel. These forces cause the lithium ion to migrate into the concrete through the pore structure and cracks (Figure 1).

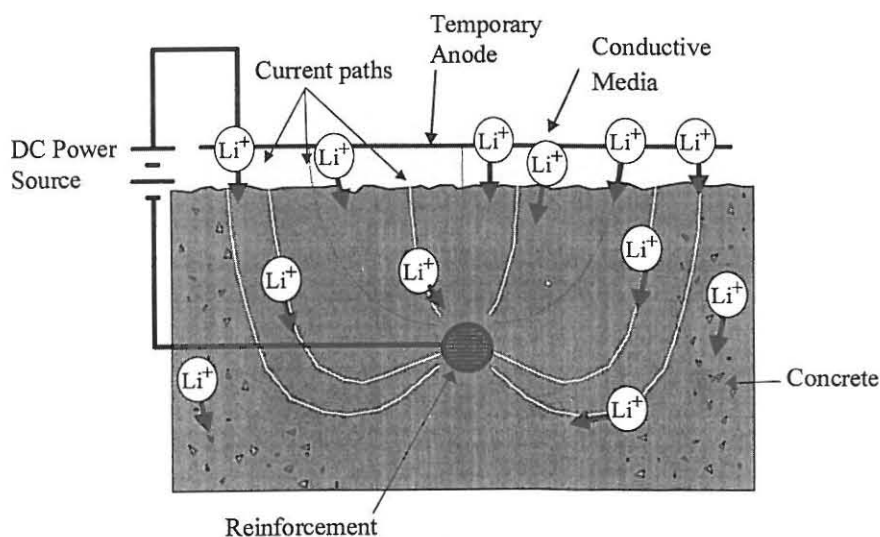


Fig.1: Schematic Showing Lithium Ion Migration During Treatment

During the initial stages of development Vector conducted a number of experiments with different lithium compounds and test slab configurations. This testing confirmed the effectiveness of electrochemically migrating lithium into concrete structures. The data also indicated that electrochemical migration would transport between 4 and 10 times as much lithium into the concrete as would penetrate under simple ponding conditions (to comparable depths). Within this range, the amount of lithium transport tended to vary depending upon proximity to the reinforcing steel, since nearer to the steel the electric field intensity increased.

It was also recognized at that time that certain massive structures such as pier footings and abutment walls, would have relatively little reinforcing steel to act as a cathode. For these types of structures, experiments were set up to determine how well the lithium migration would perform. It was discovered that lithium migration did occur, but at a slower rate. Special measures were therefore devised to speed up the lithium impregnation process for massive structures with relatively little reinforcing steel.

To maximize the lithium impregnation in massive structures, "wells" can be cored or drilled into the structure (being careful to avoid any reinforcing steel that may be present in the area of the hole). These wells serve as reservoirs for lithium, and will act as a direct route for the lithium to enter the interior of the structure. Placement of additional anodes inside these wells aids to drive the lithium ions into the surrounding concrete. In structures with little reinforcing steel additional cathodes may also be placed in the structure. In a similar manner to the anode wells, a series of holes are drilled into the structure, interspersed at regular intervals. These "auxiliary" cathodes are comprised of regular "black steel" rebar cut to an appropriate length, and then grouted into the holes. Prior to installation and grouting, the cathodes are first connected to electrical leads, which will become wired into the system. The cathodes are the only component of the system that are permanent. Once the treatment is complete the entire system will be removed from the structure except for these cathodes. The auxiliary cathodes will remain permanently grouted inside of the structure, and will not be visible.

PROJECT SUMMARIES

Bridge Deck Treatment; Arlington, Virginia; 1995

During the summer of 1995 an Electrochemical Chloride Extraction project was planned for a bridge deck in Arlington, Virginia. The bridge in question was the 34th Street overpass of I-395. The total treatment area was 720 m² (7,750 ft²), in two spans. Due to the recognized potential for ASR in this structure, a decision was made to combine a lithium treatment with the standard ECE procedure. To enable this, a solution of lithium borate was substituted for the regular electrolyte (water). Installation of the system proceeded much as it would for a regular ECE project, however a special system was devised to continuously re-circulate the electrolyte.

