

# Measurements of Thermodynamic Data of Water in Na-Bentonite in the Standard Condition by Relative Humidity Method

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**Keywords:** Geological disposal, bentonite, montmorillonite, swelling stress, Gibbs free energy

## ABSTRACT

Buffer material (compacted bentonite) composing engineered barrier in the geological disposal of a high-level radioactive waste develops swelling stress by penetration of groundwater from the surrounding rock mass. In previous studies, we measured the activity of water and the Gibbs free energy of water in Na-montmorillonite which is the major component of Na-bentonite by vapor pressure method, and reported a model to analyze the swelling stress of bentonite based on thermodynamic theory. However, data for the vapor pressure of water in bentonite are limited. In this study, we determined the activities of water and the Gibbs free energy by measuring relative humidity (RH) and temperature for water in Na-bentonite and Na-montmorillonite. We also analyzed the swelling stress of bentonite based on the thermodynamic model and compared to data reported up to date. Kunigel-V1 and Kunipia-F (Kunimine Industries Co. Ltd.) were used as a Na-bentonite. The Na-montmorillonite contents of both bentonites are approximately 51 and 99%, respectively. Bentonite powder dried was placed in a polyethylene bottle in an amount of 3.00g each, and slowly adsorbed water vapor in a vacuum chamber. Next, RH and temperature sensors and polyethylene bottles with bentonite were placed in the vacuum chamber, and the chamber of which inside pressure was reduced to -95kPa or less was submerged in a water bath at 25°C. The RH and temperature in the chamber and the weight of the bentonite were measured after 24 hours. The bentonite sample was returned to the chamber again and the water content of the bentonite was reduced by evacuating for a while, and then the chamber was submerged in the water bath again. This operation was repeated every 24 hours. Thus, RH and temperature were measured as a function of water content (*ca.* 10-100%). The activities of water and the Gibbs free energies of water for both bentonites decreased with decreasing water content in water contents lower than approximately 40%. This trend is the same as the trend in the past studies. The swelling stress of bentonite calculated using thermodynamic data obtained in this study were generally in good agreement with the measured data.

## 1. INTRODUCTION

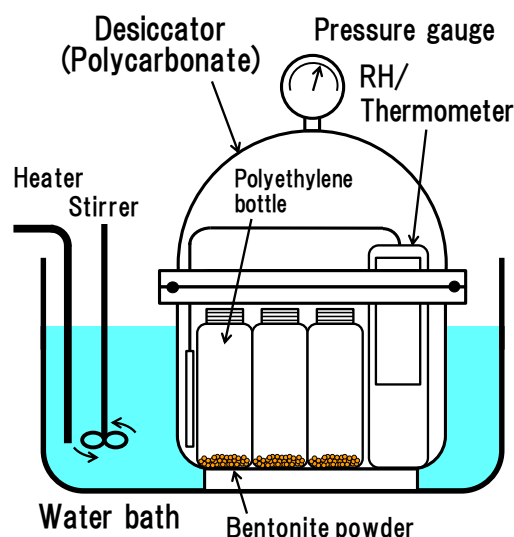
Buffer material (compacted Na-bentonite) composing engineered barrier in the geological disposal of a high-level radioactive waste (HLW) develops swelling stress (swelling pressure) by penetration of groundwater from the surrounding rock mass after the closure of the disposal tunnels. In the past studies, we measured the activities of water and the relative partial molar Gibbs free energies of water in Na-montmorillonite which is the major component of Na-bentonite used as a buffer material by vapor pressure method, and proposed a thermodynamic model to analyze the swelling stress of bentonite based on thermodynamic theory (*e.g.* Sato, 2007, 2008a, 2008b). However, the thermodynamic data of water in bentonite are limited.

In this study, we measured the thermodynamic data of water (activity of water and relative partial molar Gibbs free energy of water) in Na-bentonite and Na-montmorillonite by measuring relative humidity (RH) and temperature. Furthermore, we also analyzed the swelling stress of bentonite based on thermodynamic model and the thermodynamic data of water, and compared with the measured data.

