THRESHOLD EFFECT OF LiOH, LiCl OR LiNO$_3$ ON ALKALI-SILICA REACTION

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Abstract

Use of lithium compounds can limit the development of Alkali-Silica Reaction (ASR) in concrete. The aim of this study is to assess the effect of lithium compounds on mechanism of ASR.

Our approach uses chemical method which allows a quantitative measurement of the specific degree of ASR. We use a chemical concrete sub-system called model reactor involving the main ASR reagents: chert aggregate, portlandite and mixture of different ratios: LiOH/NaOH or lithium salts/NaOH. The measured reaction degrees are porous volume and absolute density on flint aggregate but also molar fraction of silica dissolved and molar fraction of silanol inside aggregate due to breaking up siloxane bonds.

The results show that alteration by ASR depends Li/Na ratio for a same proportion of hydroxide ions. This evolution is not graduated, unlike it appears a threshold effect. Indeed, below threshold Li/Na ratio, ASR occurs but from this value, ASR is very limited.

Keywords: alkali-silica reaction, chert aggregate, reaction degree, inhibitor, lithium

1 INTRODUCTION

Alkali-silica reaction (ASR) is well known to pose a durability problem to concrete. It can induce cracking and damage in concrete structures.

The origin of the reaction is a chemical reaction between three essential compounds included in concrete: moisture, a sufficiently high alkali concentration and a pessimum amount of reactive silica in the aggregate. The high alkali concentration will in turn produce a high hydroxyl ion concentration to maintain charge balance with the presence of portlandite. Different methods have been made to mitigate or prevent ASR. The addition of lithium salts is one of these methods. Using lithium compounds to mitigate the effects of ASR expansion was first reported by McCoy and Caldwell in 1951 [1]. Since, many papers on mortar bars or concrete [2-11] have reported reducing or suppressive effects on expansion due to ASR. But the mechanism (or mechanisms) by which lithium acts, is not well understood [12]. The general aim of this study was to contribute to the understanding of lithium's role on the alteration mechanism of ASR by quantitative measurements of specific reaction degrees. Like Mitchell et al. [13], our work used a chemical concrete sub-system. The use of model reactors constituted from chert aggregate, portlandite and alkaline solution like NaOH, KOH or LiOH allowed to show, in our previous study [14], that reaction degrees evolved greatly with NaOH and KOH and hence ASR developed. On the other hand, with LiOH, the result was totally opposite. ASR progressed very little and showed LiOH as an inhibitor of ASR. In this study, the main aim was to evaluate the influence of lithium compound type and Li/Na ratio on alteration mechanism of ASR

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without changing hydroxyl ion concentration. Mixtures of different ratios: LiOH/NaOH or lithium salts/NaOH were used in model reactors.

2 MATERIALS AND METHODS

2.1 Reactive aggregate used

The material used in this study is a "chert type" reactive aggregate coming from the north of France. This material chose for its high potential reactivity so as to assess the effectiveness of lithium compounds on alteration mechanism of ASR. A characterisation has been given by Bulteel et al. [15]. A short description follows. X-ray fluorescence analysis gives a composition close to 99% SiO_2. X-ray diffraction analysis detects only quartz lines in this aggregate. Elements other than Si have not been studied. The quartz crystal lattice is characterised by ^{29}Si solid NMR spectroscopy [16]. This crystal lattice is constituted by Q_4 SiO_2 tetrahedra and Q_3 $SiO_{5/2}H$ "silanol" tetrahedra. The Q_3 molar fraction measured by thermogravimetry is close to 0.07. The mineralogy of the material is determined by optical microscopy. This aggregate is essentially micro to crypto crystalline (microquartz) and contains radial fibers (chalcedony). The crystal size is variable but in general particularly small: a few microns. However, a few grains present a development of chalcedony zones. The material has a specific porosity about 3 mm^3/g by BJH analysis. Its absolute density measured by helium pycnometer analysis is about 2.57g/cm^3.

