

# Thermo-hydro-chemical processes influence on buffer material degradation in high level radioactive waste disposal

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**Key words:** high-level radioactive waste, buffer material, bentonite degradation, performance assessment, geological disposal

## Abstract

The concept of geological disposal for high-level radioactive waste (HLW) is based on a multi-barrier system that comprises the natural geological barrier provided by the repository host rock and its surroundings, as well as an engineered barrier system (EBS) that includes the waste form, waste canisters, buffer materials and backfill. The multi-barrier system is expected to perform its desired functions and isolate the waste from the biosphere to achieve the performance of the HLW disposal. Due to the interaction processes of radionuclide decay heat, hydraulic and water-mineral reaction in the radioactive waste repository, the bentonite buffer material degradation that results from the external temperature and pressure warrants investigation. Smectite, a swelling clay mineral, is the main mineral in bentonite from 65 to 90 wt%. However, seldom addressed in Taiwan is the influence of thermo-hydro-chemical (T-H-C) processes on buffer material degradation in the EBS of HLW disposal repository, as related to the chemical reaction of smectite clay dehydration. Therefore, we adopted the chemical kinetic model of smectite illitization to calculate the transformation amount of smectite-to-illite caused by the higher temperature of waste decay heat. The results show that smectite illitization is deemed insignificant for the anticipated geological repository conditions. The results can form the advanced research results in evolution of bentonite degradation for the performance assessment and safety analysis on the final disposal of HLW in Taiwan.

## 1. INTRODUCTION

The safety concept of a geological repository for the disposal of radioactive waste is based on a multi-barrier system that includes the natural geological barrier and engineered barrier system (EBS). The natural geological barrier is provided by the repository host rock and its surroundings, and the EBS comprised the waste form, waste canisters, buffer materials and backfill. The multi-barrier system should perform its desired functions to isolate the waste from the biosphere. The EBS design used in Taiwan is shown in Figure 1.

The buffer should have the functions, i.e. low water permeability, micro-porous structure, self-sealing, canister support, high swelling capacity, colloid filtering, inhibition of microbial development, resistance to rock shear movements, retardation of radionuclide, and must be able to effectively isolate waste for at least 100,000 years. Bentonite has been used as a buffer material in most HLW repository concepts. Smectite clay is the main mineral component of bentonite material and plays a key role in the characteristic domination of buffer physical

and chemical behavior. The thermal constraint in EBS for most HLW repository concept at the bentonite/canister interface should remain the bentonite buffer temperature at temperatures beyond 100 °C. However, the long-term functions of buffer clay could be lost through smectite illitization under prevailing temperature and temperature gradient conditions that arise from waste decay heat. Therefore, the influence of higher waste decay temperatures on bentonite performance requires investigation.

The chemical evolution of bentonite buffer and bentonite degradation in the EBS of HLW disposal repository caused by thermals affecting smectite illitization and smectite dehydration are topics seldom discussed in Taiwan. Therefore, in this study, we used the chemical kinetic model of smectite illitization to calculate the transformation amount of smectite-to-illite caused by higher temperatures of waste decay heat. The results indicated that smectite-to-illite conversion could cause volume shrinkage due to loss of interlayer water of smectite and lead to the bentonite buffer compression.

Therefore, investigating the evolution of bentonite degradation on the final disposal of HLW can provide further insights into performance assessments for the long-term safety analysis of radioactive waste disposal sites.

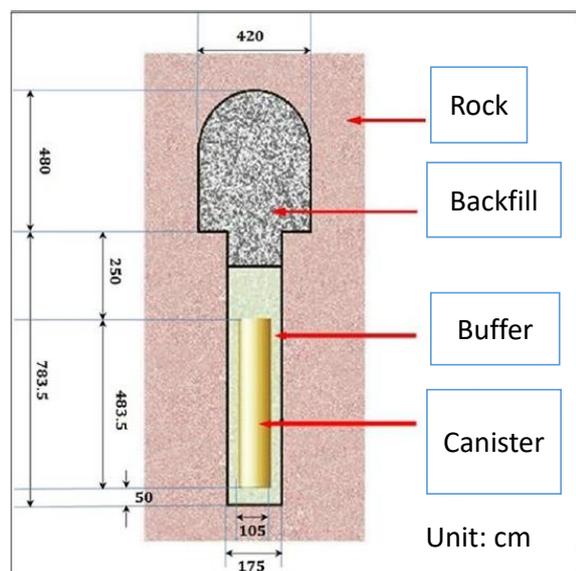


Figure 1 Schematic of EBS design.

