# EXPERIMENTAL INVESTIGATION OF THE MECHANISMS BY WHICH LINO<sub>3</sub> IS EFFECTIVE AGAINST ASR

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#### Abstract

Various series of experiments on concretes, cement pastes, reactive aggregates, and a variety of silica and glass materials have been performed with the objective to determine which mechanism among those proposed in the literature better explain the effectiveness of LiNO<sub>3</sub> against ASR. The principal conclusions are the following: (1), the amount of amorphous reaction gel found in the Libearing concretes, the only product observed and which has the typical textural characteristics of classical ASR gel, is proportional to concrete expansion, thus is likely expansive while containing lithium in significant proportions; (2), the formation of Li-Si products in contact with the reactive phases which could eventually act as a physical barrier against silica dissolution was not observed, except for samples subjected to very high temperatures and pressure conditions (e.g. in the autoclave) or at relatively lower temperature for very particular materials (e.g. obsidian), and (3), the most likely mechanism explaining the effectiveness of LiNO<sub>3</sub> against ASR is a reduction in the dissolution of reactive silica.

Keywords: alkali-silica reaction, lithium nitrate, pore solution, reaction mechanisms, silica dissolution

# 1 INTRODUCTION

Many studies showed that various lithium salts can reduce ASR expansion in concrete when used in sufficient amounts.  $LiNO_3$  proved to be one of the most effective salts. However, its effectiveness varies with the concrete alkali content and the type of reactive aggregate to counteract, irrespective of its degree of expansivity (in control concrete) and its petrographic nature [1, 2]; actually, the mechanisms involved are still not well understood. As discussed by Tremblay et al. [3] in more details and according to the literature, different mechanisms can be proposed to explain the beneficial effect of  $LiNO_3$  against ASR, which can be grouped in two main categories:

- Silica dissolution is significantly reduced or suppressed:
- (a) due to a pH decrease in the concrete pore solution;
- (b) due to some other change(s) in the chemistry of the concrete pore solution, or

(c) due to the early formation, at the surface of or somehow surrounding the reactive silica, of a Li-Si reaction product, crystalline or amorphous, which acts as a physical barrier against further reaction.

• <u>Silica dissolution is almost unchanged or remains significant, but the concrete expansion is significantly reduced or suppressed</u>:

(d) due to the formation of a crystalline and non-expansive Li-Si reaction product;

(e) due to the formation of a Li-Si amorphous reaction product (i.e. gel) which is, however, non-expansive or much less-expansive than the classical expansive ASR gel, or

(f) due to limited polymerization of the dissolved silica, which thus mostly remains in solution without forming an expansive gel.

A number of experiments were carried out either on concretes specimens, cement paste samples, reactive aggregates, and a variety of silica/glass materials immersed in control or lithiumbearing solutions. The results of those experiments are summarized and analysed hereafter in view of determining the most probable mechanisms explaining the beneficial effect of lithium-based admixtures in controlling expansion due to ASR. A better understanding of such mechanisms would greatly help in making decisions regarding the use of LiNO<sub>3</sub> in concrete incorporating ASR-susceptible aggregates.

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## 2 MATERIALS AND METHODS

# 2.1 Pore solution chemistry of cement paste and concrete specimens

As detailed elsewhere, cement paste cylinders [4] and concrete prisms [2] were made with or without LiNO<sub>3</sub>, using a [Li]/[Na+K] of 0 (controls) or 0.74, and different alkali contents. Various reactive and non-reactive aggregates were used for making the concretes. All specimens were stored above water at various temperatures (23, 38, and 60°C for cement pastes; 38 and 60°C for concretes). At different times, their pore solution was expressed under high pressure (1000 MPa for cement pastes; 1400 MPa for concretes) and analyzed for Na, K, Li, and Si, using ICP (Inductively Coupled Plasma). The [OH<sup>-</sup>] was also determined by titration, and the pH values were calculated accordingly.

## 2.2 Visual examination and microanalysis of concrete specimens

# Visual and SEM examinations

At different times/expansions, the concretes were visually examined under the stereomicroscope. Fragments of several concretes incorporating different reactive aggregates and containing  $LiNO_3$  or not, were then examined under the scanning electron microscope (SEM).

# Visual examination under ultraviolet light after uranyl acetate treatment

After 2 years at 38°C or 6 months at 60°C, a large number (42) of concrete prisms were broken perpendicular to their length in order to obtain a quite even broken surface which was then submitted to the uranyl acetate test, following AASHTO procedure T 299-93 [5].

