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A novel assessment of the Electrochemical Lithium Impregnation Treatment used to mitigate Alkali-Silica Reaction in Concrete

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ABSTRACT

Lithium compounds are used to prevent alkali–silica reaction (ASR) in concrete. If lithium is mixed in wet concrete, the swelling effects of ASR are mitigated. Electrochemical lithium impregnation techniques have been also used successfully on a number of older structures. This paper evaluates the electrochemical penetration and ASR performance of lithium in hardened concrete. Reactive Colombian aggregate and commercial cement were used to prepare mortar mixes and lithium nitrate performance was evaluated using the accelerated ASTM C1260 Mortar-Bar Method. Two penetration methods were used to introduce lithium into concrete. First, concrete was mixed with lithium in the mix water and expansion was measured using ASTM C1260. Second, lithium ions were migrated into ASTM 1260 mortar bars using an electric field.

A novel experimental method was developed for electrochemical treatment and assessment of the mortar bars. Samples were cast in ASTM C490 molds used in determining the length change of mortar bars ($25 \times 25 \times 250$ mm). Stainless steel electrodes were used in the migration cells, which were filled using 0.3M KOH + 0.1M NaOH in the cathode reservoir and 30% LiNO₃ in the anode reservoir. Voltages of 15 and 20 Volts were applied for 4 days. After electrochemical treatment, samples were tested to ASTM C1260. Compressive strength tests were carried out to determine the effects of lithium. Results indicate that lithium significantly mitigates the reactivity of aggregate and the ionic lithium migration seems to be more effective than initial mixing.

Keywords: alkali-silica reaction (ASR), electrochemical lithium impregnation, lithium migration

Introduction

The alkali-silica reaction (ASR) is one of concrete's many pathologies that need special care when it is involved, or potentially involved, in the construction of a concrete structure. This reaction takes place when alkali ions, such as Na^+ and K^+ react with a specific type of reactive silica compounds present in the concrete aggregates, forming a gel that absorbs water and increases its volume causing an increase of pressure inside the concrete [5]. The result on the large scale of this microscopic reaction is cracking of the hardened concrete, causing severe damage to the structure.

Therefore, many studies have been conducted in order to understand and analyze the occurrence of this phenomena and, even more importantly, ways to prevent and mitigate ASR. One successful way to partially prevent ASR occurrence is by adding lithium salts to the concrete [1]. This admixture may slow down the reaction when applied on fresh concrete and it can also work when applied to hardened concrete via an electrochemical processes [2] [3].

The adding of lithium as an admixture is a way of preventing the reaction from happening, or, at least, making it occur at a lower rate [4]. Giving the hardened concrete an electrochemical treatment is a way of controlling the ongoing ASR. This treatment can be carried out because of concrete's structure, in which the pores can be used for ion migration. For this to happen, two electrodes must be placed on the concrete so that lithium ions may be forced into the concrete thought its pores by the electrical field that is applied. Adapting Electrochemical Chloride Extraction technology, a method was implemented to electrochemically drive lithium ions into the concrete.

Although several reports on experimental electrochemical lithium impregnation on real structures (i.e., bridge decks) have been published [3] [6], real tests are expensive and and are limited. This paper shows research to investigate small scale laboratory experiments, which can also be effective. In this work the electrochemical penetration and ASR performance of lithium nitrate in hardened concrete has been assessed. For this, a reactive Colombian aggregate and high alkali cement were used to prepare mortar mixes and two methods of impregnation were investigated. Concrete was mixed with lithium in the mix water and lithium ions were migrated into ASTM 1260 mortar bars using an electric field. After the treatment, expansion was measured using ASTM C1260.

Experimental Procedures

Materials

A reactive Colombian aggregate from a quarry located in the southern Pacific area of the country was used. It was crushed and prepared in order to obtain the grading requirements of ASTM C1206.

The aggregate was mainly particles from igneous origins, such as basaltic andesite and volcanic tuffs, with porphyritic texture, characterized by considerably big crystals of plagioclase, pyroxenes, micas upon others, floating on a microcrystal (holocristalline), volcanic glass (holohyaline) or mixed (hipocrystilline) matrix, with partially or totally devitrified sectors, with some amorphous silica content.

