

STUDY OF LITHIUM TREATMENTS IN MITIGATING ALKALI-AGGREGATE REACTION

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Abstract

In recent years, the efficiency of lithium-based compounds in mitigating the alkali-silica reaction ASR has been considered in the prevention and repair of structures affected by this phenomenon.. With regard to treatment, the main challenge nowadays is how to ensure the adequate impregnation of concrete with the lithium solution. The main purpose of this paper is to present a research program in laboratory conditions that studied the efficiency of some types of treatment by using a product based on lithium nitrate. The treatments sought to prevent or minimize the residual expansion of the alkali-aggregate reaction (AAR), in particular the ASR, when it is already under way. The experimental program was conducted in mortar bars, from an adaptation of ASTM C 1260. The treatments were performed after the specimens reached a level of expansion predetermined at about 0.18%. The treatments tested were: vacuum impregnation with lithium, total saturation in lithium, surface saturation in lithium, water immersion and wrapping in plastic film. After each exposure/treatment condition, the specimens were returned to the accelerated expansion attack process for two years in order to evaluate the effectiveness of each treatment in reducing residual expansions. The results demonstrated the efficiency of the lithium-based composite in mitigating residual expansions at values up to 75%.

Keywords: mortar; expansion; alkali-aggregate reaction; treatment; lithium.

1 INTRODUCTION

The alkali-aggregate reaction (AAR) was discovered around 70 years ago and to this day there are no fully effective methods to fight this phenomenon in concrete, once it has begun. Thus, the best alternative is prevention of the reaction. Yet, many old structures were built without the necessary measures for lack of knowledge on the subject and today they are facing the deleterious effects of the AAR, and therefore need to be treated and restored.

AAR mitigations methods, and specifically those against the alkali-silica reaction (ASR), can be divided into two categories, namely: mitigation of the reaction's symptoms and treatment of the reaction's causes [1,2]. The methods to mitigate the symptoms of the reaction include structural reinforcements and cuts into the structure, with the aim of preventing or releasing the deformations, respectively. The structural

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reinforcements are performed by encapsulating the affected structural element with a non-reactive concrete, which can also be protended. The cuts into the structure are performed especially in dams. The treatment of the cause of the reaction comprises two methods: controlling the amount of humidity that reaches the structures and treatment based on lithium. Humidity control is achieved by improving the structures' drainage systems through grout injections in the cracks, microcement, polyurethane, epoxy and application of impermeable coating, like membrane and sealers. Lithium-based treatments comprise surface treatment, electrochemical impregnation and vacuum impregnation. [1, 2, 3]

In recent years, the efficiency of lithium compounds in mitigating the AAR has been assessed both in terms of prevention (used as a chemical additive in the concrete admixture)[4] and in the repair of affected structures [5]. Today's main challenge, as regards the treatment of structures with lithium compounds focusing on the cause of the reaction, is how to ensure the adequate introduction of this solution into the concrete. Several approaches have been described in the literature. This study aimed to assess the effectiveness of some lithium-based treatments in reducing ASR expansions in the presence of a reactive mylonite. This research comprises a larger R&D project by FURNAS/ANEEL, called "Identification of reactive aggregates and fighting the alkali-aggregate reaction in dams", which is developed in partnership with the Federal University of Goiás, and is the object of Cândido's master's degree dissertation [6].

2 EXPERIMENTAL PROGRAM

2.1. Materials

The present study selected a type of aggregate known to be reactive in the field – mylonite – responsible for deteriorating some foundation structures in Brazil, specifically in the metropolitan area of Recife [7].

The mylonite studied derives from some type of granite that underwent a process of dynamic metamorphism, and comprises basically feldspars, quartz and micas, having a fine grain size. Its structure is foliated and marked by thin layers of mica and quartz / feldspars stretched out in a slight mineral orientation. Feldspar occurs in the form of irregular crystals, mostly saussuritized (altered to sericite). Some feldspar crystals have a graphic texture, with a flame-like or worm-like shape. The quartz occurs in large crystals, some times with serrated edges, or forming recrystallized microcrystalline aggregate, with the grains stretched out according to the rock's foliation, or tending to polygonization. These crystals have a high undulatory extinction above 30°. The biotite and muscovite micas are associated in the form of long thin pallets; some are chloritized biotites. Some opaques appear as irregular crystal in association with the biotite.

The portland cement used in the mortars is a pure cement, without any kind of admixture, and its characteristics are shown in Table 1.

The lithium nitrate solution employed in this study is a commercial product, and its main characteristics are described in Table 2.

2.2. Methods

Tests prior to the treatments

The tests prior to the treatments aimed to bring about the ASR in the laboratory, to expansion rates close to the Brazilian limit of 0.19% for the ASR[8], following the accelerated mortar bar method [9,10]. This limit was adopted taking into account the need for a minimum level of deterioration to facilitate the penetration of the lithium nitrate solution in the mortars and thus gain greater efficiency. Other researchers [1] also adopted the limit of 0.19% in their studies to perform treatments in mortar bars with several types of lithium compounds.