## SIMS microanalysis

After 2 years at 38°C, polished sections of two non-expanding concretes were analyzed using a Micro-SIMS (Secondary Ion Mass Spectrometer equipped with a microbeam), for assessing the spatial distribution of lithium in concrete. These two concretes, both containing  $LiNO_3$  at a [Li]/[Na+K] of 0.74, were made with a non-reactive limestone and a reactive rhyolite, respectively.

## 2.3 Composites of aggregate particles and cement paste in NaOH+LiNO<sub>3</sub> solutions

Aggregate particles polished, embedded in cement paste, with the composites immersed in NaOH+LiNO<sub>3</sub> at  $80^{\circ}C$ 

Particles from one glassy highly-reactive volcanic rock (obsidian), one highly-reactive aggregate (rhyolite), and one moderately-reactive aggregate (granitic rock), 10/14 mm in size, were sawed and polished on one face, then embedded in cement paste containing LiNO<sub>3</sub> at a [Li]/[Na+K] of 0.74. These composite specimens were then immersed at 80°C in a 1N NaOH + 0.74N LiNO<sub>3</sub> ([Li]/[Na] = 0.74) solution. After 28 days, the specimens were broken along the original polished aggregate interface which was treated with a 10% HCl solution to remove the residual cement paste adhering to the surface. The products from ASR or from reaction(s) incorporating lithium, if present, are considered not affected by this treatment. Both the aggregate polished surface and the cement paste surface in immediate contact were analyzed by X-ray diffraction (XRD) and observed under the SEM.

# Composites of aggregates and cement paste, sawed, polished, and immersed in NaOH and NaOH+LiNO3 at 80°C

Sections were sawed in prisms, 75 by 75 by 300 mm in size, made of cement paste and 10/14 mm particles of three reactive aggregates (rhyolite, Spratt limestone, and greywacke). The sections were polished on one (sawed) face, immersed in 1N NaOH (control) or 1N NaOH + 0.74N LiNO<sub>3</sub> ([Li]/[Na] = 0.74) solutions at 80°C, periodically examined, and analyzed under the SEM after 28 days.

# 2.4 Aggregate particles immersed in Li solutions

## Polished aggregate particles immersed in LiOH for one hour at 350°C (in autoclave) or 6 months at 80°C (obsidian)

Particles of obsidian, 4 highly-reactive aggregates (greywacke, rhyolite, Spratt limestone, and clayey limestone), 3 moderately-reactive aggregates (granitic rock, dolostone, and chloritic schist), and one non-reactive aggregate (pure limestone), were sawed, polished on one (sawed) face, and immersed for one hour in a 1N LiOH solution in the autoclave at 300 psi (350°C). In addition, one obsidian particle was immersed for 6 months in a 1N LiOH solution at 80°C. The polished surfaces were analyzed by XRD before and after immersion, with the obsidian particle immersed for 6 months in 1N LiOH at 80°C also observed under the SEM.

## Polished aggregate particles immersed for 28 days in NaOH+LiNO<sub>3</sub> at 80°C

Polished particles of the same aggregates were immersed for 28 days in a 1N NaOH + 0.74N LiNO<sub>3</sub> ([Li]/[Na] = 0.74) solution at 80°C. The polished surfaces were analyzed by XRD before and after immersion.

#### Aggregate powders (150-300 $\mu$ m) immersed for 28 days in various Li solutions at 60°C

Three reactive aggregates (rhyolite, Spratt limestone, chloritic schist) and obsidian were finely ground. 20-g samples of 150-300  $\mu$ m particles were immersed for 28 days in 40 ml of the following solutions at 60°C: (1), 0.38N NaOH + 0.30N KOH (control); (2), 1N LiOH; (3), 0.8N (Na,K)OH + 0.28N LiNO<sub>3</sub> ([Li]/[Na+K] = 0.35), and (4), 0.8N (Na,K)OH + 0.59N LiNO<sub>3</sub> ([Li]/[Na]+[K] = 0.74). The test containers were shaken manually for one minute every day for the first 5 days, then every 3 days until 28 days. After 1, 3, 7, and 28 days, the solutions were sampled (one mL) and chemically analysed for Na, K, and Li, by ICP.

