RESEARCH ON THE SUPPRESSION EXPANSION DUE TO ASR. EFFECT OF COATINGS AND LITHIUM NITRATE

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Abstract

This paper concerns with the study of the use of coatings and lithium nitrate to control the alkali-silica reaction (ASR) development in a concrete affected by this reaction. Seven coatings were selected in order to enclose different types of coating systems, which were exposed in natural and accelerated test conditions. In order to study the modifications produced by lithium nitrate in the expansive properties of ASR products, immersion and electrical migration conditions were used to drive the lithium ion into concrete.

In this paper the results of physical, chemical and microstructural tests in the un-treated and treated concretes were evaluated and discussed.

Keywords: ASR, concrete, coatings, lithium nitrate, mitigation

1 INTRODUCTION

The occurrence of alkali-silica reaction (ASR) in several concrete structures in the last few years worldwide has point the need for the improvement of preventive measures to inhibit these reactions not only in affected structures but also in new structures. In Portugal this form of concrete degradation was discovered in the last decade in important structures, namely dams and bridges. The most applied preventive and remedial measures against this expansive reaction are those which control the factors that induce its development, e.g. by controlling the ingress of water in the concrete.

The water ingress control in concrete by the application of coatings is one way to prevent this deterioration. However, the coatings have to fulfil some requirements:

- They must be chemically resistant, namely to the alkalinity of concrete;
- They must have sufficient adhesion and permeability to water vapour. This is particularly important when concrete has a high level of humidity;
- They must prevent water absorption;
- They must have adequate deformability to support the residual expansion of the concrete.

Considering the great number of cases in the ASR literature of the employment of coatings presenting many contradictory results, some researchers have implemented another method based on the modification of the expansion properties of the ASR products, namely by the use of lithium salts. The use of lithium compounds to control expansion due to ASR was first reported by McCoy and Caldwell (1951) [1]. They conducted an investigation on the potential use of chemical admixtures to prevent or minimize ASR-induced expansion and damage. After McCoy and Caldwell many other researchers have studied this subject [2, 3, 4, 5, 6, 7, 8]. The incorporation of lithium into a fresh concrete mix is relatively simple, however its application to a hardened structure is more difficult [9], being normally ineffective in massive structural members, due to the difficulties in the penetration of lithium ion in the concrete. An adaptation of the Electrochemical Chloride Extraction (ECE) has been studied by some researchers [10] in order to shorten the time of treatment and to increase the efficiency of lithium impregnation. The ECE is a treatment process specially developed to extract chlorides in a contaminated concrete structure. It 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 drive-in lithium ions into concrete [9].

The study presented in this paper is part of an extensive work developed in the National Laboratory of Civil Engineering (LNEC, I. P.), a public institution of the Portuguese Ministry for

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Public Works, Transports and Housing, aiming the study of the behaviour of different coatings and lithium nitrate in the mitigation of ASR in concretes suffering from this pathology.

2 MATERIALS

2.1 General

In this work samples extracted from railway concrete sleepers, which are cracked by ASR and delayed ettringite formation (DEF), were employed [11]. Several railway concrete sleepers were used, which were produced by the same plant and at the same day. From each sleeper a total of 17 cores (74 mm in diameter) were taken by drilling.

2.2 Surface Coating Treatment

The concrete cores, 160 mm high, were prepared by careful abrasion in order to remove any loose materials and to obtain an even surface. Before the products application the cores were dried (relative humidity (RH) less than 5% measured at surface by a portable humidimeter). This RH of the concrete was chosen in order to guarantee the best conditions for the application of the coating systems. Each coating system was applied in a total of thirty cores extracted from two concrete sleepers manufactured at same day and same hour, being the remaining four cores left uncoated to act as a control (reference). Two of the three kind of surface treatments defined by the European Standard EN 1504-2 [12] for protection and repair of concrete structures were selected for these study – one hydrophobic impregnation and six coatings, which are presented on table 1.

2.3 Lithium Treatments

Concrete cores cutted and rectified with 50 mm high were prepared as previously described. These samples were then subjected to three lithium ingress conditions as follows: immersion; wetting/drying cycles (W/D); and electrochemical migration (ECM) (Figure 1) with 20, 40 and 60V.

