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

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- Introduction

- A Thermodynamic Model of Swelling Stress (Pressure) of Bentonite

- Measurements of Water Vapor Pressure by Relative Humidity (RH) Method

- Activity of Water & Relative Partial Molar Gibbs Free Energy vs. Water Content

- Model Analysis of Swelling Stress of Bentonite

- Conclusions

- Buffer material (compacted bentonite) composing engineered barrier in the geological disposal of a HLW develops swelling stress by penetration of groundwater from the surrounding rock mass.

- 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, and proposed a thermodynamic model to analyze the swelling stress of bentonite based on thermodynamic theory [eg., 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-bentonite and Na-montmorillonite by measuring relative humidity (RH) and temperature. Based on the thermodynamic data of water and the thermodynamic model developed so far, we calculated the swelling stress of bentonite and compared with measured data.
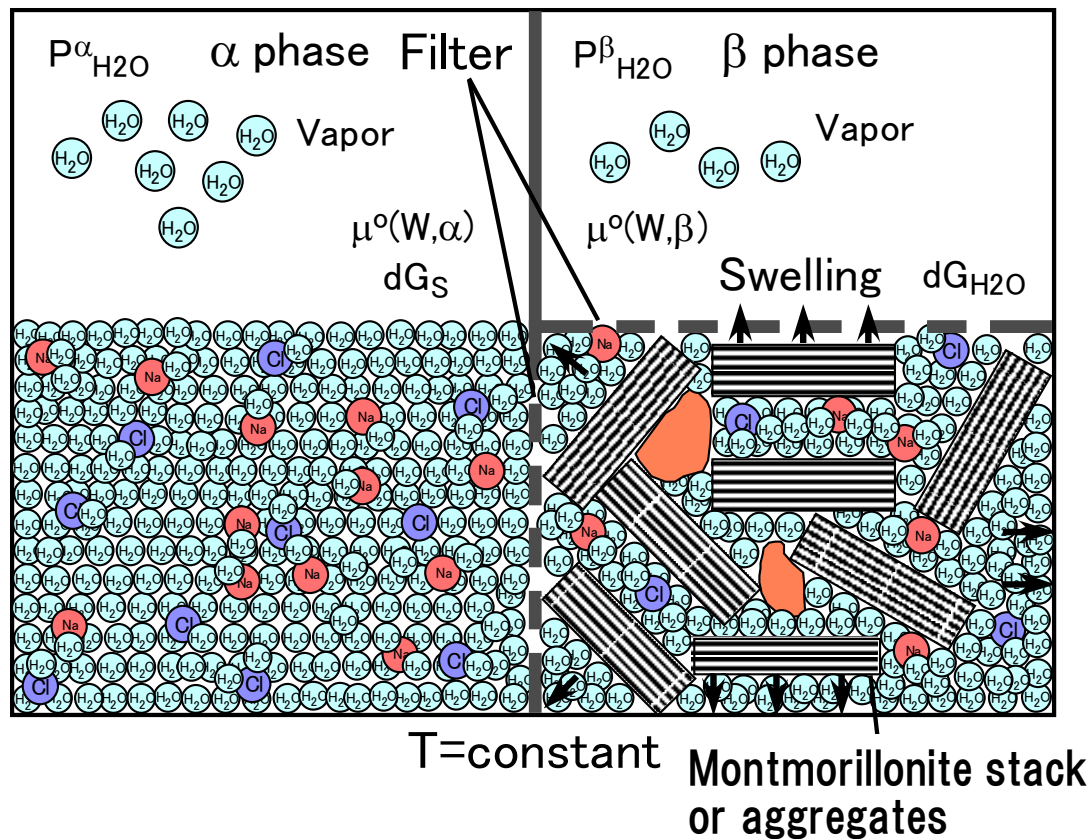
[1] H. Sato：ICONE15-10207 (2007).
[2] H. Sato：Phys. and Chem. of the Earth 33, pp.S538-S543 (2008a).
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A conceptual model on the chemical potential balance of water in the equilibrium state between an electrolyte solution (α phase) & bentonite (β phase) saturated with the solution through filter

P^{α}_{H2O}　α phase　Filter　P^{β}_{H2O}　β phase

Vapor

Vapor

$\mu^o(W,\alpha)$　$\mu^o(W,\beta)$

dG_S　Swelling　dG_{H2O}

T=constant

Montmorillonite stack or aggregates

(Fig. H. Sato: MRS Symp. Proc. Vol.1124 (2009))

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

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

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}.

