

INVESTIGATION ON LITHIUM MIGRATION FOR TREATING ALKALI-SILICA REACTION AFFECTED CONCRETE

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ABSTRACT

Alkali-silica reaction (ASR) is one of the major deterioration mechanisms that affect numerous concrete structures worldwide. During the reaction, hydroxyl and alkali (sodium and potassium) ions react with certain siliceous compounds in the aggregate, forming a hygroscopic gel. The gel absorbs water from the cement paste and swells, possibly leading to deleterious expansion and cracking of the structure. Once ASR is detected in existing structures, there are no treatments to stop it and prolong their service life.

Lithium is known to alter the reaction, as it binds to the alkali-silica gel and the latter is no longer expansive. Indeed, the use of lithium-based admixtures has been acknowledged as a preventive measure for over 50 years. In existing structures, nevertheless, the use of admixtures is no longer possible and lithium ions need to be transported into the cementitious matrix. Amongst other transport mechanisms, such as capillary absorption and diffusion, ionic migration is the most effective.

In order for ionic migration to occur, power should be supplied between two electrodes, immersed in electrolytes. The reinforcement bar is often used as cathode and, therefore, attracts cations, such as lithium ions. Pore solution works as catholyte. The anolyte, on the other hand, should be a lithium compound solution. Although several studies have been conducted on the use of electric field to drive lithium ions into concrete, so far, there is no agreement on the conclusions. It is necessary to fully understand lithium migration into concrete before developing a possible treatment against ASR. This paper presents preliminary results on the investigation of the influence of different lithium compounds used as anolyte during migration through experimental testing.

Key-words: Alkali-silica reaction, repair, electrochemical method, migration.

INTRODUCTION

Concrete structures worldwide are affected by Alkali-silica reaction (ASR). In 1992, Poole [1] reported that only few countries had not reported structures damaged by ASR and all continents presented affected structures. As it is a slow degradation mechanism that takes from 5 to 15 years to take place, cases are still being discovered.

In this process, alkali and hydroxyl ions from the pore solution react with reactive siliceous compounds from the aggregate, producing a hygroscopic gel. As it absorbs water from the surrounding cement past, the gel swells and this might lead to expansion and further cracking of the concrete element.

Preventive methods against ASR, such as limiting the alkali content of the concrete mixture or the use of supplementary cementitious materials, are already well established. However, if the reaction has already taken place, there are no treatment procedures currently available, in order to prolong the service life.

The incorporation of lithium-based admixtures has been recognized as one of the preventive methods, as it can reduce and even prevent ASR deleterious expansion [2]. While in new concrete structures, lithium ions are mixed in the fresh mixture, in hardened elements, they need to be transported into the cementitious

matrix. In this case, ionic migration is the most effective transport method, as it leads to higher penetration depths and concentration of lithium ions compared to diffusion and capillary absorption [3,4]. Migration occurs when an electric field is formed between two electrodes immersed in electrolyte solutions. In concrete (and mortar), the pore solution works as electrolyte. The reinforcement bar is often used as one of the electrodes. The other is usually placed externally, immersed in an electrolyte solution.

Several authors have investigated the use of ionic migration to drive lithium ions into ASR affected concrete (e.g. [4-11]). Nevertheless, there is no consensus on whether lithium migration is an effective treatment against ASR deleterious expansion. In fact, better understanding the principles of lithium migration and its effect on ASR affected concrete is still necessary. The present paper brings preliminary results on the investigation of the influence of the anolyte solution on lithium migration through experimental testing.

EXPERIMENTAL

Materials and specimen preparation

Cylindrical mortar specimens (diameter of 98 mm and height of 50 mm) were cast with water to cement ratio (w/c) of 0.5 and sand to cement proportion of 3:1, according to EN 196 1:2005. The specimens were cured in a fog room for 36 days. Portland cement type CEM I 42.5 N, standard sand with D_{max} of 2.00 mm (according to EN 196 1:2005) and deionized water were used.

