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Effects of $LiNO_3$ on Alkali-Silica Reaction and Comparison with the Effects of Fly Ash on Reaction

Estudo dos Efeitos do $LiNO_3$ na Reação Álcali-Sílica e Comparação com os Efeitos da Cinza Volante na Reação

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Abstract

Lithium-based additives have shown satisfactory results in the expansion reduction due to alkali-silica reaction (ASR), but many doubts remain about the mechanisms of ASR. The study herein assessed the effects of a lithium nitrate based ($LiNO_3$) chemical addition, using several dosages, in order to understand its expansion mechanisms due to ASR. The study of the effects of $LiNO_3$ on ASR was conducted by the accelerated mortar bar method (ASTM C-1260), using two kinds of reactivate aggregates, consequently, the test lasted up to 30 days. Mortar bars were also molded with a fly ash (FA) based mineral addition to compare the effects of a mineral addition with a chemical one on the expansion due to ASR. The results from the ASTM C-1260 test indicated that the LiNO3 addition was effective in the expansion reduction, but presented different addition values for the acceptable threshold of 0.10% at 14 days for each kind of aggregate. It was also observed that mixtures containing $LiNO_3$ reduced the expansion up to 30 days, while for the mixtures containing fly ash the expansion continued to increase throughout the test. The test indicated that the dosages of lithium addition (Li_2O/Na_2O_{eq}), efficient in the expansion reduction for the acceptable threshold of 0.10% at 14 days, were very high when compared to those found in the literature. Folliard et al. (2003), states that the use of cement with a high alkali content (Na_2O_{eq} = 0.9 ± 1.0%) and the modification of the ASTM C-1260, would be the best solution to obtain lithium addition values compatible with field applications.

Keywords: alkali-aggregate reaction, expansion, lithium composed, mortar.

Resumo

Várias pesquisas realizadas com compostos a base de lítio tem mostrado resultados satisfatórios na redução da expansão associada à reação álcali-sílica (RAS), mas ainda existem muitas dúvidas sobre seus mecanismos de ação. A presente pesquisa avaliou os efeitos de uma adição química a base de nitrato de lítio ($LiNO_3$), utilizando várias dosagens, com o objetivo de entender seus mecanismos de ação sobre a expansão associada a RAS. O estudo dos efeitos do $LiNO_3$ na RAS foi feito pelo método acelerado das barras de argamassa (ASTM C-1260), utilizando dois tipos de agregado reativo, levando o ensaio até 30 dias. Foram moldadas também barras de argamassa com uma adição mineral a base de cinza volante com o objetivo de comparar os efeitos de uma adição mineral com uma química na expansão devido a RAS. Os resultados do ensaio da ASTM C-1260 indicaram que as adições de lítio foram efetivas na redução da expansão, mas apresentaram valores de adição diferentes para o limite aceitável de 0.10% aos 14 dias para cada tipo de agregado. Foi observado também que as misturas contendo $LiNO_3$ reduziram a expansão ao longo dos 30 dias, enquanto nas misturas contendo cinza volante a expansão continuou a aumentar ao longo do teste. O ensaio indicou que as dosagens de adição do lítio (Li_2O/Na_2O_{eq}) eficazes na redução da expansão foram muito elevado em relação aos encontrados na literatura, mostrando que segundo Folliard et al. (2003), o uso de cimento com elevado teor de álcalis (Na_2O_{eq} = 0.9 ± 1.0%) e a modificação da ASTM C-1260, seria a melhor solução para obter valores de adição de lítio compatíveis com o de uso em campo.

Palavras-chave: reação álcali-agregado, expansão, compostos de lítio, argamassa.

