

## Ca $L_{2,3}$ -edge near edge X-ray absorption fine structure of tricalcium aluminate, gypsum, and calcium (sulfo)aluminate hydrates

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### ABSTRACT

Tricalcium aluminate (cement clinker phase), gypsum, katoite, ettringite, and calcium monosulfoaluminate hydrate (abbreviated as kuzelite) are the major minerals in the hydration reaction of tricalcium aluminate in the presence of gypsum and have critical impacts on the kinetics and thermodynamics of early-age cement hydration mechanisms. Here, spectroscopic analysis of these minerals is conducted using scanning transmission X-ray microscopy (STXM). Their Ca  $L_{2,3}$ -edge near edge X-ray absorption fine structure (NEXAFS) spectra are measured and correlated to the known Ca coordination environments. The results indicate that these minerals have unique Ca environments that can be differentiated from one another based on the intensities and positions of the absorption peaks at 346.5–348.5 and 350.5–351.5 eV. It is concluded that Ca in tricalcium aluminate (cubic and orthorhombic polymorphs) and katoite is in cubic-like coordination with negative  $10Dq$ , whereas Ca is in an octahedral-like coordination with positive  $10Dq$  in ettringite, gypsum, and kuzelite. For tricalcium aluminate, the Ca atoms in both polymorphs are in similar chemical environments with slightly more distortion in the orthorhombic polymorph. As a common issue in STXM experiments, absorption saturation of NEXAFS spectra is also investigated. It is demonstrated that the optical density difference between pre- and post-edge absorption levels provides a reliable indication of the sample thickness in the systems studied. The present work provides a reference for the STXM study of the calcium (sulfo)aluminate reactions in cement hydration and natural aqueous environments, and in the former case, provides a more complete understanding of a system that may serve as a low-C alternative to Portland cement.

**Keywords:** Tricalcium aluminate, calcium aluminate hydrate, calcium sulfoaluminate hydrate, STXM, NEXAFS, Ca  $L_{2,3}$ -edge, absorption saturation