Apparatus and procedure

Lithium migration test was performed in the set-up described by ASTM 1202 - Standard Test Method for Electrical Indication of Concretes Ability to Resist Chloride Ion Penetration. As shown in Figure 1, the specimen is placed between two electrolyte chambers, each with a stainless steel electrode. Once the electric potential is applied between the electrodes, cations are attracted by the cathode (negative electrode), whereas anions move in the opposite direction, towards the anode (positive electrode).

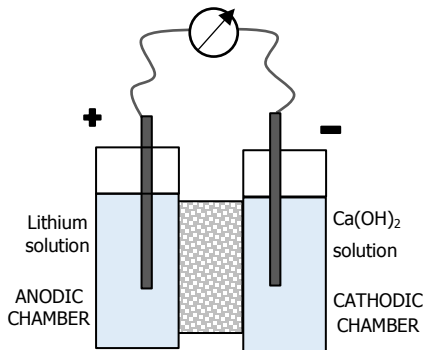


Figure 1- Schematic diagram of the experimental set-up

The catholyte in all tests was a saturated Ca(OH)_2 solution. The anolyte, on the other hand, was the investigated lithium solution, according to Table 1. The maximum concentration of lithium in each salt solution is the saturation concentration. Each solution was tested with two replicates, during one week under 40 V. Passing current and catholyte temperature were continuously monitored, while electrical resistance of the cell and electrolyte pH were measured four times during the experiments. The cell electrical resistance was measured with a multimeter, at 120 Hz in the resistance mode. From the resistance, the resistivity can be calculated with Equation 1:

$$\rho = R \cdot \frac{A}{L} \quad \text{Equation 1}$$

where R is the electrical resistance (Ω), A is the specimen surface area (m^2) and L is the thickness of the specimen (m).

The pH of the electrolytes were obtained with a pH-meter, when it was possible. In the case of very alkaline

solutions (pH > 13) or high lithium ion concentration, pH test strips were used. Electrolyte samples were collected three times during the test and were analyzed by Inductively Coupled Plasma (ICP), in order to obtain the concentration of sodium, potassium, lithium and calcium (the latter only in anolyte).

The effect of the anolytes on diffusion was also investigated in experiments in the same set-up, but without current. Each solution, as described in Table 1, was tested for a week. Samples of the electrolytes were collected in the beginning and at the end of the experiment for further chemical analysis by ICP. Resistivity and pH were also measured at those occasions.

Table 1- Lithium solutions used as anolytes

Solution	Concentration (M)	Solution	Concentration (M)
Li ₂ CO ₃	0.2 (saturated)	LiNO ₃	0.2
LiOH	0.2	LiNO ₃	4.9
LiOH	4.9 (saturated)	LiNO ₃	7.8 (saturated)

Results

Migration test

In Figure 2 (a) it is possible to observe the current density that passed through all the specimens during the migration experiment. Test LiNO₃ – 4.9 M (2) presented connection issues, as it can be seen in the current density plot. The general behavior can be divided into three parts: in the first couple of hours, there is a rapid current increase, followed by a slower drop until around the third day. Finally, the current density stabilizes until the end of tests in the majority of the cells. The initial behavior was also noted by other authors [8,10] and it is believed to be due to the complete saturation of the specimens [8]. On the other hand, the final results are different from what was reported by Pacheco and Polder [8]. In their work, the current density dropped to values lower than 5 A/m² until the end of the experiment. The temperature of the catholyte during the experiment can be seen in Figure 2 (b). The rise of temperature in all cells influenced the resistivity values, as it will be further discussed.

