

Interlayer structure model of tri-hydrated low-charge smectite by X-ray diffraction and Monte Carlo modeling in the Grand Canonical ensemble

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ABSTRACT

The present study aims primarily at refining a structure model for interlayer cations and H₂O molecules in tri-hydrated (3W) smectite ($d_{001} = 18\text{--}19 \text{ \AA}$). The $<2 \mu\text{m}$ fraction of the SWy-2 source clay (low-charge montmorillonite) was saturated by Mg²⁺, Ca²⁺, Ba²⁺, or Na⁺ cations, before collection of X-ray diffraction (XRD) patterns at 98% relative humidity. Experimental d_{001} values derived for the essentially homogeneous 3W hydrates provided volume constraints for Grand Canonical Monte Carlo (GCMC) simulations. Computed atomic density distribution of interlayer species were used in turn to calculate XRD intensities of 00 l reflections. The agreement between calculated and experimental 00 l intensities allowed validating the GCMC results of both interlayer H₂O content and distribution of interlayer species (cations and H₂O molecules). Computed atomic density profiles do not correspond to the usual model of three discrete planes of H₂O molecules but rather exhibit two sharp planes of H₂O molecules wetting the clay surfaces (at $\sim 2.7 \text{ \AA}$ from the clay layer surface). Additional H₂O molecules belong to cation hydration shells or define a poorly organized ensemble filling internal voids. This alternative model suggests that the stability of the 3W hydrate results from the dual interaction of some H₂O molecules with interlayer cation, through their second hydration shell, and with the 2:1 clay surface. Computed atomic density profiles were approximated to propose an interlayer structure model for 3W smectite. This simplified model includes two sets of two planes (symmetrical relative to the interlayer mid-plane) for H₂O molecules and one set for interlayer cations. This model allows reproducing experimental XRD patterns for the different samples investigated and thus represents a valid set of parameters for routine quantitative analysis of XRD profiles in an effort to determine smectite reactivity close to water-saturated conditions. Implications of such studies are crucial to provide experimental constraints on the behavior of the main vector of element transfer under conditions common in surficial environments and prevailing in waste repositories. In addition, the present study provides an experimental validation of structure models derived from the widely used ClayFF model, and thus allows its use to predict the fate of water in clayey systems close to water-saturated conditions.

Keywords: Crystal structure, smectite-water, tri-hydrated, water in smectite interlayer, montmorillonite, X-ray diffraction, Monte Carlo, simulation