THRESHOLD EFFECT IN ALKALI-SILICA REACTION INHIBITION ON MICRO-MORTARS AND MORTARS WITH LiOH

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Abstract

Lithium compounds can mitigate alkali-silica reaction (ASR). The aim of this study was to investigate the potential occurrence of the threshold effect (previously observed in model reactor tests) in an actual cementitious matrix (mortars) and to improve the understanding of lithium role on the alteration mechanism of ASR.

This study is based on the expansion tests of micro-mortar bars (1×1×4cm³) at 80°C, 100% R.H. and mortar bars (4×4×16cm³) at 60°C, 100% R.H. Mixes were made using a flint aggregate, an OPC and lithium and sodium hydroxides. ToF-SIMS was used to determine the location of lithium in mortar bars only.

The threshold effect was observed in micro-mortar and mortar bars, respectively at a Li/Na_{eq} ratio of 0.20 and 0.41. Observations of polished sections of mortar bars in ToF-SIMS reveal that lithium is within the flint particles when the reaction is inhibited; this questions the mechanism of a protection barrier inhibiting ASR.

Keywords: ASR, inhibition, lithium hydroxide, flint aggregate

1 INTRODUCTION

The first report of lithium's capacity to inhibit alkali-silica reaction (ASR) was first made by McCoy & Caldwell in 1951 [1]. Since then, this capacity has been investigated to a great extent and many studies, carried out on mortar and concrete bars, have confirmed that lithium has a reducing or suppressing effect on ASR expansion [2-6]. Notwithstanding the efforts by the research community, the mechanisms by which lithium inhibits ASR remain unclear [7]. However, three hypotheses are commonly drawn: 1/the lithium-containing reaction products would form a protection barrier around the aggregate [8], 2/lithium-containing reaction products would be little or non-expansive [9] and 3/the stability of silica would increase in the presence of lithium in the pore solution [10].

The goal of this paper is to contribute to the understanding of ASR inhibition: firstly, by studying the expansive behaviour of a flint aggregate thanks to tests on micro-mortar and mortar bars and secondly, by locating lithium in the mortar bars thanks to Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

This study is a continuation of the work of Bulteel on model reactors [11,12]. The latter work pointed out the existence of a threshold effect of LiOH on ASR inhibition. Indeed, the inhibition of ASR is not proportional to the quantity of lithium introduced and once a certain quantity of lithium (or a certain Li/Na ratio) is reached, expansion is very limited and further addition of lithium is therefore no longer needed. Using the same materials (an alkali-reactive flint aggregate) and adding the alkalis under the same form (lithium and sodium hydroxides in different proportions to make Li/Na ratios vary but keeping the hydroxyl ions quantity constant), it is intended to observe a correlation between the behaviour of the physico-chemical parameters in model reactor and the expansive behaviour in cementitious material. To complete this study, polished sections of mortar bars are observed using ToF-SIMS. This technique has recently been used to detect lithium in ASR-related studies as its mass is too low to be observable by the current techniques used in the field of cementitious materials (such as EDX for example) [13-15].

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2 MATERIALS AND METHODS

2.1 Materials

The aggregate used in this study is a flint aggregate from Northern France known for its reactivity, a detailed characterisation can be found in [16]. To briefly sum up, the aggregate is composed of 99% silica. A petrographic study revealed that silica is mainly under the form of microquartz and that chalcedony can be found as well.

The cement used is an Ordinary Portland Cement (OPC); its chemical composition is given in Table 1. Its sodium oxide equivalent content (Na_2O_{eq}) is 0.8%.

Additional alkalis were introduced under the form of sodium and lithium hydroxides. Hydroxides were chosen in order to make the Li/Na_{eq} ratio vary while keeping the quantity of hydroxyl ions constant.

2.2 Mix designs and thermal treatments

Micro-mortar bars

Micro-mortar bars ($1\times1\times4cm^3$) were made based on the French standard AFNOR XP P18-594 [17] with the fraction 0.16/0.63mm of crushed flint aggregate, the water to cement ratio (w/c) was 0.35 (this w/c ratio is higher than the one proposed by the standard – 0.30 – as the mix happened to be too stiff to provide a correct moulding) and the cement to aggregate ratio (c/a) was 2.

