Development of a Thermodynamic Model for Swelling Stress of Bentonite: Measurements of Thermodynamic Data of Water in Na-Bentonite

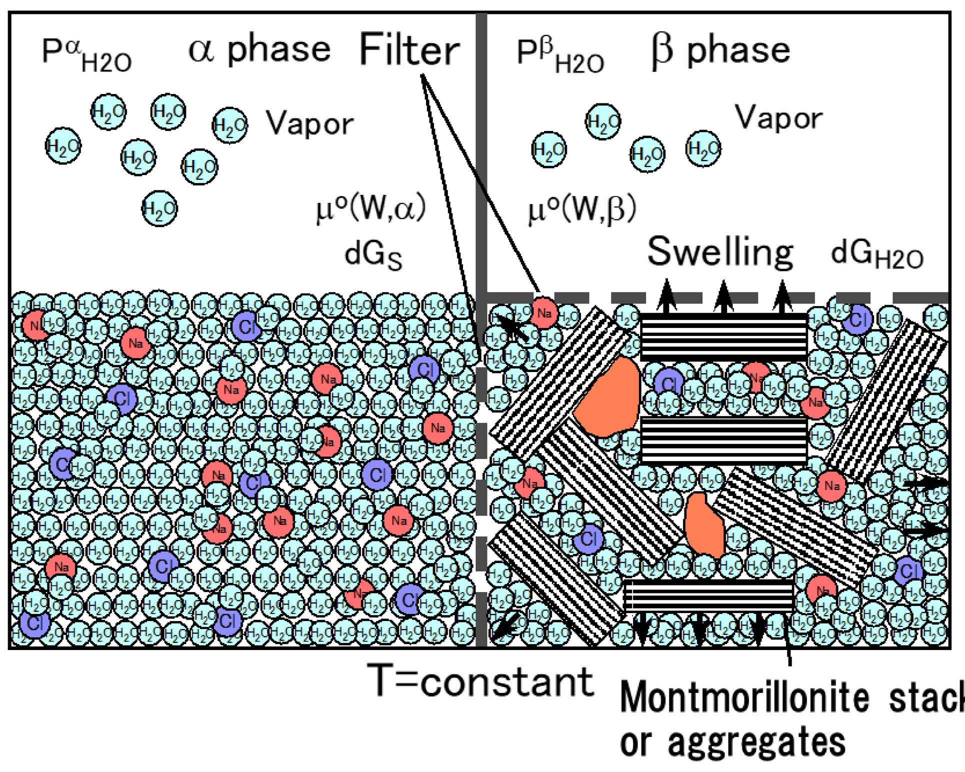
Haruo SATO, Faculty of Environmental, Life, Natural Science & Technology, Okayama University
E-mail: sato.haruo@cc.okayama-u.ac.jp / ph3c5tsu@s.okayama-u.ac.jp

Introduction

- Buffer material (compacted bentonite) composing engineered barrier in the geological disposal of a high-level radioactive waste (HLW) develops swelling stress by penetration of groundwater from the surrounding rock mass.
- In previous studies, we measured the thermodynamic data of water (the activity of water & the relative partial molar Gibbs free energy of water) in Na-montmorillonite which is the major component of Na-bentonite by vapor pressure method, and proposed a thermodynamic model to analyze the swelling stress (pressure) 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 in Na-montmorillonite and Na-bentonite by measuring relative humidity (RH). We also analyzed the swelling stress of bentonite based on the thermodynamic model developed so far & the thermodynamic data of water, and compared with measured data.

A Thermodynamic Model of Swelling Stress of Bentonite

<A conceptual model of thermodynamic model>



A conceptual model on the chemical potential balance of water in the equilibrium state between an electrolyte solution & bentonite saturated with the solution through filter

When the α & the β phases are in equilibrium state by penetration of the solution to the bentonite, the chemical potentials (μ^0) of the waters between both phases are equivalent.

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

In this system, the difference of the Gibbs free energies (dG) of the waters between both phases in equilibrium state acts as swelling energy of the bentonite.