## 2. MEASUREMENTS OF THERMODYNAMIC DATA OF WATER IN BENTONITE

Figure 1 shows a concept of the measurements of water vapor pressure by RH method. Kunigel-V1 and Kunipia-F bentonites (provided from Kunimine Industries Co. Ltd.) were used as a Na-bentonite in the experiments. The Na-montmorillonite contents of both bentonites are approximately 51% (Yamamoto *et al.*, 2022) and 99%, respectively. Bentonite powder which was dried at 105°C over 24 hours in an oven was placed in a polyethylene bottle in an amount of 3.00g each (repeatability  $n = 3$ ), and slowly adsorbed water vapor with 100% RH and -99kPa or less in a vacuum chamber (polycarbonate desiccator) for about 9 months. The water content of the bentonite was checked by weighing periodically. This adsorption of water vapor to bentonite was continued to be about 100% water content.

Next, RH and temperature sensors and polyethylene bottles with moisturized bentonite powder were placed in a vacuum chamber, and the chamber of which inside pressure was reduced to -95kPa (6.3kPa with absolute pressure) or less was submerged in a constant temperature water bath at 25°C. The RH and temperature in the chamber were measured after 24 hours and the



**Figure 1: Concept of the measurements of water vapor pressure by relative humidity method.**

weight of the bentonite was measured. The bentonite sample was returned to the chamber again and the water content of the bentonite was reduced by evacuating for a while, and then the chamber was submerged in the constant temperature water bath again. This operation was repeated every about 24 hours. Thus, RH and temperature were measured as a function of water content (*ca.* 10-100%).

### 3. THERMODYNAMIC MODEL FOR SWELLING STRESS OF BENTONITE

Figure 2 shows a conceptual model of the chemical potential balance of water in the equilibrium state between an electrolyte solution ( $\alpha$  phase) and bentonite ( $\beta$  phase) contacted with the solution through filter at standard temperature (25°C) (Sato, 2008, 2009, Sato and Fukazawa, 2016). Both phases are connected only through filter, and upper spaces are also independent. 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  $\beta$  phase increases with increasing water content of the bentonite. This means that the relative partial molar Gibbs free energy ( $dG$ ) in the  $\beta$  phase increases with increasing water content of bentonite. When both phases reach equilibrium state, the chemical potentials of waters between both phases are equivalent as follows:

$$\mu^0(W, \alpha) = \mu^0(W, \beta) \quad (1)$$

where,  $\mu^0(W, \alpha)$  and  $\mu^0(W, \beta)$  are the chemical potentials of waters in the  $\alpha$  phase and the  $\beta$  phase at 25°C, respectively (J/mol).

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:

$$dG = dG_S - dG_{H_2O} \quad (2)$$

where,  $dG$  is the difference of the relative partial molar Gibbs free energies of waters between the  $\alpha$  phase and the  $\beta$  phase in equilibrium state (J/mol), and  $dG_S$  and  $dG_{H_2O}$  are the relative partial molar Gibbs free energies of waters in the  $\alpha$  phase and the  $\beta$  phase, respectively (J/mol). If the  $\alpha$  phase is the pure water system,  $dG_S = 0$ .

The chemical potentials of waters in the  $\alpha$  phase and the  $\beta$  phase when both phases are in equilibrium state are, respectively, described as follows:

$$\mu^0(W, \alpha) = dG_S = RT \ln \left( \frac{P_{H_2O}^\alpha}{P_{H_2O}^0} \right) \quad (3)$$

$$\mu^0(W, \beta) = dG_{H_2O} + \int_{P_{ext}^0}^{P_{ext}} V_w dp = RT \ln \left( \frac{P_{H_2O}^\beta}{P_{H_2O}^0} \right) + \int_{P_{ext}^0}^{P_{ext}} V_w dp \quad (4)$$