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

Chemical potentials (μ^o) of waters in both phases (α & β) when both phases reached equilibrium by penetration of solution to bentonite (25℃)

$$\mu^o(W, \alpha) = RT \ln\left(\frac{P_{H2O}^\alpha}{P_{H2O}^o}\right) \quad \text{........ (3)}$$

$$\mu^o(W, \beta) = RT \ln\left(\frac{P_{H2O}^\beta}{P_{H2O}^o}\right) + \int_{P_{ext}^o}^{P_{ext}} V_w dP \quad \text{..... (4)}$$

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

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

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

$$= dG_S - dG_{H2O} \quad (5)$$

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

$$dP_{ext} = \frac{RT}{V_w} \ln\left(\frac{P_{H2O}^\alpha}{P_{H2O}^o}\right) - \frac{RT}{V_w} \ln\left(\frac{P_{H2O}^\beta}{P_{H2O}^o}\right)$$

$$= \frac{dG_S - dG_{H2O}}{V_w} \quad \text{........ (6)}$$

dP_{ext}: swelling stress (Pa)

V_w: specific volume of water at 25℃ (18.0686cm^3/mol)

P_{H2O}^α: vapor pressure in the α phase at 25℃ (Pa)

P_{H2O}^β: vapor pressure in the β phase at 25℃ (Pa)

P_{H2O}^0: vapor pressure of pure water at 25℃ (3.168kPa)

R : gas constant (8.314J/mol/K)

T : absolute temperature (K)

Activity of water

$$a_{H2O}^{o} = \frac{P_{H2O}^{\beta}}{P_{H2O}^{o}} \qquad (7)$$

Relative partial molar Gibbs free energy

$$dG_{H2O}^{o} = RT \ln\left(\frac{P_{H2O}^{\beta}}{P_{H2O}^{o}}\right)$$

$$= RT \ln(a_{H2O}^{o}) \qquad (8)$$

Relation of activity of water with RH

$$\boxed{a_{H2O}^{o} = \frac{RH}{100}} \qquad (9)$$

Relation of relative partial molar Gibbs free energy with RH

$$\boxed{dG_{H2O}^{o} = RT \ln\left(\frac{RH}{100}\right)} \qquad (10)$$

a_{H2O}^{o} : activity of water

dG_{H2O}^{o} : relative partial molar Gibbs free energy

P_{H2O}^{β} : vapor pressure of water in the β phase at 25℃

P_{H2O}^{o} : saturated vapor pressure of water at 25℃ (3.168kPa)

