Formation of Calcium-Iodide Ion-pair in the Interlayer of Ca-montmorillonite

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1. Introduction

Mechanistic understanding of the sorption phenomena of highly soluble fission products onto montmorillonite, a 2:1 phyllosilicate that comprises the majority in mineral components of the engineered barrier system (EBS) of deep geological repository (DGR) for high level radioactive waste (HLW), is essential for accurately assessing the radiological risks associated with a DGR after its closure. The montmorillonite is generally classified according to its principal interlayer cations, and the most abundant forms utilized and found in nature are Na- and Ca-type montmorillonites. Thus far, the thermal, hydrodynamic, mechanical, and chemical (THMC) properties of Na-montmorillonite-rich bentonites (e.g., MX-80, Kunigel V1, etc.) have been extensively investigated as reference clays for the EBS of DGR in numerous countries, whereas Ca-type clays have received rather less attention. However, several studies [1,2] have demonstrated that Ca-montmorillonite can exhibit comparable or even greater swelling pressure than Na-montmorillonite at high initial dry density, and most commercially available Ca-bentonites indeed satisfy the hydromechanical criteria required as an EBS material when formed into densely compressed blocks (dry density > 1.6 g·cm^{-3}) [3,4]. In this framework, Korea Atomic Energy Research Institute (KAERI) introduced Bentonil-WRK (Clariant Korea) as a new Ca-type reference research bentonite in 2021, and extensive experimental studies on its sorption properties with major radionuclides are in progress.

Iodine (I) is of specific interest in the safety assessment of a DGR for HLW due to its significance in the waste inventory, the long half-life of I-129 radioisotope (t$_{1/2}$ = 1.57×10^7 years), and its high solubility in natural waters. Dissolved I species can exist as iodate (IO$_3^-$) or iodide (I$^-$) depending on the Eh and pH of solution, with iodide predominating under reducing conditions. Generally, the chemisorption of iodide onto clay minerals has been considered very weak or even negligible, but a recent study indicated the formation and concentration of a neutral NaI(aq) ion-pair within the interlayer of Na-montmorillonite [5]. Such ion-pairing is more likely to occur in the interlayer of Ca-montmorillonite since the ionic interaction between I$^-$ and Ca^{2+} would be much stronger than that of Na$^+$ due to the charge difference; this inspired the authors to conduct systematic experiments on the sorption of iodide onto Ca-montmorillonite. In this work, pH-dependent chemisorption of iodide onto Ca-montmorillonite purified from Bentonil-WRK was examined by batch experiments, and the sorption thermodynamics was evaluated by adopting the characteristic ion-pairing mechanism in a modeling of sorption data. In addition, the basal plane spacing (d001) of I$^-$-sorbed clay analytes prepared in high [I(−I)]$_{total}$ conditions was analyzed by means of X-ray diffractometry (XRD) and transmission electron microscope (TEM), and the increase in d001 and reduction in the layer corrugation were confirmed, signifying that a CaI$^+$ ion-pair was predominantly formed in the interlayer of Ca-montmorillonite.

2. Experimental

Aqueous samples were prepared with ultrapure water (Merck Millipore, Milli-Q Direct 8), where their pH and ionic strength were precisely controlled using concentrated HCl (Sigma-Aldrich, 99.999 %), CaOH$_2$ (Sigma-Aldrich, 99.995 %), and CaCl$_2$ (Sigma-Aldrich, ≥ 99 %) solutions. The I(−I) stock solution was produced by diluting a 57 wt. % HI solution (Sigma-Aldrich, 99.99 %) while trace amount of I$_2$(aq) and I$_3^-$ species were fully reduced to I$^-$ by adjusting the pH of stock solution to be 7−8 using a CaOH$_2$ solution. Montmorillonite, with a 95 wt. % mineral purity, was separated from raw Bentonil-WRK bentonite by performing the physical and chemical treatments detailed in elsewhere [6]. The purified Bentonil-WRK montmorillonite was further reacted with 1 M CaCl$_2$ solution for 198 hours to exchange the interlayer cations with Ca^{2+} and achieve homoionic Ca-montmorillonite. Subsequently, the clay suspensions were dialyzed against ultrapure water and lyophilized.

Batch sorption experiments were conducted under the aqueous conditions of [I(−I)]$_{total}$ = 0.05−0.20 mM, S/L = 5 g·L^{-1}, I = 0.01 M CaCl$_2$, pH$_c$ 4−9, and T = 25 ± 2 °C for 198 hours where pH$_c$ denotes the negative logarithm of proton concentration corrected from the measured pH [7]. After the sorption equilibrium was attained, the supernatants were separated by centrifugation at 5000 rpm for 10 minutes, and aliquots of the supernatants were acidified to determine the remaining concentrations of dissolved Al(III) and I(−I) by inductively coupled plasma-mass spectrometry (Perkin Elmer, NexION 350X) and UV-vis spectrophotometry (Varian, Cary 5), respectively. The quantified Al(III)

concentrations in the all analytes were below the detection limit (5 ppb) while UV-vis absorbance of a blank clay supernatant (without I(−I) spike) was also negligible, which signify that the centrifugal separation was successful. A parameter estimation code PEST [8] coupled with PHREEQC [9] was employed to thermodynamically model the sorption data where the diffuse double layer model was adopted to correct electrostatic term in the assessment of surface complexation of I^- with edge sites of montmorillonite.