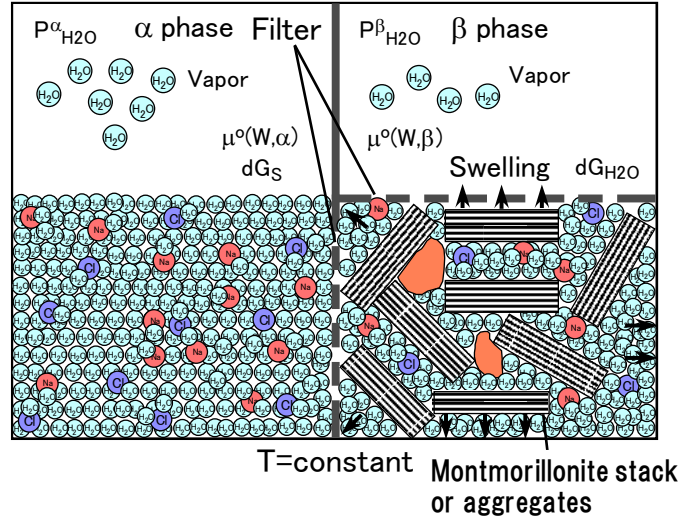
Since the chemical potentials of waters in both phases are equivalent, the swelling energy of bentonite is derived as follows, based on Eqs. (1) to (4):

$$RT \ln \left( \frac{P_{H_2O}^\alpha}{P_{H_2O}^0} \right) = RT \ln \left( \frac{P_{H_2O}^\beta}{P_{H_2O}^0} \right) + \int_{P_{ext}^0}^{P_{ext}} V_w dp \quad (5)$$

$$\therefore \int_{P_{ext}^0}^{P_{ext}} V_w dp = (P_{ext} - P_{ext}^0) V_w = RT \ln \left( \frac{P_{H_2O}^\alpha}{P_{H_2O}^0} \right) - RT \ln \left( \frac{P_{H_2O}^\beta}{P_{H_2O}^0} \right) = dG_S - dG_{H_2O} \quad (6)$$

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

$$dP_{ext} = \frac{RT}{V_w} \ln \left( \frac{P_{H_2O}^\alpha}{P_{H_2O}^0} \right) - \frac{RT}{V_w} \ln \left( \frac{P_{H_2O}^\beta}{P_{H_2O}^0} \right) = \frac{dG_S - dG_{H_2O}}{V_w} \quad (7)$$



**Figure 2: A conceptual model of the chemical potential balance of water in the equilibrium state between an electrolyte solution ( $\alpha$  phase) and bentonite ( $\beta$  phase) came in contact with the solution through filter at constant temperature.**

where,  $P_{\text{ext}}^0$  is the swelling stress (Pa),  $V_w$  the specific volume of pure water at 25°C (18.0686cm<sup>3</sup>/mol),  $P_{\text{H}_2\text{O}}^\alpha$  and  $P_{\text{H}_2\text{O}}^\beta$  the vapor pressure in the  $\alpha$  phase and the  $\beta$  phase at 25°C, respectively (Pa),  $P_{\text{H}_2\text{O}}^0$  the vapor pressure of pure water at 25°C (3.168kPa),  $R$  the gas constant (8.314J/mol/K), and  $T$  the absolute temperature (K).

Furthermore, the activity of water is defined as follows, from  $P_{\text{H}_2\text{O}}^0$ ,  $P_{\text{H}_2\text{O}}^\alpha$  and  $P_{\text{H}_2\text{O}}^\beta$ :

$$a_w^\alpha = \frac{P_{\text{H}_2\text{O}}^\alpha}{P_{\text{H}_2\text{O}}^0} \quad (8)$$

$$a_w^\beta = \frac{P_{\text{H}_2\text{O}}^\beta}{P_{\text{H}_2\text{O}}^0} \quad (9)$$

where,  $a_w^\alpha$  and  $a_w^\beta$  are the activity of water in the  $\alpha$  phase and the  $\beta$  phase, respectively, and when the  $\alpha$  phase is pure water,  $a_w^\alpha = 1$ .

The relative partial molar Gibbs free energy of water in the  $\beta$  phase at 25°C is given as follows:

$$dG_{\text{H}_2\text{O}} = RT \ln \left( \frac{P_{\text{H}_2\text{O}}^\beta}{P_{\text{H}_2\text{O}}^0} \right) = RT \ln (a_w^\beta) \quad (10)$$

The relation between relative humidity ( $RH$ ) and the activity of water is given as follows:

$$a_w^\beta = \frac{RH}{100} \quad (11)$$

Therefore, the relative partial molar Gibbs free energy is expressed as follows, using  $RH$ :

$$dG_{\text{H}_2\text{O}} = RT \ln \left( \frac{RH}{100} \right) \quad (12)$$

where,  $RH$  is the relative humidity at 25°C (%).