The thermal and chemical treatments applied to the bars differed from those recommended by the aforementioned standard. Lithium and sodium hydroxides were added through the mixing solution. Those two hydroxides were used in order to maintain a constant hydroxyl ions quantity; therefore sodium was, in a way, substituted by lithium to obtain different Li/Na_{eq} ratio (Li/Na_{eq} being the elemental ratio between the lithium brought by the mixing solution and the equivalent sodium, Na_{eq}, taking into account the sodium brought by the mixing solution and the alkalis already contained in cement). Nine ratios were tested: 0; 0.03; 0.07; 0.10; 0.13; 0.20; 0.25; 0.31 and 0.41. As the quantity of lithium in solution increases while substituting sodium, the quantity of sodium oxide equivalent, Na_2O_{eq}, decreases with lithium addition. The Na_2O_{eq} content when no lithium is added (i.e. $Li/Na_{eq}=0$) is 2.8% (0.8% of Na_2O_{eq} come from the cement itself and 2% from the mixing solution).

After mixing, the moulded preparation was allowed to set for 24h at 20°C, c. 100%RH; bars were then demoulded and their length l_0 was measured. After that, bars underwent a thermal treatment in water steam at 100°C for 4h in order to increase their mechanical resistance and certainly give a start to ASR and were then allowed to cool down to 20°C, c. 100%RH for 12 to 24h. Finally the bars were placed in water steam at 80°C for 24h and were allowed to cool down to 20°C, c. 100%RH before measurement of their length l.

Mortar bars

Mortar bars ($4\times4\times16cm^3$) were also realised based on the French standard AFNOR XP P18-594 [17]. Only the fraction 0.16/5mm of the crushed flint aggregate was used, w/c and c/a ratios were 0.5.

The thermal and chemical treatments applied to the bars were, here again, different to those proposed by the standard. Lithium and sodium were introduced in a similar way than previously described; eight mixes were tested: Li/Na_{eq} = {0; 0.03; 0.13; 0.20; 0.25; 0.31; 0.41; 0.55}. The Na_2O_{eq} content when no lithium is added (i.e. $Li/Na_{eq}=0$) is 2.8%.

After mixing, the preparation was maintained for 24h in a chamber at 20°C, c. 100%RH. After demoulding, the initial length measurement (l_0) was made and bars were placed in water steam at 60°C, 100%RH. Length measurements were realised every 13 days on a period of c. 15 weeks - which is enough for the expansion to reach an asymptote. Before each measurement, mortar bars spent at least 24h at 20°C, c. 100%RH to cool down.

2.3 Expansion measurement

Length expansion ε was calculated according to Equation 1 where l is the final length of a bar (after thermal treatment), l_0 its initial length (right after demoulding) and L the reference length (4cm for micro-mortar bars and 16cm for mortar bars).

$$\varepsilon = \frac{l - l_0}{L} \quad (1)$$

Each mix of micro-mortar and mortar bars was respectively made in a series of 4 and 3 bars. The graphs presented below are given showing the standard deviation of the average length expansion of these 4 or 3 bars.

2.4 Mass spectrometry: ToF-SIMS

Time of Flight Secondary Ion Mass Spectrometry (Tof-SIMS) analyses were carried out using a ToF-SIMS[5] instrument from ION-TOF GmbH. A 25keV Bi_3^+ primary ions beam was used in burst-alignment mode; only secondary positive ions were detected. Images were obtained with 100 scans over an area of 500x500µm² (512x512 pixels). Analyses were carried out on polished sections of mortar bars. As the polishing operations were found to contaminate samples surfaces, the latter were cleaned before analysis thanks to an O_2^+ sputter beam (2kV, 500nA, non-interlace mode) for 4 minutes over an area of 800x800µm². The cleansing operation was monitored until complete stabilization of the intensities of the secondary ions of interest.

3 RESULTS

3.1 Micro-mortar bars

The expansion according to the Li/Na_{eq} ratio for micro-mortar bars (Figure 1) reveals that the inhibition is not proportional to the quantity of lithium introduced. In fact, when not enough lithium is introduced the inhibition can be either non-existent (at Li/Na_{eq}=0 and Li/Na_{eq}=0.03, expansions are respectively 0.70 and 0.69%) or weak (expansions are respectively 0.54 and 0.52 for Li/Na_{eq}=0.07 and Li/Na_{eq}=0.10). A significant decrease of the expansion is then observed between 0.10 and 0.20 and reaches a phase of complete inhibition with an expansion inferior to 0.06%. This is the threshold effect previously observed by Bulteel in model reactors [11].