This aggregate is crushed to 0.16-0.63 mm and homogenized for this study.

### 2.2 Determination of reaction degrees

The determination of reaction degrees is based on ASR mechanism which is described using different models [17-21] and can be written in two main steps (eg. here for NaOH):

Formation of Q_3 sites (step 1) due to a first siloxane bonds breaking up by hydroxyl attack:

$$SiO_2 + NaOH \rightarrow SiO_{5/2}Na + 0.5\ H_2O \tag{1}$$

From a structural point of view, SiO_2 represents a Q_4 silicon tetrahedron sharing 4 oxygens with 4 neighbours, and using a simplified notation, $SiO_{5/2}Na$ represents the Q_3 tetrahedron sharing 3 oxygens with 3 neighbours.

Dissolution of silica (step 2) due to continued hydroxyl attack of the Q_3 sites to form Q_0 silica ions:

$$SiO_{5/2}Na + NaOH + 0.5\ H_2O \rightarrow (H_2SiO_4)^{2-} + 2\ Na^+ \tag{2}$$
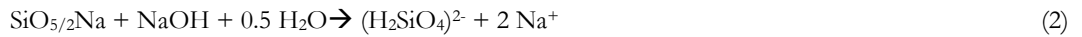
These silica ions respect the Iler equilibrium [22] according to pH.

Afterwards, precipitation of silica ions by the cations of the pore solution of concrete is likely to give C-S-H and/or C-N-S-H phase formation.

In this study, the use of the chemical method [16] allowed quantification specific reaction degrees of ASR based on steps (1) and (2), which are defined as follows:

$$FMQ_4 = moles\ of\ Q_4\ sites/moles\ of\ initial\ silica \tag{3}$$

$$FMQ_3 = moles\ of\ Q_3\ sites/moles\ of\ initial\ silica \tag{4}$$

$$FMQ_0 = moles\ of\ dissolved\ sites/moles\ of\ initial\ silica \tag{5}$$

$$FMQ_4 + FMQ_3 + FMQ_0 = 1 \tag{6}$$

2.3   Methods for assessment and analysis
General

The chemical method based on using a model reactor allowed the determination of reaction degrees, obtained by solid characterisation after the reaction. The following protocol was used [23]:
Start:

A mixture of 1g of 0.16-0.63 mm crushed aggregate and 0.5g $Ca(OH)_2$ was introduced in a closed stainless steel container. After 30 minutes preheating up to 80°C, 10 ml of solution based on 0.79 mol/l hydroxyl concentration and different Li/Na ratio given in Table 1 was added. The container was then autoclaved for 168 hours at 80°C to accelerate ASR under controlled temperature.

Stage 1:

After 168 hours of the reaction, the aggregate is constituted by Q_4 tetrahedra that have not reacted (sound silica) and by the Q_3 tetrahedra (i.e. $SiO_{5/2}Na$, $SiO_{5/2}CaSiO_{5/2}$ and $SiO_{5/2}H$) which constitute the degraded silica.

Stage 2:

Selective acid digestion with 250 ml cold 0.5M HCl solution followed by filtration leads to the removal of the soluble reaction products (($H_2SiO_4)^{2-}$, $(H_3SiO_4)^-$, Na^+, Ca^{2+}, C-S-H and/or C-N-S-H) but also reagents (NaOH and $Ca(OH)_2$). During this chemical treatment the Q_3 tetrahedra $SiO_{5/2}Na$ and/or $SiO_{5/2}CaSiO_{5/2}$ are protonated to form silanols $SiO_{5/2}H$ with a release of Na^+ and/or Ca^{2+} cations.

The porous volume (V_p) and the absolute volume (V_{abs}) are measured on the remaining aggregate residues. The porous volume is obtained by the BJH method from the nitrogen adsorption and desorption curves measured on an ASAP (Accelerated Surface Area and Porosimetry) analyzer. The absolute volume is obtained from a helium pycnometer analyzer.