#### Dissolution of silica, silicate, and aggregate particles immersed for 28 days in various Li solutions at 80°C

Particles of various reactive and non-reactive materials (see Table 3) were immersed for 28 days in the above four solutions at 80°C. Opal and chalcedony particles were also immersed in 1N NaOH with various concentrations of LiNO<sub>3</sub> (i.e. 0.1, 0.2, and 0.3N for chalcedony; 0.75 and 1.0N for opal), with a few particles also transferred in the 1N NaOH control solution after 28 days in a 1N NaOH + 0.5N (chalcedony) or 1.0N (opal) LiNO<sub>3</sub>. Only one particle, weighing 1.0 g  $\pm$  0.1, was tested per container with 200 ml of solution, supported on a plastic grid. After cleaning its surface with distilled water and drying for 3 hours at 80°C, its mass was periodically measured up to a maximum of 28 days, depending on the test solution used and the kinetics of dissolution, with a precision of 0.0001 g. XRD was performed after the tests on reacted particles of opal and chalcedony.

# 3 RESULTS

# 3.1 Pore solution chemistry of cement paste and concrete specimens

The main conclusions drawn from the chemical analysis of the pore solution of the cement pastes and concretes (details given in Bérubé et al. [4] and Tremblay et al. [2]) are the following:

- For all mixtures incorporating LiNO<sub>3</sub>, the [Li]/[Na+K] in solution ranged between 0.30 and 0.45, which is about half of the original (mixture) ratio of 0.74. In fact, Li ions are incorporated in greater proportion than Na and K ions into the cement hydrates [4]. Consequently, the [Na+K] significantly increased in the presence of LiNO<sub>3</sub>, while the pH decreased just by about 0.1. Nevertheless, the expansion due to ASR was largely reduced in the corresponding concretes [2].
- In the presence of LiNO<sub>3</sub>, after cement hydration was mostly completed, the [Li] and [Li]/[Na+K] in the pore solution were quite stable in the absence of reactive aggregates (i.e. for pure cement pastes and non-expansive concretes made with non-reactive aggregates). However, in the presence of reactive aggregates, the higher the concrete expansion and the related amount of reaction products observed (see Section 3.2), the higher was the decreases in the [Li] and [Li]/[Na+K]. This suggests that: (1), Li ions are incorporated within some reaction products, amorphous (gel) or crystalline in nature; (2), Li ions are progressively and more rapidly incorporated within these products than Na and K ions, and (3), a certain amount of expansive gel is formed due to ASR, which likely contain Li.
- In the presence of LiNO3 or not, silicium in solution is always close to the detection limit.

#### 3.2 Visual examination and microanalysis of concrete specimens

#### Visual examination and scanning electron microscopy

Characteristic reaction products from ASR (siliceous gel and microcrystalline products) were observed visually and under the SEM in the control concretes showing high expansion. On the other hand, only traces of amorphous gel containing Si, Ca, Na, and K, and possibly also Li (this element is too light to be detected with the SEM) were observed in the Li-bearing concretes without any noticeable difference in morphology and chemical composition with respect to classical ASR gel. Moreover, no other type of reaction product was observed at the surface of the reactive aggregate particles (as a protective coating) or elsewhere in the cement paste. These observations apply, whatever the reactive aggregate that was used in concrete and the effectiveness of LiNO<sub>3</sub>.

## Visual examination under ultraviolet light after uranyl acetate treatment

The amounts of alkali-bearing gel observed under ultraviolet light on the broken concrete sections after the application of uranyl acetate was proportional to concrete expansion (due to ASR), whatever the reactive aggregate in concrete. For all concretes made with LiNO<sub>3</sub> and showing no or limited expansion, no or only traces of gel were observed.

#### SIMS microanalysis

The micro-SIMS analyses showed that lithium was everywhere within the cement paste of the two concretes tested, containing reactive aggregates or not, without any local concentrations (Figure 1). It is likely that lithium precipitated from the pore solution when specimens were dried for analysis, and that Li-bearing reaction products were not present in the concretes, even the one made with the highly-reactive rhyolite and for which LiNO<sub>3</sub> was very effective in controlling expansion in concrete due to ASR [2].

# 3.3 Composites of aggregate particles and cement paste in NaOH+LiNO<sub>3</sub> solutions

Aggregate particles polished, embedded in cement paste, with the composites immersed in NaOH+LiNO3 at 80°C

Reaction products (crystalline or amorphous) were not detected by XRD neither observed by SEM on the polished surface of the reactive aggregate particles tested nor on the surface of the cement paste which was in immediate contact with these polished aggregate surfaces during immersion.