The slope of the bridge deck eliminated any possibility of ponding the electrolyte on the surface. However, because of the value of the lithium borate, it would be necessary to continuously re-use the solution. It was calculated that the lithium content would not be depleted from the electrolyte until after 3 or 4 weeks of continuous treatment. To maintain a steady supply of electrolyte to the entire surface, a method was devised to pump the lithium solution to the high end of each span, and then allow it to flow by gravity to a collection area at the low end. From here the pump would repeat the process, and in this manner a circulating system was created so that none of the electrolyte would be wasted. A sandwich type of system was laid on the surface of the bridge deck consisting of the titanium anode mesh between two layers of synthetic felt. Once saturated with electrolyte, the felt maintained electrical continuity, and a constant supply of lithium ions to the concrete between periods of pump activity. To complete the installation, a layer of plastic was rolled out over the entire system to prevent evaporation of the electrolyte, and sustain maximum performance throughout the treatment.

The total treatment period lasted approximately 8 weeks. While it was difficult to know how much lithium was entering the concrete, samples of the electrolyte were taken during treatment and sent for testing (Table 1).

TABLE 1: Changing Lithium Concentrations in Electrolyte over Time

Lithium in Electrolyte (PPM)		
Day	Span 4	Span 5
0	4200	4200
4	-----	2554
5	2147	-----
16	-----	646
17	707	-----
24	-----	217
25	179	-----

The data shown in this table reveals that there is a rapid migration of lithium out of solution and into the concrete within the first week of treatment. After approximately 3 weeks of operation there is little lithium remaining in the electrolyte.

Subsequent to completion of the treatment concrete dust samples were removed from the deck and tested for lithium concentrations (Table 2).

TABLE 2: Lithium Concentration in Concrete Before and After Treatment

Span	Lithium (PPM)			
	At 0.6-1.9 cm		At 1.9-3.2 cm	
	Before	After	Before	After
4	89	315	25	265
5	24	343	62	203

The data obtained through this treatment showed that the electrochemical migration of lithium into concrete was quite simple to accomplish, and could be achieved in a relatively short period. Determining exactly how much lithium is required to successfully halt the expansion of the ASR gel is difficult. The target for treatment of hardened concrete is to impregnate the concrete with one part of lithium monohydrate for every two parts of sodium equivalent. In typical concrete this equates to approximately 80 PPM of lithium. However the actual amount of lithium required will vary from structure to structure, and depends upon a number of factors.

It should also be noted that due to the nature of the migration, the greatest concentrations of lithium tends to be found closer to the surface of the concrete, and within the vicinity of the reinforcing steel. Lithium concentrations will often be lower in the spaces between rebar, as well as between and below lower mats of steel.

Bridge Deck; Seaford, Delaware; 1997

In April 1997, a bridge deck being planned for chloride extraction by the Delaware Department of Transportation was discovered to be ASR prone. The bridge was located in the town of Seaford, Delaware on Stein Highway (State Route 20). The bridge was

constructed in the mid 1940's, and as such was classed as a heritage structure. The structure comprised a total of seven spans, for a total treatment area of almost 1,600 m² (17,000 ft²).

Once again lithium borate was chosen as the electrolyte for the chloride extraction. Installation of the felt and titanium anode mesh proceeded in much the same manner as it had on the Arlington project. Drain holes were drilled in the lower corners of each span. A system of drainage pipes was put in place which returned the electrolyte from each of these drains to a large storage tank (one tank was located under both the west and east ends of the bridge). From these tanks a pump re-circulated the solution to each span. The pumps were set on timers so that they operated for approximately 15 minutes out of every hour. This frequent wetting was sufficient to keep the layers of felt saturated, and maintained excellent electrical continuity between the anode mesh and the concrete.

The chloride extraction treatment had been given approximately 8 weeks for completion. Based upon experience gained from Virginia, it was known that the lithium contained within the electrolyte would be depleted within 3 to 4 weeks. It was therefore planned to replace the electrolyte halfway through the project with new lithium borate. This would ensure maximum lithium impregnation over the entire allotted treatment time. Disposal of the expended lithium solution was made simple by the local sewer facility. While the ingredients of the lithium borate solution are not toxic, they are alkaline. Therefore as was done earlier in Virginia, permission was given to dump the used electrolyte into the sewer system, providing the pH of the solution was first neutralized. When new, the pH of the lithium borate solution was approximately 13. However, during the treatment, chemical reactions had reduced the pH substantially so that it ended up between 8 and 9. Neutralizing the pH of the electrolyte was accomplished by simply adding small quantities of acid until the pH was further reduced to approximately 7.

