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Review and Strategy for Study on Korean Buffer Characteristics Under the Elevated Temperature Conditions: Mineral Transformation and Radionuclide Retardation Perspective

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In the majority of countries, the upper limit of buffer temperature in a repository is set to below 100℃ due to the possible illitization. This smectite-to-illite transformation is expected to be detrimental to the swelling functions of the buffer. However, if the upper limit is increased while preventing illitization, the disposal density and cost-effectiveness for the repository will dramatically increase. Thus, understanding the characteristics and creating a database related to the buffer under the elevated temperature conditions is crucial. In this study, a strategy to investigate the bentonite found in Korea under the elevated temperatures from a mineral transformation and radionuclides retardation perspective was proposed. Certain long-term hydrothermal reactions generated the bentonite samples that were utilized for the investigation of their mineral transformation and radionuclide retardation characteristics. The bentonite samples are expected to be studied using in-situ synchrotron-based X-Ray Diffraction (XRD) technique to determine the smectite-to-illite transformation. Simultaneously, the 'high-temperature and high-pressure mineral alteration measurement system' based on the Diamond Anvil Cell (DAC) will control and provide the elevated temperature and pressure conditions during the measurements. The kinetic models, including the Huang and Cuadros model, are expected to predict the time and manner in which the illitization will become detrimental to the performance and safety of the repository. The sorption reactions planned for the bentonite samples to evaluate the effects on retardation will provide the information required to expand the current knowledge of repository optimization.

Keywords: Korean bentonite, Elevated temperature conditions, Smectite-to-illite transformation, Radwaste disposal

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1. Introduction

Korea Atomic Energy Research Institute (KAERI) has been developing Korean deep geological disposal concepts for the high-level waste (HLW), namely Korean Reference disposal System (KRS) and KRS+ [1-3]. These KRSs need disposal areas of about 10 km^2, which is relatively large area for Korea, so siting seems a major national challenge. If the disposal density for HLW increases, it will certainly help nations like Korea, especially from the public acceptance perspective, because they have a high population and small area available for disposal.

In most countries, the thermal criteria for the engineered barrier system (EBS) is set to below 100°C due to the possible illitization, which is known to be detrimental to the performance and safety of the repository [4-7].

The illitization, a transformation of the smectite to illite, is known to affect the swelling function of the buffer and depend upon the key factors including time, temperature, and K$^+$ concentration [8-10]. In disposal, time reaches to the geological timescale so there will be enough supply of time for illitization. However, the temperature and K$^+$ concentration can be controlled by design. HLWs generate decay heats. If the spacing between the HLW increases, then the temperature of the repository decreases.

On the other hand, if the spacing between the HLW decreases, then the disposal density and the cost-effectiveness for disposal will dramatically increase [11-14]. Still, bentonite parameter characterization under the elevated temperatures (*e.g.*, over 100°C) is rare, although no significant changes in safety-relevant properties are indicated up to about 150°C. Thus, recent efforts in this field focus on validation of the buffer performance beyond 100°C. This includes the HotBENT (High Temperature Effects on Bentonite Buffers) project at Grimsel Test Site (GTS) [15].

HotBENT project plans to provide information and data for repository optimization with respect to mostly design, space and costs, followed by experiments relevant to investigating the effects of high temperatures on the bentonite and its safety functions. Its specific aims include (i) increase of database on buffer and hostrock performance under the elevated temperature conditions (*e.g.*, up to 200°C) and at realistic scales, and (ii) upscaling and changing of boundary conditions of bentonite buffers for laboratory and modelling knowledge to large scale. Also, integrating of Thermal-Hydro-Mechanical-(Geo) Chemical (THMC) modelling and lab activities is expected [15, 16].

From a KAERI's perspective, understanding the long-term behaviors and generating database relevant for the Korean buffer under the elevated temperature conditions is of crucial importance to evaluate the applicability of thermal upper limits. Yet, only a few study can be found on this issue. Cho et al., reviewed the appropriateness of the current thermal criteria for Korean reporitory based on the reported technical information [11]. Briefly, they reported that if the upper temperature limit of the reporitory is elevated from 100 to 125°C, it will increase the disposal density up to about 210%. Park and Seoung has conducted laboratory-scale experiments to investigate thermal behaviors of groundwater-saturated Korean bentonite (*i.e.*, KJ-ii) under the elevated temperature conditions (up to 250°C) based on in-situ synchrotron XRD study [12]. They found no evidence of the illitization under their experimental conditions, while found noticeable differences in the thermal behaviors of Korean bentonite and MX-80 (*e.g.*, dehydration temperatures, swelling abilities, interlayered-waters, *etc.*).

