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Dehydration of Ca-montmorillonite at the crystal scale. Part 2. Mechanisms and kinetics

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Abstract

A kinetic study of Ca-montmorillonite dehydration was performed based on information derived from X-ray diffraction (Ferrage et al. 2007, this issue) and, thus, focusing on interlayer water only. The dehydration was quantified following the two processes that were observed in the X-ray pattern modeling: the transitions between the different hydration states and small thickness decrease observed in the bi- and mono-hydrated layers. The thickness decrease of bihydrated layers with dehydration (activation energy E_a = 16 kJ/mol) was found to be controlled by a mechanism of two-dimensional diffusion of water molecules through the interlayer space, whereas for mono-hydrated layers the variation of thickness (E_a = 18 kJ/mol) occurred as a mechanism of slight local layer collapse and collapse propagation, attributed to a rearrangement of the configuration of the interlayer cation hydration shell. For the transition between the bi- and mono-hydrated state (E_a = 84 kJ/mol), the mechanism of reaction was found to evolve gradually with increasing temperature from local layer collapse and collapse propagation to a two-dimensional diffusion mechanism, as the forced diffusion of water molecules produced by the layer collapse transfers the control of the process to diffusion mechanism. This phenomenon causes the coexistence of two hydration states in a given interlayer. Finally, the transition between mono-hydrated and dehydrated layers (E_a = 132 kJ/mol) indicated the concomitance of water diffusion and local layer collapse and propagation mechanisms, although the structures were found to be homogeneous during this transition.

The determination of both mechanisms and the activation energy for these processes were used to establish a model of smectite dehydration at the crystal scale. This model can be used to calculate crystal shrinkage and interlayer water content upon dehydration, and to predict the evolution of the system.

Keywords: Crystal structure, smectite-water, diffusion, water in smectite interlayer, kinetics, smectite dehydration, mixed-layering, montmorillonite