The dG can be calculated as below assuming that the relative partial molar Gibbs free energy of water in the α phase is dG_S & that that in the β phases is dG_{H2O}.

$$dG = dG_S - dG_{H2O} \quad \cdots\cdots\cdots\cdots (2)$$

Chemical potentials (μ^0) of waters in both phases (α & β) when both phases are in equilibrium by penetration of solution to bentonite (25°C)

$$\mu^o(W,\alpha) = RT\ln\left(\frac{P^{\alpha}_{H2O}}{P^{o}_{H2O}}\right) \quad \cdots\cdots (3)$$

$$\mu^o(W,\beta) = RT\ln\left(\frac{P^{\beta}_{H2O}}{P^{o}_{H2O}}\right) + \int_{P^o_{ext}}^{P_{ext}} V_w dP \cdots (4)$$

Chemical potentials (μ^0) of waters in both phases are equivalent

$$RT\ln\left(\frac{P^{\beta}_{H2O}}{P^{o}_{H2O}}\right) + \int_{P^o_{ext}}^{P_{ext}} V_w dP = RT\ln\left(\frac{P^{\alpha}_{H2O}}{P^{o}_{H2O}}\right)$$

$$\int_{P^o_{ext}}^{P_{ext}} V_w dP = RT\ln\left(\frac{P^{\alpha}_{H2O}}{P^{o}_{H2O}}\right) - RT\ln\left(\frac{P^{\beta}_{H2O}}{P^{o}_{H2O}}\right) = dG_S - dG_{H2O} \quad \cdots\cdots (5)$$

Relation of swelling stress (dP_{ext}) with the Gibbs free energy changes ($dG = dG_S - dG_{H2O}$) of waters in both phases

$$dP_{ext} = \frac{RT}{V_w}\ln\left(\frac{P^{\alpha}_{H2O}}{P^{o}_{H2O}}\right) - \frac{RT}{V_w}\ln\left(\frac{P^{\beta}_{H2O}}{P^{o}_{H2O}}\right) = \frac{dG_S - dG_{H2O}}{V_w} \quad \cdots\cdots (6)$$

dP_{ext}: swelling stress (Pa)
V_w: specific volume of water at 25°C (18.0686cm³/mol)
P^{α}_{H2O}: vapor pressure in the α phase at 25°C (Pa)
P^{β}_{H2O}: vapor pressure in the β phase at 25°C (Pa)
P^{o}_{H2O}: vapor pressure of pure water at 25°C (3.168kPa)
R: gas constant (8.314J/mol/K)
T: absolute temperature (K)

Measurements of Thermodynamic Data of Water in Montmorillonite & Bentonite

<Relation of thermodynamic parameter with relative humidity (RH)>

Activity of water

$$a_{H2O} = \frac{P^{\beta}_{H2O}}{P^{o}_{H2O}} \quad \cdots\cdots\cdots\cdots (7)$$

Relative partial molar Gibbs free energy

$$dG_{H2O} = RT\ln\left(\frac{P^{\beta}_{H2O}}{P^{o}_{H2O}}\right) = RT\ln(a_{H2O}) \quad \cdots\cdots\cdots\cdots (8)$$