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1. Introduction

The Alkali-Silica Reaction (ASR) is a pathological phenomenon that occurs internally in concrete structures due to the chemical reaction between some mineralogical constituents contained in the aggregates and alkali hydroxides (mainly from cement and other sources, for example, mixing water, aggregates, pozzolans and external agents) released during the hydration process of Portland cement, which are dissolved in the concrete pore solutions. The reaction results in the formation of an expanding water-absorbing hygroscopic gel, which occupies the concrete pores, hence swelling in the presence of water. After filling the pores, the gel promotes the appearance of interstitial pressures that can cause cracks and shifts in the concrete structures, causing structural as well as operational problems. This reaction is the most prevalent type of Alkali-Aggregate Reaction (AAR) and this particular phenomenon has been widely examined and is better understood, since it usually occurs more rapidly, depending on the forms of reactive silica minerals involved. Conducting previous studies to understand the characteristics of the concrete materials used in a new construction can reduce the possibility of ASR, especially when measures are adopted to attenuate the favorable conditions for its occurrence, thus avoiding possible damage to the concrete structures. These measures can be divided into three: using cement with low alkali content, using non-reactive aggregates, and including chemical or mineral additions to the concrete. However, each of these measures is limited. For example, mineral additions such as silica, fly ash and pozzolans are already being used in many concrete constructions to prevent ASR, but not all mineral additions are equally effective and the amount of these additions to control ASR may not be acceptable for other reasons.
The need to find alternative means to prevent the damage caused by ASR and has led research studies to focus on the use of chemical additions. The chemical additions became another addition alternative to prevent ASR, as long as they do not affect the mechanical properties of concrete, also considering that this addition may be just delaying the reactive evolution.
McCoy and Caldwell [1] were the first to report that ASR expansion could be inhibited by some chemical additions. Since then, measures using chemical additions to inhibit ASR have increasingly received attention. This initial study and subsequent studies showed that certain chemical substances, such as lithium mixtures, can reduce the expansions caused by ASR. The lack of understanding the mechanism or mechanisms by which these chemical substances reduce the expansions and their effects on the properties of concrete is perhaps the greatest obstacle to the practical use of such chemical additions. Without understanding the control mechanism and its effects on the properties of concrete, it is difficult to predict the efficiency of a chemical addition, in order to predict its performance control or to recommend dosages (MONTEIRO and KURTIS [2]). Another obstacle to the practical use of chemical additions is associated to environmental factors, such as water projects, the most susceptible to this pathology, as there is a great risk of contaminating the water, fountain springs and soils.
Of all the studies using chemical additions, the most satisfactory results were those obtained using lithium compounds, due to its particular efficiency in reducing ASR expansion. Research has shown that all the lithium compounds studied, including LiF, LiCl, LiBr, LiOH, LiOHxH2O, LiNO3, LiNO2, Li2CO3, Li2SO4, Li2HPO4 and Li2SiO3 are effective in reducing expansions caused by ASR in concrete, provided they are used in appropriate dosages. Several mechanisms describing the effects of lithium-based compounds to reduce ASR-related expansion have been proposed, with studies such as those by Ramyar et al. [3], Feng et al. [4] and Schneider et al. [5] which showed that lithium alters the composition of the ASR gel, resulting in a product with little or no ability to absorb water and to expand. Compared with the other lithium-based compounds, the researchers believe that the lithium nitrate (LiNO3) represents the most promising one. The use of LiNO3, an entirely soluble neutral salt, does not generate a significant increase in the concentration of hydroxyl ions and thus reduces the risk of ASR acceleration, while improving its effects.
There are several studies using lithium-based compounds, but there are still many questions to be clarified as to its effect (MO [6]).
Despite the wide use of mineral additions in many projects, the availability of mineral additions that are effective in preventing ASR may be limited in certain regions and the demand may exceed the local source, and also not all of these additions are equally effective for this role and the amount for ASR control may not be acceptable for other reasons. Thus, it would be advantageous to use the lithium-based compounds in the prevention of ASR due to its easy accessibility and efficiency, as long as the amount is also acceptable due to other reasons.
This research contributes with the study of a LiNO3-based chemical addition in the expansion due to ASR, through the accelerated mortar bar method, observing its effects in reducing the expansion and compared to a mineral fly ash-based additive.