Based on thin section microscopically analysis, the internal composition of the constituents was determined, and, it was found that some aggregates presented specific characteristics that could make them potentially reactive or harmful. This was the case for the basaltic andesite with holohyaline or hipocrystalline texture, with tuffs, cherts, quartzite and polycrystalline quartz, representing a 70% of the sample. Figure 1 shows a thin section of the aggregate used.



Figure 1. Sand particles (#100)

Commercial blended limestone cement was used. Results for the alkali oxides determined by XRF were 0.11% for Na₂O and 0.7% for K₂O. The total alkali contribution of cement Na₂O was 0.57 percent. A commercial lithium based admixture was used, which was a solution containing 30 percent lithium nitrate (LiNO₃).

Mix Design

Two different kinds of mortar mixtures were prepared according to the ASTM 1260 mortar-bar method. The proportion used was 1 part of cement to 2.25 parts of dry graded aggregate by mass. The water to binder ratio was set equal to 0.47 by mass. A group of standard mixtures was cast without the ASR inhibitor and another group of mixtures was cast mixing with the ASR inhibitor.

The dosage recommended by the admixture's supplier corresponds to the standard dosage reported by McCoy and Caldwell's [1], where the molar ratio of lithium to alkali metals ([Li]/[Na+K]) is equal to or greater than 0.74. The amount of ASR inhibitor depends on the alkali content of the cement used, in which 4.6 litres should be used for every kilogram of total alkali expressed as sodium equivalent. In order to keep the water to binder ratio constant, the free water content was adjusted (0.85 liters of water were subtracted for each litre of ASR inhibitor used).

Experiments

ASR was investigated measuring the expansion of mortar bars according to the accelerated ASTM C1260 Method, in which samples are subjected to high temperatures and high NaOH concentrations. After casting, mortar bars are stored at laboratory temperature for 1 day and then demolded and immersed in tap water at 80 °C (176 °F) for 1 day. After the second day, mortar bars are removed from water and the zero length reading is taken as a reference. Mortar bars are then immersed in a 1 N NaOH solution at 80 °C (176 °F), and length change is monitored several times per week.

A total of four different groups of samples were tested: a reference without ASR inhibitor, a sample in which the ASR Inhibitor was mixed together with the raw materials,

and two samples in which lithium ions were migrated electrochemically after mortar hardening through the application of an electric field at different voltages.

A novel experimental setup was developed for electrochemical treatment and assessment of the mortar bars. The cell consists of two reservoirs, each containing stainless steel electrodes and electrolyte. The mortar bars (cast in standard ASTM C490 molds) were located between the two reservoirs and an electrical field was applied between the metallic electrodes. For these tests, the catholyte consists of a solution of 0.3 M KOH + 0.1 M NaOH, saturated with Ca(OH)₂. The anolyte consists of the ASR inhibitor (30% lithium nitrate solution). Voltages of 15 and 20 Volts were applied for 4 days . After that treatment, samples were tested conventionally according to the ASTM C1260 standard. For each experiment, three replicates were used and the results correspond to the average of those. Table 1 shows a summary of bar expansion tests carried out.

SAMPLE	MIXING RAW MATERIALS	CURING (ASTM 1260 - AFER DEMOLDING)	IMPREGNATION TREATMENT (AFTER CURING)	BAR EXPANSION MEASUREMENT (AFTER IMPREGNATION)
Ref (reference)	Cement + Reactive aggregate	Hot curing (80 °C) during 24 hours	None	Measurement during 26 days in ASTM C1260 conditions
LM (lithium mixed)	Cement + Reactive aggregate + 30% lithium nitrate	Hot curing (80 °C) during 24 hours	None	Measurement during 26 days in ASTM C1260 conditions
ET1 (Electrochemical treatment 1)	Cement + Reactive aggregate	Hot curing (80 °C) during 24 hours	Electrochemical impregnation 15V- 4 days	Measurement during 26 days in ASTM C1260 conditions
ET2 (Electrochemical treatment 1)	Cement + Reactive aggregate	Hot curing (80 °C) during 24 hours	Electrochemical impregnation 20V- 4 days	Measurement during 26 days in ASTM C1260 conditions

Table 1. Summary of expansion tests



Figure 2. Setup of the electrochemical impregnation treatment developed

The compressive strength was measured at early (1 or 2 days) and later ages (38 days) to determine the influence of lithium on the mechanical properties of mortar. Normal

and hot curing (ASTM 1260) conditions were investigated. For this, a hydraulic testing machine was used in accordance with ASTM C109: "Compressive Strength of Hydraulic Cement Mortars" (ASTM-C109).