RH : relative humidity at 25℃ (%)
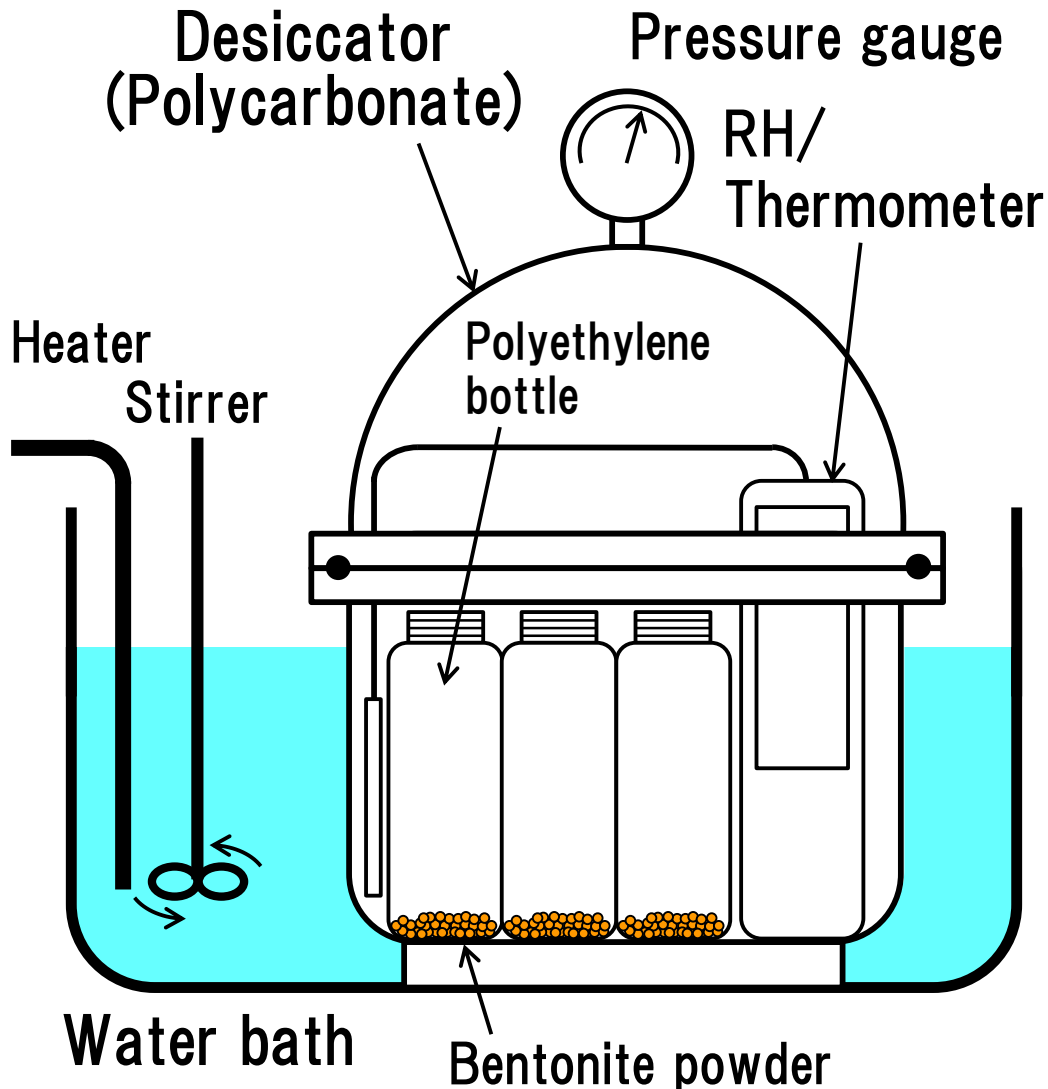
R : gas constant (8.314J/mol/K)

T : absolute temperature (273.15+t (℃), K)

Desiccator
(Polycarbonate)

