



# Smectite alteration and its influence on the barrier properties of smectite clay for a repository

Jae Owan Lee<sup>a,\*</sup>, Il Mo Kang<sup>b</sup>, Won Jin Cho<sup>a</sup>

<sup>a</sup> Korea Atomic Energy Research Institute, P.O. Box 105, Yusong, Taejeon 305-600, Korea

<sup>b</sup> Korea National Oil Corporation, 1588-14, Gwanyang-dong, Dongsan-gu, Anyang, Gyeonggi-do 431-711, Korea

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## ABSTRACT

Hydrothermal tests were conducted to investigate smectite alteration and its influence on the barrier properties of a smectite clay for a repository. Examinations of the X-ray diffraction patterns of the starting material and reacted samples and the silica release rate in the solution revealed that the smectite was transformed into randomly interstratified illite–smectite by a smectite-to-illite conversion when it was hydrothermally treated under a potassium concentration of 0.5 M, maintaining a 1 g/20 ml of solid sample-to-solution ratio. Temperature was observed to be a key factor controlling the conversion reaction. The smectite alteration affected the barrier properties of smectite clay for a repository: when the temperature increased, the percentage of the expandable smectite layers in the randomly interstratified illite–smectite decreased, the layer charge was more negative, and the cation exchange capacity and the sorption capacity for the cesium and nickel ions were reduced.

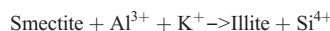
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## 1. Introduction

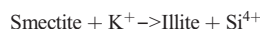
The major functions of the buffer in a high-level waste (HLW) repository are to inhibit the penetration of groundwater and to retard the release of radionuclides from the radioactive wastes to the surrounding environment. Smectite clay has been considered favorably as such a buffer material because of its high swelling and sorption capacities. However, when the smectite clay is exposed to an elevated temperature due to heat from radioactive decay and the particular geochemical conditions of a repository for a long time, it may be transformed into other minerals (e.g., illite, chlorite, etc.) which leads to a decrease in the swelling and sorption properties of the smectite clay and consequently increases its water penetration and radionuclide transport properties (Pusch and Carlsson, 1985; Bucher and Müller-Vonmoos, 1989). Therefore, an understanding of smectite alteration and its influence on the barrier properties of a smectite clay is essential to evaluate the long-term barrier performance of a buffer for a HLW repository.

Smectite alteration, especially smectite-to-illite conversion which may occur under commonly-prevailing pH conditions, has drawn considerable interest in the last few decades due to the implication of its reaction for clay diagenesis and migration of petroleum as well as the long-term barrier performance of a smectitic buffer for a repository. Very many investigators (Eberl, 1978; Roberson and Lahann, 1981; Inoue, 1983; Howard and Roy, 1985; Huang and Otten,

1987; Proust et al., 1990; Güven and Huang, 1991; Velde and Vasseur, 1992; Huang et al., 1993; Cuadros and Linares, 1996; Huertas et al., 2001; Bauer et al., 2005; Sato et al., 2005; Bauer et al., 2006) have studied the reaction mechanism and kinetics of smectite-to-illite conversion. On the basis of those studies, smectite-to-illite conversion has been suggested by a general consensus to proceed by two different mechanisms. One is a solid-state one-to-one transformation where T–O–T layers are conserved, and the reaction proceeds with a replacement of the tetrahedral Si<sup>4+</sup> by Al<sup>3+</sup> until the layer charge deficiency is sufficiently developed to dehydrate the interlayer cations, and a collapse occurs (Hower et al., 1976):



The other is a mechanism in which a destruction of the T–O–T layers provides the source of aluminium for the transformation, which thus consumes more smectite than it produces illite (Boles and Franks, 1979):



where the ratio of smectite consumed to illite produced is approximately 1.6:1, and no external source of aluminium is required. However, no consensus has been reached on which mechanism prevails because the reaction depends on different test conditions. The kinetics of a smectite-to-illite conversion has been studied to obtain a rate law for the overall conversion process (Pytte and Reynolds, 1989; Velde and Vasseur, 1992; Huang et al., 1993; Wei et al., 1993; Cuadros and Linares, 1996; Huertas et al., 2001). Most of these studies are based on field observation of clay diagenesis, while there

\* Corresponding author. Tel.: +82 42 868 2852; fax: +82 42 868 8850.