#### Composites of aggregates and cement paste, sawed, polished, and immersed in NaOH and NaOH+LiNO; at 80°C

Typical ASR gel was observed on the exposed polished surfaces of all reactive aggregate particles for the test specimens immersed in the NaOH control solution. However, reaction products (crystalline or amorphous) were not observed for specimens immersed in the LiNO<sub>3</sub>-bearing solution.

## 3.4 Aggregate particles immersed in Li solutions

# Polished aggregate particles immersed for one hour in 1N LiOH at 350°C (in the autoclave)

After autoclaving, a well-crystallized Li-silicate, Li<sub>2</sub>SiO<sub>3</sub>, was detected in significant amounts by XRD on the polished surfaces of obsidian and the three reactive aggregates tested for which LiNO<sub>3</sub> proved to be effective in concrete (i.e. rhyolite, dolostone, and granitic rock, using a [Li]/[Na+K] < 0.74; [2]). It was also detected, however just in traces, on the surface of one (i.e. clayey limestone) of the 4 other reactive aggregates tested, for which a greater LiNO<sub>3</sub> ratio was needed in concrete (i.e. [Li]/[Na+K] > 0.93 or more; [2]), while not detected for the three other aggregates (Spratt limestone, greywacke, chloritic schist). Secondary portlandite was also detected after autoclaving on the surface of all aggregates containing calcite in large amounts (Spratt limestone, clayey limestone, chloritic schist, and the non-reactive pure limestone). More information in this respect can be found in [3].

### Obsidian particle immersed for 6 months in 1N LiOH at 80°C

After the immersion test, the obsidian was covered with a layer of Li<sub>2</sub>SiO<sub>3</sub> (Figure 2), identified by XRD. A finely-dispersed whitish product, which could be crystalline or amorphous (not analyzed by XRD), also precipitated at the bottom of the test containers.

## Polished aggregate particles immersed for 28 days in 1N NaOH+0.74N LiNO<sub>3</sub> at 80°C

Surprisingly, for each of the 8 aggregates tested, the XRD results were exactly the same before and after the immersion test, no crystalline Li-product being detected on the polished surfaces.

## Aggregate powders (150-300 $\mu m$ ) in (Na,K)OH (control), LiOH, and (Na,K)OH+LiNO<sub>3</sub> at 60°C for 28 days

The [K] and [Na] in the (Na,K)OH control solution were quite constant for all 4 materials tested (Figure 3A). Figure 3B shows that the [Li] in the LiOH solution decreased for each material, more rapidly for obsidian. As illustrated in Figures 3C and 3D for rhyolite, for each material, the [Na] and [K] in the (Na,K)OH+LiNO<sub>3</sub> solutions were quite stable over time, while the [Li] significantly decreased, more rapidly in the solution with more LiNO<sub>3</sub> (Figure 3C vs. 3D). This is in good agreement with the results from concrete pore solution chemistry (Section 3.1) where Li ions were consumed more rapidly than Na and K ions. The consumption of Li after 28 days is given in Table 1. The results clearly suggest that a Li-bearing reaction product is formed. A finely-dispersed whitish product was effectively always observed in the test containers (in the presence of lithium). The largest quantity was obtained for the obsidian immersed in the LiOH solution and also corresponds to the largest Li decrease in solution (~83% after 28 days; Table 1). This whitish product was not chemically analyzed neither analyzed with the SEM or by XRD; it could thus be crystalline or amorphous but it likely contains, in addition to Li, Si in significant amounts, and some Na and K as well.

# Dissolution of silica, silicate, and aggregate particles in NaOH, LiOH, and NaOH+LiNO3 at 80°C for 28 days

In absence of Li, all reactive materials tested presented significant mass losses (Table 2). The extremely-reactive opal and the three highly-reactive cryptocrystalline varieties of quartz (chalcedony, red chert, green chert) were completely dissolved after 1, 11, 15, and 15 days, respectively. For all materials tested, this dissolution occurred without the formation of any reaction product, thus suggesting that the dissolved silica remained in solution. However, when the percentage of dissolution

was important in the absence of lithium, a translucent colloidal material, likely a silica gel, was generally observed in the test solution.