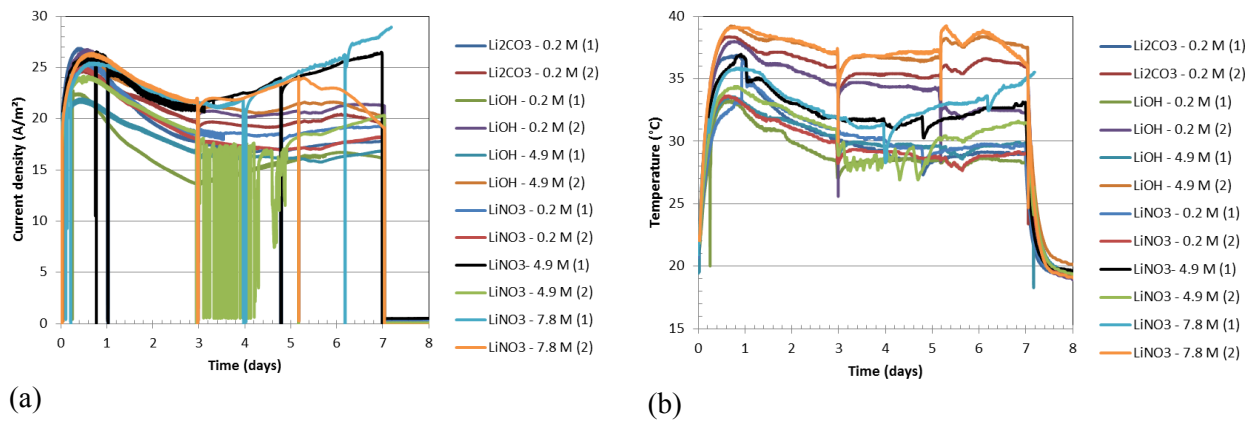


Figure 2 - Current density variations (a) and catholyte temperature (b) during migration test

According to Equation 2, the total charge can be calculated by the integration of the current plot.

$$Q = \int_0^T i(t)dt \quad \text{Equation 2}$$

where Q is the charge that passed through the specimens (in C), i is the current (in A), T is the total time of the experiment (in s) and t is time (in s).

Table 2 presents the total charges that passed through the cells according to each lithium solution used as anolyte. Three solutions exhibited deviation above 10% between replicates, LiNO₃ 4.9 M and LiOH 0.2 and 4.9 M. In the first case, connection problems in one of the cells explain that variation. However, that is not the case with the last two. Therefore, further experiments might be needed to explain this. Overall, it is

possible to observe a tendency of the charge to increase with the anolyte concentration. It is interesting to note that, when comparing solutions of different compounds, but with same concentration, charge values did not vary by more than 3.5%, indicating that the type of compound does not play an important role on the charge.

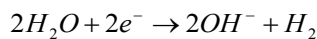
Table 2 - The charge passed of tested solutions

Concentrations	0.2 M			4.9 M		7.8 M
Lithium compound	Li ₂ CO ₃	LiOH	LiNO ₃	LiOH	LiNO ₃	LiNO ₃
Charge (C)	94758	91361	92644	93443	100058	112435
*CV (%)	3.8	14.3	2.1	10.9	11.8	3.2
Average charge (C)	92921			96751		-
*CV (%)	1.5			3.4		-

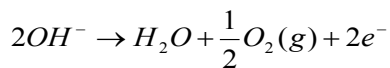
*CV: coefficient of variation

In Figure 3, the electrical resistivity variations during the experiments are exhibited. The initial resistivity of most cells was around 45-50 Ω.m. Comparing Figures 2 and 3, it is possible to notice that, during the experiment, the variations in resistivity and temperature are related: higher temperature led to lower resistivity values and vice versa. These findings are different from what was reported by Pacheco and Polder [8], where increasing resistivity was noted until the end of the experiment.

Variations in pH in catholyte and anolyte are related to the cathodic and anodic reactions, respectively, as shown in Equation 3. The reaction that takes place in the anode depends on the pH of the surrounding solution.

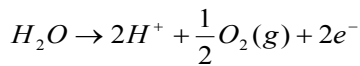


Cathodic reaction



Anodic reaction (high pH)

Equation
3



Anodic reaction (low pH)

