ALKALI SILICA REACTION MITIGATING PROPERTIES OF TERNARY BLENDED CEMENT WITH CALCINED CLAY AND LIMESTONE

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Abstract

A promising way to reduce CO_2 is using blend with a high level of substitution by widely available Supplementary cementitious materials (SCMs) such low grade calcined clay and limestone. Further, blended systems have well established benefits in terms of durability.

ASR is the most important durability issue not related to reinforcing steel. Prevention is critical as sources of non-reactive aggregates are increasingly scarce. Since ASR occurs between alkalis in pore solution and reactive silica, most mitigation methods rely on empirical tests through SCMs. The effectiveness of SCMs in mitigating ASR is attributable mainly to the inhibition of silica dissolution when Al ions provided by the SCMs. Due to uncommon usage in the field, the mechanisms which underlie the properties of such blends are still not wholly understood. In this study, we demonstrate the performance of blends with high level of replacement (reaching 50%) of cement with limestone and calcined clay.

Keywords: Alkali silica reaction, ternary blended cement, limestone, calcined clay

1 INTRODUCTION

Concrete structures are often subject to degradation due to the alkali silica reaction (ASR). ASR is a reaction between amorphous silica from aggregates and the alkalis from the pore solution of the cement paste. This results in an expansive gel which induces cracks until a complete deterioration of the concrete. Despite decades of study, the chemistry of ASR gels remains poorly understood. Knowledge of the chemical composition is essential for understanding and predicting ASR expansion behaviour and developing effective mitigation measures.

The use of supplementary cementitious materials to control the expansion is well established and a number of reviews have been published[1,2].However, the role of SCMs and their mechanisms in mitigating ASR remain unclear. Some researchers have shown that mineral additions lead to a reduction in the concentration of alkali-hydroxides in the pore solution of concrete, the amount of reduction is being directly linked to the SCM replacement levels. The reduction was thought to be the principal factor in the mitigating properties, however, field experience shows expansions in very low alkali systems. Therefore, it has been also suggested that the presence of alumina in SCMs contributed some way to prevent the release of alkali back to the pore solution. However, Chappex et al. [3] showed that this effect is extremely small. Alumina is an inhibitor of silica dissolution [4]. Based on these observations, the use of alumina-rich SCMs, such as calcined clays containing metakaolin should be favoured for the purpose of mitigating ASR effects. By changing the chemical environment of the aggregates, the chemical composition of the ASR can be impacted with beneficial and /or detrimental effects. The effect of Ca was studied by Hou et al.[5] but the effect of uptake of al by gels remains unknown.

In this study, we investigate the chemical composition of ASR gels in the aggregates in -portland cement and in limestone--calcined clay cement (LC3) by EDS mapping.

2 MATERIALS AND METHODS

2.1 Materials and mix designs

Three different binders are studied, a ternary blended cement with a substitution of 30% by calcined clay and 15% of limestone noted "LC3-50 (50%)", a ternary blended cement with a substitution of 30% by commercial metakaolin from Burgess and 15% of limestone noted "LC3-50 (95%)" and a CEM I noted "PC". The alkali content is adjusted to be identical by adding NaOH in water during the mix. The aggregate used was a highly reactive North American river aggregate (Jobe). This sand has several potentially reactive facies. A good proportion of chert, especially in the coarser fractions, there is identified and some chert grains may contain chalcedony. In addition, this sand contains various types of volcanic rock: andesite / basalt,

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which contains the matrix of volcanic glass in some cases. A volcanic rhyolite rock types was also observed; its matrix consists of microcrystalline silica. These various volcanic facies type have a high potential reactivity of alkali (RAS). They are rather abundant in coarser sand fractions.

Mortars bars were cast with the same Water/Binder ratio of 0.46, the amount of plasticizer was adjusted to obtain a workable mixture. Some mortar bars were cast with inset metal measurement studs to monitor expansion. The aggregate to cement ratio was 3. The mortars bars were first cured for 28 days at 20 °C and 95 %RH. They were then put in alkaline solution containing 0.32 mol/l NaOH as it is close to the pore solution and at 38 °C to accelerate the expansion. As a control, a batch was cured in 1.6 mol/l, matching the reported alkali pessimum for Jobe reported in the literature[6,7].

2.2 Methods for assessment and analysis

General

Expansion was measured almost weekly following ASTM C1293-08b[8] at 38°C. Depending on the results of expansion, mechanical properties such as flexural strength, compressive strength and elastic modulus were measured (data not showed).

Then, at these times, samples were taken for SEM analysis on a FEI Quanta 200. A high resolution montage of 144 pictures at a magnification of 800× was acquired to analyse a representative amount of aggregates. The amount of degradation in the aggregates was quantified by the image analysis method developed by Dunant [9]. First, the aggregate particles are identified by a combination of grey level and shape. Then the dark areas, corresponding to cracks and gel in the aggregates are thresholded and measured.

SEM-EDS mapping

The scanning electron microscope is used with Bruker XFlash 4030 EDS detector with 30 mm active surface. The microscope was operated at 15 kV accelerating voltage and 12.5 mm working distance. The system was configured to carry out EDS element mapping with magnification 400X, the image resolution was 1024×768 and the pixel size $0.246 \times 0.246 \mu$ m.

The following elements were quantified from the spectra: Al, Si, Na, K. The quantification of elements was carried out by Esprit software using a profile fit with standards and PhiRhoZ matrix corrections. The calculations are automated and require around 1 h per frame. The results are expressed in atomic percent. Custom MATLABTM software was used to treat the data. And it plotted in a ternary diagram for further analysis as atomic percentage. Part of the plot >95 atomic-% Si contains a high intensity peak and was deliberately truncated from the display to better visualize other phases.

