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A thermodynamic model of effect of temperature on swelling stress of buffer material in geological disposal

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Abstract

Buffer material composing engineered barrier in the geological disposal of a high-level radioactive waste is affected by decay heat from vitrified waste. Swelling stress (pressure) distribution is formed in parallel with the formation of temperature distribution in the buffer material by penetration of groundwater. We have reported a thermodynamic model of swelling stress of Na-bentonite including montmorillonite under standard temperature (25 °C) in previous studies. In the conventional model, swelling stress was calculated based on the difference between the relative partial molar Gibbs free energies of interlayer water and external water of montmorillonite. In this study, we discussed the effect of temperature on the swelling stress of Na-bentonite from the viewpoint of thermodynamics. The effect of temperature on the swelling stress of Na-bentonite was based on Clausius–Clapeyron's equation. By applying the conventional model to this theory, an advanced thermodynamic model which can calculate the effect of temperature on swelling stress was derived. Key parameter in the model is the relative partial molar enthalpy. The relative partial molar enthalpy of interlayer water of Na-montmorillonite which is the major component of Na-bentonite was approximately 0 in montmorillonite partial densities lower than 1.25 M m^{-3} and decreased in montmorillonite partial densities higher than 1.25 M m^{-3}. This indicates that swelling stress gradually decreases with the increase in temperature in montmorillonite partial densities higher than 1.25 M m^{-3}. Degree of decrease in swelling stress was 10–20% in the comparison between 25 and 60 °C. Considering design density of buffer material in repository, it is considered that we realistically need not consider the effect of temperature.

Introduction

The temperature of buffer material composing engineered barrier in the geological disposal of a high-level radioactive waste rises by decay heat from vitrified waste. Swelling stress (pressure) distribution is formed by the formation of water content distribution in parallel with the formation of temperature distribution in the buffer material by penetration of groundwater from the surrounding rock mass. Furthermore, since the major component of buffer material is bentonite, swelling stress is also affected by water chemistry (water quality of groundwater), and Thermo-Hydro-Mechanical-Chemical (T-H-M-C) coupled process progresses in the buffer material for a long time.

Many studies on swelling stress (pressure) of bentonite have been reported up to date, but studies on the influence of temperature are limited. For example, the swelling stress (pressure) of Na-bentonite (Kunigel-V1® and Kunigel OT-9607®) is indicated to tend to decrease with an increase of temperature, according to the JAEA database on fundamental properties of buffer material [1]. Villar et al. [2] have reported that the swelling stress of the FEBEX bentonite was the same tendency. On the other hand, Pusch et al. [3] have reported both cases that the swelling stress of the MX80® bentonite decreased and increased with an increase of temperature. Recently, some studies have reported that the swelling stress of bentonite increased with an increase of temperature [4, 5]. Thus, the effect of temperature on the swelling stress of bentonite is still controversial and is not always sufficient.

In this study, we analyzed and discussed the effect of temperature on the swelling stress of Na-bentonite, based on thermodynamic theory and thermodynamic data.

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Thermodynamic models of swelling stress

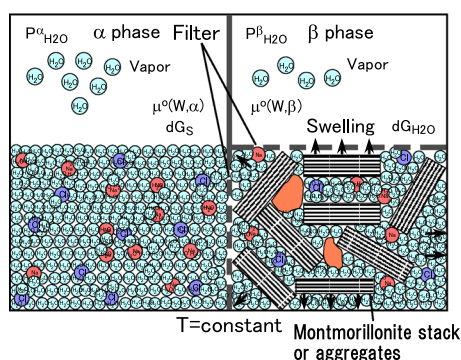### Conventional thermodynamic model of swelling stress at standard temperature

Figure 1 shows a conceptual model on the chemical potential balance of water in the equilibrium state between an electrolyte solution (α phase) and bentonite (β phase) contacted with the solution through filter at standard temperature [298.15 K (25 °C)] [6–8]. Here, the α phase is an electrolyte solution, the β phase is the bentonite, and both phases come in contact through filter (which does not deform). Upper spaces in both phases are the vapor pressures in equilibrium state with the electrolyte solution and moisturized bentonite, respectively. By penetration of the solution to bentonite, the bentonite gradually swells and the vapor pressure of water in the β phase increases with an increase of water content of the bentonite. This means that the relative partial molar Gibbs free energy (dG) in the β phase increases with an increase of water content of bentonite. When the α phase and the β phase reach equilibrium state, the chemical potential of waters between both phases are equivalent as follows:

$$\mu^0(W, \alpha) = \mu^0(W, \beta), \tag{1}$$

where $\mu^0(W, \alpha)$ and $\mu^0(W, \beta)$ are the chemical potential of waters in the α phase and the β phase, respectively (J mol^{-1}).