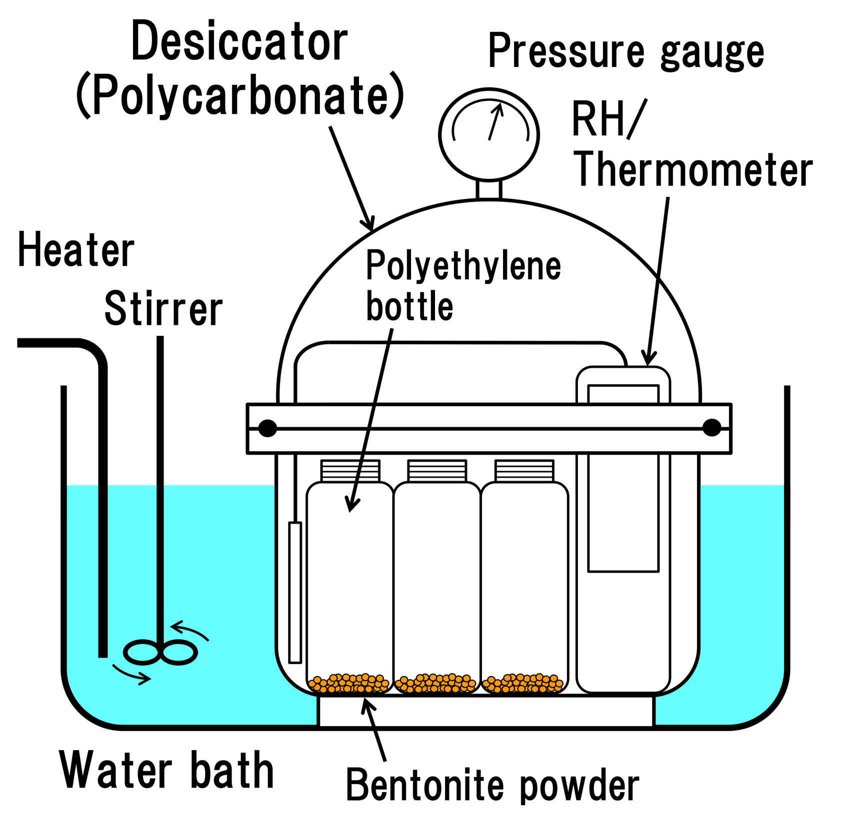
Relation of activity of water with RH

$$a_{H2O} = \frac{RH}{100} \quad \cdots\cdots\cdots\cdots (9)$$

Relation of relative partial molar Gibbs free energy with RH

$$dG_{H2O} = RT\ln\left(\frac{RH}{100}\right) \quad \cdots\cdots\cdots\cdots (10)$$

a_{H2O}: activity of water
dG_{H2O}: relative partial molar Gibbs free energy
