

## Assessment of Illitization Behavior of Bentonite Buffer Materials for Engineered Barrier Systems under K<sup>+</sup>-Rich, High-Temperature Conditions

Si Eun Park<sup>1)</sup>, Junhyuk Ham<sup>1)</sup>, Seunghyun Kim<sup>2)</sup>, Yunju Lee<sup>2)</sup>, Ji Hyun Kim<sup>1)\*</sup>

<sup>1)</sup>Department of Nuclear Engineering, Ulsan National Institute of Science and Technology, 50 UNIST-gil, Eonyang-eup, Ulsu-gun, Ulsan, 44919, Republic of Korea

<sup>2)</sup>Department of Joining Technology, Korea Institute of Materials Science, 797, Changwon-daero, Seongsan-gu, Changwon-si, Gyeongsangnam-do, 51508, Republic of Korea

\*Corresponding author: kimjh@unist.ac.kr

\***Keywords** : Bentonite buffer material, Illitization, Deep geological repositories, Raman spectroscopy

### 1. Introduction

Bentonite is widely used as a buffer material in the engineered barrier system (EBS) for deep geological disposal of high-level radioactive waste because of its high swelling capacity, low hydraulic conductivity, and self-sealing behavior upon hydration. These properties enable bentonite to function as an effective hydraulic barrier that limits groundwater inflow and contributes to radionuclide containment. In many repository concepts, however, the maximum allowable buffer temperature has traditionally been limited to approximately 100 °C because elevated temperatures may induce mineralogical alteration, thereby degrading swelling capacity and compromising long-term isolation performance.[1]

With increasing international interest in improving disposal efficiency, the need to verify the stability of bentonite under conditions exceeding 100 °C has been continuously emphasized. In particular, prolonged exposure to K<sup>+</sup>-rich groundwater at elevated temperature may accelerate illitization, that is, the transformation of swelling smectite into non-swelling illite or mixed-layer illite/smectite phases.[1,2] Because such mineralogical changes directly reduce swelling and sealing performance, systematic evaluation of the thermochemical stability of candidate buffer materials is essential for ensuring the long-term safety of disposal systems.

Accordingly, this study compares two Na-type bentonites, GBM (Granular Bentonite Mixture) and GTC4, to evaluate their illitization behavior under K<sup>+</sup>-rich, high-temperature conditions. In particular, GTC4 was included to assess the feasibility of a domestically available alternative buffer material for repository applications in Korea. The objectives of this study are to analyze K<sup>+</sup>-dependent structural and mineralogical changes under high-temperature conditions using Raman spectroscopy, to determine the K<sup>+</sup> concentration range at which illitization becomes evident, and to compare the K<sup>+</sup> concentration-dependent illitization sensitivity of GBM and GTC4.

### 2. Experimental

Two Na-type bentonites were used in this study: GBM, a Wyoming-derived Na-bentonite, and GTC4, a Na-

exchanged bentonite produced by Clariant in Korea. Groundwater collected in Korea was used as the base solution and was chemically characterized by inductively coupled plasma-optical emission spectroscopy (ICP-OES) to determine its ionic composition. The chemical composition of the base groundwater is summarized in Table 1. KCl was then added to prepare solutions with K<sup>+</sup> concentrations of 0, 0.01, 0.1, and 0.5 M (0 M denotes the base groundwater without KCl addition). For each test, 3 g of bentonite was mixed with 30 mL of the prepared groundwater solution, and the mixture was subjected to hydrothermal reaction experiments at 120 °C for 168 hours. After the reactions, the samples were dried, ground, and subsequently analyzed using Raman spectroscopy, which is highly sensitive to changes in chemical bonding. Raman spectra were collected using a 785 nm excitation laser with an exposure time of 8 s and 25 accumulations.

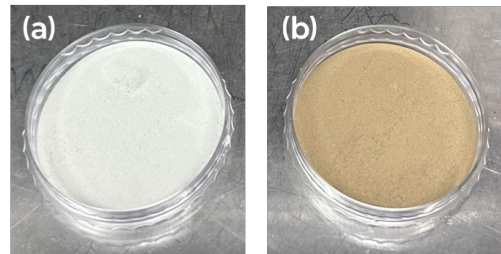


Fig. 1. Photographs of the bentonite buffer materials used in this study: (a) GBM and (b) GTC4.

Table 1: Chemical composition of Korean groundwater.

Element	Concentration (mg/L)
K	2.426
Na	27.566
Ca	33.215
Mg	8.348
Li	0.056
Sr	0.280
Fe	2.926
Mn	0.403
Zn	0.057
Al	0.006

### **3. Results and Discussion**

After hydrothermal treatment, the Raman spectra exhibited systematic changes with increasing  $K^+$  concentration, indicating that the mineralogical response of the bentonite strongly depended on the chemical environment. A clear difference was observed between the two Na-type bentonites: illitization in GBM was detected only at 0.5 M  $K^+$ , whereas GTC4 showed illitization at 0.01, 0.1, and 0.5 M  $K^+$ . These results suggest that the threshold  $K^+$  concentration for mineralogical alteration is lower for GTC4 than for GBM, while GBM maintains comparatively higher structural stability over a wider  $K^+$  concentration range under the same hydrothermal conditions.

The different illitization behaviors of GBM and GTC4 are likely associated with differences in their initial interlayer cation environments. Although both materials are classified as Na-type bentonites, GBM is a natural Na-type bentonite, whereas GTC4 is a Na-exchanged bentonite, and this difference may influence the stability of the interlayer structure under  $K^+$ -rich hydrothermal conditions.

### **4. Conclusions**

This study investigated the illitization behavior of two Na-type bentonite buffer materials, GBM and GTC4, under  $K^+$ -rich, high-temperature conditions using Raman spectroscopy. Under hydrothermal treatment at 120 °C for 168 h, GBM showed illitization only at 0.5 M  $K^+$ , whereas GTC4 exhibited illitization at 0.01, 0.1, and 0.5 M  $K^+$ . These results reveal a clear difference in  $K^+$  concentration-dependent illitization sensitivity between the two bentonites.

Overall, this work provides useful experimental evidence for evaluating the thermo-chemical stability of bentonite buffer materials and for selecting suitable candidates for deep geological disposal systems. Further long-term and multi-technique investigations will be necessary to establish the applicability of domestic bentonite alternatives under repository-relevant conditions.

### **REFERENCES**

- [1] J.S. Kim, W.J. Cho, S. Park, G.Y. Kim, and M.H. Baik, "A review on the design requirement of temperature in high-level nuclear waste disposal system: based on bentonite buffer," *Journal of Korean Tunnelling and Underground Space Association*, Vol. 21, No. 5, pp. 587-609, 2019.
- [2] C. Liu, Y.G. Chen, and Z. Sun, "An experimental study on the montmorillonite illitization process in Na-Gaomiaozi bentonite for Chinese EBS," *Bulletin of Engineering Geology and the Environment*, Vol. 84, Art. 438, 2025.