Stage 3:

After thermal treatment of the residual solid at 1000°C, the silanol groups are condensed to give back silica Q_4 and release water following :

$$2\ SiO_{5/2}H\ \rightarrow 2\ SiO_2 + H_2O \tag{7}$$

Measurement of the water loss by thermogravimetry allowed calculation of the quantity of Q_3 tetrahedra in the aggregate sample (FMQ_3 defined in Equation 4). The weight of the residual silica made it possible to determine by difference the quantity of dissolved silica (FMQ_0 defined in Equation 5).

3   RESULTS
3.1   Evolution of chemical reaction degrees

The variation of molar fractions FMQ_4, FMQ_3 and FMQ_0 according to Li/Na ratio obtained by different mixtures of LiOH or $LiNO_3$ or LiCl with NaOH solutions in the model reactors as shown in Figures 1, 2 and 3 give prominence to two very different effects on ASR. For Li/Na ratio superior to 0.43, the values of FMQ_4, FMQ_3 and FMQ_0 were stable. These values showed that ASR progressed very little as they were near of their initial values. Indeed, FMQ_4 passed from 0.93 to about 0.85 and formed Q_3 and Q_0 quantities are very small with FMQ_3 from 0.07 to about 0.09 and FMQ_0 close to 0.05 in spite of a longer time of attack (168 hours). On the other hand, for Li/Na ratio inferior to 0.43, the values of FMQ_4, FMQ_3 and

FMQ$_0$ evolved with the decrease of Li/Na ratio showing that ASR progressed. FMQ$_4$ highly decreased from 0.85 to 0.03 whereas FMQ$_3$ and FMQ$_0$ increased from 0.09 to 0.43 and from 0.05 to 0.54 respectively. The curve drawings for each molar fraction in Figures 1, 2 and 3 are similar whatever lithium compounds used in the mixtures (Table 1): LiOH or LiNO$_3$ or LiCl with NaOH solutions. Only, LiOH/NaOH mixture presented evolution of chemical reaction degrees slightly more marked between 0.32 and 0.43 for Li/Na ratio.

3.2 Evolution of physical reaction degrees

Figure 4 shows porous volume according to Li/Na ratio for the three model reactors studied. The curves described two parts. One part where all the results of measurement stayed similar to initial value (some mm^3/g) when Li/Na ratio was superior to 0.43. In this case, the material was not degrading. Second part, porous volumes for the three model reactors highly increased as soon as Li/Na ratio was inferior to 0.43 to reach values from 120 to 160 mm^3/g. Even if general trend of three curves was similar, the mixtures with NaOH and LiOH presented an increasing faster than mixtures with NaOH and LiNO$_3$ or LiCl. These values of porous volume showed high alteration of chert aggregate.

The evolution of absolute density according to Li/Na ratio for the model reactors based on different mixtures with NaOH and LiOH, LiNO$_3$ or LiCl presented in Figure 5 shows again curves with two major trends with nevertheless a few differences between the model reactors. On the one hand, for high Li/Na ratio, all the measurements of absolute density were near initial value (2.57 g/cm^3). Chert aggregate seemed few altered. Indeed, the results of absolute density gave the same values close to 2.54 g/cm^3 for mixtures with NaOH and LiNO$_3$ or LiCl when Li/Na ratio was superior to 0.38 and values slightly weaker at 2.51 g/cm^3 for mixtures with NaOH and LiOH for Li/Na ratio superior to 0.43. On the other hand, for Li/Na ratio inferior to 0.38 or 0.43 for respectively lithium salts and lithium hydroxide, absolute densities for the three model reactors highly decreased up to 2.02 g/cm^3. These values of absolute density showed high degradation of chert aggregate. Little differences appeared between the mixtures based on lithium salts and lithium hydroxide. Firstly, on the values Li/Na ratio where absolute density started to change: 0.38 for lithium salts and 0.43 for lithium hydroxide. Secondly, absolute density decreased faster with lithium hydroxide than lithium salts.