P^{β}_{H2O}: vapor pressure of water in the β phase at 25°C
P^{o}_{H2O}: saturated vapor pressure of water at 25°C (3.168kPa)
RH: relative humidity at 25°C (%)
R: gas constant (8.314J/mol/K)
T: absolute temperature (K)



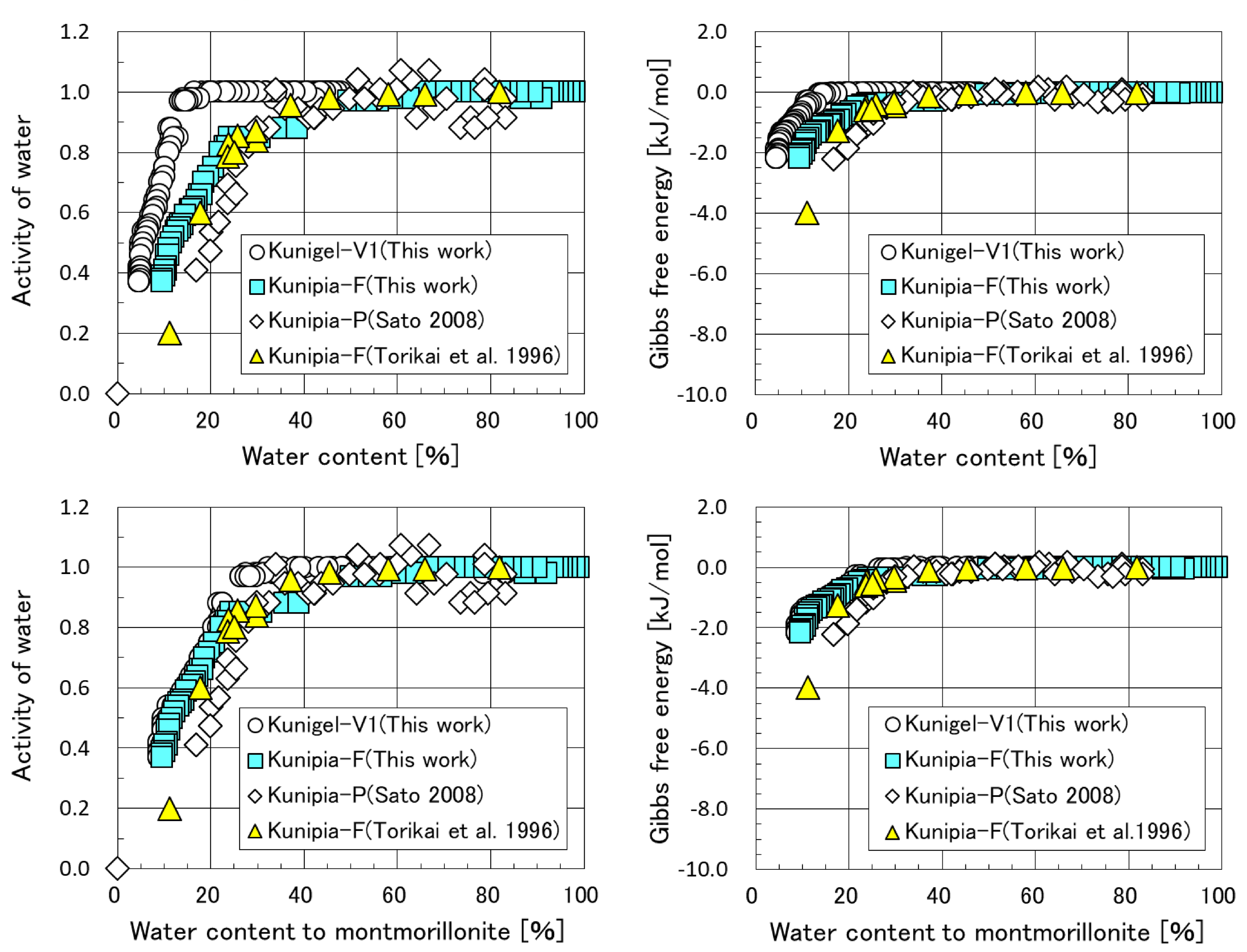
Concept of measurement of water vapor pressure by RH method