Pressure gauge

RH/
Thermometer

Heater

Stirrer

Polyethylene
bottle

Water bath

Bentonite powder

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℃, 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℃, measure every 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%)
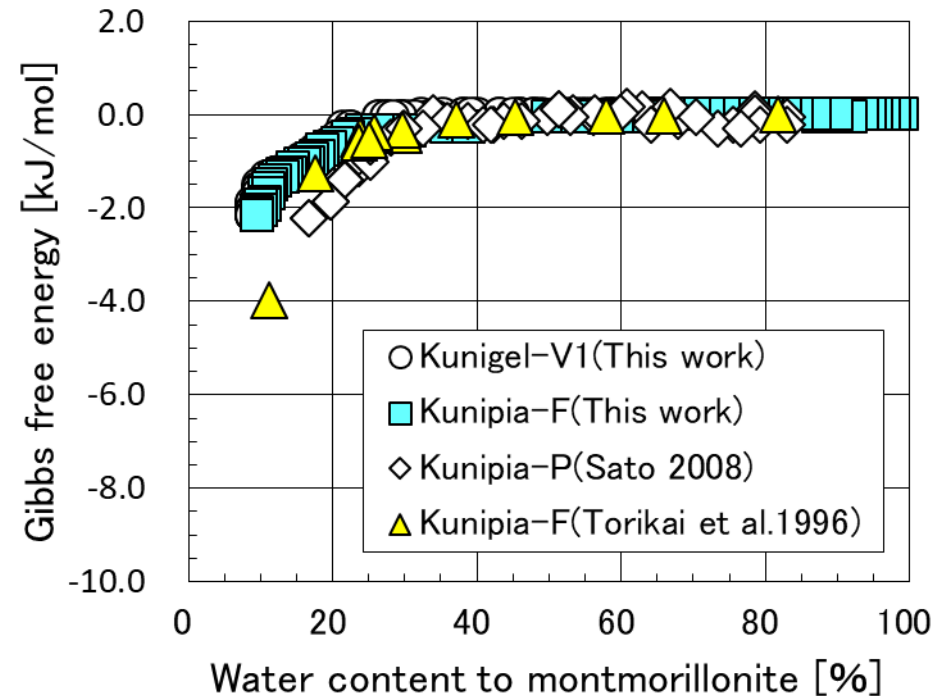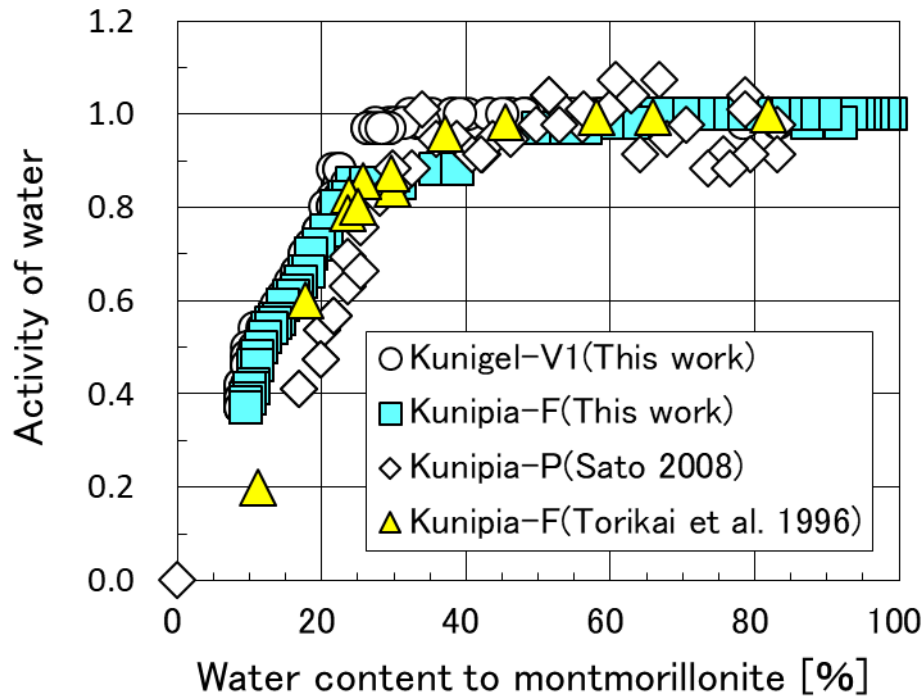
Activity & Gibbs Free Energy vs. Water Content (1/2)

