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Minerals in cement chemistry: A single-crystal neutron diffraction study of ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 27H_2O$

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Abstract

Ettringite, reported with ideal formula $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, is recognized as a secondary-alteration mineral and as an important crystalline constituent of Portland cements, playing different roles at different time scales. It contains more than 40 wt% of H_2O. The crystal structure and crystal chemistry of ettringite were investigated by electron microprobe analysis in wavelength-dispersive mode, infrared spectroscopy, and single-crystal neutron diffraction at 20 K. The anisotropic neutron structure refinement allowed the location of (22+2) independent H sites, the description of their anisotropic vibrational regime and the complex hydrogen-bonding schemes. Analysis of the difference-Fourier maps of the nuclear density showed a disordered distribution of the inter-column ("free") H_2O molecules of the ettringite structure, modeled (in the structure refinement) with two independent and mutually exclusive configurations. As the disorder is still preserved down to 20 K, we are inclined to consider that as a "static disorder." The structure of ettringite is largely held together by hydrogen bonding: the building units [i.e., SO_4 tetrahedra, $Al(OH)_6$ octahedra, and $Ca(OH)_4(H_2O)_4$ polyhedra] are interconnected through an extensive network of hydrogen bonds. The ettringite of this study has ideal composition $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 27H_2O$, with (Mn+Fe+Si+Ti+Na+Ba) < 0.04 atoms per formula unit. The effect of the low-temperature stability of ettringite and thaumasite on the pronounced "Sulfate Attack" of Portland cements, observed in cold regions, is discussed.

Keywords: Ettringite, Portland cement, crystal chemistry, single-crystal neutron diffraction, infrared spectroscopy, hydrogen bonding