2. Materials and experimental program

2.1 Materials

The mortar bars were prepared with one type of cement and two types of reactive aggregates, in accordance with ASTM [7]. The lithium nitrate and the fly ash were used as additions in the mixtures. The cement used was the CPV-ARI-PLUS with an alkali content (%Na2Oeq) of 0.70%. The aggregates used had high reactivity according to the mortar bars' expansion test, in accordance with ASTM [7] and they are: basalt and gravel. Table [1] shows the chemical composition of the cement and fly ash. The lithium nitrate used was a commercial product with 95% purity.

2.2 Mixing characteristics of the mortar bars

The expansion tests were performed to analyze the behavior of the aggregates under potential reactivity, and to study the effects of LiNO3 in reducing the expansion of the mortar bars, in accordance with ASTM [7]. According to the test method, three mortar bars for each type of mixture were prepared. The dimensions of the bars were: 25mm x 25mm x 285mm, with a cement/aggregate ratio of 1:2.25 and water/cement ratio of 0.47 (mass).
The prisms remained cast for 24 hours in a suitable environment and after the mold was removed, they were fully immersed in water at a temperature of 80 oC for an additional 24-hour period. After this procedure, the reference length was determined and the prisms were kept in a sodium hydroxide (NaOH) solution at 1 N at 80 oC for 28 days. The readings of the length changes were periodically measured and the results were expressed in percentage

Table 1 – Chemical composition of cement and fly ash (wt, %)

Material	Composition (%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SiO_3	Na_2O	K_2O	Na_2O_{eq} (*)
Cement	18.97	4.80	2.52	59.17	5.30	3.53	0.13	0.87	0.70
Fly ash	44.26	21.73	13.15	2.22	0.23	0.19	-	-	0.48

(*) $\%Na_2O_{eq} = \%Na_2O + 0.658.\%K_2O$

of expansion, corresponding to the averages of three mortar bars for each type of addition.
For the tests, the control mortar bars, which did not contain the addition of LiNO3 ,were prepared and the bars containing various dosages of LiNO3, according to the molar concentration ratio of lithium oxide by the molar concentration of sodium oxide (Li/Nae) were used. The molar ratios used for the dosage of LiNO3 were as follows: Li/Naeq = 0.72, 0.79, 0.86, 0.93, 1.5, 3.0 and 4.5. Equation [1] was used to calculate the dosage of LiNO3, and Table [2] shows the amount of the mortar bars' component materials for each dose of the addition.

$$M = 2 . \frac{M_0}{M_{Na_2O}} . P_m . A_m . B_m . \frac{1}{n_O N_O} \quad (1)$$

Where M is the amount of LiNO3 to be added to the mixture (g), M0 is the molecular weight of LiNO3 (g/mol), MNa2O is the molecular weight of Na2O (g/mol), Pm is the amount of cement to be used in the preparation of the bars (g), Am is the molar ratio Li/Naeq required, Bm is the amount of Na2Oeq in the cement (%), n0 is the molar amount of Li per mixture mole and N0 is the pure percentage of Li in the mixture.
The required LiNO3 dosage was added to the mixing water, but if the lithium compound is in the form of an aqueous solution (solution with 30% of LiNO3), the amount of water in the solution should be removed from the mixing water in order to keep the same water/cement ratio required by the standard (FOLLIARD et al. [8]).
Mortar bars with a fly ash mineral-based addition were also prepared, in order to compare the expansive behavior of these ones with the mortar bars prepared with the LiNO3-based chemical addition. The replacement of fly ash by part of the cement in the mortar bars were prepared in different dosages for each aggregate and without using any additive, in order to obtain expansions of less than 0.10% at 14 days of testing: for basalt, 60% of cement and 40% of fly ash; and for gravel, 70% of cement and 30% of fly ash. Table [3] shows the amount of component materials in the mortar bars with the replacement of a part of the cement by fly ash for the aggregates used.