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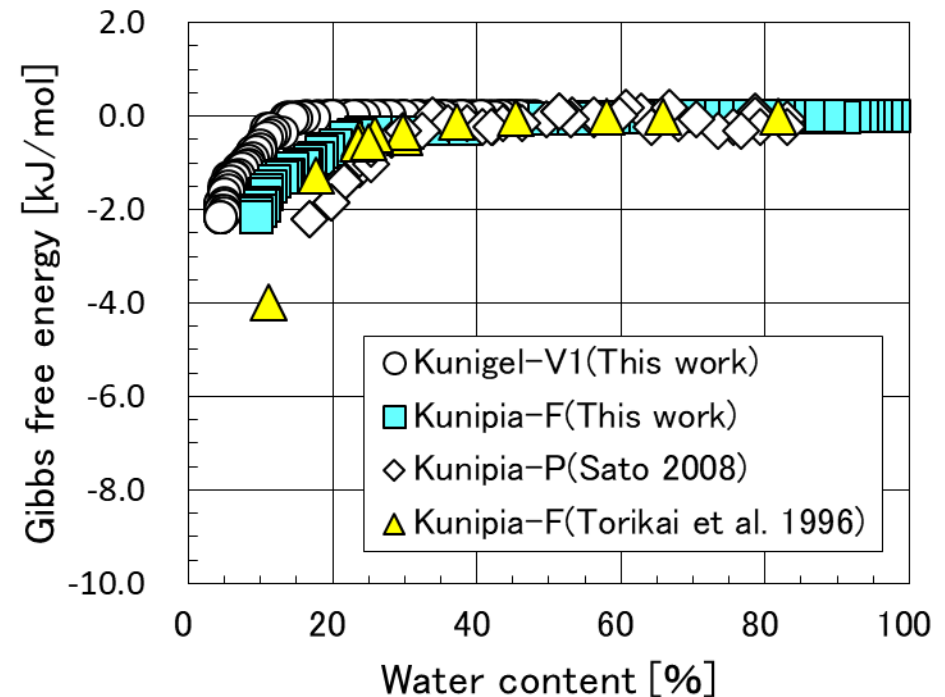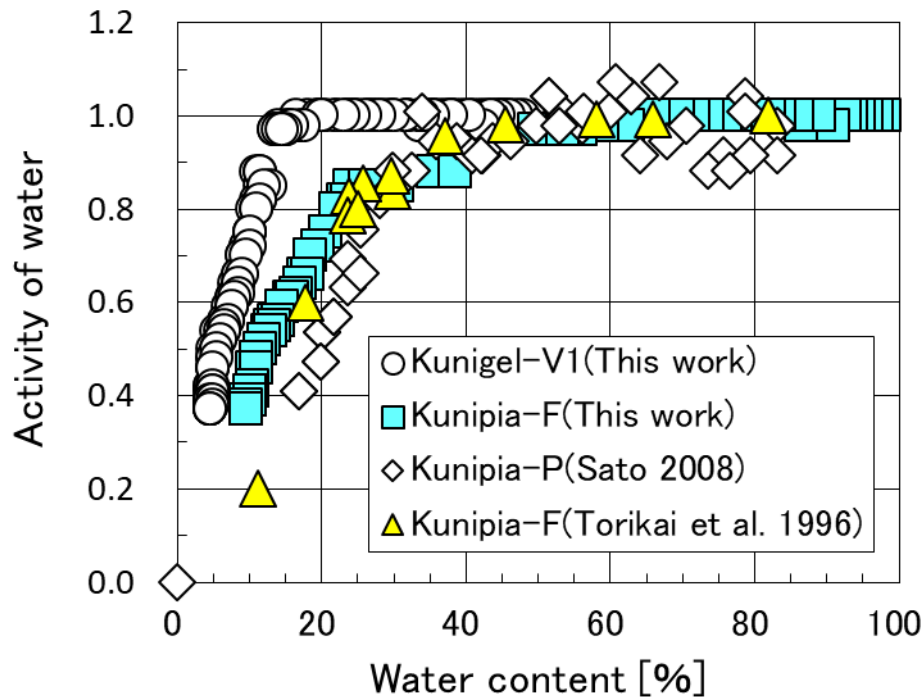
Activity of water (a_{H2O}^o) (left) & relative partial molar Gibbs free energy (dG_{H2O}^β) (right) vs. water content of bentonite (W_C)

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

- Both of the activity of water and the relative partial molar Gibbs free energy are lower in Kunipia-F and Kunipia-P than in Kunigel-V1 (the higher montmorillonite content is the lower both parameters are)

- Data of Kunipia-F are equivalent to data obtained by vapor pressure method [Torikai et al. 1996]

Activity & Gibbs Free Energy vs. Water Content (2/2)

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Activity of water (left) & relative partial molar Gibbs free energy (right) vs. water content to montmorillonite