The cement:aggregate proportion used in the mortars was 1:2.25, in mass, and the water/cement ratio was equal to 0.47. Immediately after casting, the bars were cured for 24 hs in a wet chamber, and were then demolded and cured in water at 80°C for another 24 hs. After curing, the bars were individually measured and transferred to an airtight container filled with an aqueous solution of NaOH at 1N, at 80°C. From this point, readings were taken periodically until an expansion close to the desired one was reached, when the mortar bars were removed from the solution and submitted to the different exposure/treatment conditions described below.

Exposure/treatment conditions

The mortar bars were removed from the test when they reached an expansion of approximately 0.19%, which occurred on day 11 of the test. After cooling, the surface of the bars was then rinsed in running water and placed in a climatic test chamber (40°C ± 0.5°C and R.H. 30% ± 0.5%) to dry in 3 days. After drying, R.H. was kept at 30% ± 0.5% and the temperature reduced from 40°C to 35°C for an hour. The temperature was then again reduced from 35°C to 30°C and then from 30°C to 25°C, keeping each interval at one hour of duration. When the reduction of temperature was concluded, the bars remained in the climatic chamber until the next day for stabilization, when they were removed and submitted to the different conditions of exposure/treatment, as described henceforth.

In the first condition of exposure, the mortar bars were wrapped in a fine plastic film for a period of 7 days, as shown in Figure 1. The second condition involved immersing the mortar bars in deionized water for the same period, as shown in Figure 2.

In the case of treatments with lithium nitrate, the third condition involved total saturation, by immersing the bars in the solution for 7 days, as shown in Figure 3. A fourth treatment was performed with the lithium solution, but only by means of surface saturation. In this case, the saturation involved immersing 5 mm of the three mortar bars in the solution, also for a period of 7 days (Figure 4).

The fifth and last treatment involved vacuum impregnation with the lithium compound. After the pre-established drying period, the mortar bars were placed inside an acrylic vacuum chamber, made specifically for this treatment (Figure 5). The stages of the vacuum impregnation treatment were thus conducted:

- application of 0.5 atm. vacuum until constancy;
- introduction of lithium solution in the vacuum chamber until the bars were completely immersed (Figure 6);
- application of vacuum for an additional 7 hs;
- removal of vacuum;
- after removal of vacuum the specimens remained immersed in the LiNO₃ solution for another six days and a half.

Residual expansions

After concluding all treatments, the mortar bars returned to the attack condition so as to determine residual expansions and thus investigate the efficacy of the treatments. To this end, the bars were stored in an airtight container, called reactivity box, with relative humidity above 95% and constant temperature of (60 ± 2)°C. The post-treatment readings began one day after the storage of the bars in the reactivity box and were periodically performed for 2 years. The change in exposure conditions, after the treatment, was adopted for closer proximity with a real-life situation and to prevent the lithium in the treated mortar bars from reacting with the external NaOH solution or lixiviating part of the alkaline solution in the pores.

3 RESULTS AND DISCUSSION

3.1 Tests prior to the treatments

Figure 7 shows the evolution of the average expansions until they reached values closer to the Brazilian limit of 0.19%, which happened at 11 days of age, when the bars were removed and submitted to the different exposure/treatment conditions. This figure shows the high reactive potential of this rock, since the expansions did not stop, but rather developed high rates until around 20 days into the test, reaching values above 0.40%.

3.2 Residual expansions after the treatments

Figure 8 shows the average residual expansion results during the time the mortar bars were submitted to the different types of exposure/treatment conditions.

Comparing to the condition in which the bars were wrapped in plastic film, all the other conditions tested were able to mitigate the residual expansions right after the early post-treatment ages. The expansions in this reference condition continued to grow in the course of time while in the conditions treated with the lithium solution, the expansions yielded considerably lower results in the course of the investigation.

4 DISCUSSION

According to the results shown in Figure 8, it can be seen that up to approximately 5 months into the tests, expansions grew in all the conditions tested, but at lower growth rates for the treatments involving lithium. All three conditions tested with lithium produced similar expansion behaviors. After that age, surface treatment with lithium distances a little from the other conditions involving total saturation and vacuum impregnation. After approximately 7 months, the expansions in all the conditions tested tend to stabilize up to the test age of 2 years. Figure 9 shows expansions when the ages of 7, 12 and 24 months are compared.

