

Effect of a Hydrothermal Reaction on the Expandibility, Layer Charge, and CEC of Smectite Clay

스멕타이트 점토의 팽창도, 충전하, 양이온 교환능에 대한 열수반응의 영향

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Abstract

In a HLW repository, the buffer is exposed to an elevated temperature due to a radioactive decay and geochemical conditions for a long time and such a hydrothermal condition may cause a significant loss of its barrier function. This study carried out hydrothermal tests with a domestic smectite clay to investigate the changes in the expandibility, layer charge, and cation exchange capacity of the smectite. When the temperature and potassium concentration in solution was increased for the hydrothermal treatments, the expandibility decreased, the layer charge negatively increased, and the CEC also decreased.

Key words : HLW repository, buffer, smectite clay, hydrothermal reaction, expandibility, layer charge, cation exchange capacity

요 약

고준위폐기물처분장에서 완충재는 오랜 기간 동안 방사성핵종의 붕괴열과 여러가지 화학조건의 지하수에 노출되며, 이러한 열수조건은 완충재물질의 차수 및 핵종저지 방벽성능에 심각한 영향을 줄 수 있다. 본 연구에서는 국산 스멕타이트를 대상으로 열수실험을 수행하고, 열수반응에 의한 스멕타이트 점토의 팽창도, 충전하, 양이온교환능의 변화를 조사하였다. 열수실험 결과, 온도와 용액 중 칼륨농도를 증가시켰을 때, 스멕타이트의 팽창도는 감소하였고, 충전하는 더 큰 음전하를 가졌으며, 양이온교환능도 감소하였다.

중심단어 : 고준위폐기물처분장, 완충재, 스멕타이트 점토, 열수반응, 팽창도, 충전하, 양이온교환능

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I. Introduction

A repository for high-level radioactive wastes (HLW) in Korea will be constructed in bedrock at a depth of several hundred meters below ground surface. The present disposal concept [1, 26] makes use of a room-and-pillar design. The waste containers are deposited in an array of large-diameter boreholes drilled on the floors of the emplacement rooms, and, after their disposition, the gap between the container and the wall of the borehole is filled with a buffer material. In the HLW repository, the major functions of the buffer are to inhibit the penetration of groundwater and to retard the release of radionuclides from the radioactive wastes to the surrounding environment. The smectite clay has been considered as a suitable buffer material because of its low permeability and high sorption capacity. However, when a smectite clay is exposed to elevated temperature due to radioactive decay and different geochemical conditions for a long time, it may be altered mineralogically and consequently lose its barrier function as the buffer of a repository. That is, a decrease in the permeability and sorption properties of the smectite clay occurs, thereby increasing the water penetration and radionuclide transport. Therefore, understanding the alteration of the smectite clay under hydrothermal conditions is essential to evaluate the long-term performance of the smectite clay in a HLW repository.

The hydrothermal reaction of the smectite clay has drawn considerable interests due to the implication of the reaction for the genesis as well as the long-term barrier performance of a bentonitic buffer for a HLW repository. Numerous studies have been carried out to evaluate the reaction mechanism, its dependency on environmental factors, and its reaction kinetics under natural conditions [2-8] or experimental conditions [9-16]. However, there are not much data on the effect of the hydrothermal reaction on the expandibility, layer charge, and cation exchange capacity which may affect the barrier performance properties such as the permeability and sorption capacity of the smectite clay.

In this study, hydrothermal tests were carried out with a domestic smectite clay. The mineralogical alteration of the

smectite was identified by examining its X-ray diffraction patterns, and the effect of a hydrothermal reaction on expandibility, layer charge, and cation exchange capacity was investigated.

II. Materials and Methods

1. Solid sample

The solid sample used for the hydrothermal tests is natural smectite fractioned into the <2 μm size from bentonite [17] which was taken from Kyeongju, Korea. The bentonite contains smectite (78 %), feldspar (20.1 %), quartz (1.7 %), and some impurities. The <2 μm fraction of the bentonite was separated by the centrifugation method, and the physicochemical and mineralogical properties of the separated natural smectite are as summarized in Table 1.

