

Spectroscopic and Thermodynamic Insights into pH-Dependent Fe Incorporation and Phase Transformation in Hydrotalcite-group Structures

JIAXING BAN^{1,2,3}, BIN MA⁴, JOHN L. PROVIS¹,
 BARBARA LOTHENBACH² AND SERGEY V.
 CHURAKOV^{1,3}

¹Paul Scherrer Institute

²Empa

³University of Bern

⁴North China Electric Power University

Magnesia-based cements (Mg cements) are emerging as a low-carbon alternative to traditional Portland cement (PC), potentially resulting in lower CO₂ emission during production without compromising performance. Hydrotalcite-group layered double hydroxide phases (HT) play a crucial role in various applications of Mg cements, including heavy metal immobilization and corrosion resistance. Iron, which originates from supplementary cementitious materials, corrosion of steel reinforcement, and nuclear waste disposal systems, can be incorporated into the HT structure, influencing its thermodynamic stability and functional properties. However, the pH-dependent mechanisms of Fe incorporation and the resulting phase transformations in HT are poorly understood, particularly within the broad pH range characteristic of Mg cements.

This study explores the pH-dependent incorporation of Fe into HT using advanced synchrotron-based X-ray absorption spectroscopy (XAS) (Fig 1a) combined with thermodynamic modeling (Fig 1b). Our results show that increasing pH generally enhances Fe incorporation into the HT structure. However, at elevated temperatures (65°C), high pH levels (>11) suppress Fe incorporation, potentially altering HT formation and stability. Higher pH increases the solubility of Al and Fe in HT, leading to a higher divalent-to-trivalent ratio in the main layer and resulting in expanded unit cell parameters. Notably, the incorporation of iron into HT delays the formation of iron hydroxides (Fe(OH)₂ or Fe(OH)₃) in cement, mitigating volumetric expansion in cement system upon oxidation of steel. These findings provide valuable insights into the Fe-HT interaction in Mg cement systems, and in hydrotalcite-group minerals more generally, aiding in optimizing cement formulations for applications in waste stabilization, corrosion-resistant infrastructure, and sustainable construction.