In this system, the difference of the relative partial molar Gibbs free energies (dG) of waters between both phases in equilibrium state acts as swelling energy of the bentonite. The dG can be calculated as follows:

$$dG = dG_S - dG_{H_2O}, \tag{2}$$

where dG is the difference of the relative partial molar Gibbs free energies of waters between the α phase and the β phase in equilibrium state (J mol^{-1}), and dG_S and dG_{H2O} are the relative partial molar Gibbs free energies of waters in the α phase and the β phase, respectively (J mol^{-1}). When the α phase is the pure water system, $dG_S = 0$.

The chemical potential of waters in the α phase and the β phase when both phases are in equilibrium state are, respectively, described as follows:

$$\mu^0(W, \alpha) = RT \ln\left(\frac{P^{\alpha}_{H_2O}}{P^0_{H_2O}}\right) \tag{3}$$

$$\mu^0(W, \beta) = RT \ln\left(\frac{P^{\beta}_{H_2O}}{P^0_{H_2O}}\right) + \int_{P^0_{ext}}^{P_{ext}} V_w dP. \tag{4}$$

Since the chemical potential of waters in both phases are equivalent as shown by Eq. (1), the swelling energy of bentonite is derived as follows:

$$RT \ln\left(\frac{P^{\alpha}_{H_2O}}{P^0_{H_2O}}\right) = RT \ln\left(\frac{P^{\beta}_{H_2O}}{P^0_{H_2O}}\right) + \int_{P^0_{ext}}^{P_{ext}} V_w dP$$

$$\therefore \int_{P^0_{ext}}^{P_{ext}} V_w dP = \left(P_{ext} - P^0_{ext}\right) V_w = RT \ln\left(\frac{P^{\alpha}_{H_2O}}{P^0_{H_2O}}\right)$$
$$- RT \ln\left(\frac{P^{\beta}_{H_2O}}{P^0_{H_2O}}\right) = dG_S - dG_{H_2O}. \tag{5}$$

Therefore, if V_w can be regarded as a constant between P^0_{ext} and P_{ext}, swelling stress ($dP_{ext} = P_{ext} - P^0_{ext}$) can be finally calculated from the following relations:

$$dP_{ext} = \frac{RT}{V_w} \ln\left(\frac{P^{\alpha}_{H_2O}}{P^0_{H_2O}}\right) - \frac{RT}{V_w} \ln\left(\frac{P^{\beta}_{H_2O}}{P^0_{H_2O}}\right) = \frac{dG_S - dG_{H_2O}}{V_w}, \tag{6}$$

where dP_{ext} is the swelling stress (Pa), V_w the specific volume of pure water at 25 °C (18.0686 cm^3 mol^{-1}), P^{α}_{H2O} the vapor pressure in the α phase at 25 °C (Pa), P^{β}_{H2O} the vapor pressure in the β phase at 25 °C (Pa), P^0_{H2O} the vapor pressure of pure water at 25 °C (3.168 kPa), R the gas constant (8.314 J mol^{-1} K^{-1}), and T the absolute temperature (K).

An advanced thermodynamic model of swelling stress at arbitrary temperature

The effect of temperature on the swelling stress of bentonite cannot be evaluated by the conventional model. The change in vapor pressure with respect to temperature

Fig. 1 A conceptual model of the chemical potential balance of water in the equilibrium state between an electrolyte solution (α phase) and bentonite (β phase) came in contact with the solution through filter at constant temperature [6–8]

change is given by Clausius–Clapeyron's equation if vapor is an ideal gas.

$$\frac{dP}{dT} = \frac{PdH_v(s)}{RT^2} \tag{7}$$

Vapor pressures of waters in both phases at arbitrary temperature are given as follows, by giving initial and boundary conditions to Eq. (7).

