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CONTROLLING ALKALI-SILICA REACTION BY UNDERSTANDING THE CONTRIBUTION OF ALUMINIUM PROVIDED BY SUPPLEMENTARY CEMENTITIOUS MATERIALS

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Abstract

The mechanism by which SCMs control alkali-silica reaction is not well understood. Some previous studies, principally done on synthesized cement phases show the immobilization of alkali ions in the C-S-H phase. The assimilation of Si by C-S-H is involved in the alkali fixation. The better ASR resistance of aluminium rich SCMs was often attributed to the alkali fixation potential of Al in C-S-H. However, this behaviour has never been confirmed in real cement pastes.

It is showed here that the aluminium incorporation in C-S-H has no contribution on the alkali immobilization. It is proposed that the role of aluminium takes place in the aggregates. Aluminium ions can limit the dissolution of amorphous silica of the aggregates. The study of aggregates reacted fraction confirms the inhibiting effect of aluminium on the ASR gel formation. This approach indicates a new mechanism controlling ASR in presence of aluminium in the pore solution.

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Keywords: Alkali silica reaction, supplementary cementitious materials, C-S-H, blended pastes, pore solution extraction, aluminium, dissolution ¶

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1. INTRODUCTION

The deleterious effects of ASR in new structures can be avoided by using supplementary cementitious materials (SCMs). However, the exact mechanism by which this is brought about is unclear. A better understanding of the role of SCMs would be a very useful step forward to the prediction of the precise amount of substitution for a given type of reactive aggregate to avoid or significantly reduce ASR expansion. It was already showed [1-4] that SCM substitution decreases the pH of the cement paste pore solution over and above that expected by simple dilution. Studies [5, 6], on synthetic cement phases, indicate that an increase of the Si/Ca ratio increases the immobilization of sodium and potassium ions in the C-S-H. This lowers the pore solution alkalinity and its capacity to dissolve silica in the aggregates.

There are several indications that show that aluminium rich SCMs, such as fly ash, slag or metakaolin are more efficient against ASR than pure silica additions such as silica fume, which may only have a temporary effect [7-9]. In the study of Hong and Glasser [6], the replacement of silanol sites by aluminium in synthesized C-S-H, indicated a role of the aluminium on alkali fixation. However, synthesized C-S-H did not have the same compositions as found in real pastes. The first part of this study aimed to investigate the effect of aluminium incorporation in C-S-H on the fixation capacity of alkalis in real blended pastes.

Several researchers from geology and marine chemistry showed that aluminium in solution is able to reduce or even stop silica dissolution e.g. [10-12]. All these studies deal however with conditions very different from concrete. The second part of this study tries to confirm this mechanism for concrete conditions, with highly alkaline and calcium saturated pore solutions.

2. EXPERIMENTAL PROGRAM

The aim of the experimental study was to make blended pastes containing comparable C-S-H phases. Pastes with three substitution levels of 5, 10 and 15% of metakaolin were cast with a water to binder ratio of 0.5. To obtain pastes with the same Si/Ca ratio of C-S-H but no aluminium, the same substitution levels were cast with silica fume and inert quartz filler, following the Figure 1. The aim was to provide the same amount of added silica, but in one case an additional amount of aluminium. The composition of the materials used is presented in Table 1.

The C-S-H compositions in the blended pastes were studied by EDS micro analysis (Bruker AXS XFlash Detector 4030 133eV) in the scanning electron microscope (FEI Quanta 200). The paste samples were cut at different ages chemically dried with isopropanol to stop hydration and impregnated with an epoxy resin. The samples were mechanically polished down to 1 micron with diamond pastes. Around 100 measurement points were made for the inner and for the outer C-S-H product.

A batch of pastes was pressed in an adapted device in order to extract the pore solution at the ages of 28, 90 and 300 days. The solutions were analyzed by inductive coupled plasma (ICP) to determine the amount of ions present in the pore solutions.

In order to see the effect of aluminium ions on the ASR gel formation, reactive aggregates were placed in simulated pore solutions with and without aluminium ions at 60°C in order to accelerate the reaction. Reacted fraction analysis by SEM imaging was done at several time steps [13]. The aluminium containing solution had a concentration of 4.5 mM of aluminium, was portlandite saturated and contained 0.6 M of sodium hydroxide.

3. RESULTS AND DISCUSSION

Figure 2 shows the distribution of Si/Ca in function of the Al/Ca for the outer C-S-H points at 300 days. It appears that the metakaolin blended pastes, corresponding to the aluminium rich systems, have the same distribution of Si/Ca ratios as the silica fume - quartz systems. As expected, the higher the substitution level, the higher was the Si/Ca ratio. The Al/Ca ratio of the metakaolin blended pastes increased with substitution level, whereas the silica fume – quartz systems had a constant Al/Ca ratio of approximately 0.07, independent of the substitutions level. The same tendencies were observed at 28 and 90 days and for the inner product.