## 2. TEMPERATURE WITHIN BUFFER

Heat decay is expressed as power  $P(t)$ , where  $t$  is time in years, and  $a_i$  is the coefficient Time and coefficient are depicted in Table 1 (SKB, 2009).

$$P(t) = \sum_{i=1}^7 a_i \exp(-t/t_i) \quad (1)$$

Table 1 Time and coefficient  $a_i$

$i$	$t$ [years]	$a_i$	$i$	$t$ [years]	$a_i$
1	20	0.060147	5	2000	0.025407
2	50	0.705024	6	5000	-0.009227
3	200	-0.054753	7	20000	0.023877
4	500	0.249767			

Table 2 Parameters for heat transport simulation.

Parameter	Units	Description	Buffer	Backfill	Host rock
$\rho$	$g/cm^3$	Density	1.95	1535	2750
$C_p$	$J/kg \cdot K$	Heat capacity	830	830	712
$T_{int}$	$^{\circ}C$	Initial temperature	25	25	29
$k$	$W/m \cdot K$	Thermal conductivity	1.1	1.1	2.91
$n$	-	Porosity	0.435	0.46	-
$\rho_D$	$g/m^3$	density	1.56	-	-

The initial canister power was 1315 W. COMSOL Multiphysics software was used to simulate the temperature evolution in the EBS. COMSOL is a finite element software tool that allows partial differential equations to be solved in two-dimensional (2D) and three-dimensional (3D) domains; the solutions can be visualized or further

processed (COMSOL, 2016). The parameters for heat transport simulation in the buffer, backfill, and host rock are shown in Table 2. The finite element mesh of the whole system (i.e. the host rock and EBS) is shown in Figure 2.

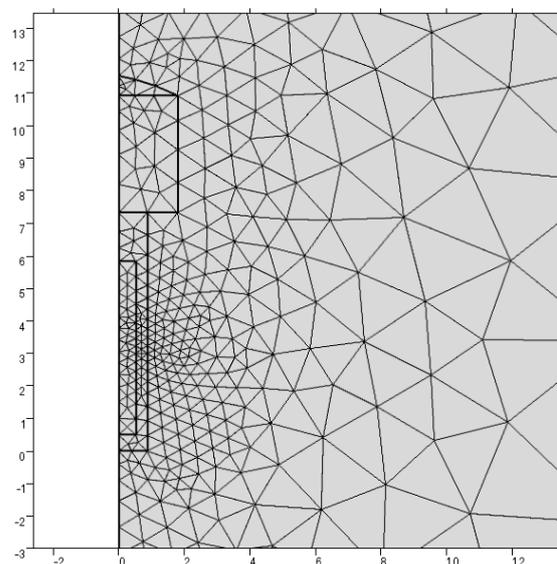


Figure 2 Finite element mesh for EBS and host rock.

## 3. SMECTITE HYDRATION PROPERTY

Montmorillonite is a swelling clay of the smectite group and the main mineral in bentonite (65 to 90 wt%). Na-type smectite has superior swelling and lower permeability, and thus is favored as a buffer. The isomorphous substitution of  $Al^{3+}$  and  $Mg^{2+}$  in smectite octahedral sites, or of  $Si^{4+}$  by  $Al^{3+}$  in smectite tetrahedral sites, generates an excess negative charge on the smectite structure; this is compensated for by the adsorption of cations on the smectite layers. Figure 3 shows the smectite clay mineral structure. If the interlayer of smectite adsorbs water, that water is called interlayer water. Colten-Bradley (1987) and Ransom and Helgeson (1994) stated that the smectite interlayer includes three discontinuous basal spacings of  $\sim 10\text{\AA}$ ,  $\sim 12.6\text{\AA}$  (one-layer of water molecules),  $\sim 15.7\text{\AA}$  (two-layer of water molecules) in a subsurface hydrogeological environment. The interlayer region in the silicate structure can be considered to be a solvent; the water is the solute dissolved in the solvent, and the solution is called a solid-solution. Using  $O_{10}(OH)_2$  as a base crystal-chemical unit, Ransom and Helgeson (1989) expressed hydrated Na-smectite ( $Na_{0.3}Al_{1.9}Si_4O_{10}(OH)_2 \cdot nH_2O$ , where  $n$  is the number of moles of water in the fully hydrated Na-smectite). The chemical and thermodynamic properties of interlayer water differ from those of pore water. Interlayer water can be considered as water bonded to a mineral, forming a hydrated mineral. When dehydration occurs, the interlayer water will be released from the hydrated smectite to form  $H_2O$  and a homologous anhydrous 2:1

layer-silicate counterpart. This behavior is analogous to the reversible intracrystallization reaction of a solid-solution (Ransom and Helgeson, 1994, 1995; Liu and Lin, 2005).



