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Investigation of smectite hydration properties by modeling experimental X-ray diffraction patterns: Part I. Montmorillonite hydration properties

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ABSTRACT

Hydration of the <1 μm size fraction of SWy-1 source clay (low-charge montmorillonite) was studied by modeling of X-ray diffraction (XRD) patterns recorded under controlled relative humidity (RH) conditions on Li-, Na-, K-, Mg-, Ca-, and Sr-saturated specimens. The quantitative description of smectite hydration, based on the relative proportions of different layer types derived from the fitting of experimental XRD patterns, was consistent with previous reports of smectite hydration. However, the coexistence of smectite layer types exhibiting contrasting hydration states was systematically observed, and heterogeneity rather than homogeneity seems to be the rule for smectite hydration. This heterogeneity can be characterized qualitatively using the standard deviation of the departure from rationality of the 00*l* reflection series (ξ), which is systematically larger than 0.4 Å when the prevailing layer type accounts for ~70% or less of the total layers (~25% of XRD patterns examined). In addition, hydration heterogeneities are not distributed randomly within smectite crystallites, and models describing these complex structures involve two distinct contributions, each containing different layer types that are interstratifed randomly. As a result, the different layer types are partially segregated in the sample. However, these two contributions do not imply the actual presence of two populations of particles in the sample.

XRD profile modeling also has allowed the refinement of structural parameters, such as the location of interlayer species and the layer thickness corresponding to the different layer types, for all interlayer cations and RH values. From the observed dependence of the latter parameter on the cation ionic potential (v/r; v = cation valency and r = ionic radius) and on RH, the following equations were derived:

$$\text{Layer thickness (1W)} = 12.556 + 0.3525 \times (v/r - 0.241) \times (v \times \text{RH} - 0.979)$$
$$\text{Layer thickness (2W)} = 15.592 + 0.6472 \times (v/r - 0.839) \times (v \times \text{RH} - 1.412)$$

which allow the quantification of the increase of layer thickness with increasing RH for both 1W (one water) and 2W (two water) layers. In addition, for 2W layers, interlayer H_2O molecules are probably distributed as a unique plane on each side of the central interlayer cation. This plane of H_2O molecules is located at ~1.20 Å from the central interlayer cation along the c^* axis.