

STUDY OF THE KINETICS OF HYDRATION OF INDUSTRIAL GRANULATED BLAST FURNACE SLAGS: A STRUCTURAL INVESTIGATION

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Introduction

Currently used as cement constituent (CEM II, III or V), granulated blast furnace slag induces various short and long term effects on mechanical strength and durability of the concrete. Many factors could be invoked among which the composition¹. To explain these differences, it is important to understand the hydration mechanisms of ground granulated blast furnace slag (GGBS) and the kinetic of formation of the hydration products. In our study, two GGBS with different origins were put in contact with a cement pore solution and hydration was stopped after times ranging from 24 h to 7 days. The change in structure after each time step was investigated using multi-nuclear high resolution solid state NMR. The different phases detected were quantified to draw the kinetic of the hydration.

Materials and methods

In this study, which is part of an RFCS research project called ActiSlag, we selected two GGBS samples from different sources, based on their difference in compressive strength (mix of 75 wt% GGBS and 25 wt% clinker) despite their rather close chemical composition. At 2 days their compressive strength is completely different, 4.3 MPa and 15.6 MPa respectively, whereas they are closer at 91 days, 53.6 MPa and 62.4 MPa respectively. The two samples labelled GGBS4.3 and GGBS15.6 in accordance with their respective compressive strength at 2 days, were initially fully characterised by a combination of techniques including SEM and multinuclear Solid State NMR.

As the aim of this work is to identify and quantify the phases formed during hydration of GGBS alone, neither clinker nor binder were added. However to stay as close as possible to real conditions, a mix of GGBS and Portlandite (Ca(OH)_2) (weight ratio of 1:3) was hydrated with a solution of KOH (0.071 mol L^{-1}) and K_2SO_4 (0.115 mol L^{-1}) with a liquid/solid weight ratio of 1.2. After various delays, the pastes were dipped in acetone for 2 minutes, filtered on a Büchner filter and finally dried in a vacuum (10^{-3} bar) for 15 minutes. The obtained samples were then characterised shortly after the hydration stoppage to prevent any possible alteration.

The environment of silicon and aluminium were studied by High Resolution Solid State ^{29}Si and ^{27}Al NMR. ^1H - ^{29}Si and ^1H - ^{27}Al Cross Polarization Magic Angle Spinning (CP-MAS) experiments were performed to edit specifically the signals corresponding to hydrated phases. The ^{29}Si MAS and ^1H - ^{29}Si CPMAS experiments were acquired on a Bruker AVANCE 400 MHz spectrometer ($B_0 = 9.4\text{T}$, $\nu_{\text{RF}}(^1\text{H}) = 400 \text{ MHz}$, $\nu_{\text{RF}}(^{29}\text{Si}) = 79.4 \text{ MHz}$, $\nu_{\text{rot}} = 10 \text{ kHz}$), whereas the ^{27}Al MAS and ^1H - ^{27}Al CPMAS experiments were acquired on a Bruker AVANCE 750MHz spectrometer ($B_0 = 17.6\text{T}$, $\nu_{\text{RF}}(^1\text{H}) = 750 \text{ MHz}$, $\nu_{\text{RF}}(^{27}\text{Al}) = 195.5 \text{ MHz}$, $\nu_{\text{rot}} = 30 \text{ kHz}$). All the spectra obtained were then simulated using the DMFit software². The CPMAS experiments were first simulated to determine the positions and width of the signals consistent with hydrated phases. These parameters were then used to simulate the quantitative MAS spectra and determine the proportions of Si and Al in each of the detected phases.