Considering that efficiency is represented by the percentage in expansion reductions in relation to the condition used as reference, it can be considered that this efficiency is practically the same for all the lithium treatments. In Figure 10 efficiencies at 2 years can be observed, which achieved about 75% in the presence of lithium treatments. The water-immersion condition also reduced expansions by around 45%. This reduction can possibly be explained by the fact that water saturation would have lixiviated the Na and K alkalis in the pore structure of the mortar, which could have reacted to cause residual expansions. This same behavior was seen by [11] as well in a treatment conducted on concrete specimens.

In view of the results obtained in the present study, lithium proved its potential in reducing residual expansions, although the different techniques using this product did not show practical differences in efficacy in the mortar tests. The literature shows that lithium is effectively capable of interfering in the ASR, by changing the nature of the reaction and, consequently, mitigating the expansions. Lithium is capable of modifying, at an atomic level, the physical-chemical, crystallographic and structural characteristics of the products in the AAR producing lithium incorporated compounds with a lower expansion capacity, according to studies with X-ray diffraction, infrared spectroscopy and magnetic nuclear resonance [12, 13].

However, for laboratory studies with concrete [14] involving lithium saturation of cores taken from ASR-affected structures, while reductions in residual expansions were observed (to the order of 24%), greater efficacy was expected of lithium. In this same line, there are other studies [5] on concrete showing also the low-depth penetration of lithium in field treatments, even though lengthier studies would be required.

Based on the above, and on the potential that this product has in mitigating expansions, according to the 2-year-long laboratory monitoring shown in this paper, despite the challenges regarding its penetration capacity in concrete, continued studies are needed involving field monitoring of structures along time, among other complementary tests.

5 CONCLUSIONS

All the mortar treatments with a lithium nitrate solution were capable of mitigating residual expansions in the presence of reactive mylonite rock. The efficiency of the treatments with lithium in this study, regardless of the condition – surface saturations, total saturations or vacuum impregnations -- , proved very similar, of about 75%. Comparing the three types of lithium-based treatments in terms of the results obtained, the surface saturation was the condition that produced the best prospects in this investigation, both technically and economically, since its efficiency in mitigating expansions was virtually the same as the other conditions tested.

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Specific gravity (g/cm ³)		3.11	
Fineness	Residue in 75 µm sieve n. 200 (%)	0.2	
	Residue in 45 µm sieve n. 325 (%)	1.2	
	Specific area (cm ² /g)	4420	
Setting times	Initial (h:min)	2:40	
	Final (h:min)	4:20	
Autoclave expansion (%)		0.1	
Compressive Strength (MPa)	3 days	35.1	
	7 days	38.4	
	28 days	45.2	
Chemical Components (%)	Loss on ignition	2.72	
	Insoluble residue	0.60	
	Sulphur trioxide (SO ₃)	3.14	
	Magnesium oxide (MgO)	3.02	
	Silicon dioxide (SiO ₂)	19.31	
	Iron oxide (Fe ₂ O ₃)	2.57	
	Aluminum oxide (Al ₂ O ₃)	3.92	
	Calcium oxide (CaO)	62.3	
	Free calcium oxide (CaO)	1.7	
	Total Alkalis	Sodium oxide (Na ₂ O)	0.68
		Potassium oxide (K ₂ O)	2.08
		Alkaline equiv. (Na ₂ O _{eq})	2.05
	Soluble-in-water alkalis	Sodium oxide (Na ₂ O _{eq})	0.31
		Potassium oxide (K ₂ O)	1.93
Alkaline equiv. (Na ₂ O _{eq})		1.59	
Calcium sulfate (CaSO ₄)		5.34	

Lithium nitrate (%)	30 to 40
Water (%)	60 to 70
Specific gravity (g/cm ³)	1.20
pH	7.0 to 9.5



FIGURE 1: Mortar bars wrapped in plastic film.



FIGURE 2: Immersion in deionized water.



FIGURE 3: Total saturations in lithium.



FIGURE 4: Surface saturation in lithium.

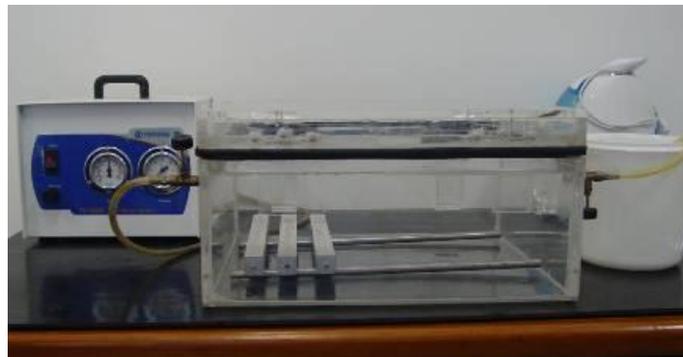


FIGURE 5: Equipment for performing treatment by vacuum impregnation with lithium.



FIGURE 6: Introduction of LiNO_3 solution into airtight chamber.