Under the elevated temperature conditions, the pressure can further be generated. In a normal condition (*i.e.*, below 100°C condition), it is known that the pressure ranges from 5 MPa to tens of MPa at about 500 meters underground. Thus, it is expected that the buffer will experience higher pressure conditions under the elevated temperatures than the normal condition. This area has not been investigated yet. Still, further efforts are needed to validate the performance and safety for the Korean buffer under the elevated temperature and pressure conditions.

Here, we review and propose a strategy to investigate Korean bentonite (Ca-type) under the elevated tem-

Table 1. Limitation of temperature in the buffer described in Posiva's Safety Case Report

Buffer (*i.e.*, bentonite)	Description in Posiva's Safety Case Report
Performance target	• Buffer shall transfer the heat from the canister efficiently enough to keep the buffer temperature < 100℃
Main rationale	• Maintaining the temperature below this upper limit prevents mineral transformation of the buffer
Related requirements	• The temperature limit is related to canister and hostrock requirements
Related design requirements	• The gap between the canister and buffer and buffer blocks and rock should be made as narrow as possible without compromising the future performance of the buffer. • The buffer shall initially provide a good contact with the host rock

peratures, from a mineral transformation and radionuclides retardation perspective. The long-term hydrothermal reactions are a prerequisite to obtain bentonite samples for the study on the mineral transformation and radionuclide retardation. The state-of-the-art synchrotron-based XRD technique with 'high-temperature and high-pressure mineral alteration measurement system', which is based on diamond anvil cell (DAC), will satisfy the smectite-to-illite transformation study. Kinetic modellings (*e.g.*, Huang and Cuadros model) will predict how and when the illitization becomes detrimental to the performance and safety of the repository. The sorption reactions planned for the bentonites (before and after the reactions) for retardation study will provide the information required to expand our knowledge for repository optimization.

2. Evaluation on Mineralogical Transformation of Korean Buffer Under the Elevated Temperature Conditions

The Safety Case Reports from Posiva describes the limitation of the buffer temperature (*i.e.*, below 100℃) in repository as one of the most important requirements [17, 18]. We briefly summarize the Posiva's performance target, main rationale, related requirements of other components, and related design requirements for the buffer in Table 1. As shown, main reasoning behind the temperature limitation in EBS is to prevent the mineral transformation in the buffer. This thermally-induced transformation is known as illitization, *i.e.*, smectite-to-illite transformation (equation (1)).

$$\textit{montmorillonite} + K^+ \, (+Al^{3+}) \rightarrow \textit{illite} + SiO_2 + (Ca^{2+}, Na^+) \quad (1)$$

This illitization process is known to highly temperature dependent and controlled kinetically. It involves mainly two aspects, for example, an increase in layer charge and the availability of K^+. That is, high concentration of layer charge and K^+ may be detrimental to the buffer function (*e.g.*, swelling ability). Thus, the smectite-to-illite conversion rates and mechanisms have focused on two types of study: one is the hydrothermal experiments, mostly of batch type, and the other is natural analoue study. Laboratory study can be controlled by several factors of interest to provide proper values to assess the safety relevant to the bentonite buffer, whereas the natural analogue study cannot be controlled but rely on the domestic geological environment and history. Thus, the approaches are quite different for the two types of study and we review the hydrothermal experimental study in this work. We note that KAERI starts a natural analogue study relevant to the Korean bentonite through other project.