The experimental set up is described in more details by Durdzinski et al. [10].

3 RESULTS

3.1 Expansion versus damage

Figure 1 shows the expansion after the samples had reached equilibrium with their environment after 1-2 week as function of time for the portland cement in NaOH solution with two concentration 0.32M and 1.6M and for ternary blend with calcined clay and limestone. We can observe that the expansion was more important in portland cement than in LC3 systems. In the 1.6M, the expansion seemed to be faster but stabilize after a while. However in the lower concentration solution, the expansion increased slower without stabilisation. The LC3-50 (50%) did not expand in 150 days.

In figure 2, we observe the expansion as a function of damages. We can observe that the portland cements had a high expansion with relatively few damages. Whereas, in LC3-50 systems the expansion was lower but the damages were important.



FIGURE 1: Expansion as a function of time after immersion in Na OH solution for three different cements with Jobe sand. PC 0.32M is immersed in 0.32 NaOH solution whereas PC 1.6 M is immersed in 1.6 M NaOH solution. The dotted line indicates the limit of innocuous behavior on concrete at one year according to ASTM C1293-08b[8].



FIGURE 2: Expansion as a function of damages after immersion in Na OH solution for three different cements with Jobe sand. PC 0.32M is immersed in 0.32 NaOH solution whereas PC 1.6 M is immersed in 1.6 M NaOH solution.

3.2 Aggregate composition by SEM-EDS

In this part, we illustrate a method to track the ASR gel compositions formed in the aggregates in different systems in Al-Si-Na+K plot. We focused on expansive system (PC) and a non-expansive system LC3-50 (50%).

Figure 3 shows the composition of the aggregates as detected and quantified by the method. We observe 3 types of aggregates plus the truncated one as pure Si aggregates. In this figure, we observe the aggregates before exposure in alkali solution as a reference state.

Figure 4, we plotted the data for the aggregates in PC 1.6M to emphasize the main ASR gels compositions overtime. After 150 days, we observed intermix composition but the starting composition seemed to shift to 2 main compositions respectively the red area Si~80% Na~20% and the blue area Si ~30% Na~60% Al~10%. The first composition corresponds to a pure sodium-silicate gel and the second to a stable aluminosilicate gel [11]. The two compositions were tracked into LC3-50 system and PC0.32M system (Figure 5 and Figure 6). In both systems, we can find these gels. These results were highlighted in Figure 7 and Figure 8. We observe the location of these gels in the aggregates. We see these two gels in both systems with no direct link to expansion as PC expanded and LC3-50 (50%) not.

The gel with the "red composition" seemed to be located in the boundaries of damaged zones as the gel with the" blue composition" was located inside the damaged aggregates. The remaining question was the gel with the "blue composition" is the same gel as the gel with the "red composition" but aged with an uptake of aluminium overtime?

On the BSE images of the complete system we can also notice a different state of the paste. The paste in LC3-50(50%) seemed less damaged and presented less cracks as in PC systems.



FIGURE 3: Ternary plot of Jobe aggregates without immersion in NaOH solution in linear scale.



FIGURE 4: Ternary plot of Jobe aggregates in PC 1.6 M after 150 days of immersion in 1.6M NaOH solution (log scale).



FIGURE 5: Ternary plot of Jobe aggregates in PC 0.32 M after 150 days of immersion in 0.32M NaOH solution (log scale).



FIGURE 6: Ternary plot of Jobe aggregates in LC3-50 (50%) after 150 days of immersion in 0.32M NaOH solution (log scale).



FIGURE 7: Left: BSE image of PC after 150 days of exposure Right: Same image on aggregates only with 2 ASR products with the following compositions: red Si~80% Na~20% blue Si ~30% Na~60% Al~10%



FIGURE 8: Left: BSE image of LC3-50 (50%) after 150 days of exposure Right: Same image on aggregates only with 2 ASR products with the following compositions: red Si~80% Na~20% blue Si ~30% Na~60% Al~10%

4 DISCUSSION

In this study, we shown that ternary blend cement with calcined clays and limestone can help to mitigate the ASR in term of expansion but also mechanically (data not showed but available in [12]). These results are not surprising considering the work of Chappex et al. [3,4,13], highlighting the positive effect of alumina in mitigating ASR. The values of the expansion do not cross the limit recommended by the standard [8]. However, this norm is defined for concrete consisting of poly dispersed aggregates after 1 year of exposure. The sands of this study are mono-sized and it has already been shown [14–16] that the size of aggregates plays an important role on the expansion rate after 100 days.

Moreover, this study emphasizes two interesting points:

- The expansion is not clearly related to the increase of damage within aggregates observed and quantified by image analysis. This can also suggest that a spate of expansion can be expected in the longer term.
- The chemical composition of ASR gels formed in the damaged aggregates are relatively close in expansive and non-expansive systems.

5 CONCLUSIONS AND PERSPECTIVES

The blended system containing aluminosilicate clays is a promising cement to formulate ASR-resistant concretes. The method developed there allowed to highlight the composition inside the damaged aggregates and cracks and can be used as a powerful tool to further investigate the products formed by ASR.

A new experimental campaign was launched to investigate the gels composition in the case of aggregate.with slower reactivity. The impact of the solution will also studied by immersion of samples in KOH/NaOH solutions with the concentration similar to the corresponding pore solution or in 0.32M NaOH solution.

6 ACKNOWLEDGEMENT

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