<Procedure & Condition>

① Dry Na-bentonite powder (Kunigel-V1 & Kunipia-F (Kunimine Industries Co. Ltd.), 105-110°C, 24h~, 3.00g/sample, n=3))
② Adsorb vapor to bentonite (RH=100%, lower than -99kPa, ~9 months, periodically measure the weight of water)
③ Measure RH & temperature (-101.3kPa, 25°C, measure every ca. 24h)
④ Take out sample (bentonite powder) & measure the weight of water
⑤ Draw a vacuum to lower water content
⑥ Repeat procedures ③~⑤ vs. water content (~100%)

Results & Discussion

<Thermodynamic Data of Water>

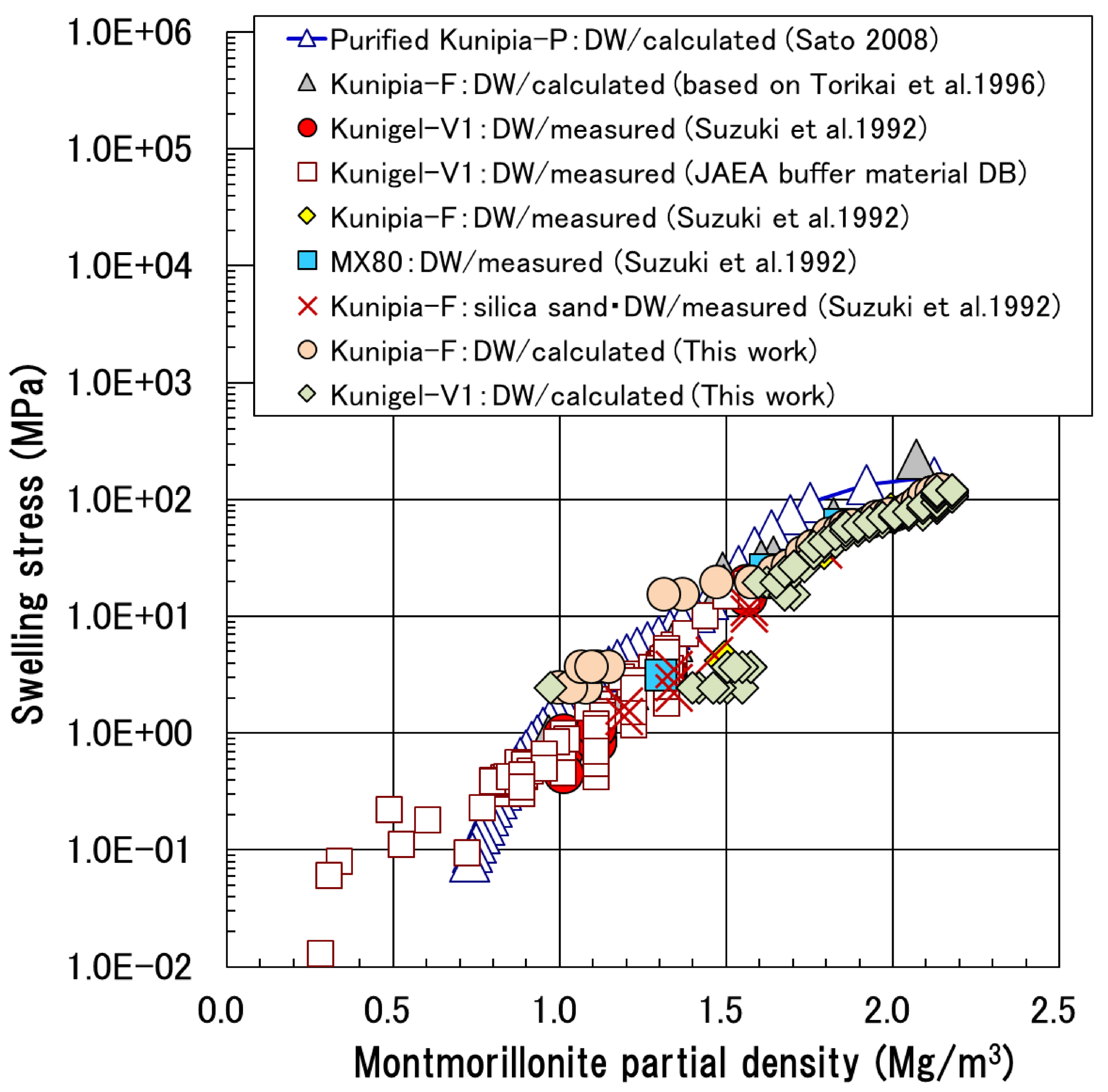


Activity of water (a_{H2O}) (left) & relative partial molar Gibbs free energy (dG_{H2O}) (right) vs. water content of bentonite (W_C)(upper Figs.) & water content to montmorillonite (lower Figs.)

$$W_c\,(\%) = \left(\frac{\text{Moisture weight}}{\text{Bentonite weight}}\right) \times 100$$

Montmorillonite content in bentonite
Kunigel-V1: 51% [NUMO 2022]
Kunipia-F: 99%

- Although both of the activity of water (a_{H2O}) and the relative partial molar Gibbs free energy (dG_{H2O}) are lower in Kunipia-F & Kunipia-P than in Kunigel-V1 in the correlation with W_C of bentonite, the plots of both bentonites (Kunipia-F & Kunigel-V1) overlap vs. W_C of montmorillonite, and montmorillonite content is concerned with water retention
- The same trend is obtained also in the past studies [Torikai et al. 1996, Sato 2007, 2008a, 2008b]



<Summary>

- We measured the thermodynamic data of water (a_{H2O} & dG_{H2O}) in Na-montmorillonite & Na-bentonite vs. water content, and calculated the swelling stress of bentonite based on the thermodynamic data & model.
- The calculated results of the swelling stress of bentonite were in good agreement with measured data. Therefore, thermodynamic model is useful for analysis of swelling stress.

References [1] H. Sato: Mat. Proc. of the Int'l Conference on Nucl. Eng. (ICONE15), ICONE15-10207, 7 pages (in pdf format) (2007). [2] H. Sato: Physics and Chemistry of the Earth, Vol.33, pp.S535-S543 (2008a). [3] H. Sato: Proc. of the 4th Japan-Korea Joint Workshop on Radioactive Waste Disposal 2008: Perspective of Sci. and Eng., pp.1-17 (2008b). [4] Y. Torikai et al.: Nucl. Technol. 115, pp.73-80 (1996). [5] H. Suzuki et al.: PNC TN8410 92-057 (1992). [6] Japan Atomic Energy Agency (JAEA): Database on Fundamental Properties of Buffer Material, "https:bufferdb.jaea.go.jp/bmsb/", downloaded 12/14 (2014).