3.2 Mortar bars

Expansion behaviour

The expansion of mortar bars according to the Li/Na_{eq} ratio (Figure 2) also displays the threshold effect. Here again, a small quantity of lithium engenders a weak inhibition: the expansion of the reference (Li/Na_{eq}=0) is 0.71% while it is between 0.51-0.55% for Li/Na_{eq}=0.03-0.20. When lithium quantity increases, the expansion knows a significant decrease between Li/Na_{eq}=0.25 and 0.41. The reaction is then fully inhibited with a corresponding expansion of 0.06%.

ToF-SIMS analysis

Two mixes were observed with ToF-SIMS: an expansive lithium-containing mix (Li/Na_{eq}=0.25) and a lithium-containing mix where ASR is fully inhibited (Li/Na_{eq}=0.41). The expansive mix displays signs of alteration such as cracks, reaction product and altered flint grains. An optical image of the area observed in ToF-SIMS for the mix at Li/Na_{eq}=0.25 is given in Figure 3. This photograph reveals the presence of cracks which extend out of the flint particles into the surrounding cement paste. The cracks are partially filled with a white reaction product. The corresponding ToF-SIMS images are given in Figure 4, the length scale is given around the image and the intensity scale is on the right. It is reminded that the intensity is not quantitative as the elements studied have different ionization potential. The particle in the upper left corner is not a flint grain, indeed flint deposits also bear scarce exotic detrital material [18]; hence, it won't be taken into consideration. The fragment Si^+ (Figure 4 a) was observed in the flint particles (reflecting the presence of silica) as well as in the reaction product filling the cracks. Calcium (Figure 4 b) was obviously found in the cement paste but also in the reaction product and it seems that it had slightly diffused in the flint grains, especially in the one on the left of the image. Sodium and potassium (Figure 4 c and d) were found in the reaction product and the surrounding cement paste. As for lithium (Figure 4 e), it seems to be particularly concentrated in the reaction product filling the cracks within the flint particles alike the other alkalis.

The non-expansive mix at Li/Na_{eq}=0.41 was also studied. As expected, it displays few signs of degradation, however altered flint grains can occasionally be found. The optical image of the area observed in ToF-SIMS is given in Figure 5. The white grain in the upper right corner seems to have undergone ASR while the other observable grains seem unaltered by the reaction. The alteration of the white grain is particularly visible in the ToF-SIMS image of the fragment Si^+ (Figure 5 a) where cracks are noticeable; these cracks contain silicium. As for the other grains, no sign of alteration were observed. Calcium (Figure 5 b) is located in the cement paste as expected and also in the cracks of the altered grain in the upper right corner of the image. Sodium and potassium (Figure 5 c and d) are particularly concentrated in the altered grain but are also observable in the cement paste. The Na^+ fragment can be spotted in some areas in the unaltered grains while the K^+ fragment is detected throughout all the unaltered grains. Finally, lithium (Figure 5 e) is observed throughout the altered grain and is especially concentrated in the cracks; it is also found throughout the unaltered grain in the lower left corner of the image.

4 DISCUSSION

The expansion tests on micro-mortar and mortar bars reveal that inhibition is not proportional to the quantity of lithium introduced in the mix. This phenomenon has already been observed in model reactor tests by Bulteel [11]. The corresponding curves are given in Figure 7 ; molar fractions of Q_4 (sound silica), Q_3 (altered silica) and Q_0 (dissolved silica), which reflect the alteration of the flint aggregate, are presented according to Li/Na ratio. In model reactors, as well as in micro-mortar and mortar bars, when a small amount of lithium is introduced, the reaction is slightly inhibited (which corresponds to a slight decrease of the expansions and the molar fractions of altered and dissolved silica or a slight increase of the molar fraction of sound silica); then lithium fully goes into action and a significant evolution of the parameters is observed. Finally, when enough lithium is added, the inhibition is complete and parameters are almost constant (expansion and molar fractions of altered and dissolved silica reach a minimum while molar fraction of sound silica reaches a maximum). This phenomenon is the threshold effect.

