

DEVELOPMENT OF AN ELECTROCHEMICAL MIGRATION CELL FOR LITHIUM IMPREGNATION LABORATORY ASSESSMENT

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Abstract

The use of lithium compounds has a positive effect in mitigating the alkali-silica reaction (ASR) in concrete. This effect has been observed on hardened concrete when it is impregnated with lithium compounds with the help of electrical methods. This paper proposes an electrochemical migration cell and an experimental setup, as an approach for simulating lithium compound treatments on hardened concrete under laboratory conditions.

Experiments were carried out in which mortar bars, cast in ASTM C490 molds, underwent an electrochemical lithium treatment and the accelerated ASTM C1260 mortar-bar method. Using a potential reactive aggregate, one set of reference bars were assessed according to the ASTM C1260 standard, whereas another set of bars underwent an electrochemical lithium impregnation treatment with the help of the migration cell designed for this purpose. Results indicate that the electrochemical cell was effective during the lithium-impregnation and the treatment reduced the effects of the ASR reaction in the mortar bars.

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

1 INTRODUCTION

Alkali-silica reaction (ASR) is responsible for the deterioration and reduction of the service life of concrete infrastructure. The result, on the large scale of this microscopic reaction, is the cracking of the hardened concrete, causing severe damage on structures [1]. Nowadays, several mitigation methods are available for new and existing structures suffering from ASR. One option to prevent ASR occurrence is adding lithium salts to concrete [2], which have been reported to slow down the reaction when applied on fresh concrete and to partially inhibit the reaction when applied to hardened concrete via an electrochemical process [3].

Commercial lithium compounds are manufactured mainly from lithium nitrate (LiNO_3), in which the inhibiting mechanism of LiNO_3 against ASR has been attributed to the development of a Li-Si barrier around the surface of the reactive aggregate [4]. That Li-Si layer allows fewer OH^- ions to reach the reactive aggregate surface, whereby the alkali silica reaction is controlled. In the same way, it has been reported that LiNO_3 admixtures decrease notably the porosity of ASR products, which cover the reacting aggregates, decreasing as well the diffusion of ions and protecting the reacting minerals from dissolution [5].

In the electrochemical lithium impregnation, the concrete pores can be used for ion migration, in which metallic electrodes drive an electrical field and the lithium ions are forced into the hardened concrete through its saturated pores. This electrochemical treatment has been reported to be successful in field structures, which require massive efforts, including technical and economic resources. Laboratory trials are also limited to big scale specimens, which are very time and money consuming.

The lack of small scale and reproducible tests to assess the performance of lithium impregnation treatments in concrete led to a research partially reported in this paper. Here, it is summarized the development of an electrochemical migration cell, proposed for laboratory assessment of lithium impregnation. Lithium ions were migrated through the electrochemical cells into ASTM 1260 mortar bars using an electric field. After the electrochemical treatment, expansion was measured following the recommendations of the ASTM C1260 mortar-bar accelerated method [6]. For this, a reactive Colombian aggregate and high alkali cement were used to prepare the mortar mixes in order to analyse the proposed impregnation method.

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2 MATERIALS AND METHODS

2.1 Electrochemical impregnation cell

A new experimental setup was developed for electrochemical treatment and assessment of the lithium impregnated in mortar samples. The electrochemical cell consisted of two reservoirs, each one containing stainless steel electrodes and electrolyte solutions, in the same way as the classical migration tests on concrete (ASTM C1202 [7] or NT BUILD 355 [8]). As for the stainless steel electrodes, 18-gauge sheets were used as shown in Figure 1. The material chosen to manufacture the cells was acrylic, which is chemically stable to the solutions used in this research. Reservoirs cells were conditioned at maximum capacities of 450 cm³. In order to prevent leakage of solutions from the reservoirs to the outside, sealing neoprene rubbers were installed between the cell and the samples.

The molds for casting samples were in accordance with the requirements of ASTM C490 [9], in which specimens are 25 by 25 by 285 mm mortar prisms. As the effectiveness of the electrochemical treatment was assessed according to the ASTM C1260 standard, mortar samples were cast using gage studs for the determination of the length change. Figure 2 shows the setup of the specimen in the impregnation cell.

