

# Long-Term Experiments for Bentonite Transformation under High Temperatures for High-Level Waste Disposal

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\*Keywords : Bentonil WRK, Bentonite, Illitization, Clay mineral, Spent Fuel

## 1. Introduction

Bentonite, as an engineered barrier material, is used in spent nuclear fuel disposal sites, and understanding its physico-chemical characteristics is very important to guarantee its performance over a long period of time. Since the clay mineral ‘Montmorillonite’ is a major component of bentonite, a mineralogical approach must be considered, especially. Mineral transformations should occur when bentonite is exposed to high temperatures (over 100 degrees Celsius) for an extended period, especially resulting in the production of illite. If illitization (the conversion of smectite to illite) were to occur, bentonite could lose its engineering properties, such as thermal conductivity, swelling pressure, and even its ability to sorb radionuclides. In this study, long-term experiments spanning 20 years have been set up to investigate the changes in bentonite performance depending on the degree of bentonite transformation, employing a very conservative experimental approach. Therefore, the research data will be used as factors for ensuring the long-term safety of a deep disposal repository for high-level radioactive wastes.

## 2. Experimental Works

### 2.1 Experimental Setup

To describe illitization, Bentonil WRK, a Ca-rich bentonite, was selected in this study because it is a material strongly considered for engineered barriers in South Korea. Bentonil WRK was reacted with different concentrations of potassium ions (in KCl) at temperatures ranging from 100 to 200 degrees Celsius. The experiments were conducted with two tracks, each serving a distinct testing purpose. The detailed experimental conditions are shown in Table 1. Figure 1 shows the bentonite reacted each solution according to the conditions outlined in Table 1. To prevent chemical reactions with the stainless steel (SUS) container, the reacted samples were initially placed in Teflon jar before being placed inside the final SUS package. Each experimental cases were loaded into an oven at a specific desired temperature, and the overall experimental setups are shown in Fig. 2.

Table 1. Experimental Conditions of Long-Term Bentonite Mineral Transformation

	S/L	Solution	Temp.	Rxn
TRACK I*	1 : 2	1 M KCl	150 °C	0.5 to 2 y
			200 °C	
TRACK II**	1 : 20	0.01 M KCl	100 °C	0.5 to 20 y
			125 °C	
			150 °C	
			175 °C	
	1M KCl	100 °C		
		125 °C		
		150 °C		
		175 °C		

\*TRACK I involves tests for mineral and physical properties, while \*\*TRACK II focuses on tests for mineral and radionuclides sorption ability.

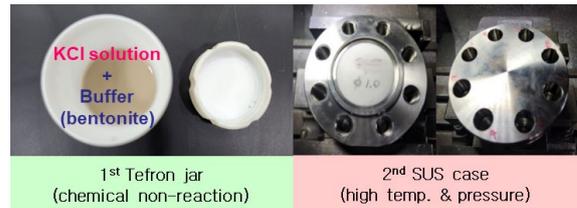


Fig. 1. Experimental setup showing the initial non-chemical Teflon jar and final SUS package.

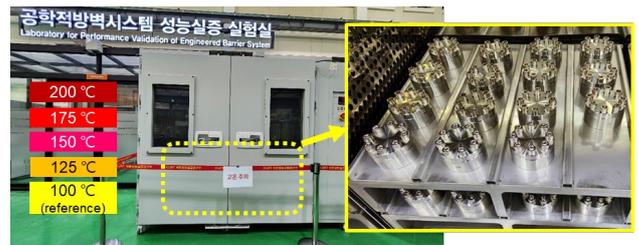


Fig. 2. Overall experimental setup under various experimental conditions.

### 2.2 Analysis

To understand the changes in the properties of bentonite, both its physical and chemical characteristics need to be measured, and the results need to be interpreted in combination. However, in this study, the focus has been on the chemical properties to uncover changes in the performance of bentonite with mineral transformation, such as alterations in chemical composition, cation exchange capacity (i.e., the sum of exchangeable cations, which influences sorption ability for cesium). Therefore, micro-XRD using a glass

capillary tube (I.D. 1.1mm), ED-XRF measuring powder, and ICP(OES/MS) analysis for quantifying elements in solution were performed.