The three tests, model reactors, micro-mortar and mortar bars all display the threshold effect with Li/Na_{eq} values at threshold of 0.43, 0.20 and 0.41 respectively. The values of threshold ratios are not comparable between one another as they have been obtained in very different experimental conditions. Mortar bar test is the accelerated experiment which is the closest to concrete material, while model reactor test takes place out of a cementitious matrix and micro-mortar bar test takes place in severe conditions of acceleration of ASR. Nevertheless, the threshold effect is observable for both experiments. Hence, the chemical parameters (molar fractions in Q_4, Q_3 and Q_0) followed in the model reactor tests translate very well the expansive behaviour of the aggregate studied and the micro-mortar bar test proves to be an efficient and quick way (a few days in the case of micro-mortar bars versus a few weeks for mortar bars) to assess the expansive behaviour of mixes regarding lithium addition.

In the mix at Li/Na_{eq}=0.25, the reaction is unimportantly inhibited (diminution of the expansion by less than 0.2% compared with the reference without lithium). Cracks and reaction products are visible, the latter are certainly of the C-(Na/K/Li)-S-H type as ToF-SIMS analyses revealed the presence of silicon, calcium and alkalis. Unlike the observations of Bernard & Leemann [13], in our case, lithium seems to correlate with sodium and potassium in the reaction products. Hence, in a mix which doesn't contain enough lithium to fully inhibit ASR, lithium is found in the reaction products.

In the mix at Li/Na_{eq}=0.41, ASR is completely inhibited. Unaltered flint grains (the three particles in the upper left corner of Figure 6) were observed; ToF-SIMS analyses confirmed the unique presence of silica. Even if ASR is inhibited, altered flint particles can occasionally be found (flint particle in the upper right corner of Figure 6). Such a particle displays cracks which seem to be filled with C-(Na/K/Li)-S-H reaction product. Unlike the precedent feature described in the case of an expansive mix (Li/Naeq=0.25), the altered grain here contains alkalis (sodium, potassium and lithium). An unaltered grain (lower left corner of Figure 6) also contains alkalis, especially lithium which is found throughout the whole grain, while sodium has a marginal presence and potassium has a low concentration.

This phenomenon of diffusion of lithium within the grains have only been observed for the non-expansive mix at Li/Na_{eq}=0.41. Hence, this feature could be indicative of the inhibition mechanism caused by lithium. Moreover, the observations made in this study question one of the mechanisms generally proposed to explain ASR inhibition with lithium: the hypothesis of the existence of a protection barrier formed by lithium-containing reaction products; in fact, no such protection barrier was observed.

5 CONCLUSION

This study on the inhibition of lithium in cementitious matrices was conducted on micro-mortar and mortar bars respectively at 80 and 60°C and 100% RH. Lithium and sodium hydroxides were added through the mixing solution and different Li/Na_{eq} ratios were tested. The quantity of hydroxyl ions was kept constant in every mixing solution.

The inhibition of ASR is not proportional to the quantity of lithium introduced in micro-mortar and mortar bars. The expansion curves of these two materials present a threshold effect, i.e.

below a certain value of Li/Na_{eq} the inhibiting effect of lithium is weak while above, the inhibition is complete. The Li/Na_{eq} threshold is 0.20 and 0.41 for micro-mortar and mortar bars respectively.

ToF-SIMS analyses enabled to make two statements about the behaviour of alkalis, and lithium in particular:

- lithium has an affinity for ASR reaction products, as well as sodium and potassium, and its location is correlated with the latter,
- lithium is found within the flint particles in the inhibited mix, a small quantity of potassium and even a smaller quantity of sodium can also be observed in the grains

The latter observation leads to the questioning of one of the commonly proposed hypothesis concerning ASR inhibition with lithium as no protection barrier made of lithium-containing products was found around the flint particles in the non-expansive mix studied.

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TABLE 1 : Chemical composition of OPC.

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O	Na_2O_{eq}	LOI
%	63.9	20.0	5.2	3.4	3.1	0.8	0.8	0.3	0.8	1.9

