In-situ hydration studies of PC: a joint laboratory powder diffraction (MoK$_{\alpha1}$) and calorimetry approach

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The multiphase nature of Portland cement (PC) and the complex interaction of its physicochemical parameters hinder a comprehensive understanding of its hydration mechanisms. PC exhibits intrinsic variability in its elemental composition, phase proportions, and textural properties (particle size distribution and specific surface area). Hydration reactions are further influenced by the incorporation of organic and inorganic admixtures. Furthermore, hydration processes are strongly dependent on thermodynamic and kinetic variables, such as the water-to-cement ratio (w/c), temperature, pressure and the alkalinity of the medium. Prior to hydration, PC contains more than six principal crystalline components: $C\bar{S}H_2$ ($CaSO_4{\cdot}2H_2O$, gypsum and/or other calcium sulfates), C_3S (Ca_3SiO_5, alite), C_3A ($Ca_3Al_2O_6$, tricalcium aluminate), C_4AF ($Ca_4Al_2Fe_2O_{10}$, tetracalcium aluminoferrite), $C\bar{C}$ ($CaCO_3$, calcite/limestone), and C_2S (Ca_2SiO_4, belite), ordered according to their hydration rates. C_3S hydrates forming crystalline portlandite (CH, $Ca(OH)_2$) and nanocrystalline calcium silicate hydrate gel (C-S-H, $(CaO)_{1.8}(SiO_2)(H_2O)_{4.0}$). C_3A reacts with gypsum to form ettringite (AFt, $Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$) or with $C\bar{C}$ and CH to produce hemicarboaluminate (AFm-Hc, $Ca_4Al_2(OH)_{13}(CO_3)_{0.5}(H_2O)_{5.5}$). C_4AF can react with C_3S and $C\bar{S}H_2$ forming CH, AFt, and an amorphous Fe-Si-H hydrogarnet ($Ca_3Fe_2(SiO_4)_{0.84}(OH)_{8.64}$), or with C_3S and $C\bar{C}$ producing CH, AFm-Hc, and amorphous Fe-Si-H [1].

To further investigate the hydration mechanisms, a multimodal approach combining isothermal calorimetry and in-situ X-ray powder diffraction (LXRPD) was employed. The sample used was PC-52.5, with $D_{v,50}$ = 10.7 µm, $V_{<3\,\mu m}$ = 18.4 vol%, and a specific surface area of 1.7 $m^2\,g^{-1}$. Six different pastes were prepared, with w/c = 0.50: i) neat, ii) 0.34 wt% of a polycarboxylate ether-based (PCE) superplasticizer (SP1), iii) 0.34 wt% SP1 + 2 wt% Master X-Seed 100 (commercial nano-seed admixture), iv) 0.34 wt% SP1 + 2 wt% Master X-Seed STE53 (commercial nano-seed admixture), v) 0.34 wt% SP1+0.05 wt% TIPA (tri-isopropanol amine) and vi) 0.34 wt% SP1 + 1 wt% $CaCl_2$. In situ LXRPD measurements were performed using strictly monochromatic MoK$_{\alpha1}$ radiation. After mixing, the pastes were injected into 1 mm borosilicate glass capillaries and sealed with UV glue to prevent water loss and carbonation [2]. LXRPD data (transmission mode) were collected at 27°C, measurements every 2 h during the first 24 h and a final dataset at 48 h. Isothermal calorimetry was conducted at 20°C and 30°C for the same pastes.

Hydration kinetics were significantly influenced by the admixtures. STE53 accelerated and intensified the reaction, reaching the highest heat flow, whereas TIPA delayed the onset of hydration but produced a peak intensity higher than the control, see Fig. 1a. The accumulated heat was greater in pastes containing STE53 and TIPA see Fig. 1b. LXRPD data were analysed by Rietveld quantitative phase analysis (RQPA) using GSAS-II, quantifying the crystalline phases and calculating the amorphous content per 100g of paste as described in [1]. Following this approach, the degree of hydration (DoH) can be determined at each hydration time, based on portlandite crystallization and C_3S dissolution, see Fig. 1c. Further details will be given at the meeting.

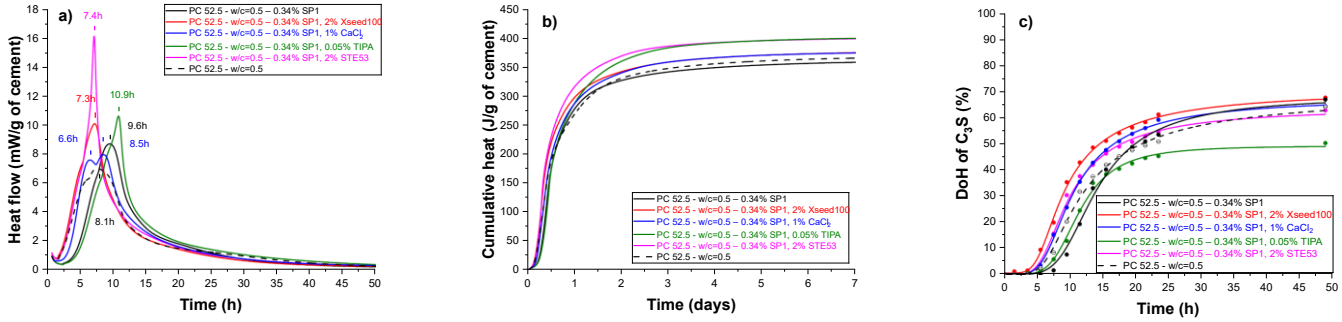


Figure 1. *Isothermal calorimetry results:* ***a)*** *Heat flow and* ***b)*** *cumulative heat traces for the investigated pastes at 30ºC.* ***c)*** *DoH obtained from MoK$_{\alpha1}$-LXRPD patterns for the in-situ hydration of the different pastes.*

[1] J. Fernandez-Sanchez *et al. J. of Appl. Crystallogr.* **2024**, 57, 10 67- 1 084. doi: 10.1107/S1600576724004527.

[2] S. Shirani *et al. Cem. Concr. Res.* **2024**, 175, 107370. doi: 10.1016/j.cemconres.2023.107370.