On the other hand, the presence of lithium in solution reduced the dissolution of all reactive materials tested (except obsidian), often dramatically, in fact for most reactive aggregates tested and the three varieties of cryptocrystalline quartz. A finely-dispersed whitish product, amorphous according to XRD and likely containing Li and Si, was always observed in the test containers, in the presence of lithium, unless no dissolution at all; and the higher the dissolution, the more abundant this product.

For chalcedony, a [Li]/[Na] of 0.2 (i.e. a 1N NaOH + 0.2N LiNO<sub>3</sub> solution) decreased the dissolution from 100% (control) to 11% after 28 days, and a ratio of 0.3 was almost sufficient to prevent any dissolution (Figure 4A); this value of 0.3 is close to the [Li]/[Na+K] in the pore solution of a concrete made with a design ratio of 0.74 [2]. A very thin coating of crystalline Li<sub>2</sub>SiO<sub>3</sub> was detected by XRD on the chalcedony surface when lithium was sufficient to prevent dissolution [3].

It was more difficult to prevent dissolution in the case of opal, by far the most reactive material tested. In NaOH + 0.25N LiNO<sub>3</sub> ([Li]/[Na+K] = 0.25) the opal grain completely dissolved after 2 days (Figure 4B), but the finely-dispersed whitish product mentioned above was now observed in significant amounts at the bottom of the test containers. In NaOH +  $0.5N \text{ LiNO}_3$  ([Li]/[Na+K] = 0.50), the mass of the particle tested decreased by about 70% after 3 days, then remained constant afterwards, and the finely-dispersed whitish reaction product was also observed in relatively small amounts. In fact, the opal completely dissolved again but a visible compact layer of reaction product deposited around the reacting particle. This product is also amorphous based on XRD. The opal thus completely dissolved after about 3 days, then leaving a particle essentially made of an empty shell of amorphous reaction product weighing about 30% of the original mass. The same observations were made in NaOH + 0.75N LiNO<sub>3</sub> ([Li]/[Na]+[K] = 0.75) except that: (1), the opal completely dissolved after about 7 days, (2), leaving a residual empty shell of reaction product corresponding to about 55% of the initial mass, and (3), the amount of finely-dispersed whitish product was still small. In NaOH +  $1.0N \text{ LiNO}_3$  solution ([Li]/[Na+K] = 1.0), amass gain of over 60% was rather observed. In this particular case, the finely-dispersed whitish product was absent; the opal again dissolved completely but the totality of the dissolved silica precipitated in the reaction shell. The 60% increase in mass is explained by the fact that this shell is composed of a hydrous and hydrated material which, in addition to the totality of the silica from the reacted opal, incorporated other substances from the solution (e.g. lithium, OH radicals, water molecules, and possibly also some NO3). It is thus obvious that the layer of reaction product around the particles did not protect the underlying opal against dissolution. The opal thus behaved very differently from chalcedony and most other reactive materials tested (except obsidian). The presence of lithium did not reduce opal dissolution, but all the silica dissolved was more or less rapidly incorporated into amorphous Li-Si reaction products (surrounding shell and finely-dispersed whitish product), depending upon the lithium concentration. The higher this concentration, the lower the mobility of the silica dissolved, the higher the amount of reaction product formed close to the reaction site (e.g. in the shell), and the lower the amount of finelydispersed whitish product in the test solution.

Obsidian, a totally amorphous volcanic glass, also performed quite differently from most other reactive materials tested. As for opal, lithium does not seem to reduce dissolution (Table 2), which, however, never exceeded 10%, and no crystalline product was detected on its surface by XRD. However, a finely-dispersed whitish product was observed at the bottom of the test containers in presence of lithium (rather than the above colloidal suspension in the NaOH control solution).

## 4 DISCUSSION

The above test results have to be analyzed in terms of degree of agreement with the various mechanisms proposed to explain the effectiveness of LiNO<sub>3</sub> against ASR. Accordingly, for each test series (no. 1 to 4.4 in Table 3), each mechanism (no. A to F in Table 3) is considered "likely" (green boxes in Table 3), "possible" (blue), "non-conclusive" (grey), "unlikely" (orange), or "impossible" (red), based on the results obtained and the reasons summarized in Table 3 and detailed in [3].