Results and discussion

Silicon environment

The main hydrated silicate phases are calcium silicate hydrates, CSH or CASH in presence of aluminium. It is generally accepted that the CSH phase has a tobermorite-like structure, which includes CaO_2 layers with sevenfold coordinated Ca^{2+} ions, where the oxygens are shared with Si^{4+} in chains of SiO_4 tetrahedra in a “dreierketten” arrangement on both sides of the CaO_2 layer.² C(A)SH are then constituted of Q^1 and Q^2 units which are well distinguished from the signal of the slag. After 24 h of hydration, evidence of silicon in hydrated phases is only detected in the best performing GGBS15.6 sample. After 48 h, as seen in Figure 1, evidence of these phases is detected in both GGBS4.3 and GGBS15.6. Interestingly, the better performing sample GGBS15.6 displays lower proportions of silicon in the unaltered slag phase (70%) and higher proportions of silicon in the hydrated phases (30%). The reactions induced by the hydration are more advanced than in GGBS4.3 where 82% of the silicon is still in the vitreous network of the slag. Moreover, in both cases the main hydrated species are Q^1 , indicating low incorporation of aluminium as well as very short chains (mainly dimers) in the silicate sheet. As the reactions advance, the proportion of Q^1 , which means dimers, increases but not the length of the chains.

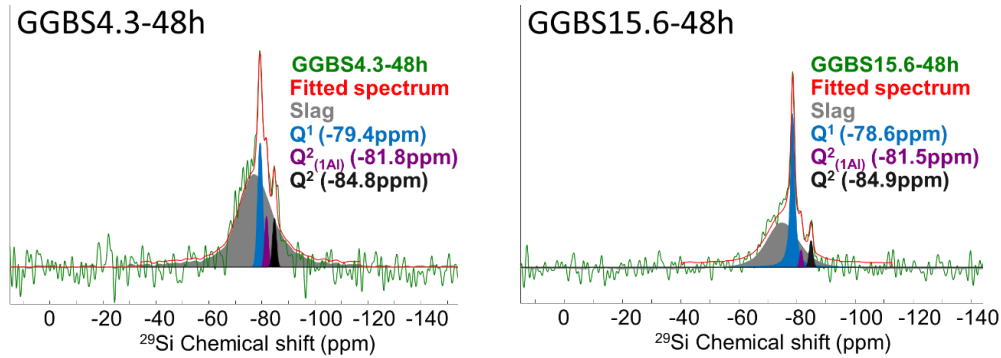


Figure 1: Experimental and fitted ^{29}Si MAS spectrum of GGBS15.6 and GGBS4.3 after 48 h of hydration

Aluminium environment

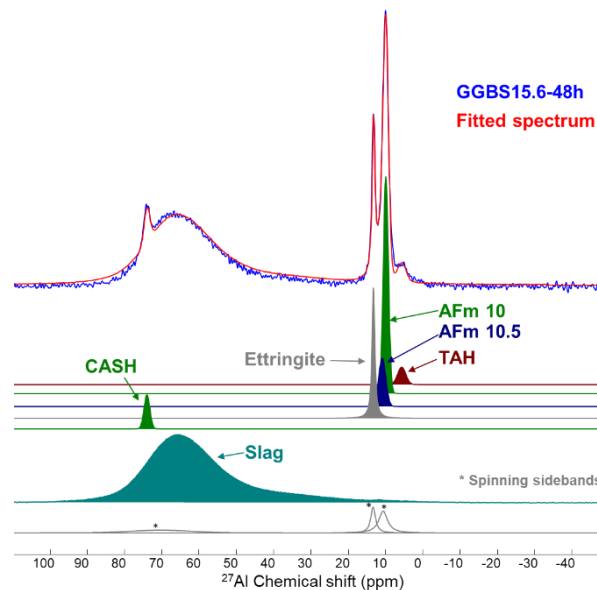


Figure 2: Experimental and fitted ^{27}Al MAS spectrum of GGBS15.6 after 48 h of hydration