Table 2. Models and information related to the hydrothermal experiments for the smectite-to-illite transformation during the thermal period

Model	Pytte	Huang	Cuadros	Karnland
$[K^+]$ supply	• Assume albite ↔ K-feldspar equilibrium	• Maximum • Temperature, time, and $[K^+]$ are controlled variables	• Maximum • Temperature, time, and $[K^+]$ are controlled variables • 11 or 60 $mg \cdot l^{-1}$ (0.3 or 1.5 $mmol \cdot l^{-1}$)	• Limited • $[K^+]$ required for complete illitization: 81 $kg \cdot m^{-3}$ • $[K^+]$ available from bentonite and groundwater: < 900 $g \cdot m^{-3}$
Conditions	• Saturated at all times	• Saturated at all times	• Saturated at all times • Maximum temp. 90℃	• Fully saturated buffer • Montmorillonite over 75%
Smectite fraction determination	• XRD measurement • Ratio between the amount of collapsed interlayers to that of swelling layers	• XRD measurement • Ratio between the amount of collapsed interlayers to that of swelling layers	• Silica measurement • Assume the silica concentration in solution correlated to the ilite amount	• By calculation
Degree of illitization (%)	0	0	9 at buffer/hostrock 12 at canister/buffer	1
Bentonite	n.a.	Naturally occurring bentonite (SWy-1)	Serrata de Nijar bentonite	Bentonite (> 75% montmorillonite content)
Reference	[19]	[8]	[9]	[20]

To estimate the degree of illitization during the thermal period, two approaches can be thought from the hydrothermal experimental results: (i) use of a kinetic rate equation assuming the expected K^+, but with no restriction on K^+ supply, and (ii) use of mass transfer constraints to determine the maximum degree of illitization allowed (*i.e.*, K^+ supply is dependent on the internal and external sources). Representatively, Pytte model and Huang model estimates no illitization at all during the thermal period [8, 19]. Cuadros and Linares model estimates 9% illitization at the buffer and hostrock location and 12% at the canister and buffer location [9]. Also, use of the input parameters of mass transfer constraints estimates only 1% of the montmorillonite to illite transformation [20]. Thus, Posiva concluded that the issue of hydrothermally-induced illitization has no significant detrimental effects on the buffer performance for the Olkiluoto repository [18]. The models and related informations are summarized in Table 2.

As mentioned above, the characteristics of Korean bentonite under the elevated temperature conditions needs to be addressed to evaluate the applicability of the thermal upper limit of over 100℃ (*e.g.*, 125℃, 150℃) in a repository design. Especially from a mineral transformation perspective, the smectite-to-illite transformation and its effects on swelling ability of the Korean bentonite under the elevated temperature conditions must be investigated. Thus, we propose three types of approaches: (i) hydrothermal experiments for the domestic groundwater saturated Korean bentonite under the elevated temperature conditions, (ii) determination of the smectite-to-illite transformation in Korean bentonite employing especially in-situ synchrotron-based XRD study, and (iii) modelling to estimate smectite-to-illite transformation rates with input data obtained from (i) and (ii).

The hydrothermal reactions will follow details described in KAERI's documentation (Document No. RWD-RGB-EP-20-01(rev.0)) on "procedure for radionuclide

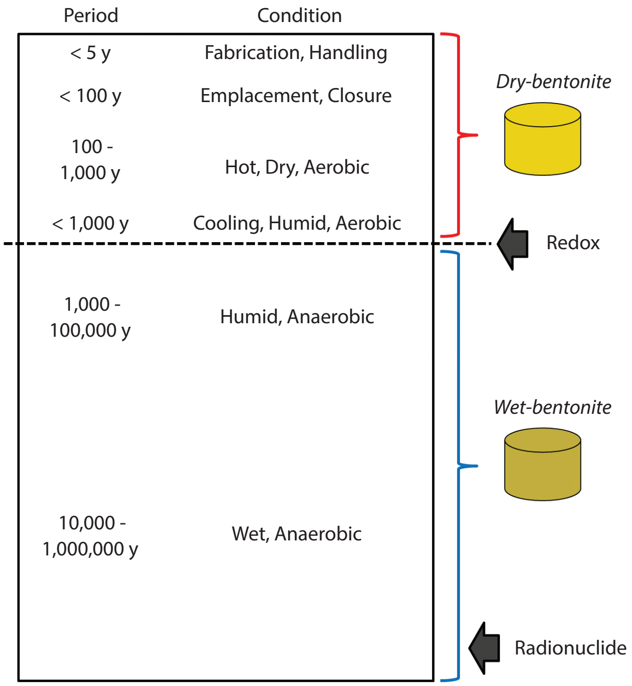


Fig. 1. Illustration for the conditions for Korean buffer with time.