The concentration of alkalis in the pore solutions is shown in Figure 3. The presence of Al in the C-S-H does not increase the alkali fixation of potassium and sodium. In fact the alkali concentrations for the metakaolin blends tends to be higher than the silica fume blends for potassium and sodium. From these results, it seems that with aluminium containing SCMs, such as metakaolin or fly ash, there must be another mechanism in addition to alkali fixation on C-S-H which makes them more efficient against ASR for a similar substitutions level.

The Figure 4 proposes the evolution of aluminium concentration in the pore solution over the time. The pore solution analysis of the blended pastes proposes an increase of the aluminium content with the increase of the substitutions level. It is visible that the aluminium concentration increases until 2.7 mM of aluminium in the pore solution for the 15% metakaolin systems. Silica fume systems do not provide additional aluminium and are not presented here.

In order to know if the aluminium species in solution have an influence on the degradation of reactive aggregates, a test was provided on reactive aggregates.
The reacted fraction of the aggregates in simulated pore solution, measured by SEM image analysis, is proposed in the graphic of the Figure 5. It is confirmed that aluminium species in pore solution effectively have an effect on the deterioration of reactive aggregates. The difference of degradation of the aggregates put at 60°C in order to accelerate the reaction is visible on the aggregates sample of the Figure 6. These are images of the bigger scale map used to calculate the reacted fracion proposed on the graphic of the Figure 5.

4. CONCLUSION

This study gives new insight into the mechanisms behind the control of ASR by SCMs. A first part of the study showed that aluminium incorporation in C-S-H in real blended pastes had no effect on the lowering of the pore solution alkalinity.
In the second part of the study, it was showed that aluminium provided by SCMs in the pore solution plays an important role in the control of aggregates deterioration. Coupled to the lowering of the pore solution alkalinity by silicon addition, aluminium is a powerful element to control ASR.

5. REFERENCES

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TABLE 1 Raw materials characterization

[%w]	SiO_2	Al_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	producer	type
OPC	21.0	4.6	64.2	1.8	2.8	0.9	0.2	0.1	Holcim	CEM I
Metakaolin	50.6	46.9	0.0	0.1	0.1	0.2	0.3	1.3	Burgess	Optipozz
Silica fume	98.3	0.2	0.2	0.1	0.0	0.3	0.0		Elkem	Microsilica 983-U
Swiss Alps aggregate	78.9	10.1	0.7	0.8	0.1	5.2	0.5	0.3		
North Am. aggregate	79.2	9.2	1.4	0.5	0.0	3.0	2.3	0.3		

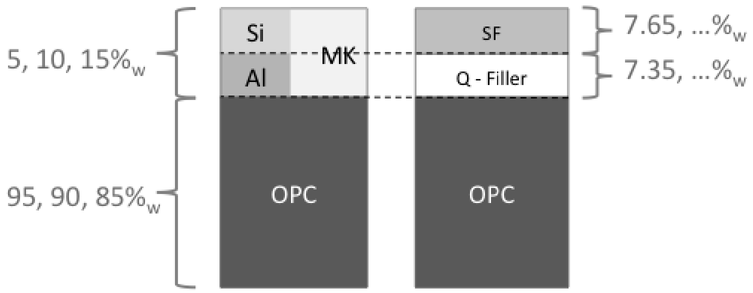

FIGURE 1: Composition of blended systems

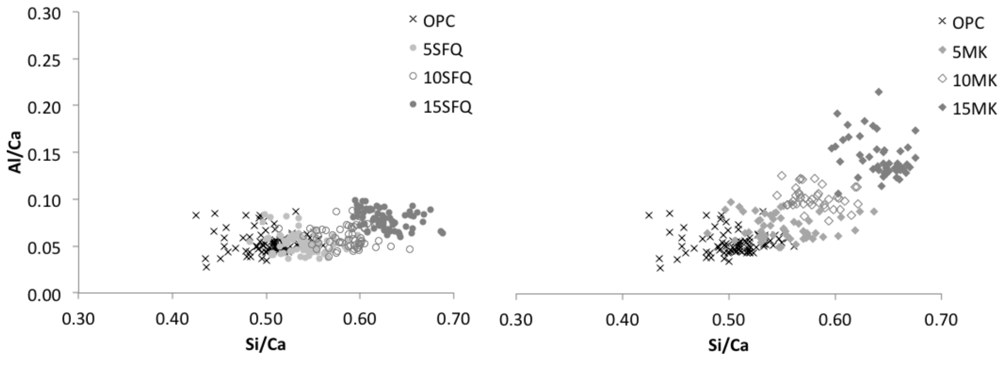

FIGURE 2: Incorporation of aluminium in the C-S-H of the different blends, at 300 days for the outer product.