As shown in Figure 2, the ^{27}Al NMR results allowed for the identification of CASH phases, Ettringite, (at least) two AFm phases (labelled AFm10 and AFm10.5, in accordance with their respective chemical shifts) and the third aluminium hydrate (TAH)³. The evolution of the proportions of aluminium in all phases after different times are shown in Figure 3. It can be seen that the dissolution rates of the two samples are dramatically different. In the case of GBS4.3 the dissolution is very slow until 24 h (only 5%), then we observe a net acceleration between 24 and 48 h and again a slow-down until 7 days. On the contrary, the dissolution is very fast before 24 h in the case of GBS15.6 (28%), followed by a slowdown and a new acceleration until 7 days. Moreover, after 7 days of hydration, around 75% of the GGBS15.6 slag has disappeared whereas only 32% of the GBS4.3 slag is dissolved. In the case of GBS4.3, the concentration of aluminium in AFm10 increases slowly from 0 to 7 days. The important dissolution of slag between 24 and 48 h seems to be related to the

rapid formation of the second AFm phase (AFm10.5) during the same period, which then disappears concomitantly with the apparition of Ettringite. In the case of GGBS15.6, the slag dissolution is rapid and intense, leading to the formation of both AFms after 24 h. Between 24 h and 48 h, the formation of AFm10 slows down with the slag dissolution and AFm10.5 seems to disappear concomitantly with the formation of Ettringite (similarly to GGBS4.3). The restarting of rapid slag dissolution seems to induce the important formation of AFm10, while the formation of AFm10.5 and Ettringite continues. The proportion of aluminium in TAH phases remains quite low in both samples. The CASH appear a little bit earlier in GGBS15.6, and their proportions increase slowly.

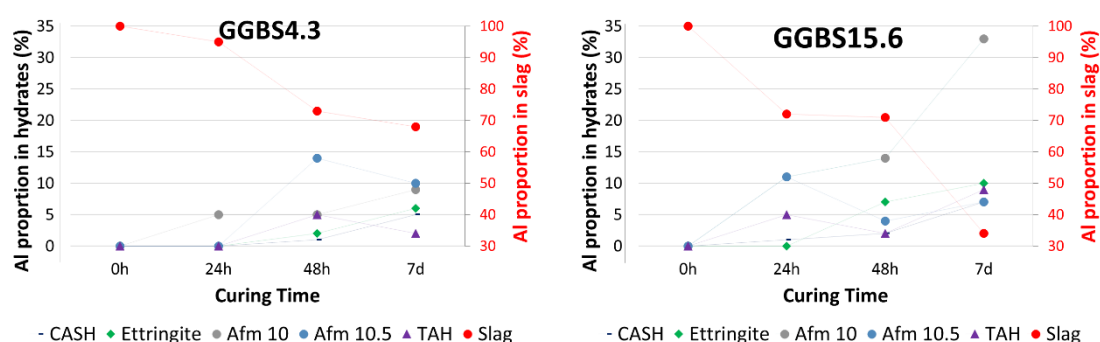


Figure 3: Evolution of the proportion of aluminium in the hydrated phases and in the unaltered slag after different curing times

Conclusion

We show that the dissolution profiles of two chemically similar GGBS samples, can be very different, leading to the formation of the same hydration products, but in very different proportions, inducing a difference in the compressive strength of the GGBS containing cement.

Acknowledgements

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References

1. A. Bougara, C. Lynsdale, N.B. Milestone, "Reactivity and performance of blastfurnace slags of differing origin", *Cem Concr Comp*, **32** 319-324 (2010).
2. I.G. Richardson, A.R. Brough, R. Brydson, G.W. Groves, C.M. Dobson, "Location of aluminum in substituted calcium silicate hydrate (C-S-H) gels as determined by ^{29}Si and ^{27}Al NMR and EELS", *J Am Ceram Soc*, **76** 2285-2288 (1993).
3. M. D. Andersen, H. J. Jakobsen, J. Skibsted, "A new aluminium-hydrate species in hydrated Portland cements characterized by ^{27}Al and ^{29}Si MAS NMR spectroscopy", *Cem Concr Res*, **36** 3-17 (2006).