It must be emphasized that the most conclusive experiments are those performed on concrete specimens stored in humid air at relatively low temperatures (38 and 60°C) and incorporating natural reactive aggregates (test series 1 and 2 in Table 3), followed by the tests on composite specimens made of reactive aggregate particles and cement paste and immersed in NaOH+LiNO<sub>3</sub> at 80°C (series 3). For their part, the test series 4.1 to 4.4 (Table 3) are all performed in the absence of cement paste and at relatively high temperatures (60, 80, or 350°C); the corresponding results must thus be used with caution, particularly those obtained at 350°C, in LiOH solution, and/or for extremely- to highly-

reactive materials such as opal, fused silica, chalcedony, chert, and obsidian. Such materials are uncommon in real concretes, at least in significant amounts, while they often performed very differently in some test series with respect to natural reactive aggregates tested in parallel.

With the attempt to quantify, to some extent, the results obtained and the evaluation made, numerical indices of +6, +3, 0, -6, or -10 have been attributed for each test series (1 to 4.4) with respect to each proposed mechanism (A to F), when this mechanism is considered "likely", "possible", "non-conclusive", "unlikely", or "impossible", respectively. For each test series, these indices were then multiplied by a weighing factor depending upon the realism of the tests performed with respect to the real life (i.e. concrete, natural reactive aggregates, etc.), as just discussed. The weighing factors used are 4 for series 1 and 2 (concretes made with natural aggregates), 3 for series 3 (specimens made of cement paste and natural aggregate particles), 2 for series 4.2, 4.3, and 4.4 (no cement paste but immersion at least in LiNO<sub>3</sub> solutions at 60 or 80°C), and 1 for series 4.1 (immersion in LiOH and at 350°C in most cases). For each mechanism, the summation of the individual indices attributed to each test series multiplied by their corresponding weighing factor has been calculated; the values obtained are: -40 (impossible), +45 (likely), -33 (unlikely), -39 (unlikely), -6 (possible), and -40 (impossible), respectively for mechanisms A to F (Table 3).

Mechanism no. B (+45), i.e. reduction/suppression of silica dissolution, is by far the most likely mechanism explaining the effectiveness of LiNO<sub>3</sub> against ASR. Mechanisms nos. A (-40) and F (-40) are considered impossible, based on concrete pore solution chemistry (series 1). Mechanisms nos. C (-33; disproved by 3 test series while not supported by any other) and D (-39; disproved by 4 test series while supported by only one), are unlikely. Mechanism no. E (-6; disproved by two test series while supported by two other) remains possible; however, it is disproved based on the examination of concrete specimens (series 2), which rather suggests that the only reaction product formed, when lithium is not highly effective, contains lithium, looks like classical ASR gel, and is expansive as well.

# 5 CONCLUSIONS

Various series of experiments were performed in this study to determine the most likely mechanism(s) by which LiNO<sub>3</sub> is effective against ASR. The principal conclusions are the following:

- One mechanism proposed is that lithium limits the polymerization of the dissolved reacted silica, thus the formation of an expansive gel. This mechanism appeared impossible since silica was found to be almost absent in the pore solution of all concretes tested, containing LiNO<sub>3</sub> or not.
- The early formation of a Li-Si product over the reactive silica which could act as a physical barrier against further reaction was not observed except at very high temperature and pressure (i.e. in the autoclave) or at relatively lower temperature for some very particular materials (e.g. obsidian).
- The reduction/suppression of silica dissolution is by far the most likely mechanism explaining the effectiveness of LiNO<sub>3</sub> against ASR, and the variations in this effectiveness as well. This mechanism is strongly supported by the facts that:
  - an amorphous gel containing Na, K, and Si, and likely also Li, was the only type of reaction product observed in concrete specimens incorporating LiNO<sub>3</sub> and a variety of reactive aggregates;
  - this gel was looking exactly like the classical ASR gel and its abundance was about proportional to the concrete expansion attained;
  - all reactive aggregates tested dissolved much less in LiNO3-bearing than in control solutions.
- Results from pore solution chemistry proved that pH is not significantly reduced in the LiNO<sub>3</sub>bearing concretes tested with respect to control specimens, such that pH reduction cannot explain a reduction/suppression in the silica dissolution.
- It remains to determine for which chemical reason the presence of lithium in the concrete pore solution can reduce/suppress the dissolution of the reactive silica and how this phenomenon can be affected by the particular reactive aggregate to counteract, irrespective of its inherent degree of expansivity (in control concretes) and its petrographic nature.
- Some of the most reactive materials tested, e.g. opal and obsidian, which are rarely present in significant amounts in concrete aggregates, often behave quite differently from the natural reactive aggregates tested in parallel. This arises the importance of testing natural reactive aggregates.