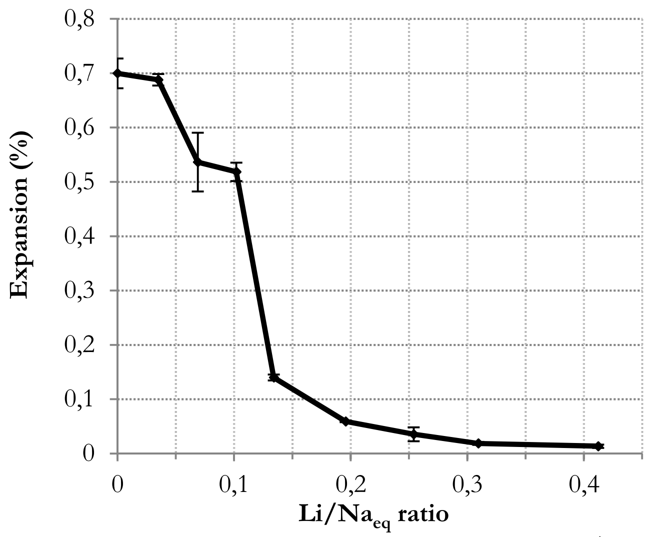

FIGURE 1 : Expansion of micro-mortar bars according to Li/Na_{eq} ratio.

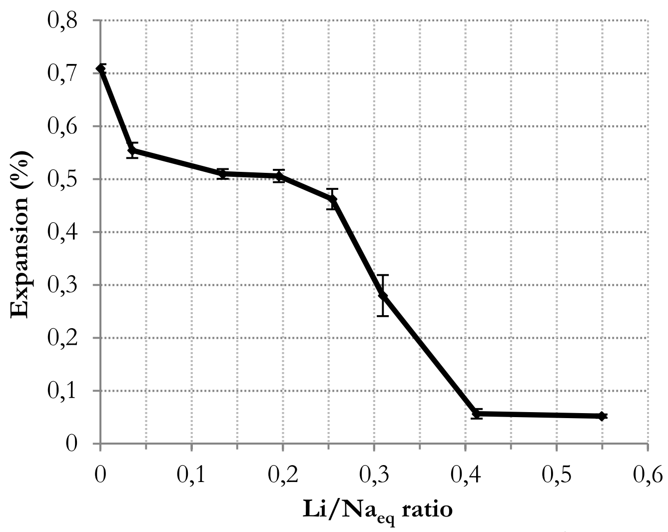

FIGURE 2 : Expansion of mortar bars according to Li/Na_{eq} ratio.

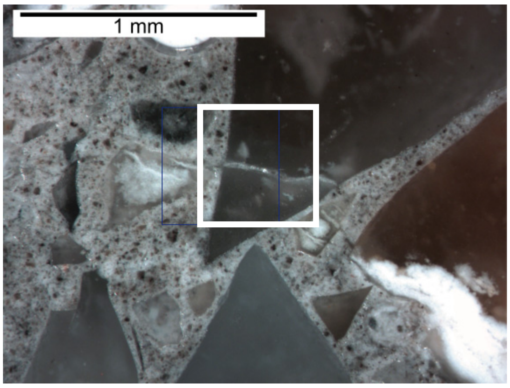

FIGURE 3 : Optical image obtained with a stereomicroscope of the area studied in ToF-SIMS (in the frame) for the mix at Li/Na_{eq}=0.25.