where *hs* denotes hydrous smectite; *as* denotes anhydrous smectite; *n* is the number of moles of water released from 1 mole of hydrous smectite. When the smectite exposes to higher temperature of waste decay heat, the reaction (2) tends to move to the right and the thermal condition could cause smectite dehydration (i.e. interlayer water was expelled of the basal spacings from ~15.7 Å to ~10 Å). In addition, smectite illitization may occur at temperatures as low as 70°C (Jenning and Thompson, 1986). Illite is a K-bearing, aluminous, non-swelling 2:1 layer clay (see Figure 3).

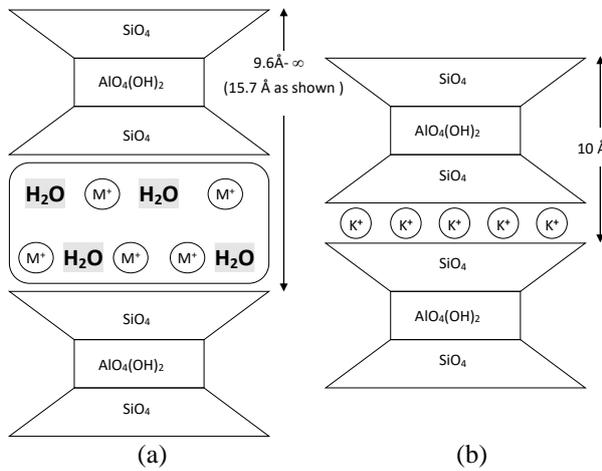
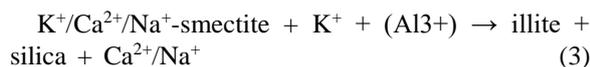


Figure 3 Clay mineral structure: (a)Smectite; (b)Illite.

When smectite minerals exposed to higher temperatures and pressures, the minerals are unstable and transform to more stable silicate phases, such as illite/smectite mixed layers, illite. The transformation process is strongly affected by kinetic and hydrologic constraints, such as time, concentration of exchangeable cations, saturation state in the bentonite and permeability of the adjacent formation (Pusch and Karnland, 1988a; Madsen, 1998; Wersin et al., 2007). This process can be written by the following chemical reaction (Karnland and Birgesson, 2006):



This leads to a devastation of smectite and to a release of Si which may precipitate as SiO<sub>2</sub> cement. Thus, the illitisation process reduces swelling capacity and plasticity of the bentonite material (Wersin et al., 2007). However, higher temperatures at the onset of the smectite-to-illite transformation are problematic in subsurface system. Furthermore, the rate of smectite illitization is influenced by dissolved potassium concentrations in groundwater. Wilson and

Bond(2016) indicated that smectite illitization would occur over many thousands of years at the temperature  $\leq 100^\circ\text{C}$  under near-neutral pH conditions. Their study shows that less than 0.003% of the smectite is transformed to illite during the 10,000 year period.

The interlayer molar volume ( $V_{il}$ ) can be determined by (Ransom and Helgeson, 1994)

$$V_{il} = \left( \frac{abc \cdot \cos(90 - \beta)}{10^{24} Z} \right) N_0 \quad (4)$$

where  $a = 5.17 \text{ \AA}$ ,  $b = 8.99 \text{ \AA}$ , and  $\beta = 100^\circ$  are parameters associated with the smectite unit-cell;  $c$  is the interlayer thickness;  $Z = 2$  is the number of units in the chemical formula of the smectite unit-cell, and  $N_0$  is Avogadro's constant.

The number of moles of water ( $n$ ) released by the dehydration of hydrous smectite is thus

$$n = \frac{\rho_{il} V_{il}}{M_w} \quad (5)$$

where  $\rho_{il}$  is the density of the interlayer water;  $M_w$  is the molecular weight of water and equals 18.05. Hawkins and Egelstaff (1980) measured the average interlayer water density as 1.05 g/cm. The  $n$  is 4.51 for ~15.7Å (two layer of water molecules) computed from the equation (5).