Since the electrochemical method presented the best result a new set of experiment was performed but in concrete cylinders with 160 mm high – Figure 2. In this case the lithium was migrated through the curved sides of the concrete core in order to guarantee a best migration efficacy.

2.4 Methods

2.4.1 Surface Coating Treatments

General

The coated and reference concrete specimens were subjected to three different test environments, which could represent the normal environmental conditions in a real structure:

- Fog chamber, with T=20ºC and RH>95%;
- Immersion in tap water, at T= 20º C;
- Outdoor exposure, urban environment.

Expansion and Mass Variation tests

Expansion measurements were performed in coated and reference concrete cores, according to the French performance test for DEF in concrete [13]. In this method the expansion is obtained by lateral length measurements in three equally spaced lines of two gauge reference studs each, with a distance of 100 mm between the two studs of a given line, so permitting three readings per core. The measurements were made at regular intervals using a SYLVAC S229 deflectometer with 0,001 mm precision adapted to the reference studs installed in the three laterals lines of each core.

Mass variation was evaluated in order to assess the increase of the weight due to the ingress of water inside the coated and reference specimens and to compare the different coating systems against their resistance to water absorption.

Atomic Absorption Spectroscopy (AAS)

About 20 g of concrete was fragmented and dried in a vacuum chamber at 40 ºC for 7 days and crushed to pass a 160 µm sieve. Then the sample was dried at 105 ºC for 15 hours. Sodium and potassium determination was performed after extraction of 1 g of concrete with 100 ml of deionised water [15]. The solution was stirred for 15 min and then left in rest for 24 hours at room temperature. Sodium (Na) and potassium (K) were determined separately on a GBC 906AA atomic absorption spectrometer and from there the Na_2O_{eq} was calculated [14].

Scanning Electron Microscope (SEM) coupled with a Energy-dispersive spectrometer (EDS)

Concrete specimens were fractured and left to dry in a vacuum chamber at 40 ºC for 14 days. Afterwards important concrete zones like pores with reaction products, interfaces and reaction rims around the aggregates were selected to be observed. Some of these samples were left as freshly broken surfaces and others were impregnated with an epoxy resin in order to obtain polished surface concrete sections. All of the samples were coated with a gold-palladium film and observed in a scanning electron microscope (SEM) JEOL JSM – 6400 coupled with an OXFORD INCA X-SIGHT EDX spectrometer. Operating conditions were set at 15 kV.

2.4.2 Lithium Treatments

General

Concrete cylindrical specimens (74 mm in diameter and 50 mm high) were used to evaluate the lithium diffusivity and migration. These specimens were pre-treated following the Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration (ASTM C 1202-05) [15] that can be described in the following steps:

- The specimens were surface dried in air for at least 1 hour, and then their curved sides were sealed with adhesive tape.
- The specimens were placed in a container and left in a vacuum chamber (less than 50 mm Hg) for 3 hours, with both end faces exposed.
- After the 3h vacuum, boiled water was drained into the container with the vacuum pump still running, and the specimens were covered with water.
- The immersed specimens were kept in the vacuum for one additional hour. After this hour the vacuum was closed and the specimens were kept soaking for 18±2 hours.

Immersion

After the pre-treatment, the bottom surface of each specimen was immersed for different periods (one to four weeks) in a 30% lithium nitrate solution. To evaluate the influence of the temperature on the lithium diffusivity the tests were done at 20º C and 38º C, respectively.

Wetting/drying cycles (W/D cycles)

Concrete specimens prepared as described above are subjected to a total of four cycles. Each cycle consists of two phases, immersion for one day in tap water at 20º C followed by drying for six days in air.

Electrochemical lithium migration (ECM)

Concrete cylindrical specimens pre-treated as described were subjected to three set of voltages (20, 40 and 60V) for one week. A concrete cylinder without lithium was also tested in the same conditions to act as a reference.

Expansion and Mass Variation tests

After these sets of tests, concrete cylinders with 160 mm high prepared using the same pre-treatment were used with a voltage of 60V. These concrete specimens were placed in a fog chamber at T=20ºC and RH>95%. Expansion and mass variation measurements were performed at regular intervals according to the French performance concrete expansion test [13].

