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 00l 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 interstratified 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:

Layer thickness (1W) = 12.556 + 0.3525 \times (v/r – 0.241) \times (v \times RH – 0.979)

Layer thickness (2W) = 15.592 + 0.6472 \times (v/r – 0.839) \times (v \times 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 H2O molecules are probably distributed as a unique plane on each side of the central interlayer cation. This plane of H2O molecules is located at ~1.20 Å from the central interlayer cation along the c* axis.

INTRODUCTION

Bentonite has been long used as buffer material for engineered barriers in municipal waste disposal sites because of its low permeability when compacted and because of its cation-retention ability. These properties also make bentonite a possible buffer material in multi-barrier designs for nuclear waste repositories. Specifically, bentonite may be used to isolate intermediate-level, long-lived wastes (ILLW wastes) from the host geological formation and from the biosphere. The retention and mechanical properties of this material are mainly influenced by its smectite component. The high smectite content provides bentonite with a self-healing capacity and the ability to sorb cations, the latter being enhanced by the high surface area of smectite. Sorption would help limit or delay possible radionuclide migration. Both properties result from the specific hydration/expansion ability of this mineral component.

However, interactions between the nuclear waste package and the bentonite barrier could possibly alter these properties. For example, concrete as a civil engineering material or as a component of the waste package will produce alkali-rich, high-pH aqueous solutions (“pH plume”) during alteration. The effect of such solutions on smectite has been widely studied (Mohnot et al. 1987; Carroll-Webb and Walther 1988; Carroll and Walther 1990; Chermak 1992, 1993; Eberl et al. 1993; Huang 1993; Bauer and Berger 1998; Bauer et al. 1998; Bauer and Velde 1999; Cama et al. 2000; Taubald et al. 2000; Huertas et al. 2001; Rassineux et al. 2001; Claret et al. 2002). Smectite in the bentonite can be affected also by a thermal pulse resulting from the radioactivity of the waste package. By analogy with burial diagenesis in sediments