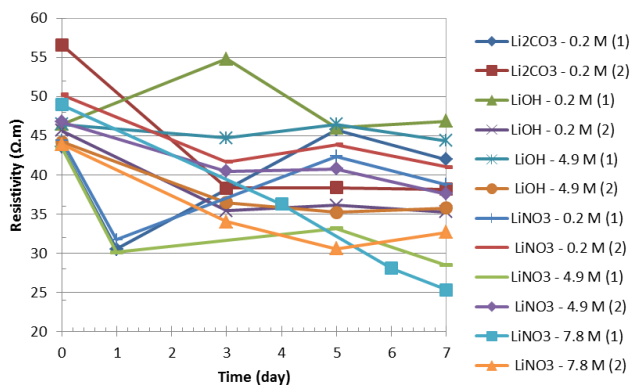


Figure 3 - Electrical resistivity variations during migration experiment

The pH variations during the experiment can be seen in Figure 4. Cells Li₂CO₃ 0.2 M (1) and LiNO₃ 0.2M, 4.9M and 7.8 M (1) did not have their pH measured because of problems with the pH probe. As for the pH behavior of the catholyte solutions, with the exception of LiOH – 0.2M (1), the initial values were around 12 and they increased slightly throughout the test. The progress of the anolyte pH, on the other hand, as it is shown in Eq. 3, depended on the initial value. The passing charge and the buffer capacity of the solution are also important.

All LiNO₃ solutions were initially acidic and, therefore, they presented the highest pH drops during the test. In fact, the anodes of those cells presented corrosion, due to the low pH. Both LiOH - 4.9 M solutions presented very basic initial pH (14) and it remained until the end of the experiment. It is interesting to notice that, although Li₂CO₃ – 0.2 M (2) and LiOH – 0.2 M (1) and (2) had close initial pH, LiOH solutions had better buffer capacity and the pH showed a lower decrease.

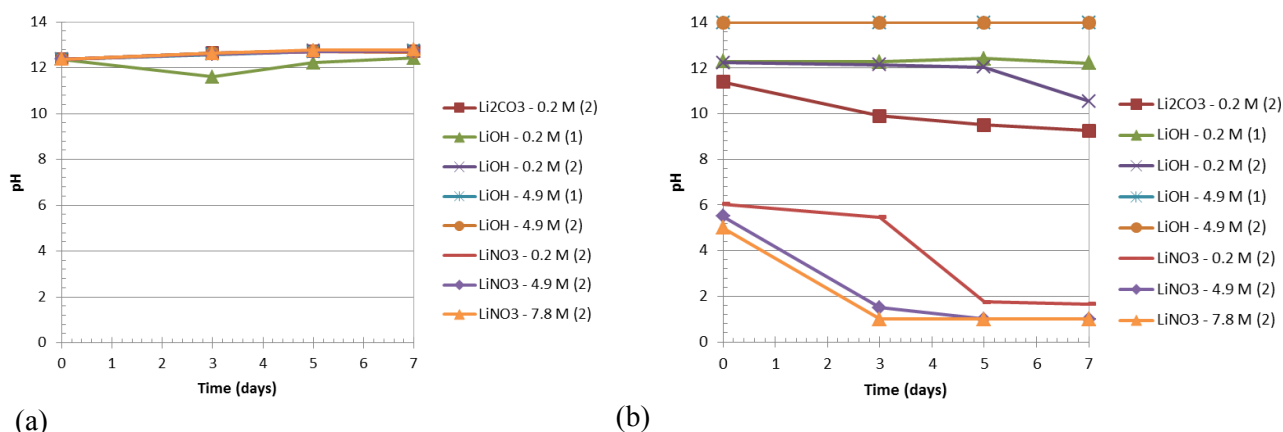


Figure 4 - pH of catholytes (a) and anolytes (b) of the migration experiment

The chemical compositions of anolyte and catholyte can be seen in Figure 5 and 6. Sodium, potassium and calcium ions move to the anolyte due to simple diffusion. No clear trend can be detected, however, it is possible to notice that LiNO₃ 7.8 M cell exhibited higher concentration of those ions by the seventh day of test. A possible explanation is that the acid pH might have led to the dissolution of the surface of the specimen. The lithium concentration in the anolyte was supposed to decrease, as lithium ions are transported into the specimen. Nevertheless, in some tests, that was not the case. Further investigation is still necessary in order to understand this. The erratic behavior of cell LiOH – 0.2 M (1) cannot be explained at the moment and further analysis is required.

Sodium and potassium concentrations in the catholytes (Figures 6 c and d) increased – potassium ions left the specimen faster because of higher ionic mobility. However, no clear trend can be noted. That is also the case for the lithium concentration in the catholytes (Figure 6 e). It is not possible to correlate the initial concentration and type of anolyte with final lithium concentration, even though higher values were observed in the cells with LiNO₃ 4.9 and 7.8 M. Lithium concentrations in the catholyte are small anyway.