Scanning Electron Microscope (SEM) coupled with a Energy-dispersive spectrometer (EDS)

The first centimetre of each sample treated with lithium was broken and dried in a vacuum chamber at 40 ºC for 14 days. Some of these samples were kept as freshly broken surfaces and others were impregnated with an epoxy resin in order to obtain polished surface concrete sections. All of the samples were coated with a gold-palladium film and analysed by SEM/EDX as previously described.

3 RESULTS

3.1 Surface Coating Treatments

Expansion and Mass Variation tests

The results of expansion and mass variation expressed as a percentage relatively to the initial measured values, obtained after 180 days of exposure of the painted and reference concretes in the different environmental conditions are presented in tables 2 and 3. Each value on the table represents the average of 3 measurements on two specimens. The reference value corresponds to the average of the two unpainted specimens taken from each sleeper. The efficacy factor is also presented in these two tables, which was obtained according to Equation 1,

$$E_{Efficacy}(\%) = \frac{E_{\mathrm{Re}f.}(\%) - E_{system-n}(\%)}{E_{\mathrm{Re}f.}(\%)} \times 100 \qquad (1)$$

being $E_{Ref.}$ the expansion value of the unpainted reference concrete specimen at 180 days and $E_{system-n}$ the expansion value of the concrete specimen coated with system *n* at 180 days.

Alkalis determination by Atomic Absorption Spectroscopy (AAS)

Table 4 presents the results of the Na_2O_{eq} content of the different coated and uncoated concretes after 180 days exposure under the three environmental conditions.

Scanning Electron Microscope (SEM) coupled with an Energy-dispersive spectrometer (EDX)

Figure 3 presents SEM images of the reference concrete before and after 180 days exposure in the fog chamber environment. The quantity of ASR and DEF products detected in the concrete after 180 days was much higher than the initially observed, being the DEF in much higher quantity than the ASR gels. The same concrete exposed to the immersion environment presents, besides the DEF, a ticker and higher quantity of ASR gel (Figure 4). These expansive products were mainly located in the paste/aggregate interfaces and in some voids inside the paste. The SEM/EDX study also showed that after 180 days the CSH gel in the reference concrete from the immersion condition is more compact than the same concrete in fog chamber environment (Figure 5) and with a lower alkali content.

The SEM observation confirms the presence of ASR and DEF products in both painted and reference concretes, but the DEF occurrence seems to be more pronounced than the ASR.

3.2 Lithium Treatments

Expansion and Mass Variation tests

The results of expansion and mass variation tests performed in the concrete treated with 60V are shown in figure 6. In comparison with the most efficient coating system employed (P7 system) the lithium migration shows a better expansion inhibition effect.

Alkalis determination by Atomic Absorption Spectroscopy (AAS)

Figures 7 and 8 presents the results of the lithium contents and Na_2Oeq (in %) of all the lithium treatments employed. According these results, the ECM method was the most efficient method in driving lithium into concrete. With only one week of treatment this method reveals to be most effective than four weeks of treatment in the immersion methods.

Scanning Electron Microscope (SEM) coupled with an Energy-dispersive spectrometer (EDX)

The ASR gel appearance (figure 9) of the concrete treated with lithium shows a alveolar structure that was associated with its less expansion behaviour and its less capability to absorb water.

4 DISCUSSION

4.1 Surface Coating Treatments

The expansion and mass variation results after 180 days exposure show that all coating systems were effective under the outdoor environmental conditions, being the P2 and P7 the only ones effectives under the both high humidity environments employed. This effect can be associated with their influence in the reduction of the water absorption as observed by the lower mass variation obtained, as compared with the reference concrete. The SEM/EDX observations, showing the presence of ASR and DEF products inside all concretes, don't present an explanation for the less expansion behaviour of P2 and P7 coating systems.

4.2 Lithium Treatments

The application of ECE method in comparison with the immersion methods has shown a great improvement in driving lithium into a concrete affected by ASR. The efficacy of the electrochemical migration treatment seems to be directly related to the voltage applied and, despite the differences obtained in the first centimetre due to the sampling, the 60V proved to be the most effective condition to drive-in the lithium. The increment of lithium was accompanied by a decrease in the alkalis availability (Table 5), which can be associated to a cation exchange mechanism.