2. Hydrothermal tests

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 solution was prepared by adding potassium chloride salt to distilled water. The test conditions, as summarized in Table 2, were

Table 1. Properties of the bentonite and its 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) <table style="margin-left: 20px;"> <tr><td>SiO₂</td><td>58.21</td></tr> <tr><td>Al₂O₃</td><td>18.31</td></tr> <tr><td>Fe₂O₃</td><td>7.85</td></tr> <tr><td>TiO₂</td><td>0.91</td></tr> <tr><td>CaO</td><td>0.15</td></tr> <tr><td>MgO</td><td>3.19</td></tr> <tr><td>MnO</td><td>0.04</td></tr> <tr><td>Na₂O</td><td>3.31</td></tr> <tr><td>K₂O</td><td>0.21</td></tr> <tr><td>P₂O₅</td><td>0.10</td></tr> <tr><td>L.O.I</td><td>7.49</td></tr> <tr><td>Total</td><td>99.75</td></tr> </table> - Structural formula (K, Na) _{0.87} (Al _{2.66} Fe ⁺³ _{0.70} Mg ^{0.64})(Si _{7.78} Al _{0.23})O ₂₀ (OH) ₄ - CEC : 96.5 cmol/kg	SiO ₂	58.21	Al ₂ O ₃	18.31	Fe ₂ O ₃	7.85	TiO ₂	0.91	CaO	0.15	MgO	3.19	MnO	0.04	Na ₂ O	3.31	K ₂ O	0.21	P ₂ O ₅	0.10	L.O.I	7.49	Total	99.75
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Table 2. Experimental design for hydrothermal tests.

Run ID	Sample	Temp (°C)	K+conc. (M)	Time (days)	Analysis/measurement
1	Smectite	-	-	-	Starting material XRD, EP, LC,CEC
2	Smectite	90	5×10^{-1}	50	XRD, EP, LC,CEC
3	Smectite	140	5×10^{-1}	50	XRD, EP, LC,CEC
4	Smectite	200	5×10^{-1}	50	XRD, EP, LC,CEC
5	Smectite	200	5×10^{-1}	50	XRD, EP, LC,CEC
6	Smectite	200	5×10^0	50	XRD, EP, LC,CEC

EP:Expandability; LC:Layer charge; CEC:Cation exchange capacity

combinations of the following variable values: an initial potassium concentration of 1×10^{-1} , 5×10^{-1} , 1×10^0 M, a temperature of 90, 140, 200°C, and a reaction time of 50 days. The internal pressure was subject to an autogenous vapor pressure of H₂O 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 minutes, and then the filtered solids were freeze-dried. The mineralogical investigations for the solid samples were conducted by means of X-ray diffraction (XRD) analysis, Electron Probe Micro Analysis (EPMA), and Cation exchange capacity (CEC) measurement.

3. Determination of the expandability, layer charge, and CEC

For the determination of the expandability (the percentage of the expandable smectite layers in the interstratified I-S, %S), the X-ray diffractions of the initial material and the reacted samples were analyzed after exchanging them with calcium ions, the reason of which was to discriminate between K-saturated smectite and true illite. The expandability was determined using a saddle/001 peak intensity ratio for the ethyleneglycolated (EG) sample [18]. Glycolations were performed under ethyleneglycol vapor at 60°C for 24 hours. In this analysis, the NEWMOD program [19] 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 from a

structural formula calculated based on 22 anion equivalents and four tetrahedral cations [20]. The structural formulae were determined from the chemical composition data of EPMA [21], where the samples for the EPMA analysis were prepared by compacting the powdered smectite into a pallet specimen. CEC was measured according to Sumner and Miller's [22] procedure using 0.1g of sample and NaCl/NH₄Cl solution.

III. Mineralogical alteration of smectite by hydrothermal reaction

The smectite alteration caused by the hydrothermal reaction was identified by examining the data sets of XRD. Figure 1 shows the XRD patterns for the starting material and the reacted samples. As shown in the Figure 1(a), when the starting material was reacted with 5×10^{-1} M of a KCl solution at the temperatures of 90°C and 140°C, there was no noticeable change in the reflection position, intensity, and width of the peak of the reacted samples. However, the XRD pattern for 200°C revealed some significant differences when compared with that of the starting material. The first- and third-order reflections