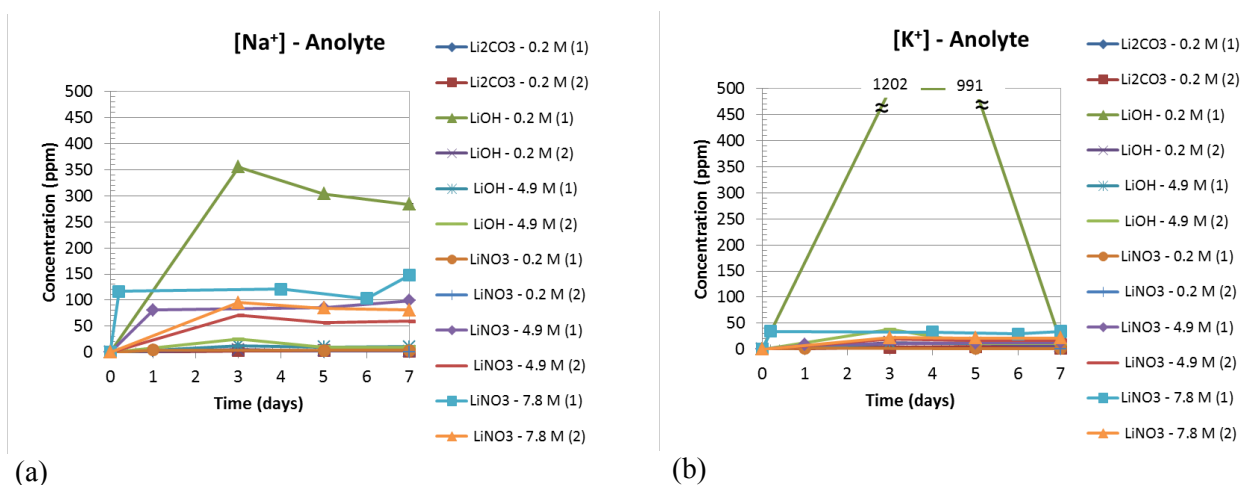


Figure 5- Concentration in anolyte solutions of sodium (a) and potassium (b) during migration experiment