Additional sorption experiments were conducted in 0.10−0.82 M CaI_2 solutions at a neutral pH_c, and powder XRD patterns of the randomly oriented I^--sorbed clays were recorded on the diffractometer (Rigaku, SmartLab SE) with a Cu Kα source at 40 kV and 50 mA. For TEM measurement, the lyophilized clay analytes were ultrasonically dispersed in a pure ethanol (Sigma-Aldrich, 200 proof) and then placed on a copper grid. Subsequently, the morphology of clay analytes was measured using a field-emission TEM equipment (Hitachi HF5000) at an acceleration voltage of 200 kV with a cold field-emission electron gun.

3. Results and discussions

The chemisorption of I^- onto the purified Ca-montmorillonite generally reached an equilibrium state within 120 hours, while the I^- sorption onto polypropylene containers or its loss through volatilization were confirmed to be negligible under the experimental conditions. The assessed sorption distribution coefficient (Kd) values gradually decrease with increasing pH_c, yet weak but observable sorption (Kd = ~10 $L \cdot kg^{-1}$) constantly remains at $pH_c > 6$. The pH_c-dependent sorption behavior under acidic conditions indicates the interaction between I^- and edge surface functionalities of montmorillonite. On the other hand, the pH_c-independent maintenance of Kd values under neutral-alkaline conditions implies that the I^- sorption also occurs in the interlayer of montmorillonite, possibly through ion-pairing mechanism, as H^+/Ca^{2+} cation exchange reaction becomes insignificant at $pH_c > 5$ [6]. The edge functionalities of montmorillonite can be simplified and divided into two major groups: amphoteric aluminol ($\equiv AlOH$) and monoprotic silanol ($\equiv SiOH$) groups. Considering the electrical charges of associated surface and aqueous species, it is assumed that the surface complexation of I^- at $pH_c < 6$ is primarily attributed to the presence of protonated aluminol sites, as indicated by its reaction formula in eq. (1). Additionally, the ion-paring of CaI^+ in the interlayer space of Ca-montmorillonite can be described as shown in eq. (2), where X represents the interlayer sorption site formed by a permanent negative structural charge.

(1) $\equiv AlOH_2^+ + I^- \rightleftarrows \equiv AlOH_2{-}I$
(2) $X_2{-}Ca + Ca^{2+} + 2I^- \rightleftarrows 2X{-}Ca{-}I$
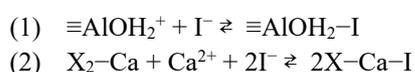
Indeed, adopting both the surface complexation (eq. (1) and ion-pairing (eq. (2)) mechanisms in the thermodynamic sorption modeling allowed a more suitable fitting of the batch data, since the I^- surface complexation with the protonated aluminol sites cannot solely explain the pH_c-independent sorption at $pH_c > 6$. For each reaction mechanism, logarithms of equilibrium constants (log K) with their uncertainties, corresponding to a 95 % of confidence level, are determined to be 0.32 ± 0.26 and 4.58 ± 0.32, respectively.

Besides, XRD and TEM analyses of the clay analytes reacted with higher $[I(−I)]_{total}$ display that d001 increases from 13.4 to 14.8 Å, while the full width at half maximum (FWHM) of the associated diffraction peak (2θ) decreases from 1.3 to 0.6º. Such expansion yet homogenization of interlayer spacing is comparable to that of $CaCl^+$ ion-paring in the Ca-montmorillonite [10], generally explained by the larger ionic radius and denser packing of CaI^+ ion-pair compared to those of free Ca^{2+} cation.

REFERENCES

[1] O. Karnland, S. Olsson, U. Nilsson, Mineralogy and sealing properties of various bentonites and smectite-rich clay materials, Swedish Nuclear Fuel and Waste Management Company, 2006, TR-06-30.
[2] B. Akinwunmi, J. T. Hirvi, S. Kasa, T. A. Pakkanen, Swelling pressure of Na- and Ca-montmorillonites in saline environments: A molecular dynamics study, Chem. Phys., Vol. 528, 110511, 2020.
[3] S. Kaufhold, W. Baille, T. Schanz, R. Dohrmann, About differences of swelling pressure-dry density relations of compacted bentonites, Appl. Clay Sci., Vol. 107, pp. 52-61, 2015.
[4] M. Kim, J. Lee, S. Yoon, S. Choi, M. Kong, J.-S. Kim, Comparison and Analysis of Physical Properties Database for Buffer Material Candidates, Korea Atomic Energy Research Institute, 2023, KAERI/TR-9795/2023.
[5] A. Miller, J. Kruichak, M. Mills, Y. Wang, Iodide uptake by negatively charged clay interlayers?, J. Environ. Radioact., Vol. 147, pp. 108-114, 2015.
[6] S. Choi, B.-J. Kim, S. Seo, J.-K. Lee, J.-S. Kwon, Characterization of the Purified Ca-type Bentonil-WRK Montmorillonite and Its Sorption Thermodynamics With Cs(I) and Sr(II), Journal of Nuclear Fuel Cycle and Waste Technology, Vol. 21, No. 4, pp. 427-438, 2023.
[7] S. Choi, J.-I. Yun, Spectrophotometric study of the uranyl monobenzoate complex at moderate ionic strength, Polyhedron, Vol. 161, pp. 120-125, 2019.
[8] J. Doherty, Calibration and Uncertainty Analysis for Complex Environmental Models, Watermark Numerical Computing, Brisbane, Australia, 2015.
[9] D. L. Parkhurst, C. A. J. Appelo, Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, U.S. Geological Survey, Reston, VA, 2013.
[10] E. Ferrage, C. Tournassat, E. Rinnert, L. Charlet, B. Lanson, Experimental Evidence for Ca-Chloride Ion Pairs in the Interlayer of Montmorillonite. An XRD Profile Modeling Approach, Clays Clay Miner., Vol. 53, pp. 348-360, 2005.