sorption onto bentonite experiment under the reducing conditions". We plan to use acid digestion vessels (*a.k.a.*, autoclaves) and the reaction periods will be 1 to 4 (or more) years. After each reaction, the vessels will be dismantled and the samples be separated by centrifugation and careful filtration. Then, the solid will be characterized by XRD, XRF, TG/DSC, *etc.* and the liquid by IC, ICP-MS, *etc.*

To determine the smectite-to-illite transformation ratios, and to provide the experimental conditions of our interest, we develop the state-of-the-art synchrotron-based XRD technique with 'high-temperature and high-pressure mineral alteration measurement system' based on diamond anvil cell (DAC). Through this system, we plan to provide the controlled temperature and pressure conditions simultaneously during the measurements. The ranges are from room temperature to at least 250°C and 5 MPa to several hundreds of MPa for the temperature and pressure, respectively.

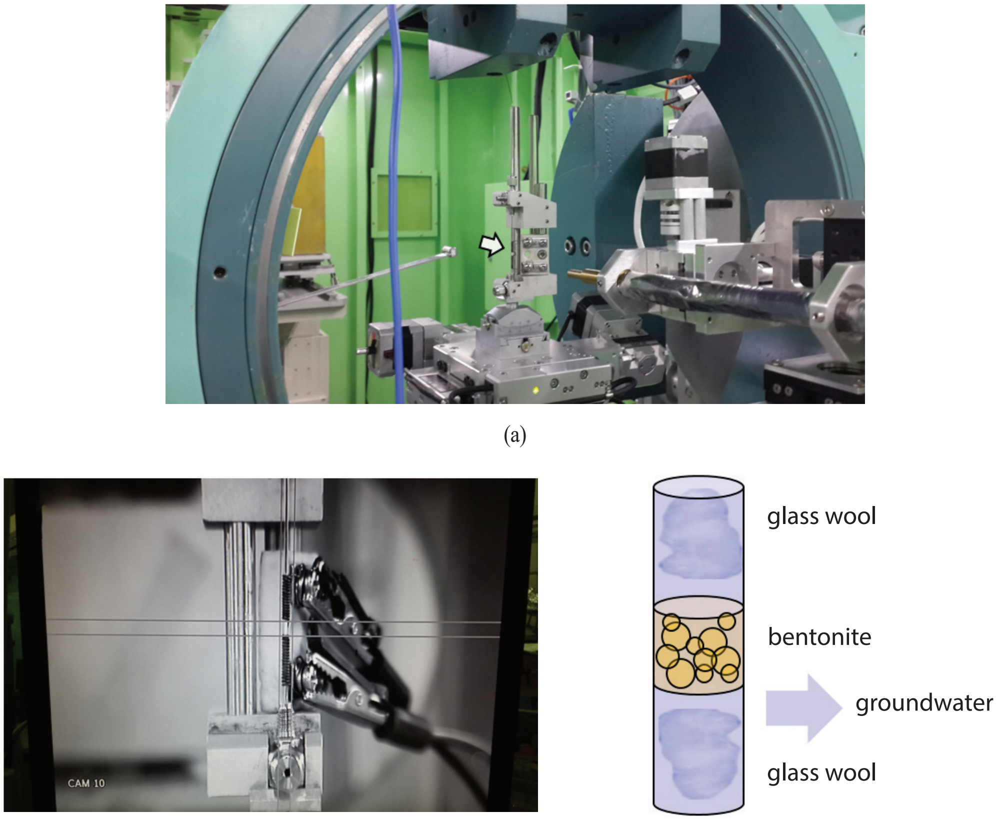
With informatin obtained from the hydrothermal experiments and spectroscopic measurements, the modelling study (*e.g.*, Pytte, Huang, and Cuadros) will predict how and when the illitization becomes detrimental to the performance and safety of the Korean buffer. We expect that the these approaches will end up providing the information required to expand our knowledge for repository optimization.

3. Evaluation on Retardation Characteristics for Korean Buffer Under the Elevated Temperature Conditions

KAERI has worked on a preliminary study to provide information relevant to Korean bentonite retardation under the elevated temperature conditions for radionuclides of interest [21]. We illustrated the conditions for Korean bentonite in a repository with time, as shown in Fig. 1 [22]. In general, it is expected that the early stage of disposal, the bentonite will be exposed to the elevated temperatures, then cooled down to the 'normal' temperature conditions. Thus, the bentonite will be dry at the early stage of disposal, and then become wet. Once the bentonite gets wet, then radionuclides will likely have a change to migrate with time.