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Aggregates	Li consumed (wt%)			
	1N NaOH + 0.35N LiNO <sub>3</sub>	1N NaOH + 0.74N LiNO <sub>3</sub>	1N LiOH	
Spratt limestone	36.4	74.9	56.3	
Rhyolite	26.3	48.9	53.8	
Chloritic schist	31.7	47.7	54.3	
Obsidian	30.5	29.2	82.5	

TABLE 1: Percentage of Li consumed after 28 days in the test solution when aggregate powders (150-300  $\mu m$ ) were immersed in various Li solutions at 60°C.

TABLE 2: Mass variation (in wt%) of various aggregates,	varieties of silica,
and silicate glass after 28 days in various Li sol	utions.

Materials	1N NaOH	1N NaOH +	1N NaOH +	1N LIOH					
([Li]/[Na+K] effective ratio <sup>1</sup> )	(no Li)	0.25N LiNO3	0.5N LiNO3	III LIOII					
Reactive and non-reactive aggregates									
Pure limestone (non-reactive)	-0.1	not tested	not tested	0.0					
Spratt limestone (1.04)	-4.4	-0.9	-0.6	-0.1					
Rhyolite (<0.74)	-7.8	-1.3	-0.9	-2.3					
Clayey limestone (>1.11)	-2.2	-0.9	-0.4	-0.1					
Greywacke (>1.11)	-8.5	-0.9	-0.4	-1.0					
Granitic rock (0.56)	-7.8	-1.3	-0.8	-1.8					
Chloritic schist (>0.93)	-4.7	-0.1	+0.8	-0.1					
Dolostone (<0.74)	-1.1	-0.8	-0.4	-0.8					
Quartz sandstone	-4.8	-0.7	+0.3	-1.2					
Quartzite (non-reactive)	-0.4	not tested	not tested	-0.4					
Reactive and non-reactive varieties of silica									
Quartz (non-reactive) <sup>2</sup>	-0.1	not tested	-0.1	0.0					
Opal (amorphous silica)	-100.0	-100.0	-71.5	$+9.4^{4}$					
Chalcedony <sup>3</sup>	-100.0	-6.3	-0.15	$0.0^{5}$					
Red chert <sup>3</sup>	-100.0	not tested +1.9		not tested					
Green chert <sup>3</sup>	-100.0	not tested	-1.9	not tested					
Fused silica (synthetic)	-13.7	not tested	$+4.4^{4}$	-3.6					
Silicate glass									
Obsidian (volcanic glass)	-7.8	not tested	-7.04	-10.2					

<sup>1</sup>Based on concrete prism tests

<sup>2</sup> Fragment from a coarse crystal

<sup>3</sup>Cryptocrystalline quartz

<sup>4</sup>Li-silicate not observed on the particle <sup>5</sup>Li-silicate observed on the particle