Based on Eq. (11), the activity of water in the condition can be determined by measuring  $RH$  and temperature. In addition, the relative partial molar Gibbs free energy can be determined based on Eq. (12).

## 4. RESULTS AND DISCUSSION

### 4.1 Correlation between Thermodynamic Data and Water Content to Montmorillonite

Figure 3 shows the correlation between the activity of water ( $a_w^\beta$ ) and water content to montmorillonite, and Figure 4 shows the correlation between the relative partial molar Gibbs free energy of water ( $dG_{\text{H}_2\text{O}}$ ) and water content to montmorillonite. For the calculation of water content to montmorillonite, the montmorillonite contents of Kunigel-V1 and Kunipia-F were assumed to be respectively 51% (Yamamoto *et al.*, 2022) and 99%.

The activities of water and the relative partial molar Gibbs free energies of water for both bentonites decreased with decreasing water content in water contents lower than approximately 40%. This trend is similar to the trend obtained in the past studies for Kunipia-F. On the other hand, the activities of water and the relative partial molar Gibbs free energies of water obtained in this study were slightly higher than conventional data (Kunipia-P of which Na-montmorillonite content is 100%). This is considered to be due to that conventional data (Kunipia-P) were obtained for completely purified Na-montmorillonite.

### 4.2 Model Analysis of Swelling Stress of Bentonite

Figure 5 shows the calculated results of the swelling stress of bentonite by thermodynamic model as a function of montmorillonite partial density and the measured data of swelling stress for various bentonites (JAEA, 2014, Sato, 2008b, Torikai *et al.*, 1996). Here, the montmorillonite

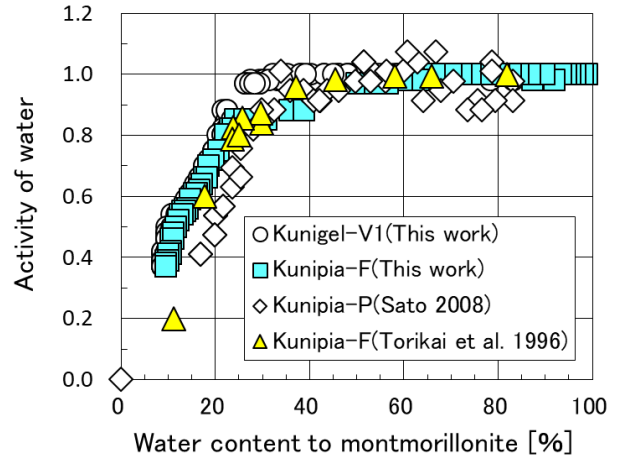


Figure 3: Correlation between the activity of water and water content to montmorillonite (Sato, 2008a, Torikai *et al.*, 1996).

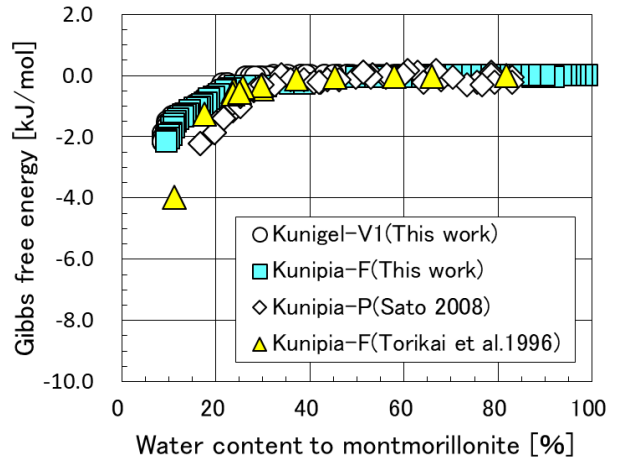


Figure 4: Correlation between the relative partial molar Gibbs free energy of water and water content to montmorillonite (Sato, 2008a, Torikai *et al.*, 1996).

partial density for water-saturated condition can be converted from water content ( $W_C$ ) by using the following relation (e.g. Sato, 2007, 2008a, 2009):

$$\rho_m = \frac{100\rho_{th} \cdot \rho_w}{W_C \cdot \rho_{th} + 100\rho_w} \quad (13)$$

where,  $\rho_m$  is the montmorillonite partial density ( $\text{Mg/m}^3$ ),  $\rho_{th}$  the solid density (particle density) of montmorillonite ( $2.7\text{Mg/m}^3$ ),  $\rho_w$  the density of water ( $0.997044\text{Mg/m}^3$  at  $25^\circ\text{C}$ ), and  $W_C$  the water content (%).