Data collected during the operation of the system included periodic sampling of the electrolyte to determine its remaining lithium content (Table 3). The volumes within both the west and east tanks are approximately equal.

TABLE 3: Changing Levels of Lithium within Electrolyte

Date	Lithium Content (PPM)		Note
	West	East	
April 25	4500	4500	Concentration of new electrolyte
April 26	2179	2771	
April 28	354	193	Electrolyte Diluted with Rain
May 2	368	309	
May 7	4500	4500	Electrolyte Replaced
May 8	1960	2430	
May 10	1160	1540	Electrolyte Diluted with Rain
May 16	1050	1300	
May 26	199	138	Electrolyte Diluted with Rain

During operation of the system several heavy rainstorms led to dilution of the electrolyte with rainwater. The resulting dilution is represented in the data of Table 2. It can however be seen that even before dilution occurred, a significant portion of the lithium had been driven into the concrete. It appears that one day after adding the lithium borate to the system, the lithium content has decreased sharply. It is unlikely that the difference between the concentration of the fresh electrolyte, and that of the electrolyte one day after is a sole result of lithium migration into the concrete. Rather it is also in part due to dilution by a small amount of water/electrolyte that was already present in the system. Even prior to the first addition of lithium, some water had been introduced into the system for testing of the plumbing system during installation.

Unfortunately since the lithium treatment was not the primary concern during this rehabilitation project, we do not have concrete samples to show what the final lithium concentrations in the structure were. Based upon observation of the disappearance of lithium from the electrolyte, and from the fact that two separate phases of application were implemented, one could assume that a significant amount of lithium was likely impregnated into the deck.

Pier Footings; New Jersey Turnpike Authority; 1999

In June of 1999 Vector installed their first system designed exclusively for alleviating ASR. As before, it was an electrochemical system requiring an anode, cathode, and a low voltage DC power supply. The site contained no chloride contamination but rather from the outset was intended to be purely a site of lithium impregnation. The project was installed for the New Jersey Turnpike Authority on 5 pier footings already suffering from the deleterious effects of ASR. Each of the pier footings was located near to a small river/wetland area. The cracking in the pier footings was in places quite severe, necessitating repair prior to lithium treatment. Another contractor was responsible for sealing and pressure grouting of the cracks before installation of the system began. The cementitious grout used for injection was made with mix water containing 10% lithium nitrate.

Treatment involved installation of titanium mesh on the top surface of each footing, as well as addition of several anode "wells" and auxiliary cathodes. The footings were approximately 6 m (20 ft) square by 1.5 m (5 ft) deep; but only contained one mat of steel about 1 m (3 ft) from the upper surface. The relatively small amount of reinforcing steel generated a concern that the lithium migration would proceed very slowly. To accelerate the treatment, a carefully spaced series of holes were drilled vertically down from the surface of each footing, to a depth of just less than 1 m. Into some of these holes steel cathodes were inserted and then subsequently connected via wire leads to the negative terminal of the power source. These cathodes were grouted firmly in place. The remaining holes each received a titanium anode, all of which were connected to the titanium mesh anode being laid upon the top surface of the footing. Electrical leads were connected from the anodes and mesh to the positive terminal on the power source. The end result was that 12-15 new cathodes had been distributed around each footing to compensate for a lack of reinforcing steel. Additionally, about 35 wells were drilled into the surface of each footing to act as reservoirs for the electrolyte, and provide an easier path for the lithium to enter the interior of the footing.

Power was turned on at this site on June 22, and treatment time was planned for 4 weeks. At the time of writing this paper, the treatment has not yet been completed and there are no results available. Concrete testing after treatment will verify how much lithium was impregnated into the footings.

CONCLUSIONS

While the problems associated with ASR daunt agencies and owners across North America, there is relatively little that can be done to cure it in existing structures. The application of lithium salts to ASR affected structures promises to provide some relief from its symptoms. When combined with an electrochemical means of migrating the beneficial lithium ions into a concrete structure, it forms a viable method of treatment.

This type of treatment is a relatively quick, non-intrusive method of giving structures added protection against the expansive nature of ASR. While continual analysis and improvement will doubtlessly make this process even more effective for mitigating ASR in a wide variety of structures, it is perhaps one of the most advantageous options available at this time.

REFERENCES

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