$$\text{Water content}\,(\%) = \left(\frac{\text{Moisture weight}}{\text{Mont. weight}}\right) \times 100$$
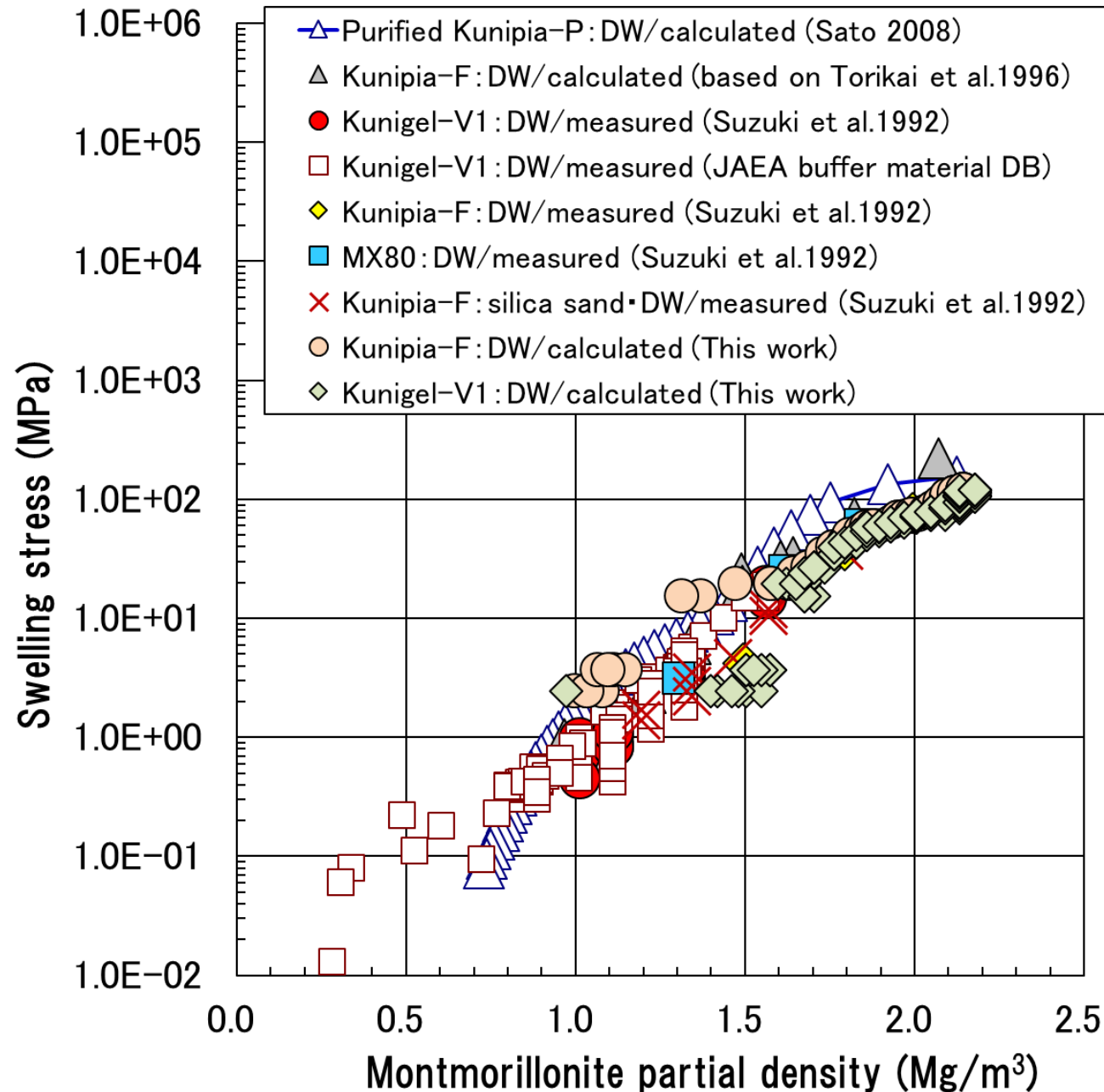
Montmorillonite content in bentonite
Kunigel-V1：51% [NUMO 2022], Kunipia-F：99%

- The plots of Kunigel-V1 & Kunipia-F (○, □) overlap, and montmorillonite content is concerned with water retention (mono-layer of hydration (water content 22.4%) from montmorillonite surface is bound and 2nd water layer (water content 44.8%) is equivalent to free water)
- Same trend also in the past studies [Torikai et al. 1996, Sato 2007, 2008a, 2008b]

- The analyzed results of swelling stress are generally in good agreement with the measured data over the montmorillonite partial density for both bentonites

→ Thermodynamic model is useful for analysis of swelling stress

Conclusions

- We measured the thermodynamic data of water (activities of water (a_{H2O}^o) & relative partial molar Gibbs free energies (dG_{H2O}^o)) in Na-bentonite and Na-montmorillonite vs. water content, and calculated the swelling stresses of bentonite based on the thermodynamic data and model.

- The calculated results of swelling stress of bentonite were in good agreement with measured data. Therefore, thermodynamic model is useful to calculate the swelling stress of bentonite.

Acknowledgements

Thank you for your attention

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Adsorption of vapor to samples (-99.5 kPa, ～9 months)

Measurements of Vapor Pressure (temperature is controlled in a water bath / periodic measurement of moisture weight)

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