In situ hydration studies of C_3S: a joint laboratory powder diffraction ($MoK_{\alpha1}$) and calorimetry approach

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Portland cement's early-age strength development depends primarily on the tricalcium silicate hydration. Ca_3SiO_5 is abbreviated C_3S and named alite in its impure form present in the cements. C_3S reacts/hydrates to form crystalline $Ca(OH)_2$ (named portlandite) and nanocrystalline calcium silicate hydrate (C-S-H) gel:

$$Ca_3SiO_5\ _{(s\text{-}cryst.)} + 5.2\ H_2O\ _{(l)} \rightarrow 1.2\ Ca(OH)_2\ _{(s\text{-}cryst.)} + (CaO)_{\sim1.8}(SiO_2)(H_2O)_{\sim4.0}\ _{(s\text{-}amorph.)}$$

The complexity of this reaction is influenced by thermodynamic and physical parameters, including temperature, water-to-solid (w/s) mass ratio, chemical admixtures and textural properties of the starting C_3S material.

To better understand the hydration reaction mechanism, a multimodal approach combining isothermal calorimetry and in situ laboratory X-ray powder diffraction has been implemented. The sample is Ca_3SiO_5, doped with 2 wt% of MgO to stabilize the T_3 polymorph, featuring a $D_{v,50}$ of 8.7 µm, $V_{<3µm}$ of 16.6 % and specific surface area value of 1.1 m^2g^{-1}. Six different pastes were prepared, with w/s=0.50: i) neat, ii) 0.1 % of a polycarboxylate ether-based (PCE) superplasticizer (SP1), iii) 0.1 %SP1+2 %Master X-Seed 100 (commercial nano-seed admixtures), iv) 0.1 %SP1+2 %Master X-Seed STE53 (commercial nano-seed admixtures), v) 0.1 %SP1+0.05 %TIPA (tri-isopropanol amine) and vi) 0.1 %SP1+1 %$CaCl_2$ (all percentages by weight of solid).

For the in situ LXRPD measurements, strictly monochromatic $MoK_{\alpha1}$ radiation was used. The above-described pastes were prepared and injected into borosilicate glass capillaries of 1 mm diameter by using a syringe. To prevent water loss and carbonation during the in situ study, the capillaries were sealed with a UV glue [1]. LXRPD data (transmission mode) were collected at 27 ºC, measuring every 2 h during the first 24 h, with a final measurement at 48 h of hydration. Isothermal calorimetry was performed at 20 ºC and 30 ºC for the same pastes.

Results indicate that pastes containing SP1 exhibit delayed but slightly enhanced hydration kinetics, see Fig 1a. The addition of admixtures further modifies this behaviour: the hydration of the $CaCl_2$ paste is strongly accelerated and enhanced, whereas those containing SP1 and TIPA are slightly retarded. As expected, the cumulative heat during the reaction is higher for the samples containing $CaCl_2$ and C-S-H seeds, see Fig.1b.

LXRPD data were analysed by Rietveld Quantitative Phase Analysis (RPQA) using GSAS-II, quantifying the crystalline phases and calculating the amorphous content per 100 g of paste as in [2]. Following this approach, the degree of hydration (DoH) can be determined at every hydration time, based on the crystallization of portlandite and the dissolution of C_3S, see Fig. 1c. The agreement between calorimetric and RQPA results is noteworthy. This multimodal approach reveals that the acceleration-to-deceleration transition occurs around 6 h, at a DoH of ≈20 % for this sample at ≈30 ºC. More details will be reported and discussed.

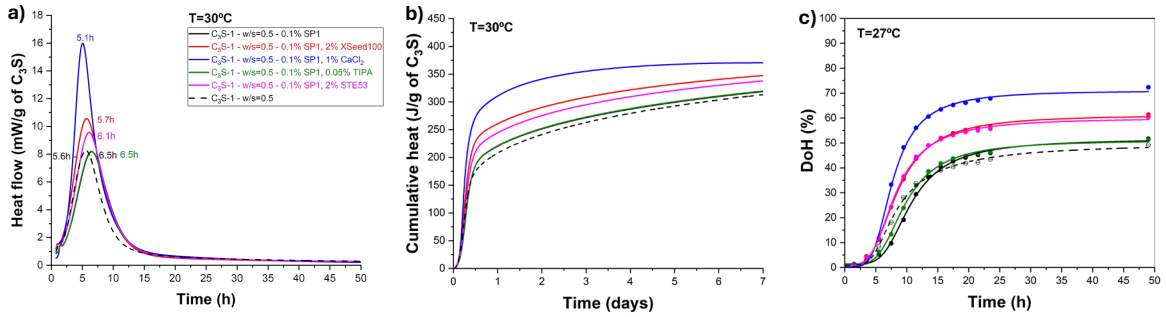


Figure 1. *Isothermal calorimetry results:* ***a)*** *Heat flow and* ***b)*** *cumulative heat traces for the investigated pastes at 30ºC.* ***c)*** *DoH obtained from laboratory $MoK_{\alpha1}$-LXRPD patterns for the in-situ hydration of the different pastes.*

[1] S. Shirani *et al. Cem. Concr. Res.* **2024**, 175, 107370. doi: 10.1016/j.cemconres.2023.107370.
[2] J. Fernandez-Sanchez *et al. J. of Appl. Crystallogr.* **2024**, 57, 1067-1084. doi: 10.1107/S1600576724004527.