	Agreement between the test results an silica dissolution reduced/			nd the following mechanism proposed <sup>1</sup> : silica dissolution takes place but			
	suppressed due		to: expansion redu		reduced/suppres	duced/suppressed due to:	
Test series	A. pH	B. Other	C.	D. Non-	E. Non/less-	F. Limited	
	decrease	chemical	Formation of	expansive	expansive gel	polymer-	
		reason	protective	crystalline		ization of	
			coating	product		silica	
1. Pore solution chemistry of cement pastes and concretes (4X factor)	Impossible (pH not reduced in presence of LiNO <sub>3</sub> )	Not conclusive (chemical analyses limited to Na, K, Li, Si, and pH)	Possible (likely formation of Si-Li reaction product, crystalline or amorphous, which may act as a protective coating: Li consumed with time, proportionally to concrete expansion, which suggests in turn that this reaction product consists at least in part in expansive gel)			Impossible (some Li ions consumed and Si almost absent in pore solution)	
2. Visual	NT -	Likely (just	Unlikely (pro	otective coating i	not observed,	Not	
examination	Not	traces of	crystalline pro	oduct not observ	ed, amount of	conclusive	
microanalysis	(pH not	product when	expansion	and absence or i	ust traces of	(Si not	
of concretes	measured)	LiNO <sub>3</sub> is very	reaction prod	uct. limited to ty	pical ASR gel.	measured in	
(4X factor)		effective)	when	LiNO <sub>3</sub> is very ef	fective)	solution)	
3. Polished						Not	
aggr.+cement	Not	Likely				conclusive	
paste in	conclusive	(reaction	Unlikely (rea	(Si not			
NaOH+/-	(pH not	products not		measured in			
(3X factor)	ineasureu)	observed)				solution)	
()II juicion)			Possible (cryst	alline product			
11 Polished		Possible	only on aggreg	ates for which	Not conclusive		
apprepates in		(reaction	LiNO <sub>3</sub> is ver	y effective in	(the product	Not	
LiOH at 350°C	Not	product absent	concrete and	d most tests	dispersed in	conclusive	
(autoclave) and	(pH not	on many	temperature/	at very nign	solution at	(Si not	
80°C (obsidian	measured)	could be finely	whitish pro	duct finely-	verified at	measured in	
only)		dispersed in	dispersed in t	he solution at	350°C could be	solution)	
(IA jacior)		solution)	80°C, which w	as not verified	amorphous)		
			at 35	0°C)			
4.2 D-1:-11		Not conclusive	Not	T.T., 131, - 1.,	Not conclusive	N	
4.2. Polished	Not	(reaction	(crystalline	(crystalline	(crystalline	not	
NaOH+LiNO3	conclusive	product could	product not	product not	product not	(Si not	
at 80°C	(pH not	be absent but	detected but	detected by	detected but	measured in	
(2X factor)	measured)	detect gel)	XRD cannot	XRD)	detect gel)	solution)	
		acteer gery	detect gel)		Lettert gely		
4.3. Ground	Net	Lintingt	Possible	Likely (reaction	n product always	Not	
or (Na K)OH	conclusive	(reaction	product	consumption	crystalline or	conclusive	
+LiNO <sub>3</sub> at	(pH not	product always	always formed	amorphous	(no XRD nor	(Si not	
60°C	measured)	formed)	which may SEM), but expansivity		measured in		
(2X factor)			protect) unknown)		solution)		
4.4. Aggregate		Likely for	Unlikely	Unlikely	Likely for some	λī	
particles in	Not	some materials	(significant	(crystalline	materials	Not	
or LiOH at	conclusive	(Si dissolution	coating only	product only	(amorphous	(Si pot	
80°C	(pH not	significantly	on opal, and	undissolved	products	measured in	
(dissolution)	measured)	reduced or	non-	chalcedony.	proportional to	solution)	
(2X factor)		suppressed)	protective)	and very thin)	dissolution)	/	
Average	Impossible	Likely	Unlikely	Unlikely	Possible	Impossible	
(summation)	(-40)	(+45)	(-33)	(-39)	(-6)	(-40)	

TABLE 3: Summary of the degree of agreement between the test results and the mechanisms proposed to explain the effectiveness of LiNO<sub>3</sub> against ASR.

<sup>1</sup> Mechanism considered : likely (green / index = +6), possible (blue / +3), non-conclusive (grey / 0), unlikely (orange / -6), or impossible (red / -10), based on the test results.



Figure 1: Micro-SIMS results for a concrete made with a highly-reactive rhyolite and a [Li]/[Na+K] molar ratio of 0.74, after 2 years in humid air at 38°C and >95% R.H. (0.01% expansion).



Figure 2: SEM views at different scales of the Li-silicate layer ( $Li_2SiO_3$ ) observed on the surface of an obsidian particle immersed for 6 months in a 1N LiOH solution at 80°C.



Figure 3: Alkali concentrations when aggregate powders (150-300  $\mu$ m) were immersed in various Li solutions at 60°C. A) All aggregates in 0.68N (Na,K)OH control solution. B) All aggregates in 1N LiOH. C) Rhyolite in 0.8N NaOH + 0.28N LiNO<sub>3</sub> ([Li]/[Na] = 0.35). D) Rhyolite in 0.8N NaOH + 0.59N LiNO<sub>3</sub> ([Li]/[Na] = 0.74).



Figure 4: Mass variation of opal and chalcedony particles immersed at  $80^{\circ}$ C in 1N NaOH (control) and 1N NaOH + LiNO<sub>3</sub> in various amounts ([Li]/[Na] from 0 to 1.0). A) Chalcedony. B) Opal.