The lower alkali content of the ASR gels in the concretes treated with lithium seems to be related to the lithium ingress. Besides, these gels present a alveolar microstructure which can be interpreted as a lower capacity to expand. Another important feature in the SEM/EDS observations was the difficulty in the detection of the deleterious ettringite. It seems that in the concrete treated with lithium the ettringite is reduced confirming the results obtained by Ekolu and co-workers [16].

5 CONCLUSIONS

This work presents the results of the application of different coatings and lithium nitrate in the mitigation of a concrete affected by ASR and DEF. Based on the obtained results it can be conclude that the efficacy of the coating systems was very dependent on the test conditions employed, being the P2 system (an cement-based polymer-modified coating system) the most effective protective coating under the high aggressive humidity testing conditions. The employed test conditions allow predicting with anticipation the inhibition behaviour of the coating systems against internal expansive reactions, confirming the importance of the experimental design conditions to simulate the real environment under which the structure is exposed and the correct use of the coating system for that environment. In fact, P3, P4, P5 and P6 systems were not effective in preventing the ingress of liquid water when exposed to immersion or fog conditions. The obtained expansion tests results of the specimens exposed to the outdoor environment show similar performance for all the coating systems, due to the slow rate of these expansive reactions in the natural environmental condition. A longer exposure time would be necessary to confirm the behaviour of these systems under this condition.

In comparison with the employment of coatings the treatment of the concrete by electrochemical migration of lithium ion was more effective in ASR and DEF expansion reduction. This method was also better than the immersion method to drive lithium ions into concrete. In terms of practical use, the lithium treatment by electrochemical migration was not very different from the well known ECE method for the chlorides extraction, being its higher cost compensated by the higher efficiency in comparison with the surface coating treatments.

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TABLE 1: Coating systems employed.

Classification	Coating System	Description
Hydrophobic impregnation	P1	hydrophobic impregnation
Coatings	P2	cement-based polymer-modified coating 1
	P3	cement-based polymer-modified coating 2 + acrylic coating with solvents
	P4	solvent free acrylic coating
	P5	white cement-based polymer-modified coating
	P6	acrylic coating with solvents
	P7	epoxy-based coating system with a crack-bridging ability of 0,158 ± 0,066 mm

TABLE 2: Expansion, mass variation and efficacy results of the concrete cores exposed to the fog chamber and immersion environmental test conditions.

Coating system	*Fog Chamber exposure*					*Immersion exposure*				
	Expansion (%)		Mass variation (%)		*Efficacy (%)*	Expansion (%)		Mass variation (%)		*Efficacy (%)*
	Reference	Painted	Reference	Painted		Reference	Painted	Reference	Painted	
P1	0,09	0,09	0,90	0,68	*0*					
P2	0,07	0,04	1,43	1,10	*43*	0,29	0,07	1,93	1,28	*76*
P3	0,14	0,10	0,98	1,04	*29*					
P4	0,09	0,10	1,38	1,38	*-11*					
P5	0,08	0,06	1,43	2,23	*25*	0,07	0,09	1,43	3,30	*-29*
P6	0,06	0,08	0,89	0,92	*33*					
P7	0,05	0,03	1,17	0,30	*40*	0,07	0,03	1,49	0,42	*57*

TABLE 3: Expansion, mass variation and efficacy results of the concrete cores exposed to the outdoor environment.

Coating system	*Outdoor environment*				
	Expansion (%)		Mass variation (%)		*Efficacy (%)*
	Reference	Painted	Reference	Painted	
P1	0,02	0,01	0,90	0,09	52
P2	0,04	-0,01	1,43	0,54	125
P3	0,01	0,01	0,98	0,04	0
P4	0,01	0,00	1,38	0,05	100
P5	0,04	0,00	1,43	0,20	100
P6	0,01	0,00	0,89	-0,11	100
P7	0,05	-0,01	1,17	0,69	122

TABLE 4: Na_2O_{eq}* (in %) content of the coated and reference concretes in the different environmental test conditions in comparison with its initial value.