### 3. Results and Discussion

At this time point, we obtained samples that had undergone a maximum 6-month reaction period (the 20-year experiment is still ongoing). The chemical composition results (ED-XRF) revealed that the concentration of calcium in the bentonite decreased, while the potassium concentration increased. This suggests a cation exchange reaction taking place at the interlayer of montmorillonite, the major mineral in bentonite. The rates of Ca-K cation exchange depended on the initial concentration of potassium in reacted solution. A 1 M concentration of potassium in solution exhibits greater affinity to induce exchange reactions compared to a 0.01 M concentration of potassium. This result aligns well with the findings from micro-XRD analysis. Track I and II samples exhibited differing trends in terms of reacted potassium concentration. These differences were corroborated by the XRD clay mineral peak intensity and the number of water-layers at the interlayer of each sample. The non-reacted (original) bentonite and samples reacted with 0.01 M potassium exhibit d-spacing values in the range of 15.23 to 14.94 Å. On the other hand, 1 M potassium reacted samples showed the d-spacing values as about 12.25 to 12.34 Å (Fig. 1). The d-spacing values obtained in this study were consistent with those reported by J. Behnsen and D.R. Faulkner(2013), who provided values under fully saturated cation conditions [1].

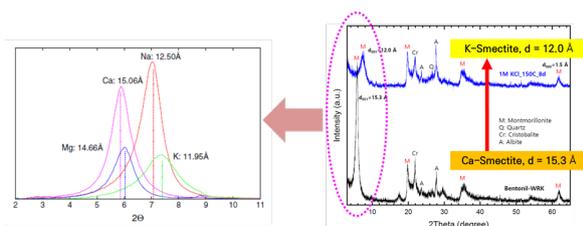


Fig 1. The XRD patterns of the reference and empirical samples. The left pattern is from J. Behnsen and D. R. Faulkner (2013), and the right pattern shows the results of Bentonil WRK (black line) and the transformed sample (blue line) under 150 °C, 1 M KCl reaction for 8 days.

Therefore, there is no evidence of mineral transformation in the bentonite samples, and differences observed in bentonite types are solely dependent on cation exchange reactions at the interlayer. For instance, the initial Ca-rich bentonite transformed into K-rich bentonite, and this change was consistent across various reaction temperatures. However, samples treated at 200 degrees Celsius and a low solid-to-liquid ratio (Track I) exhibited lower d-spacing values. This suggests that

temperatures exceeding 200 degrees Celsius may induce certain phenomena leading to mineral transformation, which could potentially compromise the integrity of the bentonite. After reacting at high temperatures, samples exhibited an increased ability to sorb cesium. This suggests that K-rich bentonite has a higher affinity for cesium compared to Ca-rich bentonite. This enhanced sorption ability can be attributed to the similar ion sizes and valences of potassium and cesium ions, facilitating their exchange.

### 4. Conclusions

Long-term experiments spanning over 20 years are being conducted to investigate the performance maintenance of bentonite as buffer material. In many countries, the design temperature of buffer material for High-Level Waste (HLW) disposal is strictly limited to no more than 100 degrees Celsius due to concerns about potential performance compromises beyond this threshold. However, in Korea, where land area is limited and population density is high, there is a pressing need to consider raising the design temperature limit to reduce the required disposal site area. For instance, raising the current standard of 100 degrees to 130 degrees Celsius could potentially halve the necessary disposal area. Therefore, our aim is to lay the groundwork for increasing the design temperature of the HLW repository. Chemical and mineralogically, the high temperature reaction does not appear to have significantly affected the original bentonite after 6 months. However, further analysis is required to ensure that the bentonite maintains its heat conduction and swellability, which are important objectives.

### REFERENCES

- [1] J. Behnsen and D. R. Faulkner (2013). Permeability and frictional strength of cation-exchanged montmorillonite. *J. Geophysical Res: Solid Earth*. 118: 2788-2798.

### ACKNOWLEDGEMENT

This work was supported by National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science and ICT, MSIT) (NRF-2021M2E3A2041312).