4 DISCUSSION

To evaluate effectively the influence of Li/Na ratio on alteration mechanism of ASR, model reactors used the same conditions with only one parameter which varied: the mixture following Table 1. The choice to autoclave for 168 hours the container allowed to reach the maximum ASR if the reaction developed [14]. To perform all the tests with hydroxyl ion concentration fixed to 0.79 mol/l allowed a good comparison of lithium ion role but also nitrate and chloride ions because a change of hydroxyl ion concentration would have had a high influence on ASR.

All chemical and physical reaction degrees (Figures 1, 2, 3, 4 and 5) showed similar evolution according to Li/Na ratio for the three model reactors studied. Inhibitor action of lithium ion did not happen progressively with increase lithium ion content in the reactor but presented a threshold effect. This threshold, about 0.43 for Li/Na ratio in the conditions studied, involved two behaviours on ASR.

For values superior to threshold, all reaction degrees evolved very little. Indeed, FMQ$_4$, FMQ$_3$ and FMQ$_0$ changed only a slightly (Figures 1, 2 and 3) near initial values indicating a very small hydroxyl attack according to Eq. (1) and Eq. (2) despite a high concentration with 0.79 mol/l. Thus, few Q$_3$ sites and Q$_0$ dissolved silica were formed. These results agree with the reduction or suppression of silica dissolution observed by Tremblay et al. [24] with the use of lithium salt (like LiNO$_3$) on reactive silica in other experiments. More, porous volume unchanged (Figure 4) and absolute density near initial value (Figure 5)

demonstrated that chert aggregate was few degraded. These results showed that ASR progresses very little with Li/Na ratio superior to about 0.43 for different mixtures of LiOH or LiNO$_3$ or LiCl with NaOH solutions. In these conditions, lithium ion was an inhibitor of ASR and nitrate and chloride ions had not any influence on mechanism.

For values inferior to threshold, all reaction degrees evolved very greatly testifying that ASR development. Indeed, the formation of Q$_3$ sites and Q$_0$ dissolved silica was due to the hydroxyl attack which consumed Q$_4$ sites. The degradation of chert aggregate also showed by high increase of porous volume and a drop of absolute density. More, these reaction degree evolutions were also quick as major part of the variation did in narrow interval between 0.4 and 0.2 for Li/Na ratio. So, inhibitor effect of lithium ion on ASR fell very quickly. It is to be noted that reaction degrees varied more quickly for LiOH/NaOH mixture than LiNO$_3$ or LiCl with NaOH mixtures. Even, mixtures with lithium salts also shifted the threshold value for the measurement of absolute density. Nitrate and chloride ions mitigated the speed of efficiency loss of lithium inhibitor effect according to the decrease of Li/Na ratio.

5   CONCLUSIONS

This study of the influence of lithium compounds and Li/Na ratio on alteration mechanism of ASR used model reactors constituted from chert aggregate, portlandite and mixture of different ratios: LiOH/NaOH or LiNO$_3$ or LiCl/NaOH. These model reactors, cured at 80°C for 168 hours with constant high hydroxyl concentration (0.79 mol/l), allowed the most favourable conditions to develop ASR and directly compare the effects of different mixtures. The comparison was based on the consistence of chemical and physical reaction degrees which presented the advantage to be specific and quantitative measurements of ASR. The results led to the following conclusions:

Inhibitor action of lithium ion did not happen progressively with increase lithium ion content in the model reactor but presented a threshold effect. In the conditions studied in this paper, the threshold was close to 0.43 the Li/Na ratio.

Above threshold value, the role of lithium ion inhibitor on ASR was efficient and nitrate and chloride ions for lithium salts had not any influence on mechanism.