Coating system	Initial	Fog chamber		Immersion		Natural	
		Reference	Painted	Reference	Painted	Reference	Painted
P1	0,096	0,053	0,074			0,038	0,082
P2	0,120	0,038	0,100	0,083	0,053	0,062	0,105
P3	0,096	0,067	0,068			0,056	0,040
P4	0,096	0,030	0,019			0,027	0,022
P5	0,095	0,038	0,061	0,038	0,031	0,043	0,082
P6	0,110	0,014	0,012			0,026	0,028
P7	0,118	0,059	0,051	0,051	0,041	0,053	0,102

$$^{*}Na_2O_{eq}(\%) = Na_2O(\%) + 0,658 \times K_2O(\%)$$

TABLE 5: Lithium increment and alkali reduction in the lithium treatments.

	Depth (cm)		Li (%)	Na_2Oeq (%)
Immersion treatments	1	20º C	0,001	0,089
		38º C	0,001	0,080
		W/D cycles	0,002	0,071
	4	20º C	0,001	0,121
		38º C	0,000	0,100
		W/D cycles	0,002	0,073
Electrochemical migration	1	20V	0,006	0,069
		40V	0,012	0,035
		60V	0,008	0,023
	4	20V	0,002	0,104
		40V	0,006	0,070
		60V	0,023	0,033

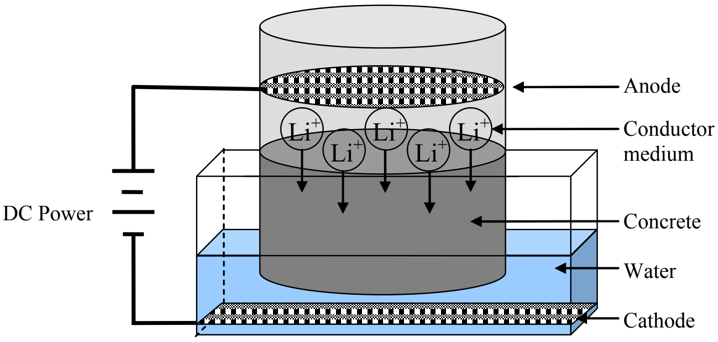

FIGURE 1: Schematic showing lithium ion migration experiment with concrete specimens 74×50 mm.

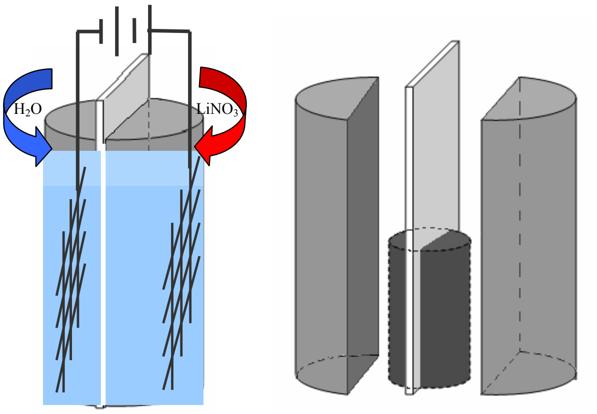

FIGURE 2: Schematic showing lithium ion migration experiment with concrete specimens 74×160 mm.

