

Influence of Illitization on the Ion-sorbing Capacity of Smectitic Clay

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1. Introduction

A high-level waste(HLW) repository uses smectitic clay as a buffer material to inhibit the penetration of groundwater and to retard the release of radionuclides from the radioactive wastes to the surrounding environment. However, when the smectitic clay is exposed to an elevated temperature due to radioactive decay heat and geochemical conditions for a long time, its physicochemical and mineralogical properties may be degraded and thus lose its barrier functions. It has been known in literature that the degradation of these properties of the smectitic clay occurs by a illitization in which the smectite transforms into illite. Therefore, an understanding of the illitization is essential to evaluate the long-term barrier performance of smectitic clay for the buffer of a HLW repository. This paper will carry out hydrothermal reaction tests with domestic smectitic clay which will be favorably considered for the buffer material of a Korean HLW repository, and also investigate the influence of illitization on the ion-sorbing capacity of the smectitic clay.

2. Materials and Methods

The solid sample used for the tests is natural smectite fractionated into a <2 μm size from a Ca-bentonite (i.e., smectitic clay) which was taken from Kyeongju, Korea. The original bentonite contains smectite (78 %), feldspar (20.1 %), quartz (1.7 %), and some impurities. The <2 μm fraction of the bentonite was separated by a centrifugation method. All the solutions were prepared by adding potassium chloride salt to de-mineralized water, except those for Run#16 and Run#18 in Table 1 which were conducted to investigate the sorption of cesium and nickel onto less altered solid material.

Tests were carried out in stainless steel pressure vessels with a Teflon liner by maintaining 1 g/20 ml of a solid sample-to-solution ratio. The test conditions were combinations of the following variable values: a temperature of 90, 140, and 200 °C, an initial concentration of KCl of 0.5 M, and a reaction time of 3, 7, 15, 28, 50 days. The distribution coefficients (K_d) of cesium and nickel ions for their sorption were determined from the following equation:

$$K_d = \frac{\text{Mass of an ion sorbed on a unit mass of a solid}}{\text{Mass of an ion per unit volume of solution}}$$

$$= \frac{(w_0 - w_1) / w}{w_1 / V} \quad [\text{L/g}] \quad (1)$$

where w_0 is the mass of an ion in the initial solution, w_1 the mass of an ion in the solution after a sorption equilibrium, w the mass of the solid, and V the volume of the solution.

Table 1. Experimental design for hydrothermal tests.

Run ID	Sample	Temp. (°C)	K ⁺ conc. (M)	Other ion conc. (M)	Time (days)	Analysis/measurement
ORM	Smectite					Starting material
1	Smectite	90	5x10 ⁻⁴	None	3	XRD, Si
2	Smectite	90	5x10 ⁻⁴	None	7	XRD, Si
3	Smectite	90	5x10 ⁻⁴	None	15	XRD, Si
4	Smectite	90	5x10 ⁻⁴	None	28	XRD, Si
5	Smectite	90	5x10 ⁻⁴	None	50	XRD, Si, EP, LC, CEC
6	Smectite	140	5x10 ⁻⁴	None	3	XRD, Si
7	Smectite	140	5x10 ⁻⁴	None	7	XRD, Si
8	Smectite	140	5x10 ⁻⁴	None	15	XRD, Si
9	Smectite	140	5x10 ⁻⁴	None	28	XRD, Si
10	Smectite	140	5x10 ⁻⁴	None	50	XRD, Si, EP, LC, CEC
11	Smectite	200	5x10 ⁻⁴	None	3	XRD, Si
12	Smectite	200	5x10 ⁻⁴	None	7	XRD, Si
13	Smectite	200	5x10 ⁻⁴	None	15	XRD, Si
14	Smectite	200	5x10 ⁻⁴	None	28	XRD, Si
15	Smectite	200	5x10 ⁻⁴	None	50	XRD, Si, EP, LC, CEC
16	Smectite	200	DW	5x10 ⁻³ M (Cs ⁺)	50	XRD, EP, LC, CEC, K_d
17	Smectite	200	5x10 ⁻⁴	5x10 ⁻³ M (Cs ⁺)	50	XRD, EP, LC, CEC, K_d
18	Smectite	200	DW	5x10 ⁻³ M (Ni ²⁺)	50	XRD, EP, LC, CEC, K_d
19	Smectite	200	5x10 ⁻⁴	5x10 ⁻³ M (Ni ²⁺)	50	XRD, EP, LC, CEC, K_d

EP: Expandability, LC: Layer charge, CEC: Cation exchange capacity, K_d : Sorption distribution coefficient