After placing the specimen in the impregnation cell, between the two reservoirs, an electrical field was applied between the metallic electrodes. For this research, the catholyte consisted of a solution of 0.3 M KOH + 0.1 M NaOH, saturated with Ca(OH)₂. The anolyte consisted of the ASR inhibitor (30% lithium nitrate solution). A Voltage of 20 V was applied to the samples during 4 days. After 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 these. Figure 3 shows a general view of the electrochemical lithium treatment.

2.2 Modified ASTM C1260

The proposed method of lithium impregnation included two main steps. First, the electrochemical treatment, which was reported in section 2.1. Second, the expansion assessment of mortar bars according to the accelerated ASTM C1260 method, in which samples were subjected to high temperatures and high NaOH concentrations. After casting, mortar bars were stored at laboratory temperature for 1 day and then demolded and immersed in tap water at 80 °C (176 °F) for another day. This high temperature curing was done in order to mature the samples prematurely. It is assumed that with this heat curing the cement matrix is hydrated in a very high percentage.

The “zero” reference length was taken before mortar bars were removed from hot water. After that initial hot curing, samples were treated electrochemically during 4 days, and finally, the electrochemical treatment was carried out. In this, the mortar bars were immersed in a 1 N NaOH solution at 80 °C (176 °F), and the length change was monitored several times per week.

2.3 Materials and experiments carried out

In order to assess the proposed method, two different groups of samples were tested: reference samples without lithium treatment, and samples in which lithium ions were migrated electrochemically after the mortar hardening through the application of an electric field. Table 1 shows a summary of bar expansion tests carried out.

The mortar mixtures were prepared according to the ASTM C1260 mortar bar method. The proportion used was 1 part of cement by 2.25 parts of dry graded aggregate by mass. The water to binder ratio was set equal to 0.47 by mass.

A commercial lithium based admixture was used, consisting of a solution of 30 percent lithium nitrate (LiNO₃). The dosage recommended by the lithium admixture’s supplier corresponded to the standard dosage reported by McCoy and Caldwell’s [10], 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 in the mortar samples, the free water content was adjusted (0.85 litres of water were subtracted for each litre of ASR inhibitor used) [1].

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 consisted mainly of 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 (holocrystalline), volcanic glass (holohyaline) or mixed (hipocristalline) matrix, with partially or totally devitrified sectors, with some amorphous silica content [1].

Based on thin section microscopic 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 [1].

Commercial blended limestone cement was used. Results for the alkali oxides determined by X-Ray Fluorescence (XRF) were 0.11% for Na₂O and 0.7% for K₂O. The total alkali contribution of Na₂O cement was 0.57 % [1].

3 RESULTS AND DISCUSSION

Expansion results are shown in Figure 4. The left side of Figure 4 shows for both samples tested the evolution of the expansion during 26 days under extreme conditions of alkalinity and temperature. The right side of the figure shows the expansion values after 26 days of extreme conditions. Results confirmed that the aggregate was potentially reactive, as previously was indicated by the petrographic analysis. In regard to 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.

An expansion decrease was observed in the lithium impregnation treatment. After 28 days, the reference (REF) showed an expansion near to 0.8%, while the electrochemical treatment showed an expansion near to 0.35%. This represents a reduction of 56% in the expansion. Although the expansion decrease was significant, it was not sufficient to mitigate the reaction to the limit given in the ASTM standard.

Figures 5 and 6 show the appearance of mortar bars after experiments. Significant deterioration in form of cracks was observed on reference samples. A distributed crack pattern, with average openings of 0.5 mm was obtained. For the electrochemically treated samples, cracks were strongly reduced, reaching openings just near 0.05 mm.

The electrical treatment also brings some additional benefits to the potential reactive samples. Lithium is a positive ion and could go into the sample, but the nitrate (which is not needed to suppress the reaction) could not. In the same way, a main beneficial effect of the electromigration is the probable removal of the sodium and potassium free alkali ions present in the pore solution [1].