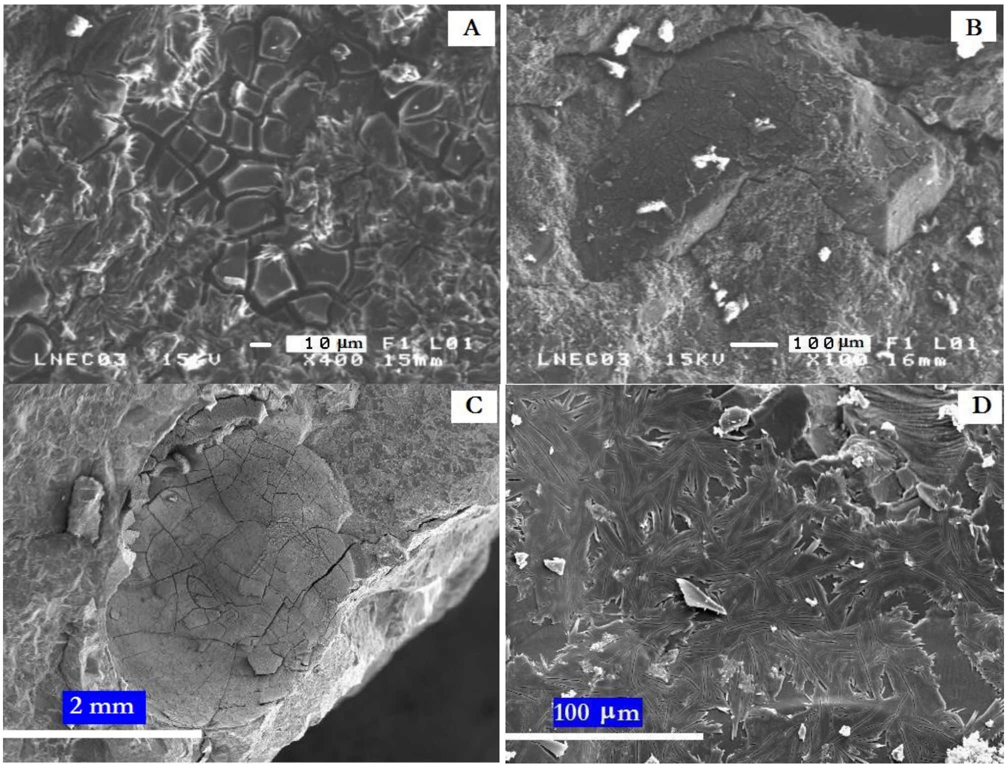

FIGURE 3: SEM images of a) ASR gel b) DEF in the concrete before testing; c) ASR gel and d) DEF after 180 days testing in the unpainted concrete tested in the fog chamber environment.

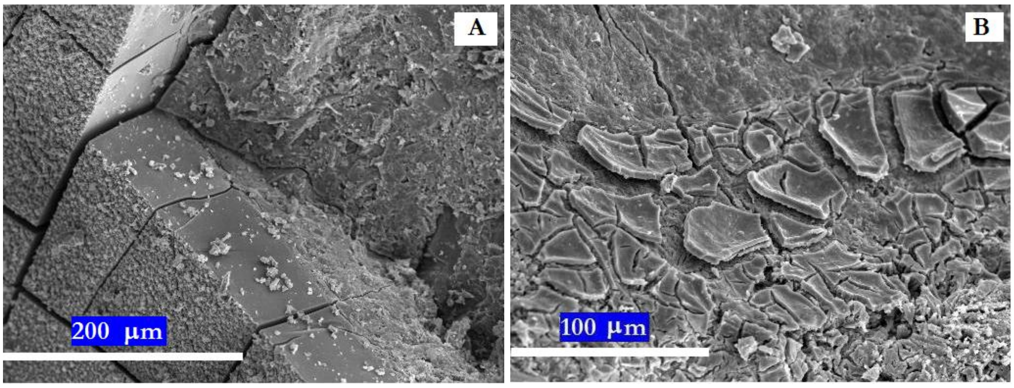

FIGURE 4: SEM images of the ASR gel of the reference specimen at 180 days of exposition in a) immersion and b) fog chamber environments being visible the high thickness of the gel formed.

