Changes in the Expandibility, Layer charge, and CEC of Smectitic Clay due to a Illitization

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1. Introduction

In a high-level waste(HLW) repository, the major fucntions of the smectitic clay for use as a buffer material are to inhibit the penetration of groundwater and to retard the release of radionuclides from the radioactive wastes to the surrounding environment. However, when the smectite 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 degradated 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 investigate changes in the expandibility, layer charge and cation exchange capacity(CEC) of the smectitic clay due to a illitization.

2. Materials and Methods

The solid sample used for the tests is natural smectite fractioned into a <2 μm size from a Ca-bentonite which was taken from Kyeongju, Korea. The original bentonite contains smecite (78 %), feldspar (20.1 %), quartz (1.7 %), and some impurities. The <2 μm fraction of the bentonite was separated by a centrifugation method.

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 ^{o}C, an initial concentration of KCl of $1x10^{-1}$, $5x10^{-1}$ and $1x10^{o}$ M, and a reaction time of 3, 7, 15, 28, 50, 80, 120 days. The expandibility(%S) that describes the percentage of expandible smectite layers in interstratified smectite/illite (S/I) was determined from oriented, ethylene glycol-solvated XRD pattern using NEWMOD [1]. The layer charges were determined from the EPMA analysis which was cast into structural formulae on the basis of 22 anion equivalents and four tetrahedral cations[2]. The cation exchange capacity (CEC) was measured according to Sumner and Miller's procedure [3] using a $NaCl/NH_4Cl$ solution.

3. Results and Discussion

3.1 Illitization Evidence

Figure 1 shows the XRD patterns for the starting material and the reacted samples with (a) 5 x 10 $^{-1}$ M KCl solution at 90 ^{o}C, 140 ^{o}C, and 200 ^{o}C and (b) 1 x 10 $^{-1}$ M, 5 x 10 $^{-1}$ M, and 1 x 10 $^{-0}$ M KCl solution at 200 ^{o}C. As shown in the Figure 1(a), when the starting material was reacted with $5x10^{-1}$ M of a KCl solution at the temperatures of 90 ^{o}C and 140 ^{o}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 ^{o}C revealed some significant differences when compared with that of the starting material. The peak near the 2θ value of 5^{o} was broad and weak although its position was at a nearly similar degree of an angle, and the peak near 10^{o} 2θ revealed a shift of its position to a lower degree, a decrease of its intensity, and a broadness of its width. It is supposed that these changes at 200 ^{o}C are attributed to the process of a illitization. Figure 1(b) also shows that this illitization is dependent upon the potassium concentration in the solution. That is, the dependency is increased with an increasing concentration of potassium.

3.2. Changes in the expandibility, layer charge, and CEC

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 ^{o}C, but a much lower value was displayed at 200 ^{o}C. The increasing potassium concentration in the solution yielded a linear decrease in the expandibility of the reacted samples. Their interlayer orderings, however, were all zero regardless of temperature and potassium concentration under given test conditions.

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 a range of less than $5x10^{-1}$ M. The increase in the net charge was dominated by a tetrahedral charge which probably resulted from an Al for a Si substitution in the tetrahedral sheet. There was no observable change in the octahedral charge.

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 given the negatively greater layer charge of the reacted samples when compared with the starting material. Probably the decrease of the CEC 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 a illitization.

4. Conclusion

The present paper 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 a illitization, by examining the XRD patterns. This paper also showed that the illitization might affect the barrier properties (e.g., expandibility, layer charge, and CEC) of thea smectitic clay for a repository. 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 was decreased, the layer charge was negatively increased, and the CEC was decreased.

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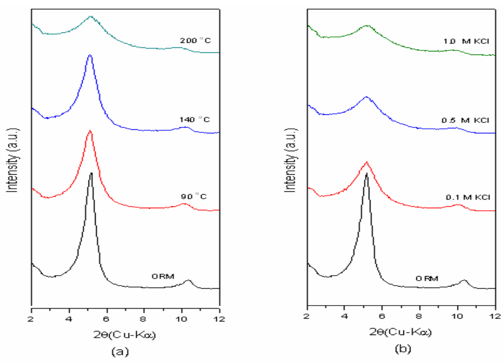

Figure 1. XRD patterns of the starting material and samples reacted under various conditions.

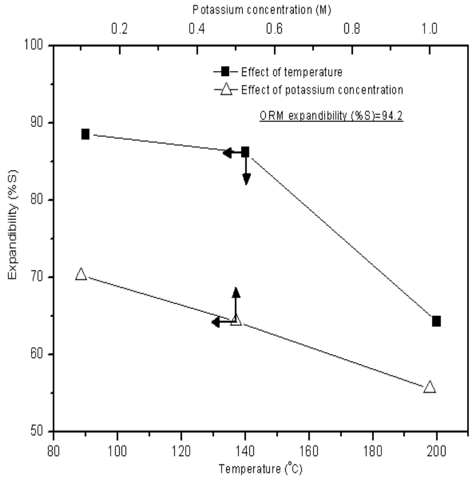

Figure 2. Change of expandibility by illitization.

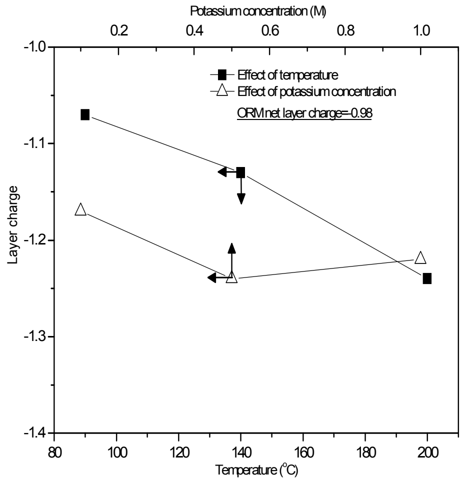

Figure 3. Change of layer charge by illitization.

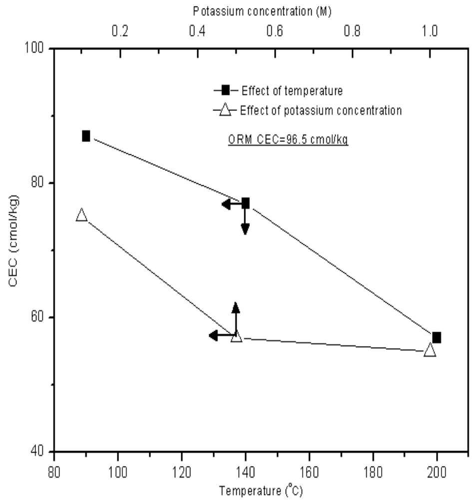

Figure 4. Change of CEC by illitization.