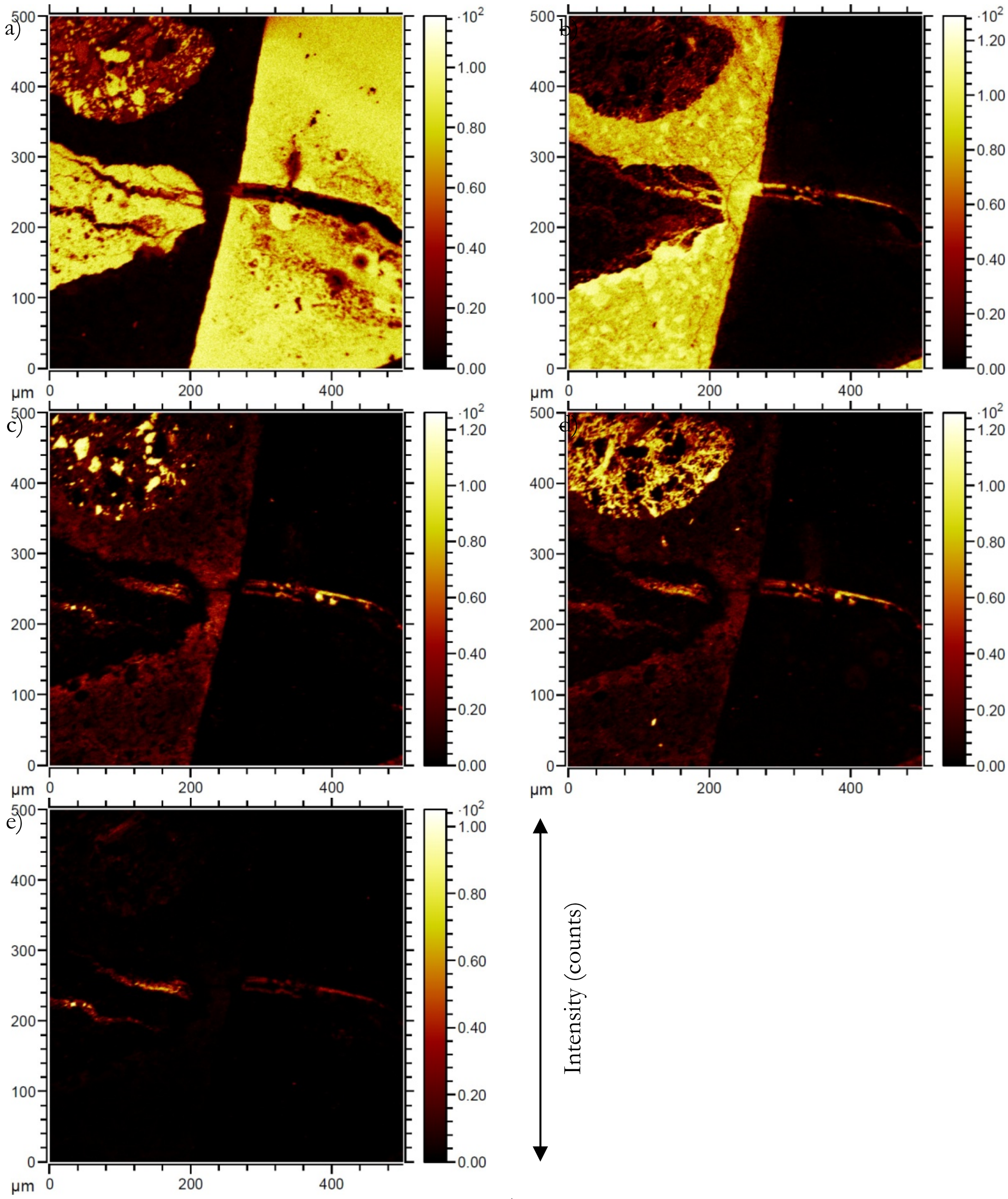

FIGURE 4 : ToF-SIMS images for the mix at Li/Na_{eq}=0.25 a) Si^+, b) Ca^+, c) Na^+, d) K^+, e) Li^+.

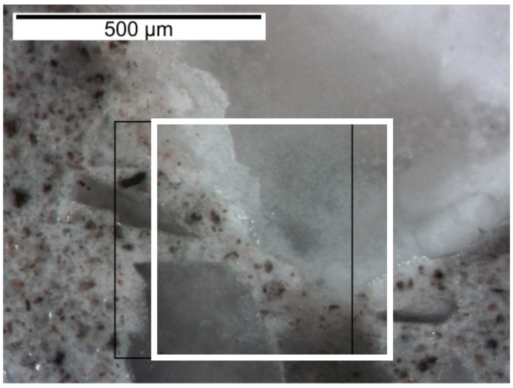

FIGURE 5 : Optical image obtained with a stereomicroscope of the area studied in ToF-SIMS (in the frame) for the mix at Li/Na_{eq}=0.41.

