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Thermodynamic Modeling of Iodide Sorption onto Ca-montmorillonite by Calcium-Iodide Interlayer Ion-Pairing

SEONGGYU CHOI[1], JA-YOUNG GOO[1], YONGHEUM JO[1,2], SANG-HO LEE[1] AND JANG-SOON KWON[1]

[1]Korea Atomic Energy Research Institute

[2]Hanyang University

Presenting Author: schoi21@kaeri.re.kr

Montmorillonite is a major component of bentonite, a clay material widely considered as engineered barriers of deep geological repository (DGR) for high-level radioactive waste (HLW). Since the post-closure risk of DGR depends on the migration of released radionuclides to biosphere, it is crucial to comprehensively understand the radionuclide sorption phenomena onto montmorillonite to accurately assess the long-term safety of DGR. Montmorillonite is further categorized by its interlayer cation composition, with Na- and Ca-dominant types being the most abundant forms discovered and utilized. Ca-bentonites offer economic advantages, and several studies [1,2] have revealed that compressed Ca-montmorillonite can display comparable to or even greater swelling pressure than that of Na-montmorillonite at high dry density. However, the radionuclide sorption capabilities of Ca-montmorillonite have received less attention than Na-montmorillonite.

Iodine (I) holds particular importance in the safety assessment of DGR for HLW, attributed to its significance in the waste inventory, the long half-life of I-129 radioisotope, and its high solubility in natural waters. Aqueous iodine predominantly exists as iodide (I^-) across broad pH-Eh ranges except under highly oxidizing or acidic conditions. Iodide sorption onto clay minerals has been generally considered very weak or even negligible. Still, a previous study has suggested the formation of NaI(aq) ion-pair within the interlayer of Na-montmorillonite [3], and this inspired the authors to comparatively evaluate the iodide sorption capability of Ca-montmorillonite since such ion-paring is expected to be stronger for Ca-montmorillonite owing to the charge difference between the two interlayer cations. In this work, the basal spacings (d_{001}) of iodide-sorbed clay samples were analyzed by XRD and TEM, and the increase in d_{001} and reduction in layer corrugation were observed as the amount of sorbed iodide increased, signifying the formation of CaI^+ ion-pair within the interlayer of Ca-montmorillonite. Further, pH-dependent iodide sorption onto Ca-montmorillonite was examined by batch experiment, and adopting the ion-paring mechanism in the thermodynamic modeling of sorption data enhanced the overall quality of modeling.

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