$$\int_{P^\alpha_{H_2O}}^{P^\alpha} \frac{dP}{P} = \int_{T_0}^{T} \frac{dH_v^0(H_2O)dT}{RT^2} \quad \therefore \ln\left(\frac{P^\alpha}{P^\alpha_{H_2O}}\right)$$
$$= \frac{dH_v^0(H_2O)}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \tag{8}$$

$$\int_{P^\beta_{H_2O}}^{P^\beta} \frac{dP}{P} = \int_{T_0}^{T} \frac{dH_v(s)dT}{RT^2} \quad \therefore \ln\left(\frac{P^\beta}{P^\beta_{H_2O}}\right) = \frac{dH_v(s)dT}{RT^2}\left(\frac{1}{T_0} - \frac{1}{T}\right), \tag{9}$$

where P^α is the vapor pressure in the α phase at arbitrary temperature (Pa), P^β the vapor pressure in the β phase at arbitrary temperature (Pa), $dH_v^0(H_2O)$ the enthalpy of vaporization of pure water (44.0 kJ mol^{-1}), $dH_v(s)$ the enthalpy of vaporization of water in the β phase (kJ mol^{-1}), and T_0 the standard temperature (298.15 K (25 °C)).

Equation (9) can be rewritten as follows:

$$\ln\left(\frac{P^\beta}{P^\beta_{H_2O}}\right) = \ln\left(\frac{P^\beta}{P^0_{H_2O}}\right) - \ln\left(\frac{P^\beta_{H_2O}}{P^0_{H_2O}}\right)$$

$$\therefore \ln\left(\frac{P^\beta}{P^0_{H_2O}}\right) = \ln\left(\frac{P^\beta}{P^\beta_{H_2O}}\right) + \ln\left(\frac{P^\beta_{H_2O}}{P^0_{H_2O}}\right)$$
$$= \frac{dH_v(s)dT}{RT^2}\left(\frac{1}{T_0} - \frac{1}{T}\right) + \ln\left(\frac{P^\beta_{H_2O}}{P^0_{H_2O}}\right). \tag{10}$$

The relative partial molar Gibbs free energies (dG^α) of waters in both phases at arbitrary temperature are given as follows:

$$dG^\alpha = RT\ln\left(\frac{P^\alpha}{P^\alpha_{H_2O}}\right) = dH_v^0(H_2O)\left(\frac{T}{T_0} - 1\right) \tag{11}$$

$$dG^\beta = RT\ln\left(\frac{P^\beta}{P^0_{H_2O}}\right) = dH_v(s)\left(\frac{T}{T_0} - 1\right) + RT\ln\left(\frac{P^\beta_{H_2O}}{P^0_{H_2O}}\right), \tag{12}$$

where dG^α and dG^β are the relative partial molar Gibbs free energies of waters in the α and the β phases (J mol^{-1}), respectively.

Since the chemical potential (μ) of waters in both phases at arbitrary temperature when both phases are in equilibrium state are equivalent, the following relations are derived.

$$\mu(W, \alpha) = dG^\alpha = RT\ln\left(\frac{P^\alpha}{P^\alpha_{H_2O}}\right) = dH_v^0(H_2O)\left(\frac{T}{T_0} - 1\right) \tag{13}$$

$$\mu(W, \beta) = dG^\beta + \int_{P^0_{ext}}^{P_{ext}} V_w dP = dH_v(s)\left(\frac{T}{T_0} - 1\right)$$
$$+ RT\ln\left(\frac{P^\beta_{H_2O}}{P^0_{H_2O}}\right) + \int_{P^0_{ext}}^{P_{ext}} V_w dP. \tag{14}$$

Therefore, swelling stress considering the effect of temperature can be finally derived as follows from Eqs. (13) and (14).

$$dP_{ext} = \frac{dH_{H_2O}}{V_w}\left(\frac{T}{T_0} - 1\right) - \frac{dG_{H_2O}}{V_w}, \tag{15}$$

where $\mu(W, \alpha)$ and $\mu(W, \alpha)$ are the chemical potential of waters in the α phase and the β phase at arbitrary temperature, respectively (J mol^{-1}), and dH_{H_2O} the relative partial molar enthalpy (J mol^{-1}), which is defined as follows:

$$dH_{H_2O} = dH_v^0(H_2O) - dH_v(s). \tag{16}$$

As described above, key parameter to evaluate the effect of temperature on the swelling stress of bentonite is the relative partial molar enthalpy (dH_{H2O}).