Below threshold value, lithium ion efficiency loss as inhibitor of ASR was very quick. ASR developed greatly between Li/Na ratio from 0.4 to 0.3 in case LiOH/NaOH solution. When LiNO$_3$ or LiCl were used, nitrate and chloride ions mitigated the speed of efficiency loss of lithium inhibitor effect according to the decrease of Li/Na ratio. The interval was from 0.4 to 0.2.

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| Table 1: Different Li/Na ratios studied in the model reactors according to lithium compounds								
Series 1			Series 2			Series 3		
LiOH (Mol/l)	NaOH (Mol/l)	Li/Na	LiNO$_3$ (Mol/l)	NaOH (Mol/l)	Li/Na	LiCl (Mol/l)	NaOH (Mol/l)	Li/Na
0	0.79	0	0	0.79	0	0	0.79	0
0.12	0.67	0.18	0.10	0.79	0.13	0.10	0.79	0.13
0.16	0.63	0.25	0.15	0.79	0.19	0.15	0.79	0.19
0.20	0.59	0.33	0.20	0.79	0.25	0.20	0.79	0.25
0.22	0.57	0.38	0.25	0.79	0.32	0.25	0.79	0.32
0.24	0.55	0.43	0.30	0.79	0.38	0.30	0.79	0.38
0.28	0.51	0.54	0.35	0.79	0.44	0.35	0.79	0.44
0.32	0.47	0.67	0.40	0.79	0.51	0.40	0.79	0.51
0.395	0.395	1	0.50	0.79	0.63	0.50	0.79	0.63
			0.60	0.79	0.76	0.60	0.79	0.76
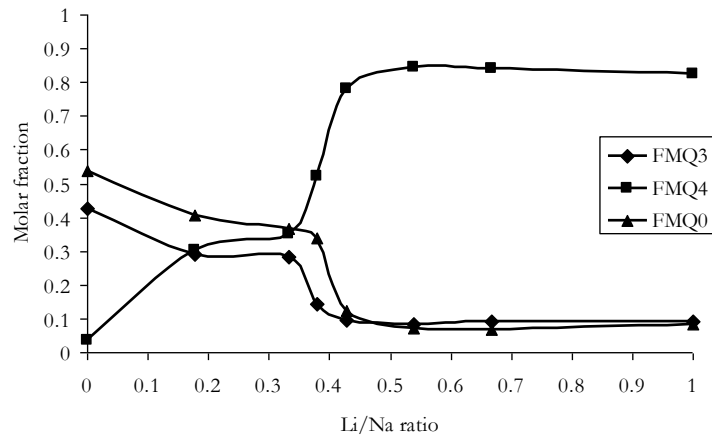
Figure 1: Molar fraction of Q_4, Q_3 and Q_0 according to Li/Na ratio for the model reactor with LiOH/NaOH after 168 hours of the reaction
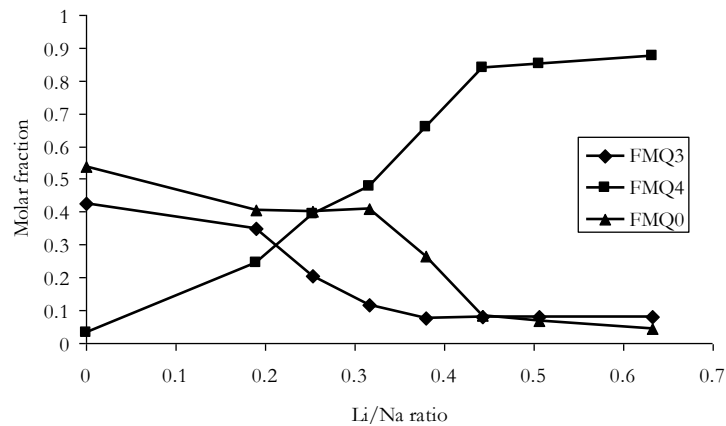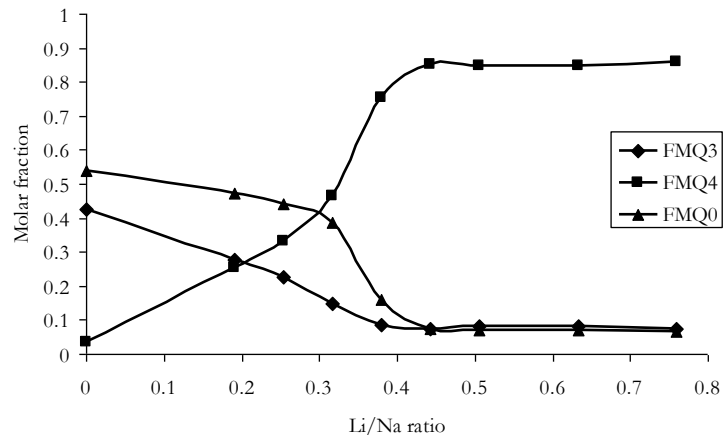