3. Results and discussions

3.1 Expansion of mortar bars with $LiNO_3$

The cement samples (bars) were prepared in order to observe the effects of LiNO3 on reducing the expansion due to ASR. Figures [1a] and [1b] show the expansion of the mortar bars prepared with LiNO3, compared to the expansion of the control mortar bars prepared without the addition of LiNO3 for the basalt and gravel, respectively. It is observed that for all dosages tested, the mortar bars showed reduced expansion for both types of aggregates. The first dosages with [Li/Nae] of 0.72 to 0.93 were used based on the literature referenced in this work, given that in the literature, these molar ratios were sufficient to reduce the expansion without

Table 2 – Components in the mortar bars with $LiNO_3$

Li/Na_{eq}	Cement (g)	Aggregate (g)	Na_2O (mol)	Addition of Li (g)	Water (g)
0.00	440	990	0.0113	0.00	206.8
0.72	440	990	0.0113	5.19	206.8
0.79	440	990	0.0113	5.70	206.8
0.86	440	990	0.0113	6.20	206.8
0.93	440	990	0.0113	6.71	206.8
1.50	440	990	0.0113	10.82	206.8
3.00	440	990	0.0113	21.65	206.8
4.50	440	990	0.0113	32.47	206.8

Table 3 – Components in the mortar bars with fly ash

Mixture	Absolute Density of Cement (g/cm³)	Absolute Density of Fly Ash (g/cm³)	Cement (g)	Fly Ash (g)	Aggregate (g)	Water (g)
Fly Ash (40%) Basalt	3.14	2.36	264	132.28	990	206.8
Fly Ash (30%) Gravel	3.14	2.36	308	99.21	990	206.8

exceeding the threshold (> 0.10%) at 14 days. For both types of aggregates these molar ratios reduced the expansion, but exceeded the threshold at 14 days, reaching high levels of expansion. According to Folliard et al. [8], for the test method ASTM [7] to be efficient in the lithium dosage, the cement used in the mortar bars must have Na2Oeq of 0.9 ± 1.0%, because the alkali content in the Portland cement is not currently specified in ASTM [7], since it was shown that the effects of alkalinity in the solution (1N NaOH) far exceed any effect of alkalinity on the cement when tested with reactive aggregates. Therefore, using a cement with low Na2Oeq ratio would result in a low content of lithium, which would be suppressed by the 1N NaOH solution. Also according to Folliard et al. [8], the lithium should be added to the immersion solution of the mortar bars in order to achieve the same molar ratio inside the bars (based on the alkalinity of the cement), this would prevent the lixiviation of lithium in the bars for the solution due to the concentration difference, avoiding high levels of lithium addition.

As the ASTM [7] test in this work used a cement with a low Na2Oeq ratio equal to 0.70% and lithium was not added to the immersion solution of the bars with the same molar ratio, the first molar ratios taken from the literature did not show the same effects on this study. Thus, the molar ratio [Li/Naeq] was increased until the expansion below the threshold of 14 days was achieved. Also with regards to the first molar ratios, there was a small difference in the expansion reduction with the ratio increase for both types of aggregates, and for the basalt, these ratios had a greater effect in reducing the expansion of the bars than for the gravel.

Increasing the molar ratio [Li/Naeq] to 1.50, there was a greater reduction in the expansion of the bars for both aggregate types, given that the lithium effect on reduction was greater for the basalt. Despite the expansion reduction of the mortar bars, this ratio exceeded the expansion threshold at 14 days.

For a molar ratio [Li/Naeq] of 3.00, there was a great expansion reduction of the bars for both types of aggregates. Despite the bars demonstrating the same reaction with the increased molar ratio for both types of aggregates, only the bars cast with the basalt reduced the expansion to the acceptable threshold at 14 days, while the bars containing the gravel exceeded this threshold.