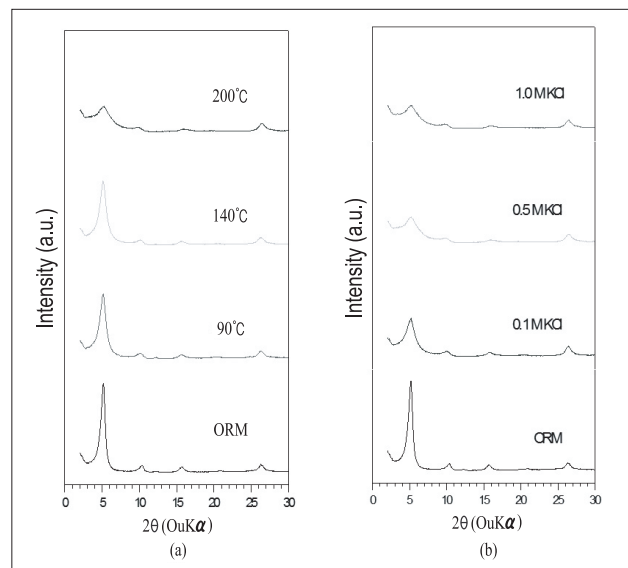


Fig. 1. XRD patterns of the starting material and reacted samples (a) with respect to temperature change at 5×10^{-1} M of KCl solution, (b) with respect to the concentration change of KCl solution at 200°C temperature.

significantly weakened and broadened; the second-order reflections moved toward the lower 2θ angle region; and the fifth-order reflection intensities increased relative to the first-order's. It is supposed that these features at 200 °C are attributed to the interlayer alteration of the smectite due to hydrothermal reaction. Figure 1(b) shows that this smectite alteration is also dependent upon the potassium concentration in the solution. That is, the dependency in the XRD pattern is increased with an increasing concentration of potassium. Based on Mering's principle (Moore and Reynolds, 1997), the peak variations shown in Figure 1 are thought to correspond to those for the randomly interstratified I-S layers. Moreover, because the reacted samples were resaturated with calcium ions to remove exchangeable potassium ions prior to the XRD measurement, the interstratificational features support the occurrence of potassium ions which had been changed into a non-exchangeable form by being fixed within the newly formed illite-like layers during the hydrothermal experiments. The percentage of the smectite layer in the randomly interstratified I-S was reduced to a minimum of 56.8 % under the experimental condition of this study, when it was determined using the saddle/001 peak intensity ratio method [18]. It follows from this that the starting smectite transforms into randomly interstratified I-S under the given hydrothermal conditions.

IV. Changes in the expandibility, layer charge, and CEC of the smectite

The expandibility, layer charge, and CEC of the starting material and the reacted samples are

Table 3. Changes in the expandibility, layer charge, and CEC of reacted smectite after hydrothermal tests.

Run ID	Expandibility (%S)	Layer charge			CEC (cmol/kg)
		Tet.	OCT.	Net.	
1	94.2	-0.3	-0.68	-0.98	96.5
2	88.5	-0.36	-0.71	-1.07	87
3	86.2	-0.41	-0.72	-1.13	77
4	64.3	-0.52	-0.72	-1.24	57
5	70.8	-0.44	-0.73	-1.17	75
6	55.6	-0.51	-0.71	-1.22	55

summarized in Table 3. After the hydrothermal reaction, the percentage of expandible smectite layers in the interstratified mixture of illite-smectite (%S) decreased with an increasing temperature and potassium concentration, as shown in Figure 2. With a temperature increase, there was a negligible decrement up to 140°C, but a much lower value was displayed at 200°C. The increasing potassium concentration in the solution yielded a linear decrease in the expandibility of the reacted samples. However, the interlayer orderings (R) in interstratified smectite/illite [19] were calculated to be all zero regardless of the temperature and potassium concentration under the given test conditions of this study.

Figure 3 is a plot of the layer charges of the initial material and reacted samples as a function of the temperature and potassium concentration. As shown in the figure, the net charge values for the reacted samples were negatively higher than that for the initial material, and they also negatively increased with increasing temperatures and potassium concentrations except for those in the range of larger than $5 \times 10^{-1}M$. The increase in the net charge was dominated by a tetrahedral charge (refer to Table 3) which probably resulted from an Al for a Si substitution in the tetrahedral sheet [23-24]. There was no observable change in the octahedral charge.

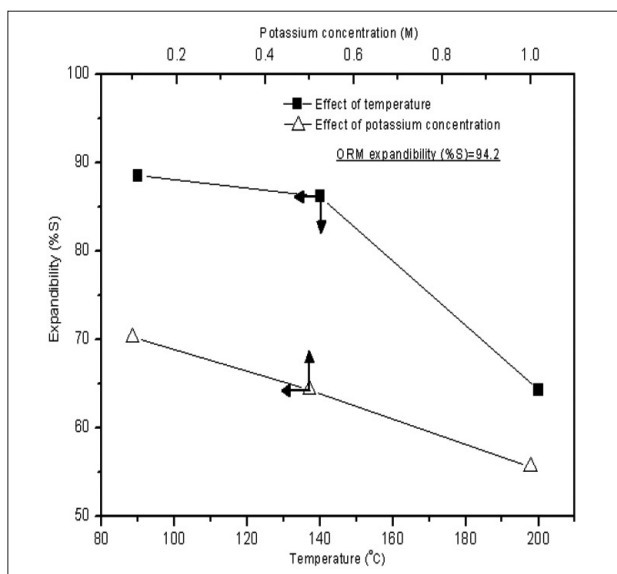


Fig. 2. Change in the expandibility of the reacted smectite.

