In-situ early age hydration of cement-based materials by synchrotron X-ray powder diffraction

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[#]**XDS. X-ray Data Services** http://www.xdataser.com/

ABSTRACT

Cement based binders are building materials of worldwide importance. Since these samples are very complex, the knowledge and control of their mineralogical composition are essential to design and predict materials with specific/improved performance [1]. Rietveld quantitative phase analysis (RQPA) allows the quantification of crystalline phases and, when combined with specific methodologies, as the addition of an internal standard or the external standard approach (G-factor), amorphous and non-crystalline phases can also be quantified. However, to carry out a proper RQPA in hydrated cementitious materials, a good powder diffraction pattern is necessary. In this work, synchrotron X-ray powder diffraction (SXRPD) has been used, allowing *in-situ* measurements during the early-age hydration process.

This work deals with the early hydration study of cement-based materials. The studied samples were: a laboratory-prepared belite calcium sulfoaluminate (BCSAF) clinker (non-active) [2] mixed with 10 wt% gypsum, labelled G10B0; two active laboratory-prepared BCSAF clinkers (activated with 2 wt% borax) [2], one mixed with 10 wt% of gypsum and the other one with 10 wt% of monoclinic bassanite, hereafter named G10B2 and B10B2, respectively; and an environmentally-friendly binder sample from Henkel, composed of calcium sulphate hemihydrate mixed with 15 wt% Portland cement (OPC) and 10 wt% Metakaolin, hereafter named H1.

Cement nomenclature will be used hereafter, i. e. C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3 and $\underline{S}$=SO_3.

RAW MATERIALS

Henkel binder_H1

Bassanite 75 wt%, Alite 15 wt%, Metakaolin 10 wt% + **15 wt% of Quartz (internal standard)**

Non-active clinker BCSAF_B0

β-C_2S 50 wt%, $C_4A_3\underline{S}$ 30 wt%, C_4AF 20 wt%

Active clinker BCSAF_B2

α'$_H$-C_2S 50 wt%, $C_4A_3\underline{S}$ 30 wt%, C_4AF 20 wt% addition of $Na_2B_4O_7{\cdot}10H_2O$ ⇨ 2.0 wt% B_2O_3

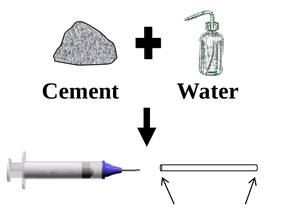
SAMPLE PREPARATION

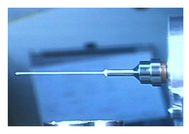
Clinker B0/B2 + 10 wt% of Gypsum or Bassanite → Cement

10 wt% of gypsum **G10B0 & G10B2**

10 wt% of bassanite **B10B2**

HYDRATION PROCEDURE



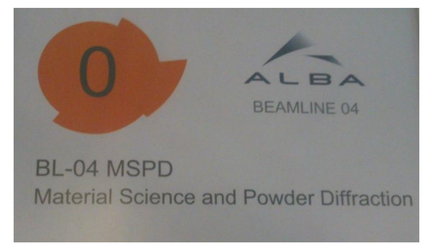


Diameter of capillaries

0.7 mm — **H1** — **w/c = 0.375**

0.5 mm — **G10B0, G10B2 and B10B2** — **w/c = 0.55**

DATA COLLECTION



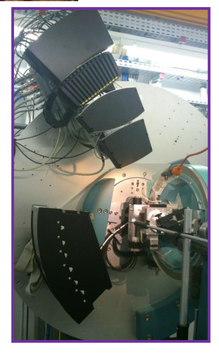
λ = 0.62 Å

Debye Scherrer configuration

Capillaries were spun

Angular range 1-35º (in 2θ)

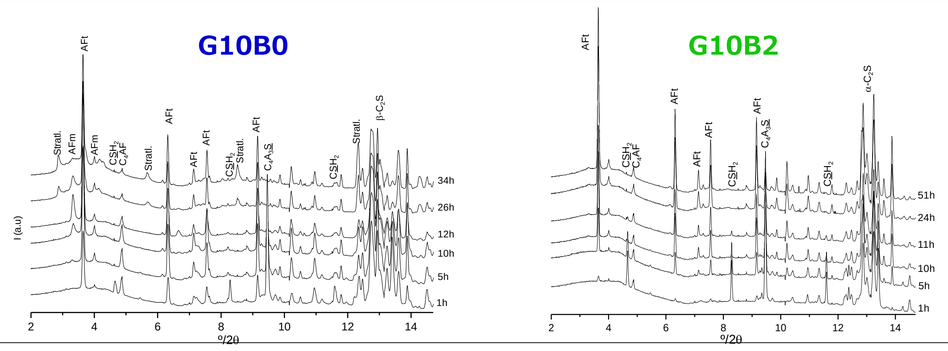
15 minutes per pattern



MYTHEN Detector

RESULT RESULTS & DISCUSSION

Influence of activation in the hydration behavior at early ages



1st Important difference in the hydration process:

Degree of reaction after 1 hour: G10B0 (α~25%); G10B2 (α~10%)

Gypsum is completely dissolved: G10B0= 5 hours; G10B2= 11 hours

Ye'elimite is completely dissolved: G10B0= 26 hours; G10B2= 51 hours (remains)

AFt crystallization after 1 hour: G10B0= 14.2(2) wt% (α~30%); G10B2= 1.9(1) wt% (α~5%)

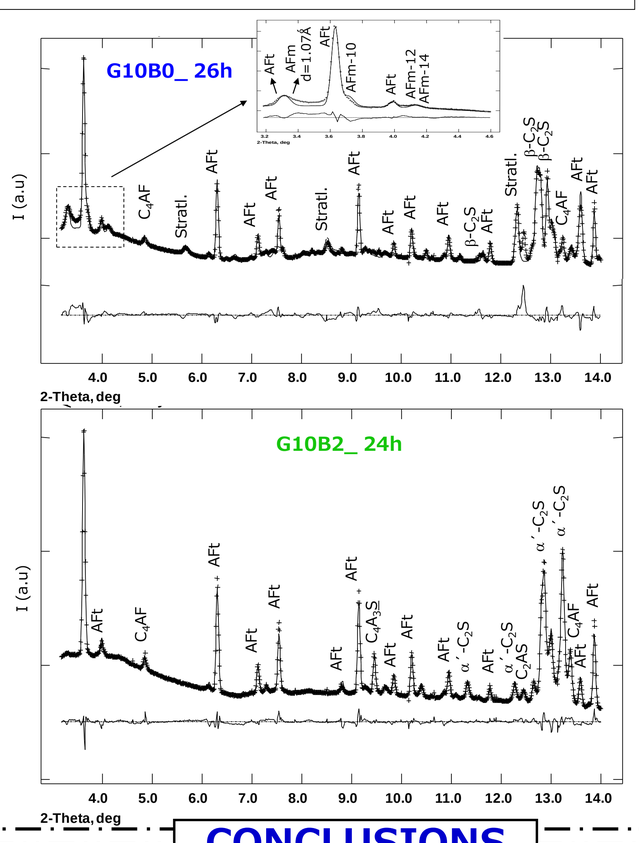
2st Important difference in the hydration process:

β-C_2S and C_4AF starts to be dissolved in **G10B0** after 1 day ⇨ crystallization of AFm type phases [2], including stratlingite.

On the other hand, for **G10B2**, α'$_H$-C_2S percentage remains constant up to 51 hours of hydration and C_4AF dissolves very slowly after 14 h.

β-C_2S reacts faster than α'$_H$-C_2S

Hydration behavior of belite is more dependent on the chemical environment (higher AH_3 content) than on its polymorphism. Furthermore, slower hydration **G10B2** led to much higher mechanical strength developments.