4 CONCLUSIONS

- The experimental procedure proposed for lithium impregnation may be applied effectively to mitigate the expansion produced by the alkali silica reaction. However, it does not completely stop the reaction under the limits given by ASTM C1260.
- Results of comparative tests show that the electrochemical impregnation is effective to mitigate ASR; however, more research is needed to determine the real effects of the treatment variables (voltage applied, time of treatment, and lithium concentration).
- It is postulated that the increased effectiveness of the electro-migration technique may also be caused by removal of alkali ions.

5 REFERENCES

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TABLE 1: Summary of tests carried out.

Sample	Mixing raw materials	Curing (ASTM C1260 - after 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
ET (Electrochemical treatment)	Cement + Reactive aggregate	Hot curing (80°C) during 24 hours	Electrochemical impregnation 20V- 4 days	Measurement during 26 days in ASTM C1260 conditions

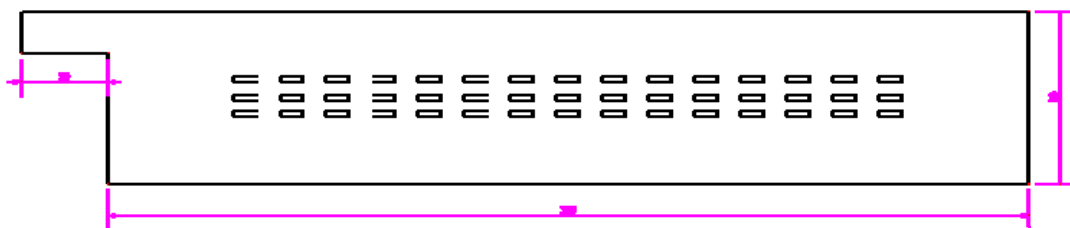


FIGURE 1: Stainless steel electrode used in the electrochemical cell for impregnating lithium salts into mortar bars.

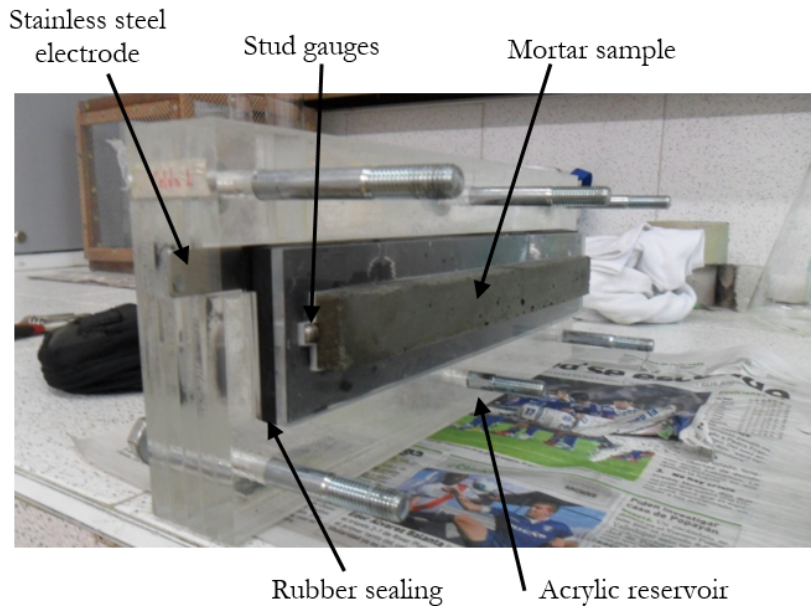


FIGURE 2: Impregnation cell set up with a mortar bar specimen inside.



FIGURE 3: Electrochemical impregnation layout during mortar bar treatment (three cells shown).