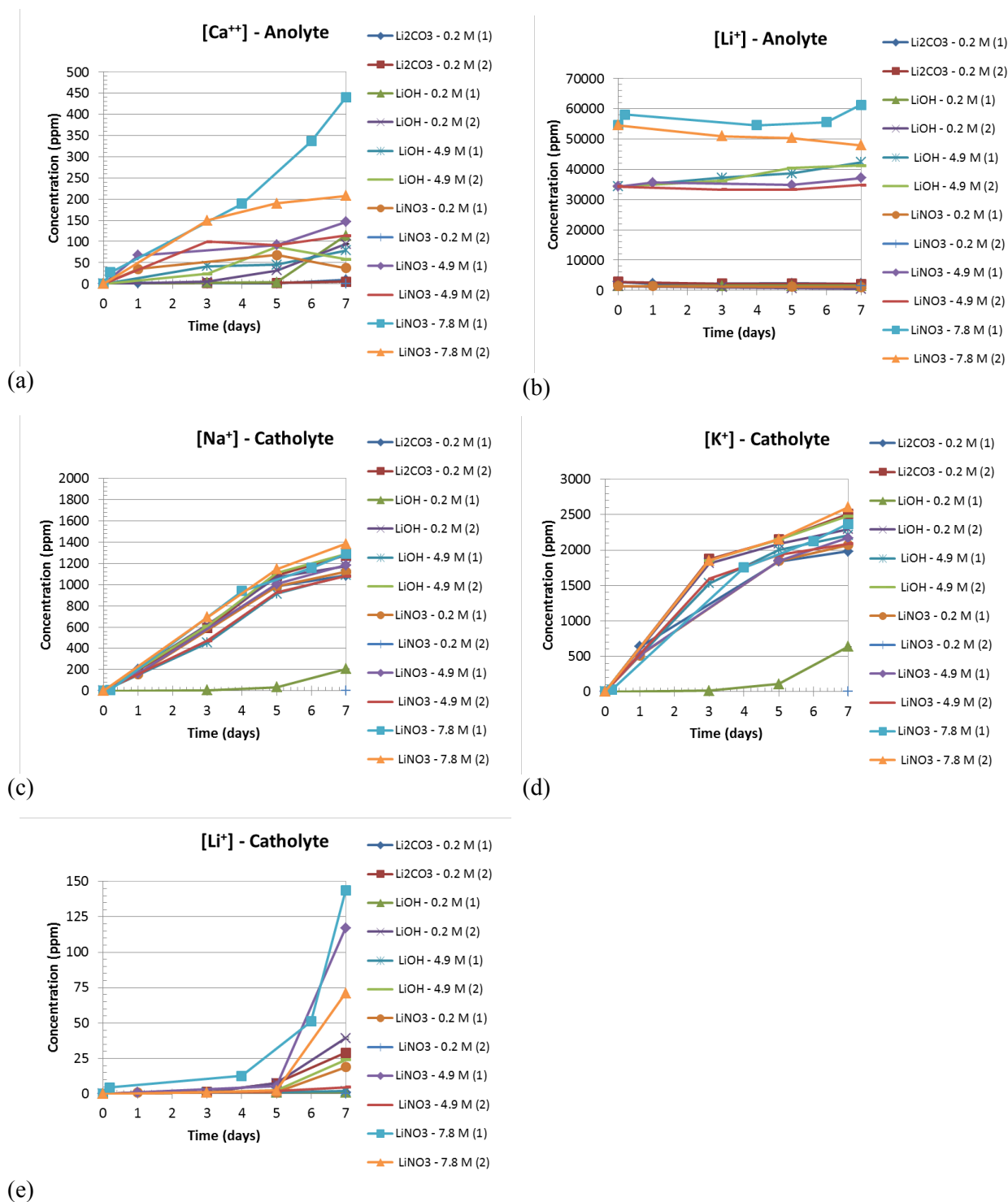


Figure 6 - Concentration in anolyte solutions of calcium (a) and lithium (b) and concentration in catholyte solutions of sodium (c) potassium (d) and lithium (e) of the migration experiment

Diffusion test

Resistivity variations during the diffusion experiment are shown in Figure 7. The room temperature remained constant during the test, at 21.5 °C. As expected, most cells did not exhibit significant variations in resistivity and, in those that varied the most, the deviation did not exceed 12%.

In Figure 8, the pH behavior in the catholyte and anolyte solutions can be observed. In the catholyte solutions, the pH remained fairly constant. In the anolyte, however, it depended on the initial solution. In the case of the LiOH and Li₂CO₃ solutions, pH remained somewhat constant until the end of the test. On the other hand, the LiNO₃ solutions were initially acidic and, by the end of the test, had their pH increased to around 11-12. This can be explained by the diffusion of OH⁻ ions from the pore solution towards those

anolytes. That was not the case of the solutions with initial pH close to 12, as this value is similar to the pH of the pore solution in the specimens.

