# Digging into different symmetries in crowded systems: C3S, C2S, C3A and all the polymorphs

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Portland cement (OPC) is the most widely used construction material worldwide, with an annual production of approximately 1.5 billion tonnes. In industrial X-ray diffraction (XRD) analysis of clinker used for OPC, increasing attention has been given to the identification and quantification of specific polymorphs of the main constituents $C_3S$ ($Ca_3SiO_5$), $C_2S$ ($Ca_2SiO_4$) and $C_3A$ ($Ca_3Al_2O_6$). These polymorphs are associated with differences in hydration reactivity, early strength development and sulfate demand, and also provide insight into kiln conditions and cooling rates during clinker production.[1]

$C_2S$ exhibits several temperature-dependent polymorphs (α, α′H, α′L, β, γ), crystallizing in space groups $P6_3/mmc$, $Pnma$, $P2_1/n$, $P2_1/n$ and $Pna2_1$, respectively. Their relative abundance reflects clinker cooling history and significantly influences reactivity. $C_3S$ occurs primarily in monoclinic polymorphs M1 and M3 (Cc and C2/c), stabilized by minor element substitution, with M1 typically exhibiting slightly enhanced intrinsic reactivity compared to M3.[2,3] In contrast, $C_3A$ polymorphism is composition-controlled rather than temperature-driven: pristine $C_3A$ crystallizes in monoclinic symmetry ($P2_1$), whereas alkali substitution (Na/K) stabilizes cubic ($Pm\bar{3}m$) or orthorhombic (Pbca) variants.

Due to the structural complexity, pseudosymmetry and severe peak overlap among multiple clinker phases, phase identification and quantitative analysis on standard laboratory XRD instruments approach practical resolution and sensitivity limits.[4] We therefore compare high-resolution synchrotron powder diffraction data from commercial clinker samples with data collected on laboratory instruments (e.g., Figure 1) using both industrially relevant measurement settings and optimized high-resolution configurations. The goal is to assess the theoretical and practical limits of polymorph discrimination and quantification under realistic industrial constraints.

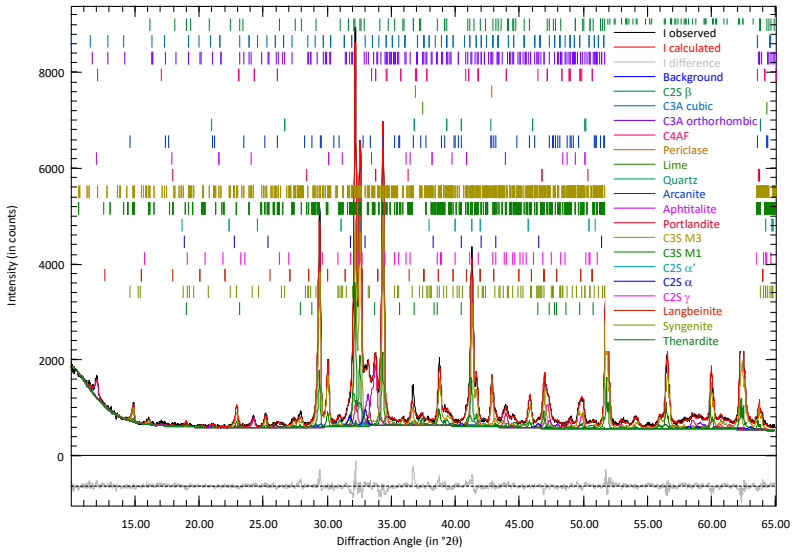



***Figure 1.*** *Rietveld refinement of NIST2686b clinker SRM*

[1] H. F. W. Taylor, *Cement Chemistry*, 2nd ed., Thomas Telford (1997).
[2] H A. G. De la Torre, M. A. G. Aranda, *Acta Cryst.* B (2003). **59**, 326–334.
[3] Y. Zhang, J. Liu, X. Chen, Z. Wang, *Int. J. Concr. Struct. Mater.* (2022). 16, 39.
[4] A. G. De la Torre, S. Bruque, M. A. G. Aranda, *Cem. Concr. Res.* (2001). **31**, 1347–1356.