By raising the molar ratio [Li/Naeq] to the same proportion (from 1.50 to 3.00 and then to 4.50), the mortar bars showed different expansion reduction reactions for both types of aggregates. The gravel bars exhibited reduced expansion within the acceptable threshold at 14 days, however the bars with basalt, with an increase in the molar ratio value, there was no expansion effect with regards to [Li/Naeq] equal to 3.00; but still kept the expansion within the acceptable threshold at 14 days.

Figure 1a – Expansion of mortar bars (basalt) over time with/without $LiNO_3$

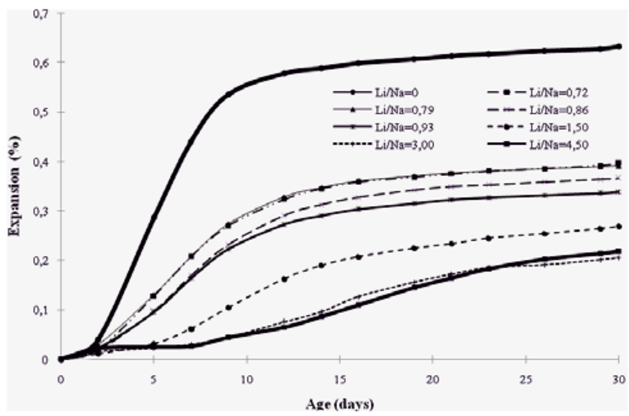
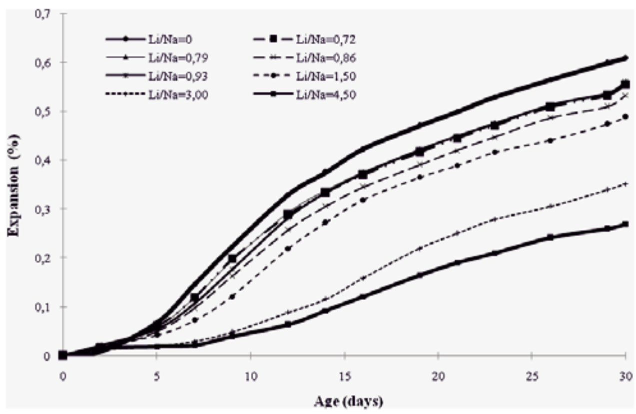


Figure 1b – Expansion of mortar bars (gravel) over time with/without $LiNO_3$



Another observation to be made is that increasing the molar ratio [Li/Naeq] at a proportion of 1.50 (1.50 to 4.50), the mortar bars showed different expansion behaviors. With the increase of [Li/Naeq] from 1.50 to 3.00, there was a significant reduction in the expansion of the bars for both types of aggregates; however with the increase [Li/Naeq] of 3.00 to 4.50, this reduction was smaller.

The bars containing gravel showed greater expansion reductions with the increase in the same proportions of the molar ratio [Li/Naeq], however for the bars cast with basalt, this reduction was smaller, given that for the molar ratio of 3.00 to 4.50, the lithium increase had no reducing effect. This decrease in the expansion reduction intensity of the bars with the increased lithium amount may be due to the existence of an addition limit in which the lithium no longer has a reduction effect on the increase, as shown by Collins et al. [9].

It was also observed that although both types of aggregates exhibit similar reactions with the molar ratio increase [Li/Naeq], the intensity in the expansion reduction was different. This shows that each type of aggregate requires a different amount of addition to reduce the expansion to acceptable thresholds, in accordance with the standard. According to Hasparyk [10], the reactivity of the aggregate governs the efficiency of the addition in reducing the silica solubility, thus the optimal concentration of additions to be used vary.