As shown in Figure 4, the CEC of the reacted samples was lower than that of the starting material, and decreased with an increasing temperature and potassium concentration, implying that the hydrothermal reaction (i.e., the illitization) affected the CEC of the reacted samples. However, this was against the expectation that the CEC would increase due to the negatively greater layer charge of the reacted samples when compared with the starting material. Probably the decrease of the CEC

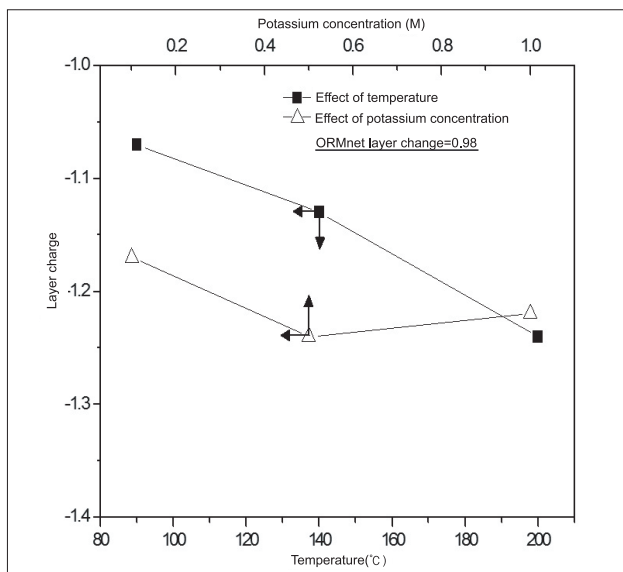


Fig. 3. Change in the layer charge of the reacted smectite.

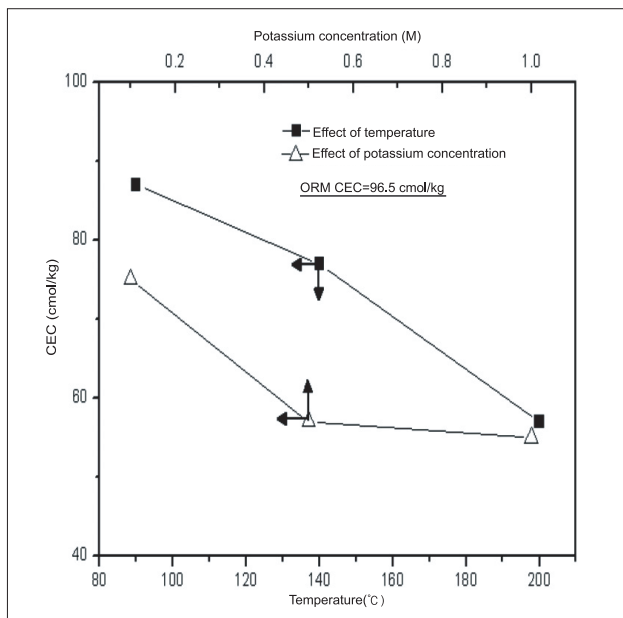


Fig. 4. Change in the CEC of the reacted smectite.

with an increase in the temperature and potassium concentration suggests that some cation exchange sites were blocked by Al or Mg hydroxides or a collapse of the interlayers due to hydrothermal reaction [25].

IV. Conclusions

The present study identified that when the smectite was hydrothermally treated under various potassium concentrations at 200°C it was converted into an interstratified mixture of smectite-illite by the hydrothermal reaction. It also showed that the hydrothermal reaction might affect the expandibility, layer charge, and CEC of the smectite. When the temperature and potassium concentration was increased for the hydrothermal treatments, the percentage of the expandible smectite layers in the interstratified I-S mixture decreased, the layer charge negatively increased, and the CEC decreased. The results obtained in this study may be used to extrapolate to the expected buffer temperature, because the reaction mechanisms are not fundamentally different at higher temperatures.

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