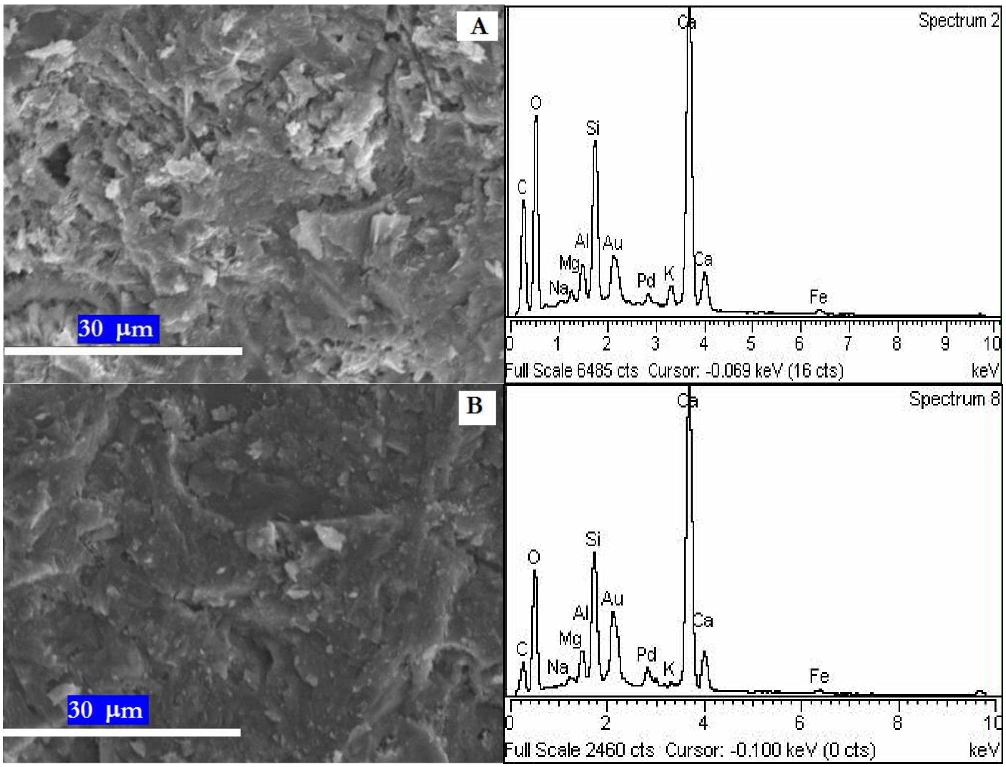

FIGURE 5: SEM/EDS images of the cement paste of the unpainted reference specimens in the fog chamber (a) and immersion (b) environments, and corresponding EDX spectrum.

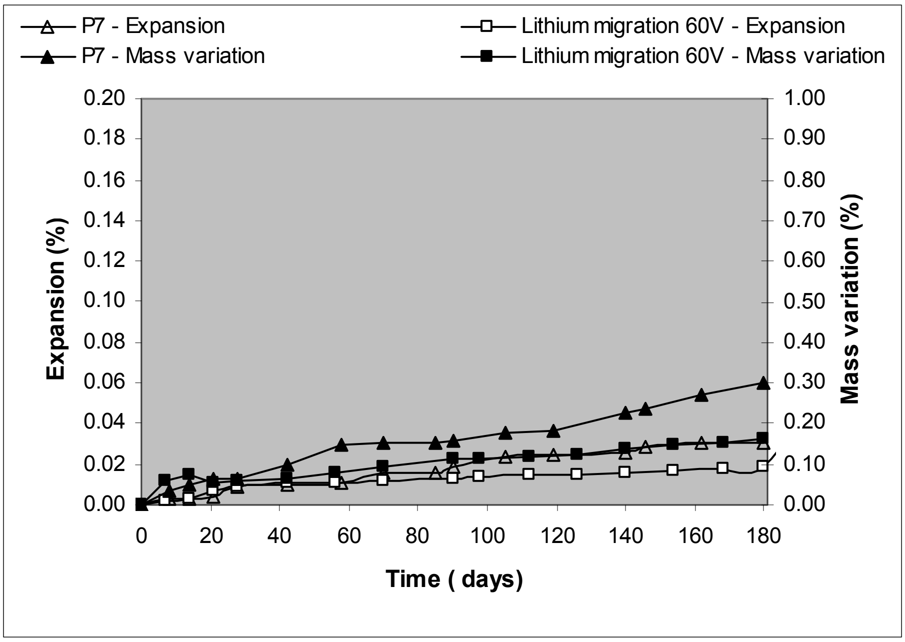

FIGURE 6 – Expansion and mass variation values for concrete specimens treated with lithium (migration with 60V) and P7 coating system in fog chamber environmental test conditions.

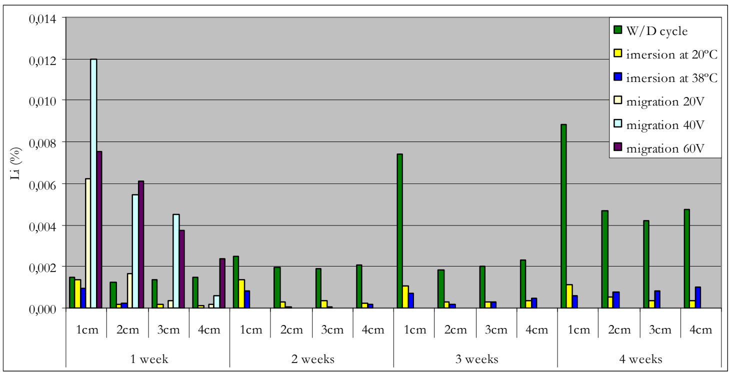

FIGURE 7: Li (%) evolution in the first's 4 centimeters depth for the concrete specimens treated with lithium by immersion at 20º C, immersion at 38 ºC, W/D cycles and by electrochemical method.