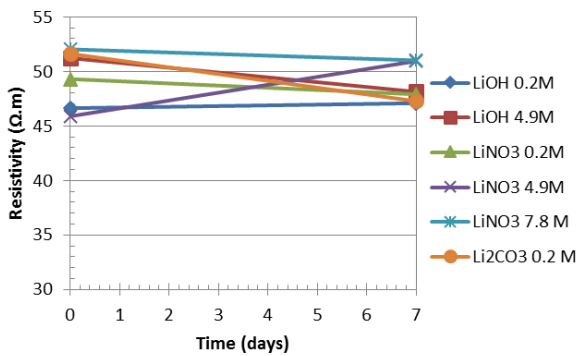
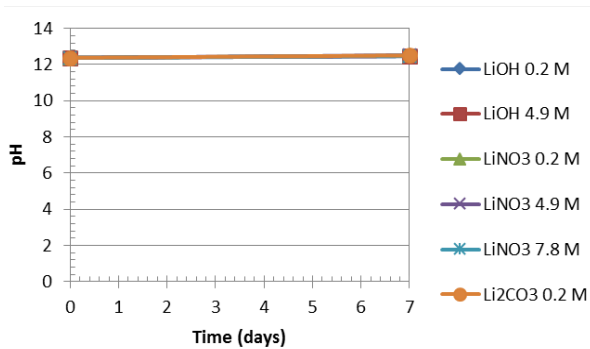
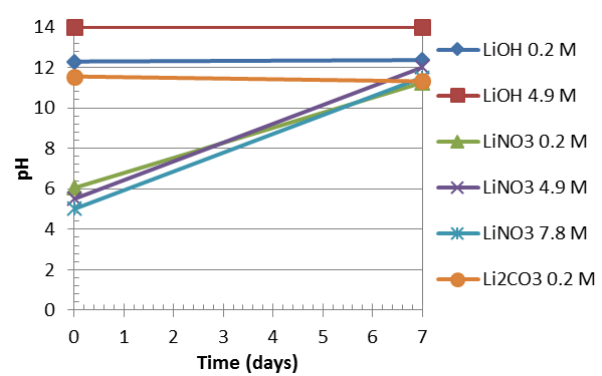


Figure 7- Electrical resistivity variations during diffusion experiment



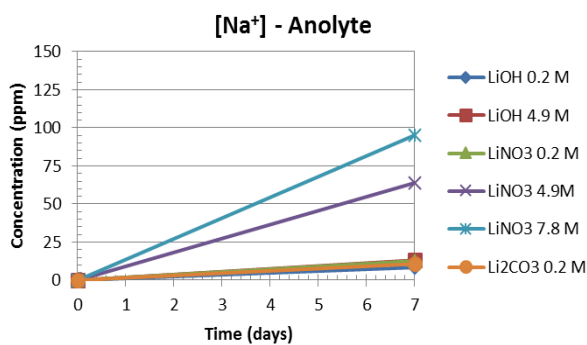
(a)



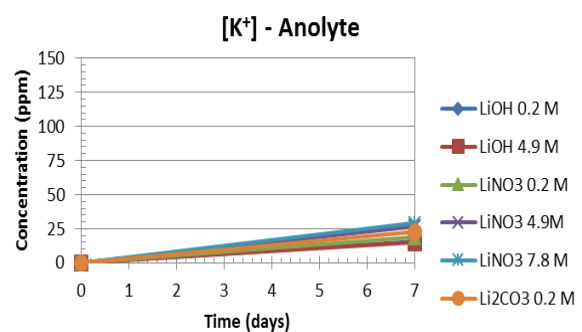
(b)

Figure 8 - pH of catholytes (a) and anolytes (b) of the diffusion test

The chemical compositions of the anolytes and catholytes before and after the diffusion experiment are in Figure 9 and 10. The final concentrations of sodium and potassium in the anolytes are comparable to the ones found at the end of the migration test. Once again, the most acid solutions (LiNO_3 – 4.9 M and 7.8 M) presented the higher concentrations of sodium and calcium ions at the end of the test. This indicates that the surface of the specimens might have dissolved due to the low pH of the solution and those ions were liberated in the anolyte. Without applied voltage, the final concentrations of sodium, potassium and lithium (Figure 10 c-e) in the catholytes are much smaller than the ones from migration, as expected. Even though, no clear trend can be noted, once again, LiNO_3 – 7.8 M exhibited the highest amount of lithium ions in the catholyte after the test. However, lithium ion concentrations in the catholyte are very low.



(a)



(b)

Figure 9 - Concentration in anolyte solutions of sodium (a) and potassium (b) during diffusion experiment