Prior to verify the bentonite performance relevant to the radionuclide retardation, thermal characteristics of the bentonite under the elevated temperature conditions need to be understood. This includes the characteristics in the absence and/or present of groundwater (*i.e.*, dry and/or wet condition), when we reconsider the thermal upper limit. Thus, we have developed an in-situ synchrotron-based method (Fig. 2) for the thermal behavior study for the Korean bentonite (Ca-type) under the elevated temperature conditions, investigated *d*-spacings of the montmorillonite in the Korean bentonite at dry and KURT (KAERI Underground Research Tunnel) groundwater-saturated conditions, and compared the behavior with that of MX-80 (Na-type) [12].

Thermal behaviors of the Korean bentonite under the



(a)

(b)

(c)

Fig. 2. (a) Experimental setup mounted for the synchrotron XRD study, (b) alignment for the bentonite, and (c) detailed description of the capillary package for groundwater-saturation environments.

elevated conditions can be summarized as follows: Korean bentonite starts losing the interlayered water molecules at lower temperatures, but keeps holding them at higher temperatures as compared with MX-80. Thus, with simple hypothesis that the *d*-spacing change of the bentonites correlates with their swelling capacity, Korean bentonite seems to keep the capacity at the elevated temperature conditions, although there is no single factor governs the swelling capacity. Detailed results on thermal behaviors (*e.g.*, dehydration, *d*-spacing, *etc.*) of Korean bentonite (Ca-type) and Na-type bentonite are summarized in Table 3.

Based on our previous experience, we plan to conduct sorption experiments for the bentonites that will be separated from batch-type hydrothermal reactions mentioned above. Results from this will be used to calculate the sorption distribution coefficients (K_d). Equation 2 shows how to calculate K_d values:

$$K_d = \frac{V}{M}\frac{(C_i - C_f)}{C_f} \tag{2}$$

where V = volume of solution, M = mass of the bentonite, C_i = initial radionuclide concentration, and C_f = final radionuclide concentration in solution.

We plan to compare the K_d values obtained here to those from KAERI's other project on sorption characteristics for the Korean bentonite under the temperature conditions below 100°C. The results from the sorption reactions planned for the bentonites (before and after the reactions) will pro-

Table 3. Thermal behaviors of Korean bentonite and Na-type bentonite under the elevated temperature conditions

	Korean bentonite (KJ-ii) (Ca-type) [12]		Bentonite (Na-type) [23]	MX-80 (Na-type) [12]
Condition	Dry	Wet	Dry	Wet
Dehydration start, ℃ (*d*-spacing contraction, %)	90 (14)	120 (12)	90 (25)	150 (33)
Complete dehydration, ℃ (*d*-spacing contraction, %)	200 (34)	> 250* (> 38)*	200 (38)	250 (48)
d-spacing restoration when cool down	slow	fast	*n.a.*	fast

* Incomplete dehydration at 250℃

vide the information required to complement and expand our knowledge on mineral transformation and radionuclide retardation of the buffer for repository optimization.

4. Summary and Outlook

The current work describes a strategy proposed for investigating Korean bentonite under the elevated temperature conditions, from a mineral transformation and radionuclides retardation perspective. This includes performing long-term hydrothermal reactions (*e.g.*, 1, 2, 3, 4 and more years) with standard Korean bentonite and groundwater, to provide samples for mineral transformation and radionuclide retardation investigation.

The bentonites undergone the reaction will be separated from the solution, then analyzed using in-situ synchrotron-based XRD technique to determine smectite-to-illite transformation. To provide and control the elevated temperature and pressure conditions during the measurements, we will develop a 'high-temperature and high-pressure condition mineral alteration measurement system' based on Diamond Anvil Cell (DAC). The kinetic modelling (*e.g.*, Huang, Cuadros, *etc.*) will be followed to predict how and when the illitization becomes detrimental to the performance and safety of the repository. The sorption reactions planned for the bentonites (before and after the reactions) will provide the information (*e.g.*, distribution coefficient K_d) to expand our knowledge for repository optimization. We believe that this work will continue to focus on generating improved data and performance assessment strategies aimed at expanding our knowledge to optimize the repository.

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