E-mail address: [jolee@kaeri.re.kr](mailto:jolee@kaeri.re.kr) (J.O. Lee).

**Table 1**  
Physicochemical and mineralogical properties of the bentonite and the separated smectite.

Sample	Properties
Bentonite	Mineral composition Smectite (78%), feldspar (20.1%), quartz (1.7%) CEC: 61.7 cmol/kg pH: 8.3
Smectite (<2 μm)	Chemical composition (wt.%) (by XRF) SiO <sub>2</sub> 58.21 Al <sub>2</sub> O <sub>3</sub> 18.31 Fe <sub>2</sub> O <sub>3</sub> 7.85 TiO <sub>2</sub> 0.91 CaO 0.15 MgO 3.19 MnO 0.04 Na <sub>2</sub> O 3.31 K <sub>2</sub> O 0.21 P <sub>2</sub> O <sub>5</sub> 0.10 L.O.I 7.49 Total 99.75 Structural formula (Ca, Na, K) <sub>0.93</sub> (Al <sub>2.57</sub> Fe <sup>+3</sup> <sub>0.78</sub> Mg <sub>0.64</sub> )(Si <sub>7.71</sub> Al <sub>0.29</sub> )O <sub>20</sub> (OH) <sub>4</sub> CEC: 96.5 cmol/kg

are not many studies based on systematic laboratory work. From these studies, it is implied that, although the most important parameters for controlling smectite-to-illite conversion are the temperature, potassium concentration, and reaction time, the proposed rate laws have limitations in their application to evaluate the extent of smectite-to-illite conversion under different repository conditions, due to an uncertainty in the parameter values. On the other hand, insufficient data has been reported regarding the influence of smectite alteration on the barrier properties such as the percentage of expandable smectite (MacEwan and Wilson, 1980; Huang et al., 1993), layer charge (Howard and Roy, 1985; Güven and Huang, 1991), cation exchange capacity (CEC) (Oscarson, and Hume, 1993), and sorption capacity (Comans et al., 1991; Ohnuki et al., 1994) of a smectite clay for a buffer of a HLW repository.

The present study, in this connection, focuses on investigating to what extent the smectite may be altered when it is hydrothermally treated under a certain potassium concentration and as a result how the smectite alteration may affect the barrier properties of a smectite clay for a Korean HLW repository.

## 2. Materials and methods

### 2.1. Materials

The solid material used for the tests was a natural smectite fractionated into a <2 μm size from a bentonite (Chun et al., 1998) which was taken from Kyeongju, Korea. The original bentonite contains smectite (78%), feldspars (20.1%), quartz (1.7%), and some impurities. The <2 μm fraction of the bentonite was separated by a centrifugation method, and the physicochemical and mineralogical properties of the separated natural smectite are as summarized in Table 1.

All the solutions were prepared by adding potassium chloride salt to de-mineralized water, except those for Run#16 and Run#18 in Table 2, which were conducted to investigate the sorption of cesium and nickel onto less altered solid material.

### 2.2. Hydrothermal experiment

Tests were carried out in stainless steel pressure vessels with a Teflon liner by maintaining a 1 g/20 ml of solid sample-to-solution ratio. The test conditions, as summarized in Table 2, were combinations of the following variable values: an initial potassium concentration of 0.5 M, a tem-