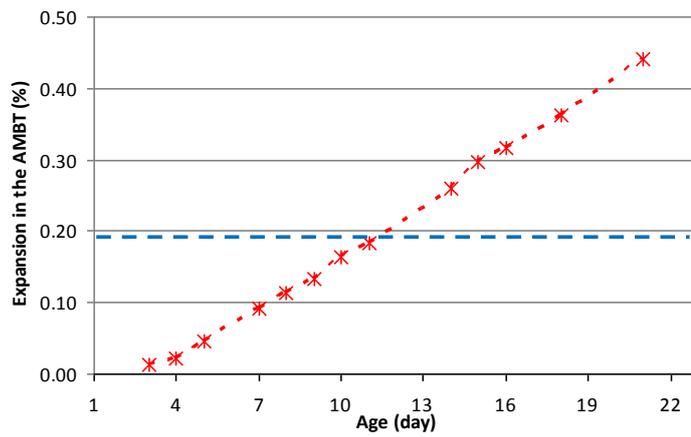


FIGURE 7: Average expansions before the treatments.

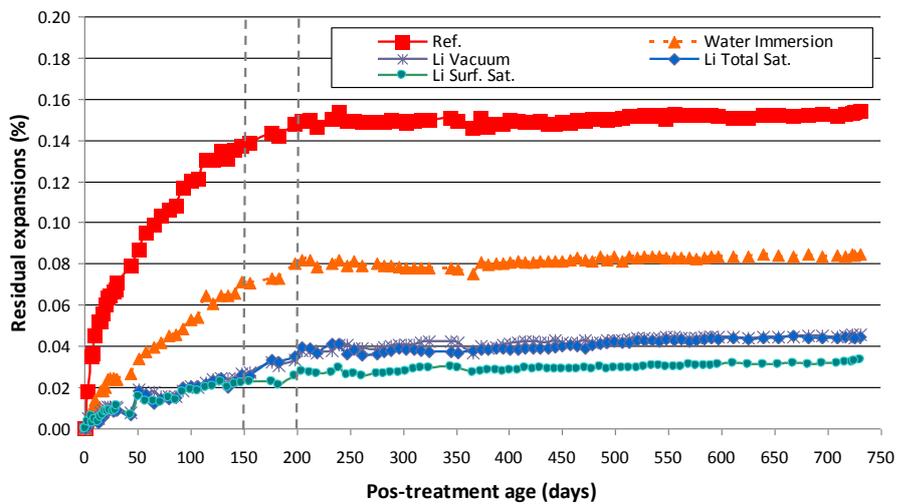


FIGURE 8: Average residual expansions of mortar bars for each type of exposure/treatment condition along 2 years.

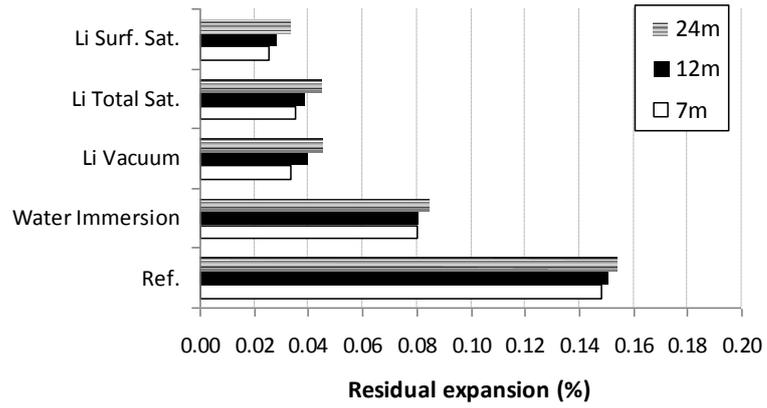


FIGURE 9: Residual expansions for 7, 12 and 24 months.

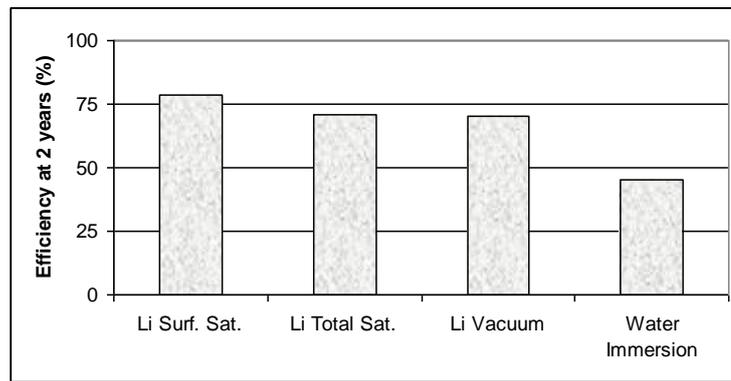


FIGURE 10: Percentage of expansion reduction compared to the reference condition at 2 years after treatment.