As shown in Fig. 5, the swelling stress of bentonite calculated using thermodynamic data obtained in this study were generally in good agreement with the measured data for various bentonites of which montmorillonite contents were different. This indicates the effectiveness of thermodynamic model.

Since the thermodynamic data of water in bentonite and montmorillonite are quite limited at the present, further acquisition of thermodynamic data is needed. In addition, bentonite is possible to alter by reaction with chemical component of groundwater. Therefore, we will measure the thermodynamic data of water also for different cations such as Ca and K in the interlayer of montmorillonite.

## 5. CONCLUSIONS

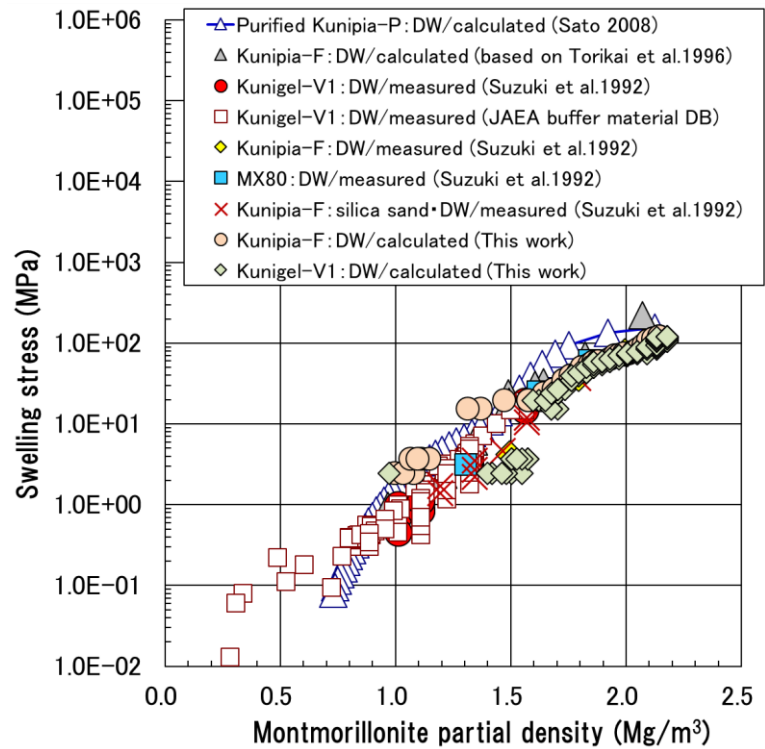
We measured the thermodynamic data (the activities of water and the relative partial molar Gibbs free energies of water) of water in Na-bentonite and Na-montmorillonite which is the major clay mineral component of Na-bentonite as a function of water content by RH method, and calculated the swelling stress of bentonite based on the thermodynamic data and model. The calculated results of the swelling stress of bentonite were in good agreement with the measured data for various bentonites of which montmorillonite contents were different over the density, and the validation of the thermodynamic model was confirmed. Since the thermodynamic data of water in bentonite and montmorillonite are quite limited, further acquisition of data is important.

## ACKNOWLEDGEMENTS

This study was conducted by Grant-in-Aid for Scientific Research of Japan Society for the Promotion of Science (JSPS) (No.20K05383), research grant of Wesco Scientific Promotion Foundation and research grant of Electric Technology Research Foundation of Chugoku. The authors would like to thank all organizations for financially supporting.

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**Figure 5: Calculated results of the swelling stress of bentonite by thermodynamic model versus montmorillonite partial density and the measured data of swelling stress for various bentonites (JAEA, 2014, Sato, 2008b, Suzuki *et al.*, 1992, Torikai *et al.*, 1996).**