Results and discussion

Relative partial molar enthalpy (dH_{H2O})

Experimental correlation of thermodynamic parameters of water in Na-montmorillonite (Kunipia-F®, provided from Kunimine Industries Co. Ltd.) as a function of water content is reported by Torikai et al. [9, 10]. Kunipia-F® is a purified bentonite, and its montmorillonite content is over 99 wt%. Also in this study, thermodynamic parameters of water in Na-montmorillonite (Kunipia-P®, provided from Kunimine Industries Co. Ltd.) were obtained as a function of water content. Kunipia-P® is bentonite which was further purified Kunipia-F®, and its montmorillonite content is approximately 100 wt%. The dH_{H_2O} data of water in Na-montmorillonite (Kunipia-F®) showed a tendency to

Table I Calculated results of swelling stress

Water content (%)	Montmorillonite partial density (Mg/m³)	dH_{H2O} (kJ/mol)	Swelling stress (MPa)		Remarks
			298.15 K (25 °C)	333.15 K (60 °C)	
42.2	1.26	− 0.10	5.96	5.31	This work
33.9	1.41	− 0.22	11.0	9.57	This work
25	1.61	− 1	46.8	40.3	Literature [9, 10]
16.8	1.85	− 1.56	122.0	111.9	This work
12.4	2.02	− 5	147.6	115.1	Literature [9, 10]

decrease with the decrease in water content in the range of water content lower than approximately 32%. The same results were obtained also for the Kunipia-P® bentonite (Na-montmorillonite) obtained in this study. This indicates that swelling stress decreases with the increase in temperature in montmorillonite partial densities higher than 1.45 Mg m⁻³. Here, the montmorillonite partial density for water-saturated condition can be converted from water content (W_C) by using the following relation [6, 11, 12]:

$$\rho_m = \frac{100\rho_{th} \cdot \rho_w}{W_C \cdot \rho_{th} + 100\rho_w}, \tag{17}$$

where ρ_m is the montmorillonite partial density (Mg m⁻³), ρ_{th} the solid density of montmorillonite (2.7 Mg m⁻³), ρ_w the density of water (0.997044 Mg m⁻³ at 25 °C), and W_C the water content.

Next, the correlation between the activity of water and water content was considered. The activity of water in Na-montmorillonite (Kunipia-F®) also showed a tendency to decrease with the decreas in water content in the range of water content lower than approximately 43%. The same trend was obtained for the Kunipia-P® bentonite [11]. This indicates that swelling stress decreases with an increase of temperature in montmorillonite partial densities higher than 1.25 Mg m⁻³. From described above, it is considered that swelling stress decreases with an increase of temperature in the range of montmorillonite partial density higher than at least 1.25 Mg m⁻³.

Effect of temperature on swelling stress of bentonite

The effect of temperature on the swelling stress of bentonite was analyzed based on the thermodynamic model revised in this study and the data of dH_{H2O}. The analysis was carried out at 298.15 K (25 °C) and 333.15 K (60 °C). The temperature condition of 60 °C is the reference case in the 2nd progress report for geological disposal [13]. The dH_{H2O} data of water in Na-montmorillonite were based on both literature data [9, 10] and experimental data obtained from vapor pressure measurements as a function of water content

and temperature in this study. The detailed experimental procedure of the vapor pressure measurements is as described in literature [12], and the measurements were carried out for the Kunipia-P® bentonite (Na-montmorillonite). The dH_{H2O} as a function of water content was calculated from Eqs. (12) and (16) based on data of vapor pressure in Na-montmorillonite as a function of temperature.

Table I shows the calculated results of swelling stress, together with the data of dH_{H2O} as a function of water content and montmorillonite partial density. As shown in Table I, the degree of decrease in swelling stress is approximately 10% at the montmorillonite partial density of 1.26 Mg m⁻³, approximately 15% at the montmorillonite partial density of 1.61 Mg m⁻³ and approximately 20% at the montmorillonite partial density of 2.02 Mg m⁻³, and the effect of temperature on swelling stress was insignificant. Considering design density of buffer material in repository, it can be said that we realistically do not need to consider the effect of temperature on swelling stress.

Thermodynamic data such as dH_{H2O} and the activity of water are presently limited to Na-montmorillonite which is the major component of Na-bentonite. Since hydration energy is dependent on interlayer cation such as Ca^{2+}, thermodynamic data of water to montmorillonite containing different interlayer cations such as Ca-montmorillonite need to evaluate the swelling stress of Ca-bentonite and the effect of temperature.

Conclusions

The effect of temperature on the swelling stress of Na-bentonite depends on the relative partial molar enthalpy (dH_{H2O}), and it is considered that swelling stress decreases with an increase of temperature in the range of montmorillonite partial density higher than at least 1.25 Mg m⁻³ from relation with water content.

Degree of decrease in swelling stress is considered small to be 10–20% in the comparison between 298.15 K (25 °C) and 333.15 K (60 °C). Considering design density of buffer material in repository, it can be said that we realistically do

not need to consider the effect of temperature on the swelling stress of Na-bentonite.

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