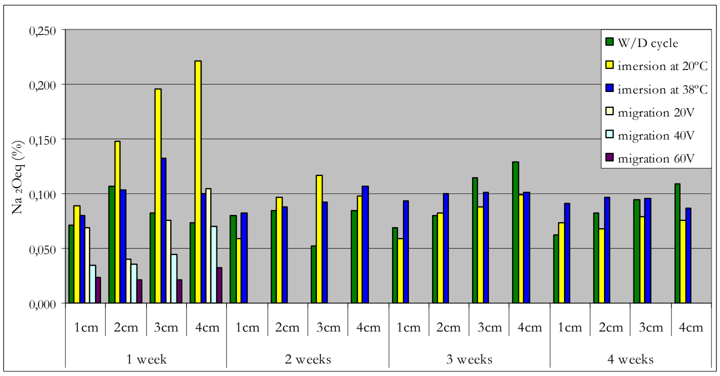

FIGURE 8: Na2Oeq evolution in the first's 4 centimeters depth for the concrete specimens treated with lithium by immersion at 20º C, immersion at 38 ºC, W/D cycles and by electrochemical migration.

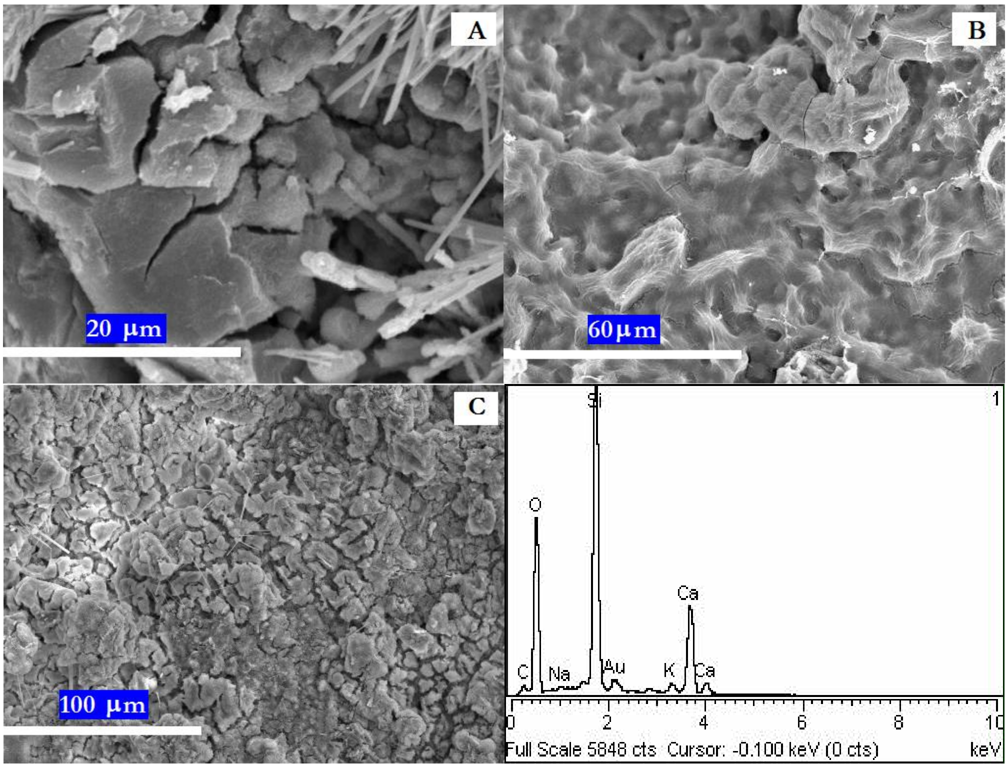

FIGURE 9: a-c) SEM picture of the ASR products in the unpainted reference specimen immersed in lithium nitrate (a, b and c), d) and corresponding EDX analysis.