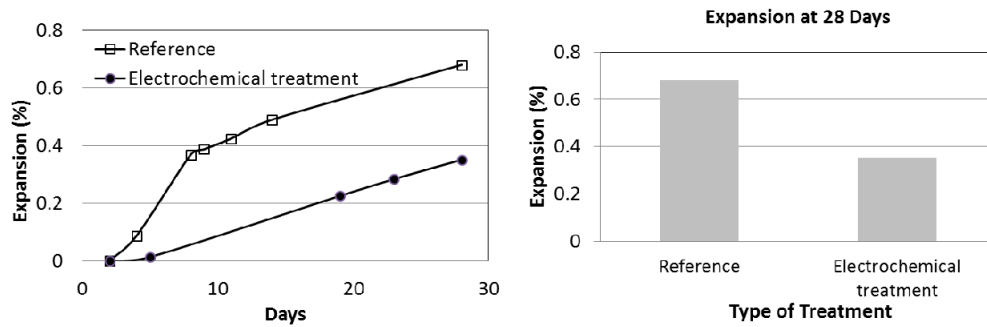


FIGURE 4: Expansion results. Left: expansion evolution for 26 days under high alkali and temperature conditions. Right: expansion after 26 days of extreme conditions of alkalinity and temperature.

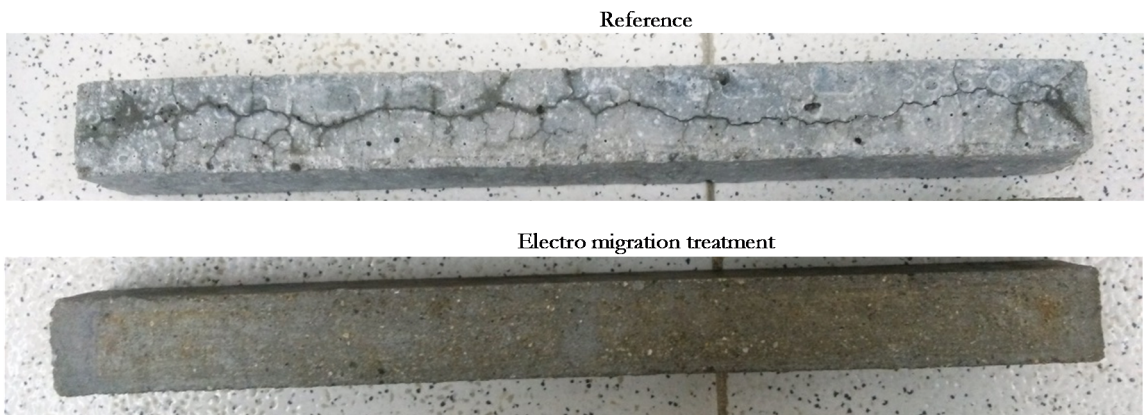


FIGURE 5: Mortar bar specimens after the test carried out. Cracks on the reference are visible.

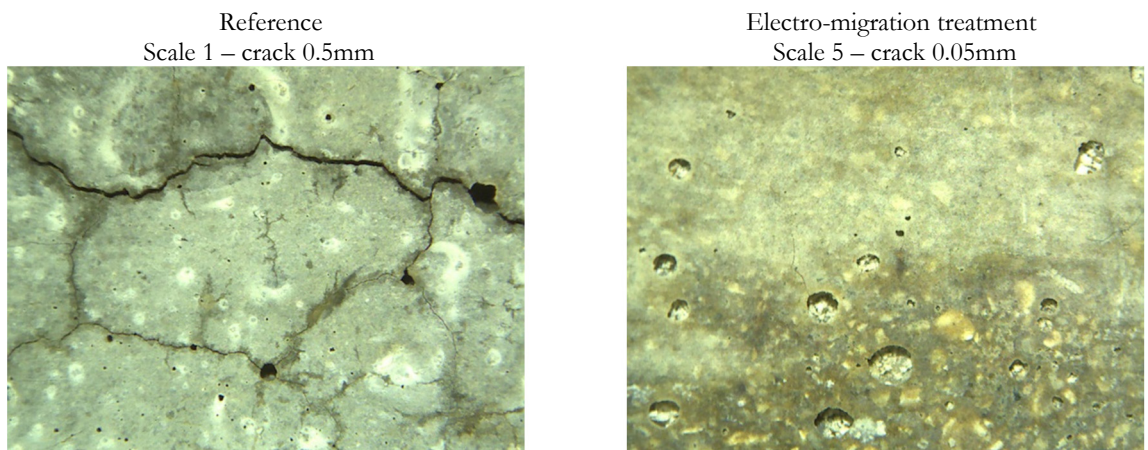


FIGURE 6: Zoomed detail on mortar bar specimens showing deterioration due to the ASR reaction.