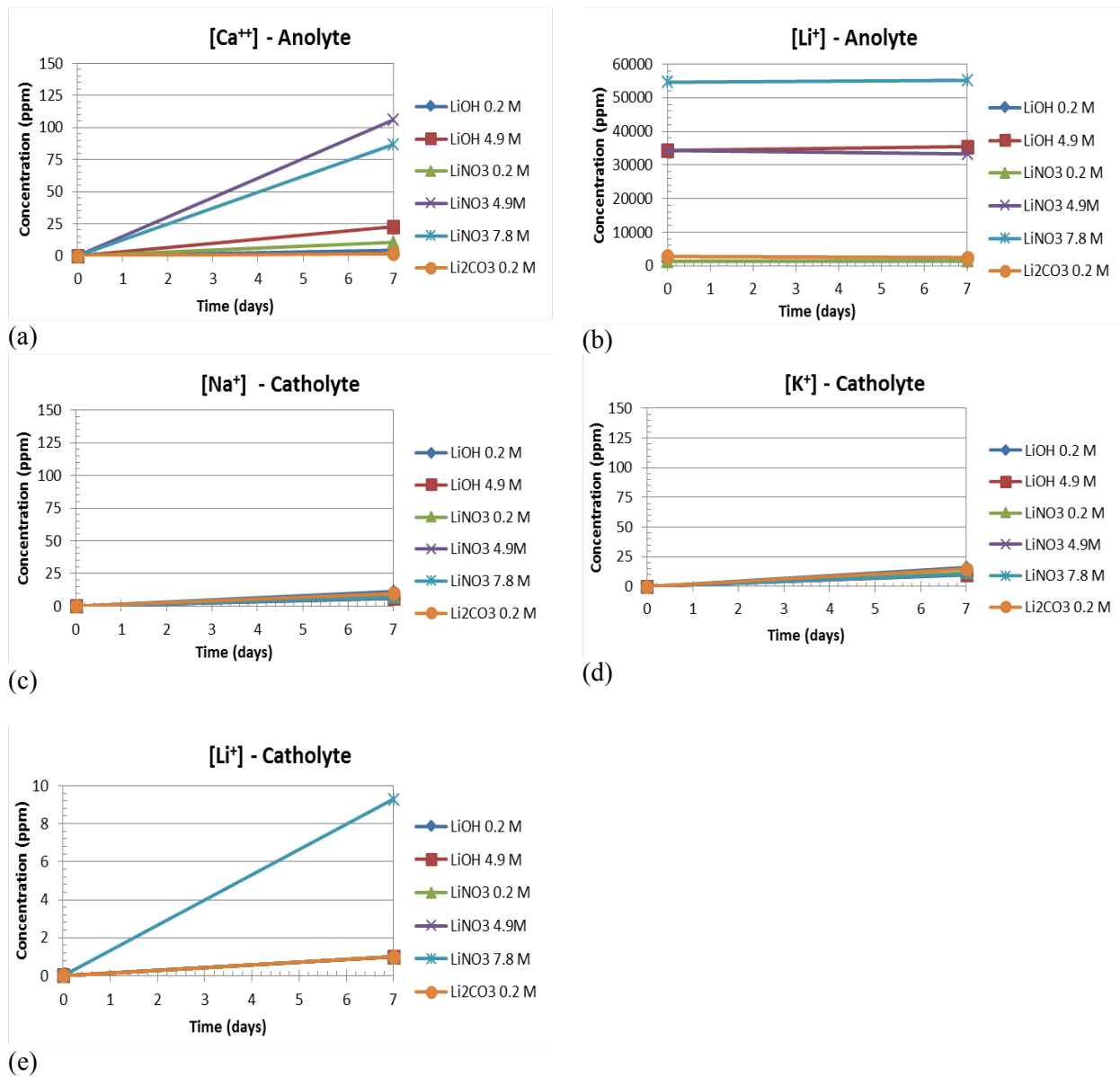


Figure 10 - Concentration in anolyte solutions of calcium (a) and lithium (b) and concentration in catholyte solutions of sodium (c), potassium (d) and lithium (e) during the diffusion experiment

CONCLUSION

According to the results of this study, using different lithium salt solutions (in terms of concentration and counter ion) as anolyte has a significant influence on the migration and diffusion process. That influence, nevertheless, is still not completely clear. In the migration experiments, the use of anolytes with higher lithium concentration resulted in higher charges that passed through the specimen. However, there is no clear relation between the anolyte concentration and the final concentrations of lithium, sodium, potassium and calcium in both chambers. That is also the case with the diffusion results.

This investigation is a work in progress. Other tests, such as obtaining lithium profile in the specimen, are still needed in order to obtain further understanding on the mechanism behind lithium migration.

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