### 3.2 Kinetic model for smectite to illite conversion

Huang et al. (1993) systematically investigated the kinetics for the conversion of a Na-saturated montmorillonite to a mixed-layer smectite/illite as a function of KCl concentration from 0.1 to 3mol/L over a temperature range of 25°C to 325°C at 500 bar in cold seal pressure vessels using gold capsules. The results of the study showed that the conversion rate can be described by a simple empirical rate equation for a Na-rich fluid as follows:

$$-\frac{dS_{sm}}{dt} = A \cdot \exp\left(-\frac{Ea}{RT}\right) \cdot C_1 \cdot S_{sm}^2 \quad (6)$$

$$C_1 = [K^+]^{\frac{1}{2}} \times \frac{[K^+]}{2} \times \frac{[Na^+]}{2.3} \quad (7)$$

where  $S_{sm}$  is the fraction of smectite layers in the  $I/S_{sm}$ ,  $t$  is the time in seconds,  $A$  is the frequency factor of  $8.08 \times 10^4 \text{ sec}^{-1}$ ,  $Ea$  is the activation energy of 28 kcal/mole,  $R$  denotes the gas constant of 1.987 cal/deg-mole,  $T$  represents the temperature in Kelvin.  $[K^+]$  and  $[Na^+]$  are the  $K^+$  ion of  $9.22 \times 10^{-5} \text{ M}$  and  $Na^+$  ion of  $1.53 \times 10^{-3} \text{ M}$  concentration in pore water compositions of granite rock in Taiwan's offshore island, respectively.

## 4. RESULT AND DISCUSSION

This study adopted the chemical kinetic model of smectite dehydration and illitization to calculate the amount of water expelled from smectite clay minerals caused by the higher temperature of waste decay heat. The results show as follow:

The heat-generating spent fuel is contained in the canister. The canister heat decay in less than 20,000 years can be calculated by the equation (1) as shown in Figure 4. We use the COMSOL model to calculate heat transport through the EBS to host rock during the 10,000 year period in the calculation. Parameters for heat transport simulation is tabulated in Table 3. Temperature profile at 1000 years is shown in Figure 5. We select the five points, A B C D E, as the represented points for temperature calculation within buffer (see Figure 6). Temperature distribution for the five represented points during the 10,000 years period is shown in Figure 7. Figure 8 shows the average temperature evolution within the buffer material. Notably, the temperature peak occurs before 10 years. After approximately 10,000 years, the thermal caused by the release of the canister had dispersed and the temperature had reduced to nearly geothermal background level. Figure 9 shows the average smectite fraction on illitization process. Less than 0.009% of the smectite is transformed to illite during the 10,000-year period because high temperatures are not retained within the buffer for extended periods. Crucially, the smectite-to-illite conversion for the performance assessment is negligible.

Ferrage et al. (2007) performed a kinetic study of smectite dehydration and reported that a smectite structure exhibits various hydration states with the intercalation of zero, one, or two planes of water molecules in the interlayer. Future study could adopt the chemical kinetic model of smectite dehydration to calculate the amount of water expelled from smectite clay minerals because of higher temperatures of waste decay heat. Thus, it can quantify the hydrous state porosity, smectite shrinkage, and swelling recovery. A literature review indicated that the horizontal confining stress from the surrounding host rock is approximately 11.43–16.55 MPa (Taipower, 2017) and the bentonite dry density is 1,533–1,692 kg/m<sup>3</sup> (density at water saturation 1,983–2,086 kg/m<sup>3</sup>), which yields a swelling pressure 4.5–16 MPa (SKB, 2010). Therefore, further investigating the swelling pressure of smectite and the confining stress of the surrounding host rock could provide further insights into the computation of bentonite consolidation and compression as well as smectite volume expansion.

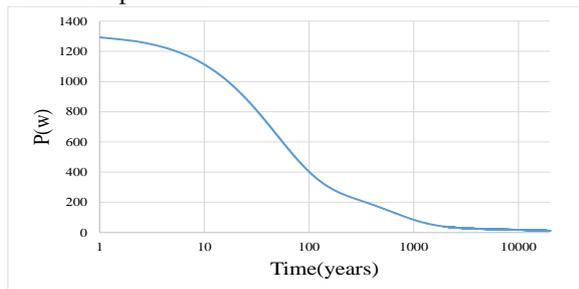


Figure 4 Canister power as a function of time.