Figure 2: Molar fraction of Q_4, Q_3 and Q_0 according to Li/Na ratio for the model reactor with LiNO$_3$/NaOH after 168 hours of the reaction

Figure 3: Molar fraction of Q_4, Q_3 and Q_0 according to Li/Na ratio for the model reactor with LiCl/NaOH after 168 hours of the reaction
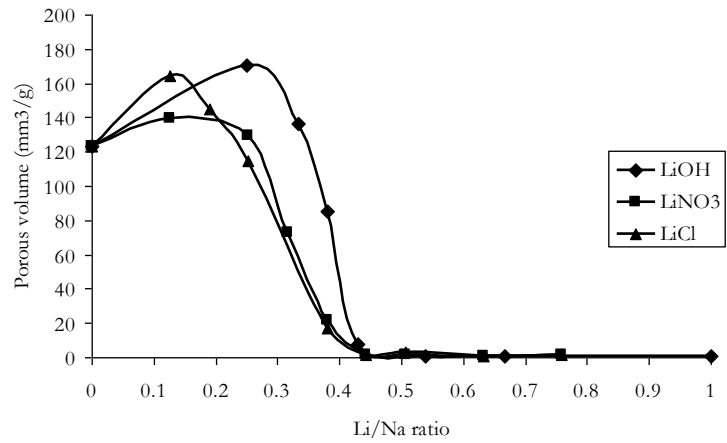

Figure 4: Porous volume according to Li/Na ratio for the model reactor with LiOH, LiNO$_3$ and LiCl + NaOH after 168 hours of the reaction
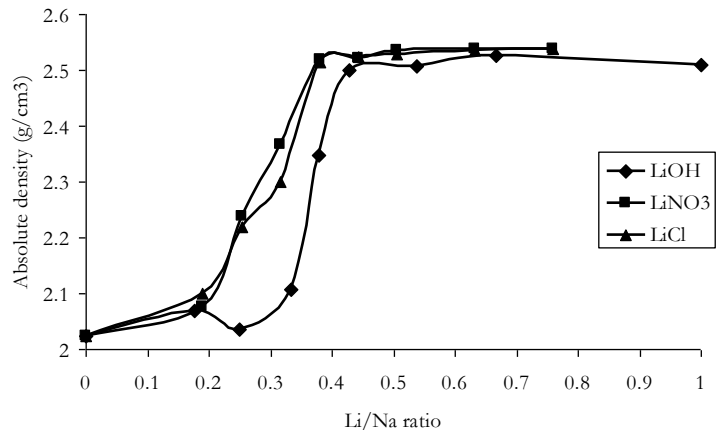

Figure 5: Absolute density according to Li/Na ratio for the model reactor with LiOH, LiNO$_3$ and LiCl + NaOH after 168 hours of the reaction