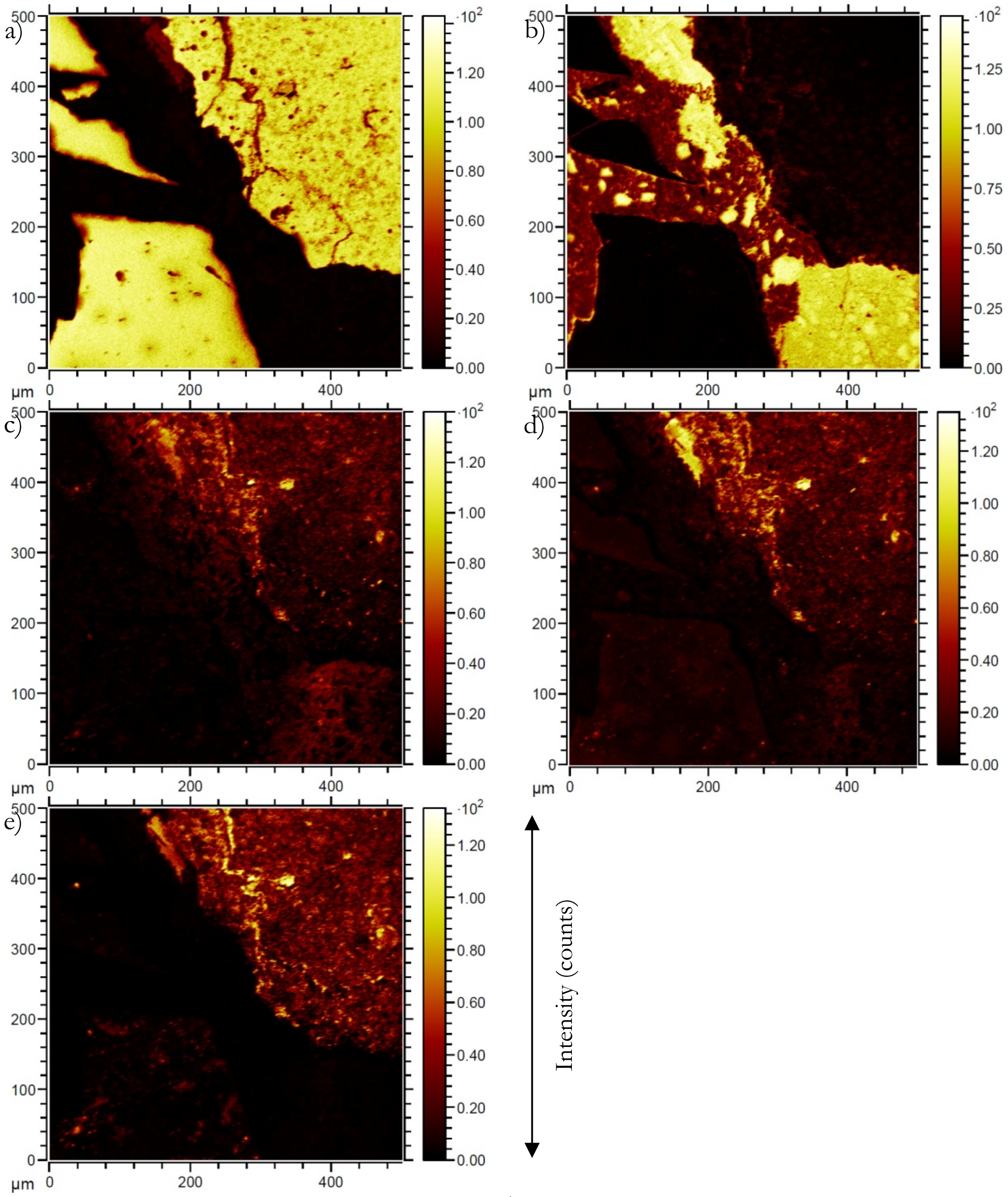

FIGURE 6 : ToF-SIMS images for the mix at Li/Na_{eq}=0.41 a) Si^+, b) Ca^+, c) Na^+, d) K^+, e) Li^+.

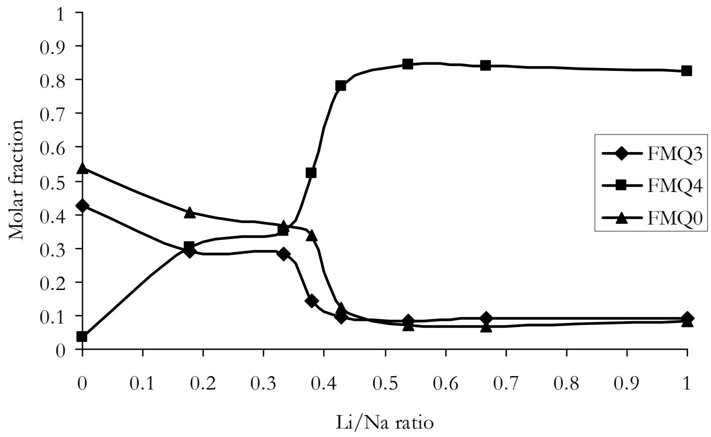

FIGURE 7 : Molar fractions in sound silica (FMQ_4), altered silica (FMQ_3) and dissolved silica (FMQ_0) according to Li/Na ratio in model reactors using flint aggregate, from Bulteel [11].