

Expansion and alteration behaviors of NH₄-montmorillonite

*Ryohei Kawakita¹, Akito Saito¹, Hiroshi Sakuma², Sohtaro Anraku³, Chie Oda³, Morihiro Mihara³, Tsutomu Sato⁴

1. Graduate school of engineering, Hokkaido University, 2. National Institute for Material Science, 3. Japan Atomic Energy Agency, 4. Faculty of engineering, Hokkaido University

Bentonite will be used as a buffer material in the geological disposal of radioactive waste due to the high swelling and cation exchange capacity of the main bentonite constituent Na-montmorillonite (Na-MMT). Replacement of the interlayer Na by other cationic species, however, can cause a significant reduction in the swelling behavior of MMT. Nitrate salts found in transuranic wastes can be reduced to form NH₄⁺ in deep underground conditions. NH₄⁺ ions could replace the interlayer Na cations of Na-MMT to form NH₄-MMT, but the swelling behavior of NH₄-MMT is not well known.

To improve understanding of the swelling behavior of NH₄-MMT, the expandability of a suite of homoionic MMT, including Na-MMT, K-MMT, Cs-MMT, and NH₄-MMT were investigated by XRD under controlled relative humidity (RH) conditions and supported by molecular dynamics (MD) calculations.

Differences in the swelling behavior of the suite of homoionic MMT were observed by XRD and could be largely explained in terms of the valence, the radius and the hydration energy of the interlayer cations. All these properties, however, are very similar for K⁺ and NH₄⁺ and so could not be used to explain the reduced swelling of K-MMT compared to NH₄-MMT under low RH conditions. Although it has been well known that K-MMT lost expandability by dehydration, it has not been well known whether this process would occur on NH₄-MMT or not.

First-principles MD calculations were conducted in a previous study (Shi et al., 2013) for NH₄-MMT containing only a small number of water molecules (less than 1.25 molecules per NH₄-MMT half unit cell). The hydrogen bonding and the network between the surface oxygen, interlayer NH₄⁺ ion and water were reported to be increased by adding more water molecules to the interlayer. The basal spacing measured by XRD under controlled RH in the current study are consistent with the interlayer containing less than one layer of water, although the interlayer charge may be different between samples. It is also difficult to make direct comparisons with Shi et al.'s calculations and experimental results because the number of water molecules in the interlayer cannot be precisely controlled experimentally.

The classical MD simulations in the current study described the mixing enthalpy of MMT / water molecules system by including the number of interlayer water molecules as a variable. The potential functions and parameters of MMT and water molecules proposed by Nakano and Kawamura (2006) and Kawamura (2008) were employed in this study. Parameters on NH₄⁺ are determined to reproduce NH₄Cl structure. The mixing enthalpy was used as an index to evaluate the swelling state stability. To consider the RH effect, the mixing enthalpy (H_{mix}) was calculated by: $H_{\text{mix}} = H_{(\text{MMT}+n\text{H}_2\text{O})} - (H_{\text{MMT}} + n\mu_{\text{H}_2\text{O}})$, where the chemical potential of water, $\mu_{\text{H}_2\text{O}}$ includes the effect of RH by: $\mu_{\text{H}_2\text{O}} = \mu^0 + RT \ln(P/P_0)$ (μ^0 : standard chemical potential, R : gas constant, T : temperature(K), P_0/P : partial pressure of water) The minimum of H_{mix} indicates the stable hydration state of the MMT. In this study, $n = 0$ to 20 water molecules were added to homoionic MMT to understand the different swelling behavior of K-MMT and NH₄-MMT under each RH condition. It was found that the series of calculated mixing enthalpy was consistent with the XRD results under controlled RH. In the NH₄-MMT system, the hydrogen bond between NH₄⁺ and surface oxygen on clay was confirmed from the radial distribution function. These hydrogen bonds make large basal spacing of NH₄-MMT rather than that of K-MMT at 0%RH, which lead to hydration at low RH condition compare to K-MMT because the expansion of smectite occurs when hydration of interlayer cation exceeds the electrostatic attraction between silicate layer and cation. This result indicates that NH₄-MMT is more

difficult to become non-expandable or less expandable mineral than K-MMT.

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