3. Results and Discussion

The alteration of the smectite samples, when they are hydrothermally treated under the potassium concentration of 0.5 M, was identified by examining the XRD patterns and silica releases into the solution. Figure 1 shows the evolution of XRD patterns for the reacted samples at 90 °C, 140 °C, and 200 °C. As shown in the Figures 1(a) and 1(b), there was no noticeable change in the reflection position, intensity, and width of the peak of the reacted samples at 90 °C and 140 °C. However, the XRD patterns for 200 °C (Figure 1(c)) revealed some differences when compared with that of the starting material. The first- and third-order reflection peaks were weak and broad although its position was at a nearly similar angle. This is a typical XRD pattern of randomly interstratified illite-smectite(I-S) which can be observed in the reaction series of a smectite with an increasing temperature and time: smectite -> randomly interstratified I-S (<65% illite) -> ordered I-S (>65% illite) -> illite. The decrease of the peak intensity and the broadness of its width, from the viewpoint of the X-ray diffractometry, are attributed to an interstratification of the illite and smectite layers with different basal spacings of their peak and thereby a layer-by-layer interference. The

percentages of the illite layer in the randomly interstratified I-S were 20.6, 25.5, 33.8, 35.7, 38.7 % for the reaction time of 3, 7, 15, 28, 50 days, respectively, when they were determined using the saddle/001 peak intensity ratio method. It follows from this that the starting smectite transforms into randomly interstratified I-S under the given hydrothermal conditions and eventually into illite with increasing time.

The profiles of the Si concentration for 90 °C and 140 °C showed a rapid increase within a short time period and then a nearly constant value, while that for 200 °C, indicating a much higher silica concentration than those for 90 °C and 140 °C, showed two distinguishable stages: a rapid increase in the silica concentration during the first 15 days and thereafter a more slowly increasing silica concentration. It is thought for the reaction at 200 °C that the first stage corresponds to a dissolution of the non-crystalline siliceous phase and the second one to a silica release from the tetrahedral sheet in the structural scheme of smectite due to the process of an illitization.

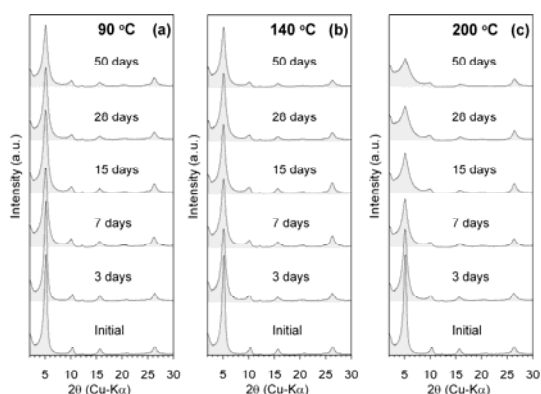


Figure 1. X-ray diffraction patterns

Figure 2 shows that the sorption distribution coefficients (K_d) of cesium and nickel ions for the reacted samples with a lower %S (Run#17 for cesium, Run#19 for nickel) are considerably lower in comparison with those of the samples with a higher %S (Run#16 for cesium, Run#18 for nickel), indicating that the sorption capacity of the smectite may be affected by the extent of a smectite alteration. These results are likely attributed to the reduction of the CEC due to the smectite-to-illite conversion. However, the change of K_d is more than 90 %, which does not correspond with ~30 % reduction in CEC. It is thought that there may be the possibility of an impact of the experimental conditions such as pH reduction or carbonate variations etc. as well as CEC on the sorption distribution coefficient, but an investigation of the possibility was not included in this study. Figure 3, which is a plot of the in-situ FT-IR spectra for the reacted samples after the sorption tests, indicates that the cesium ions were adsorbed onto the randomly interstratified I-S by a different mechanism from that of the nickel ions. The

reacted sample with the cesium ions sorbed has a distinctive band at ~685 cm^{-1} as compared with that of nickel ions. This is probably because the cesium ions may be adsorbed by a fixation to specific sorption sites of the “ditrigonal cavity” yielded in the tetrahedral layers due to a smectite-to-illite conversion [1-2], in addition to their sorption onto the interlayer and/or edge sites by ion-exchange reaction.

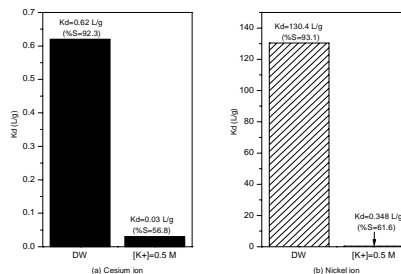


Figure 2. The Sorption distribution coefficients of cesium and nickel ions.

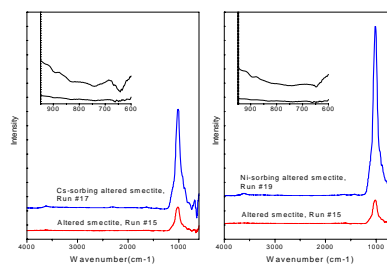


Figure 3. In-situ FT-IR spectra for the reacted samples

3. Conclusions

This study identified that when the smectite was hydrothermally treated under the potassium concentration of 0.5 M it was transformed from randomly interstratified I-S by a smectite-to-illite conversion. The temperature was a key factor controlling the conversion reaction. It was observed that such a smectite conversion might affect the ion-sorbing capacity of smectite clay. The sorption capacity for the cesium and nickel ions were reduced, when the temperature was increased. The obtained results will be used for evaluating the long-term barrier performance of smectitic clay for the buffer of a HLW repository.

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