3.2 Comparison of the effects of $LiNO_3$ with fly ash on alkali-silica reaction

The mortar bars were prepared with fly ash to compare the LiNO3 effects to fly ash expansion due to ASR. Figures [2nd] and [2b] show the expansion of mortar bars prepared with/without LiNO3 and with the addition of fly ash, for the basalt and gravel, respectively. There was a different behavior between the expansion curves of the bars with the addition of LiNO3 and fly ash. The expansion curves of the bars with LiNO3 tend to follow the development of the control bar curve without LiNO3 for both types of aggregates; on the other hand, the expansion curves of the fly ash exhibit a more rectilinear expansion development for both types of aggregates. However, it can be observed, especially in the expansion curves of the basalt bars, that LiNO3 tends to stabilize the reaction throughout the test, while the bars with fly ash continue to expand throughout the test. Ramyar et al. [11] compared the expansion effects of the mortar bars cast with the addition of lithium and fly ash through ASTM [7], taking the test up to 56 days, which demonstrated that the bars containing lithium ceased expansion at 28 days of testing, while in mixtures containing fly ash, the reactions continued, increasing the expansion throughout the 56 days of testing.

The difference in the added amount of fly ash to reduce the expansion to the acceptable threshold of 14 days for both aggregates is due to the reactivity difference of the aggregates, as explained at the end of item 3.1.

4. Conclusions

With the materials used and the test method applied in this study, the following conclusions can be drawn:

- **1.** The expansions are reduced by increasing the addition of $LiNO_{3;}$
- **2.** The test method, in accordance with ASTM [7], should be modified, keeping the same molar ratio [Li/Na_e] inside the bars with the immersion solution and the cement with Na_2O_{eq} content between 0.9 ± 1.0 should be used to obtain lithium addition values compatible with those used in the field;
- **3.** There may be a threshold value for the addition of lithium, in which there is no more increase in the expansion reduction;
- **4.** The lithium additions tend to stabilize the expansion over time, while in the fly ash additions the expansion continues to increase over time;
- **5.** The addition amount of lithium and fly ash to reduce the expansion to acceptable threshold values, in accordance with the standard, vary depending on the reactivity of the aggregate used.

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Figure 2a – Expansion of mortar bars (basalt) over time with/without $LiNO_3$ and fly ash

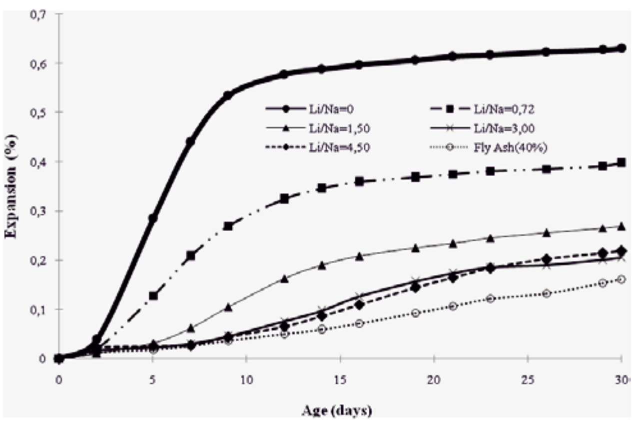
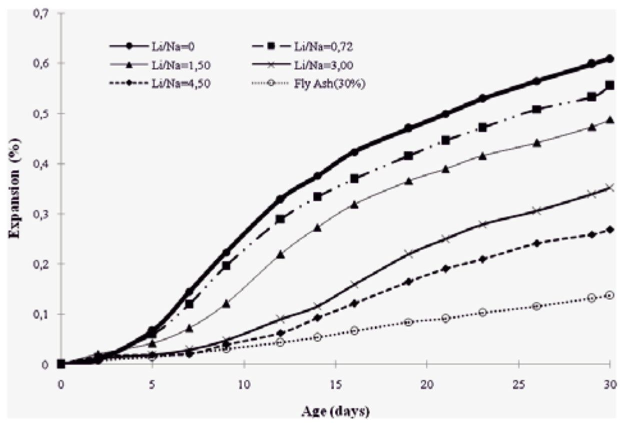


Figure 2b – Expansion of mortar bars (gravel) over time with/without $LiNO_3$ and fly ash



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