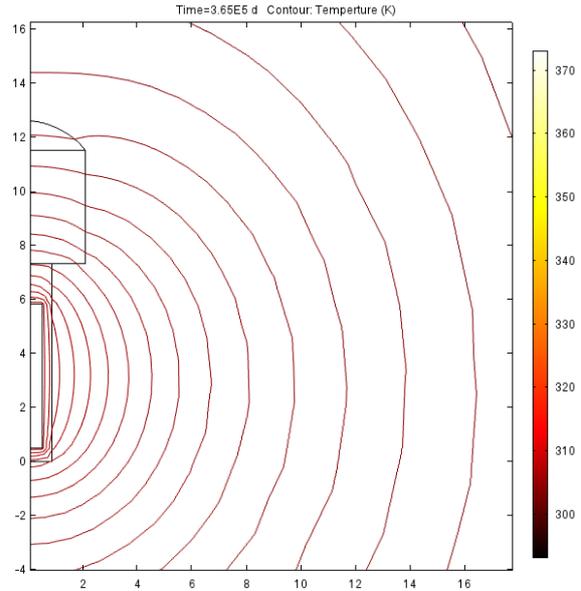


Figure 5 Temperature profile at 1000 years for simulation domain.

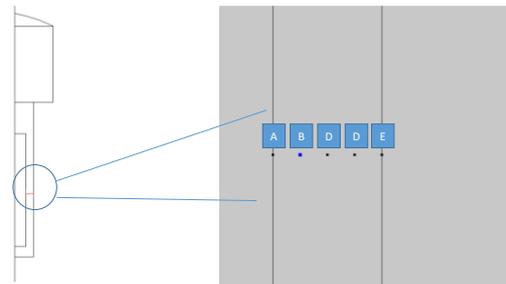


Figure 6 Points for temperature calculation within the buffer.

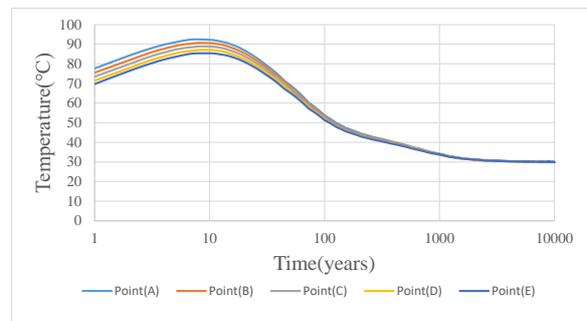


Figure 7 Temperature distribution at point A, B, C, D and E.

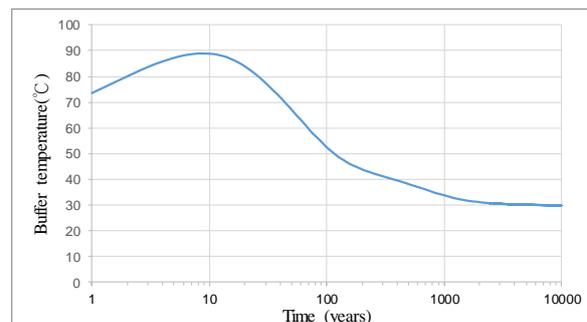


Figure 8 Average temperature evolution within the buffer material.

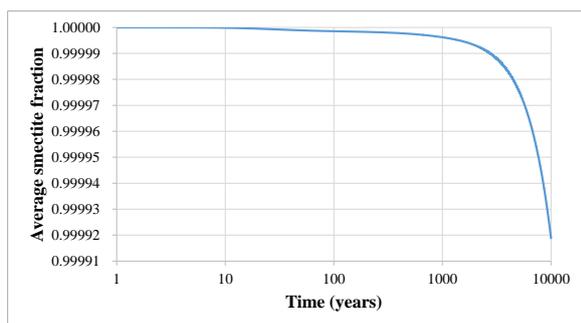


Figure 9 Average smectite fraction as a function of time on illitization process.

## 5. CONCLUSION AND SUGGESTION

This study adopted the Kinetic dehydration of interlayer water, Kinetic model for smectite to illite conversion and hydration state of the interlayer to calculate the amount of water expelled from smectite clay minerals caused by the higher temperature of waste decay heat. The results show as follows: The temperature peak occurred before 10 years. After approximately 10,000 years, the thermal caused by the release of canister has dispersed and the temperature has reduced close to the geothermal background. Less than 0.009% of the smectite is transformed to illite during the 10,000-year period. Because high temperatures are not retained within the buffer for extended periods of time. It is important to note the smectite-to-illite conversion for the performance assessment is negligible. The results can form the advanced research results in evolution of bentonite degradation for the performance assessment and safety analysis on the final disposal of HLW in Taiwan.

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