Results and discussions

Results for expansion are shown in figure 3. They confirm that the aggregate is potentially reactive as was indicated by the petrographic analysis. For all samples, the expansion was greater than 0.10 percent after 14 days in the alkaline solution. Length change measurements were taken beyond 14 days in order to understand the expansion at later ages.

For all lithium treatments a decrease in the expansion was observed; however, electrochemical tests were more effective than initial lithium mixing. At 28 days the reference (REF) showed an expansion near to 0.8%, the lithium mixed (LM) showed an expansion near to 0.5%, the electrochemical treatment 1 (ET1) near to 0.45%, and the electrochemical treatment 2 (ET2) near to 0.35%. This represents a reduction of the expansion in 37.5%, 44%, and 56%, respectively. Although the expansion decrease was significant for all treatments, none was sufficient to mitigate the reaction to the limit in the ASTM standard. Despite the use of the additive, the aggregates were still considered reactive.

The application of lithium electrochemical treatments in comparison with the directly mixing have shown a great improvement in controlling the expansion in a concrete affected by ASR. The efficacy of the electrochemical migration treatment seems to be directly related to the voltage applied, greater voltages proved to be the most effective . However for practical applications the voltage could not be too high because the joule effect and the corresponding incising in temperature. During all experiments, it was noted that the specimen temperature did not rise above 35°C



Figure 3. Length change measurements (ASTM C1260)

Figure 4 shows the appearance of mortar bars after experiments. Significant deterioration of samples is apparent after the ASTM C1260 tests. As was expected, the

pattern of damage found was in accordance with the expansion measurements. Major cracks were found for the reference samples; however, the cracking decreased when the treatment is applied. Although for lithium mixed samples seem there was a high density of cracks, they were much smaller than those of the reference.

It is believed that the electrochemical treatment is more effective than the lithium mixed because during mixing, lithium is partially adsorbed chemically by cement compounds and just a fraction remains within the pore solution to produce an ASR inhibitor effect. In contrast, during electrochemical migration almost all the lithium remains in the pore solution, where an increment in the electrical field gives more penetration into the sample.

There will also be significant direct benefits from using the electrical system. The lithium will be a positive ion and will go into the sample but the nitrate (which is not needed to supress the reaction) will not. Similarly a main beneficial effect of the electromigration will be the removal of the free alkali ions (sodium and potassium) in the pore solution. The potassium ions at the cathode are positive and will not penetrate the sample.



Figure 4. Mortar bars appearance after experiments

If lithium admixtures are to be used in new concrete structures, it will be necessary to know their effect on the compressive strength. For this, cubes under standard wet curing were tested at 1, 7 and 38 days. In the same way, samples cured using 80 °C for 1 day and standard wet curing for the remainder, were tested at 2 and 38 days. Figure 5 shows the results of compressive strength for all samples. It can be seen in the figure that regardless of the method of curing, lithium produces an increase of mortar strength for all ages. For normal curing the increase due to the lithium was around 20% and for hot curing the increase due to the lithium admixture was around 25%.

The main porpoise of the 1 day hot curing is accelerate the hydration of cement as can be seen in figure 5. However, for accelerated samples, the final strength is always lower than samples cured under standard conditions.



Figure 5. Compressive strength of samples under hot and normal curing

Conclusions

- Lithium nitrate may be applied effectively to concrete using an electro-migration technique in order to inhibit ASR.
- Results of comparative tests show that this method is more effective than adding lithium nitrate to the original mix. Moreover, as voltage (also current) increases, the linear expansion of mortar bars decreases. However, precautions should be taken due to the Joule effect when considerably high voltages are applied.
- It is postulated that the increased effectiveness of the electro-migration technique may also be caused by removal of alkali ions.
- However, in the present work, neither method was able to inhibit ASR sufficiently to meet ASTM standards.
- The lithium nitrate increases the concrete strength both in normal and hot water curing.

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