The role of calcium sulfate source

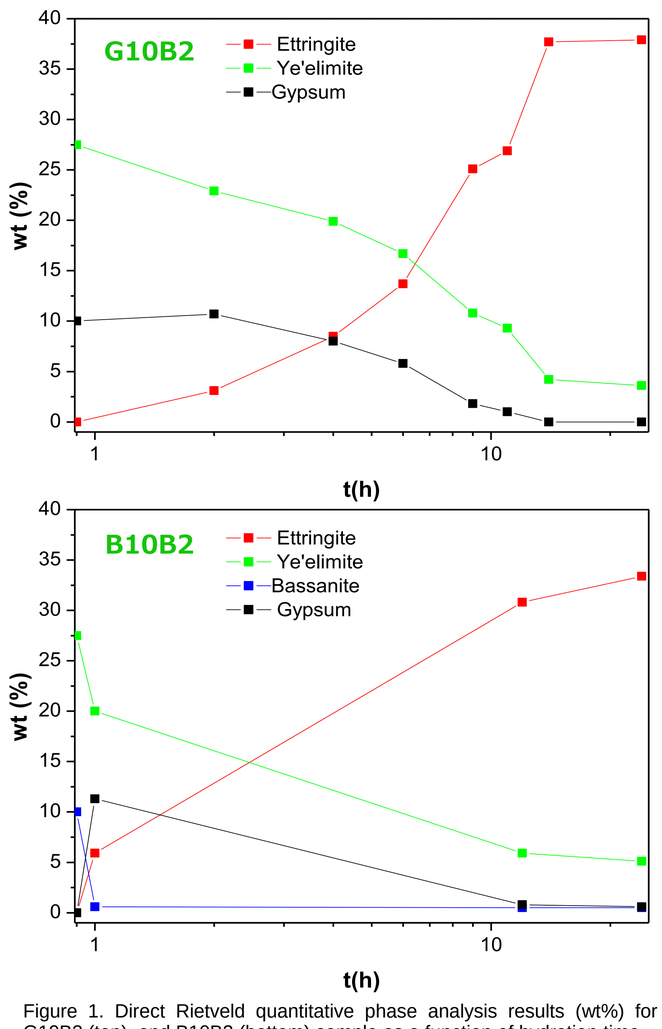


Figure 1. Direct Rietveld quantitative phase analysis results (wt%) for G10B2 (top) and B10B2 (bottom) sample as a function of hydration time.

The type of sulphate source has important consequences on the hydration of the active BCSAF cement pastes. Bassanite is quickly dissolved and it precipitates as gypsum within the first hour of hydration (in B10B2). At that time, ettringite starts to crystallize (Figure 1), and after 12 hours is almost fully crystallized, similar to G10B2.

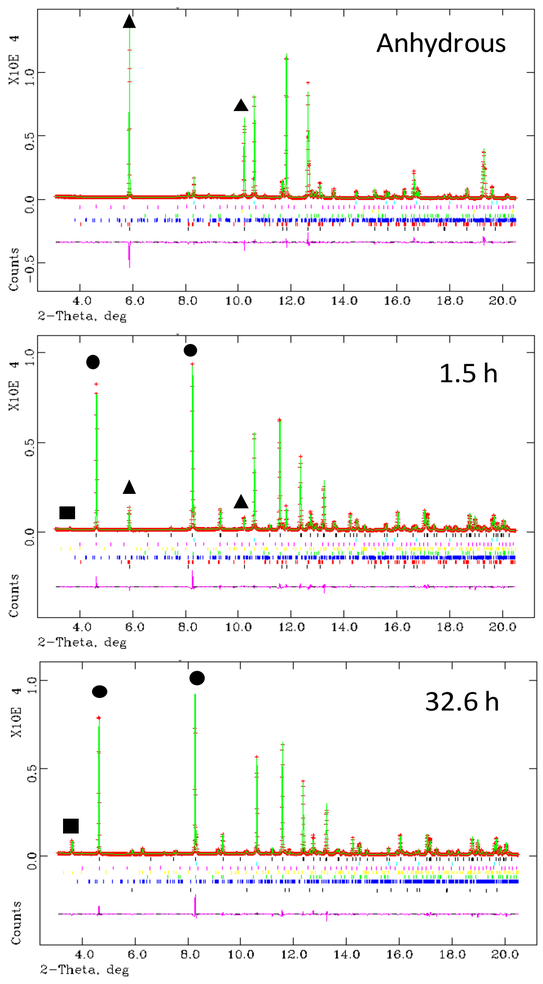


Figure 2. Rietveld plots for anhydrous (top), hydrated after 1.5 hours (middle) and 32.7 hours (bottom) H1 cement. Bassanite, gypsum and ettringite marked with triangle, circle and square, respectively.

In H1, bassanite transforms into gypsum within the first hour, being the principal hydration product; ettringite starts to be formed just after few minutes of hydration (Figure 2).

CONCLUSIONS

- ✓ Experimental setup & data analysis procedures are mature and they can be applied to several chemical reactions including hydration of cements.
- ✓ In-situ early-age hydration study of cement-based materials have been analyzed with synchrotron XRPD (SXRPD) and Rietveld methodology.
- ✓ Ye'elimite, in the B10B0 pastes, dissolves at a higher pace than in the active one (degree of reaction is α~25% and α~10% at 1 h, respectively)
- ✓ In B10B0, the presence of high amounts of ettringite at early hours of hydration implies a concomitant large amount of available aluminates, which can precipitate as stratlingite, C_2ASH_8, enhancing belite reactivity.
- ✓ The very fast dissolution of bassanite has been quantified showing the accuracy of the reported methodology.
- ✓ These results are crucial in the understanding and development of improved cement materials.

REFERENCES

[1] H. F. W. Taylor, Cement Chemistry. Telford, London, (1997).

[2] G. Álvarez-Pinazo, A. Cuesta, M. García-Maté, I. Santacruz, E.R. Losilla, A.G. De la Torre, L. León-Reina, M.A.G. Aranda, *Cem. Concr. Res.* **42** (2012) 960.

Acknowledgments: We thank the financial support by MAT2010-16213 and P11-FQM-7517.