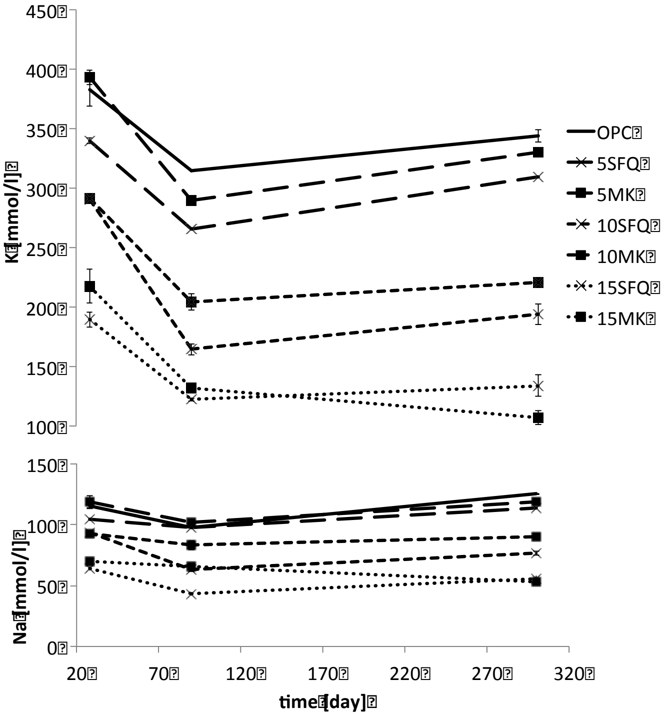

FIGURE 3: Pore solution alkali analysis of the different blended pastes

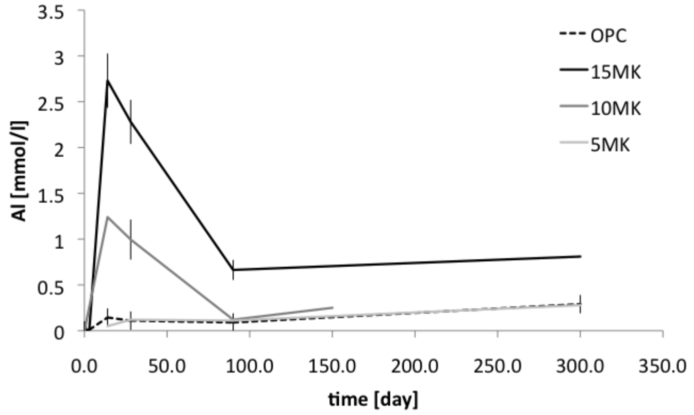

FIGURE 4: Evolution of the aluminium concentration in metakaolin blended pastes over time.

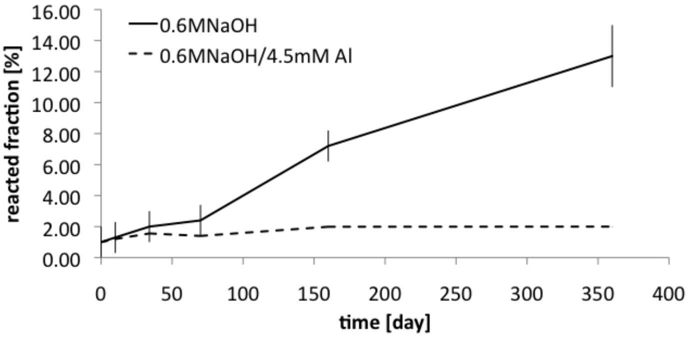

FIGURE 5: Reacted fraction of reactive aggregates in simulated pore solution without and with 4.5mM aluminium at 60°C over 1 year.

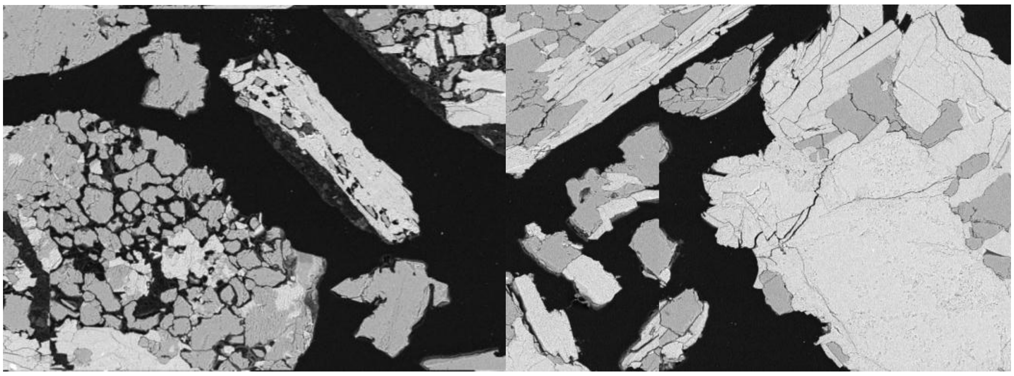

FIGURE 6: State of the aggregates after 1 year in solution without (left) and with (right) 4.5mM aluminium in solution (image width 500um)