perature of 90, 140, 200 °C, an initial concentration of CsCl of  $5 \times 10^{-3}$  M and NiCl<sub>2</sub> of  $5 \times 10^{-4}$  M, and a reaction time of 3, 7, 15, 28, 50 days. The internal pressure was subject to an autogenous vapor pressure of H<sub>2</sub>O at a given temperature of each test run. Upon termination of the runs, the vessels were quenched in iced water for their rapid cooling to a temperature of 25 °C to reduce the possibility of silica polymerization. The cooled suspension was centrifuged at 10,000 rpm for 10 min; the solution was filtered on a 0.45 μm membrane; and the filtered solids were freeze-dried. The chemical and mineralogical investigations were conducted by means of inductively coupled plasma mass spectrometry (ICP-MS) for the liquid solutions, and X-ray diffraction (XRD), Fourier transform infrared spectrometry (FT-IR), and Electron Probe Micro Analysis (EPMA) for the solid samples. In preparation for the XRD analyses, each solid sample was resaturated with calcium ions to remove the exchangeable potassium not completely fixed into the illite interlayer during the hydrothermal tests. After extra electrolytes were washed with deionized water, oriented specimens were prepared by sedimenting the treated sample onto a glass slide, followed by ethylene-glycol (EG) treatment. The XRD analyses were performed with a Bragg-Brentano diffractometer (MXP 18A RINT-2500, Mac Science Co., Ltd, Japan): Cu-Kα (40 kV/30 mA), a graphic monochromator, a 1° divergence slit, a 0.15° receiving slit, two soller slits (2.4° and 2.5°), and 1 s / 0.05° 2 step-scanning. The FT-IR analyses for investigation of the sorption mechanism of cesium and nickel onto the solid material were conducted using an *in-situ* IR cell (Graseby, Specac Co.) with the water in the interlayer of the sample removed by vacuuming under the condition of 760 mmHg and 110 °C for 24 h.

### 2.3. Determination of expandability, layer charge, CEC, and sorption distribution coefficient

The expandability (the percentage of the expandable smectite layers in the interstratified I-S, % S) was determined using a saddle/001 peak intensity ratio for the ethylene-glycolated (EG) sample (Inoue et al., 1989). Glycolations were performed under ethylene glycol vapor at 60 °C for 24 h. In this analysis, the NEWMOD program (Reynolds, 1985) was complementarily used for simulating the XRD pattern of interstratified illite-smectite (I-S) and obtaining a calibration curve between the saddle/001 peak intensity ratio and % S. The layer charge was evaluated

**Table 2**  
Experimental design for hydrothermal tests.

Run ID	Sample	Temp. (°C)	K <sup>+</sup> conc. (M)	Other ion conc. (M)	Time (days)	Analysis/measurement
ORM	Smectite					Starting material
1	Smectite	90	$5 \times 10^{-1}$	None	3	XRD, Si
2	Smectite	90	$5 \times 10^{-1}$	None	7	XRD, Si
3	Smectite	90	$5 \times 10^{-1}$	None	15	XRD, Si
4	Smectite	90	$5 \times 10^{-1}$	None	28	XRD, Si
5	Smectite	90	$5 \times 10^{-1}$	None	50	XRD, Si, EP, LC, CEC
6	Smectite	140	$5 \times 10^{-1}$	None	3	XRD, Si
7	Smectite	140	$5 \times 10^{-1}$	None	7	XRD, Si
8	Smectite	140	$5 \times 10^{-1}$	None	15	XRD, Si
9	Smectite	140	$5 \times 10^{-1}$	None	28	XRD, Si
10	Smectite	140	$5 \times 10^{-1}$	None	50	XRD, Si, EP, LC, CEC
11	Smectite	200	$5 \times 10^{-1}$	None	3	XRD, Si
12	Smectite	200	$5 \times 10^{-1}$	None	7	XRD, Si
13	Smectite	200	$5 \times 10^{-1}$	None	15	XRD, Si
14	Smectite	200	$5 \times 10^{-1}$	None	28	XRD, Si
15	Smectite	200	$5 \times 10^{-1}$	None	50	XRD, Si, EP, LC, CEC
16	Smectite	200	DW	$5 \times 10^{-3}$ M (Cs <sup>+</sup> )	50	XRD, EP, LC, CEC, K <sub>d</sub>
17	Smectite	200	$5 \times 10^{-1}$	$5 \times 10^{-3}$ M (Cs <sup>+</sup> )	50	XRD, EP, LC, CEC, K <sub>d</sub>
18	Smectite	200	DW	$5 \times 10^{-4}$ M (Ni <sup>2+</sup> )	50	XRD, EP, LC, CEC, K <sub>d</sub>
19	Smectite	200	$5 \times 10^{-1}$	$5 \times 10^{-4}$ M (Ni <sup>2+</sup> )	50	XRD, EP, LC, CEC, K <sub>d</sub>

EP: expandability; LC: layer charge; CEC: cation exchange capacity; K<sub>d</sub>: sorption distribution coefficient.

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