

A Thermodynamic Study on Swelling Stress of Bentonite as a Buffer Material Composing Engineered Barrier in Radioactive Waste Disposal



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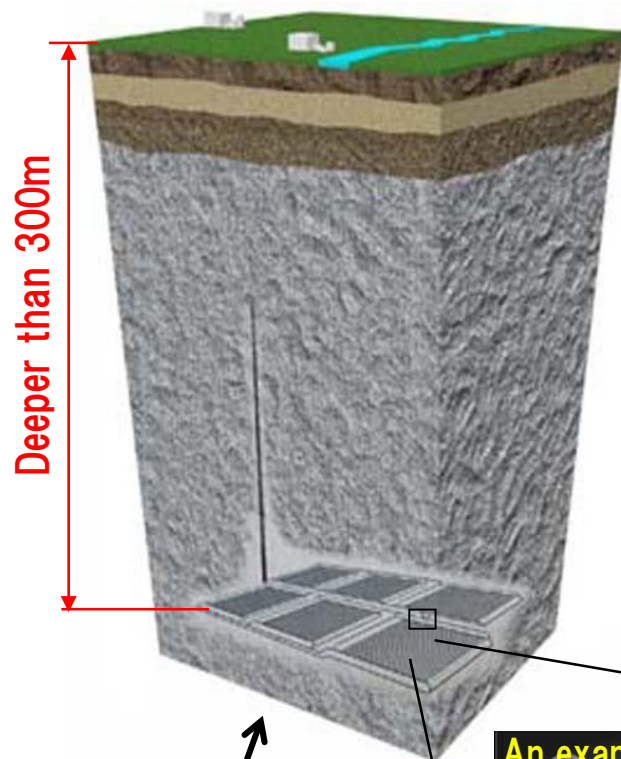
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- Introduction
- A Thermodynamic Model of Swelling Stress (Pressure) of Bentonite under Standard Condition (25°C)
- A Thermodynamic Model on the Swelling Stress of Bentonite (effect of temperature)
- Examples of Measurements of Activity ($a_{\text{H}_2\text{O}}$) & Relative Partial Molar Gibbs Free Energy ($dG_{\text{H}_2\text{O}}$) of Water
- An Example of $a_{\text{H}_2\text{O}}$ & $dG_{\text{H}_2\text{O}}$ versus Water Content
- Model Analysis of Swelling Stress of Bentonite (25°C)
- Relative Partial Molar Enthalpy ($dH_{\text{H}_2\text{O}}$) versus Water Content
- Effect of Temperature on Swelling Stress of Bentonite
- Summary

- **Radioactive wastes** generate from **nuclear facilities** such as nuclear power stations and **RI facilities** such as hospitals and research facilities. All radioactive wastes are disposed in **underground** with engineered barriers, although disposal concept and depth are different depending on origin of the waste, the kind of radiation and radioactivity level.
- Particularly, **a high-level radioactive waste (HLW)** is disposed, excavated tunnels in **deep geological formation** deeper than 300m in Japan (**geological disposal**).
- In many countries, **multi-barrier system** consisting of **engineered barrier** and **natural barrier (rock mass)** is adopted for **HLW disposal**. The engineered barrier consists of **vitrified waste (HLW)**, **overpack (carbon steel container)** and **buffer material (compacted bentonite)** from inside. The outside of the buffer material is rock mass.

A geological disposal concept of HLW



Geological Environment

Long-term stability avoiding

- Volcanic activity
- Significant fault movement
- Significant effects due to uplift/denudation
- Significant effects due to climate/sea-level change
- Presence of natural sources

Favorable geological environment

- Favorable geochemistry (e.g. chemically reducing)
- Low groundwater flux
- Rock mechanical stability
- Isolation from the human environment

Functions as a natural barrier

- Retardation & dilution/dispersion of RNs

An example of disposal Tunnel (pit disposal type)



Tunnel backfill material (bentonite + surplus soil)

Engineered Barrier

Vitrified waste

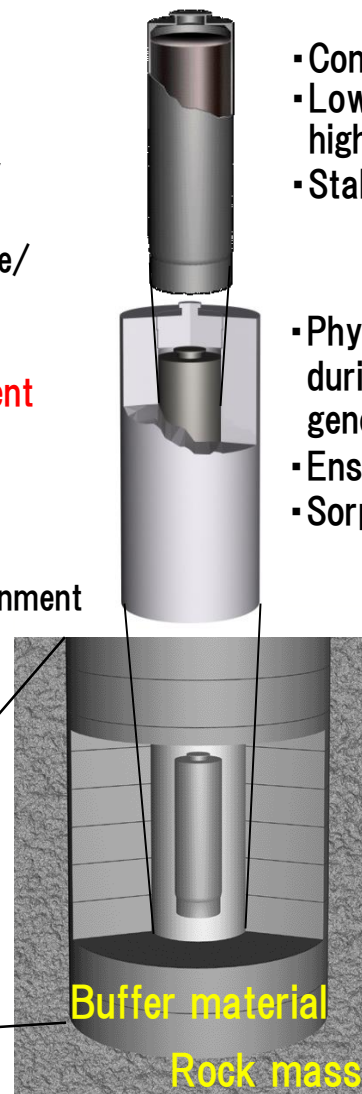
- Containment of RNs in glass matrix
- Low RN release to groundwater due to high chemical durability
- Stable under thermal & radiation loads

Overpack (19cm thick)

- Physical containment of vitrified waste during the period of high heat generation & radiation field ($\geq 1,000\text{yr}$)
- Ensuring reducing conditions
- Sorption of RNs onto corrosion products

Buffer material (70cm thick)

- Low permeability
- Low solute diffusivity (diffusion field)
- Retardation of RN migration (sorption)
- Swelling & plasticity
- Chemical buffering
- Low solubilities of many RNs in porewater
- Filtration of colloids, organic matter & microbes



- After being disposed, **bentonite** which is the major component of **the buffer material** composing **engineered barrier** in the geological disposal of a HLW develops **swelling stress (swelling pressure)** by penetration of groundwater from the surrounding rock mass, and this parameter is important in designing buffer material and analyzing long-term behaviour.
- In the past studies, we developed **a thermodynamic model** which can calculate the swelling stress of bentonite under **standard condition (25°C (=298.15K))**, based on **the thermodynamic data (activity of water & relative partial molar Gibbs free energy)** of interlayer water in **Na-montmorillonite which is the main component of Na-bentonite** and **thermodynamic theory [e.g., Sato 2007, 2008a, 2008b]**.

(H. Sato:ICONE15-10207 (2007),

H. Sato:Phys. and Chem. of the Earth 33, pp.S538-S543 (2008a),

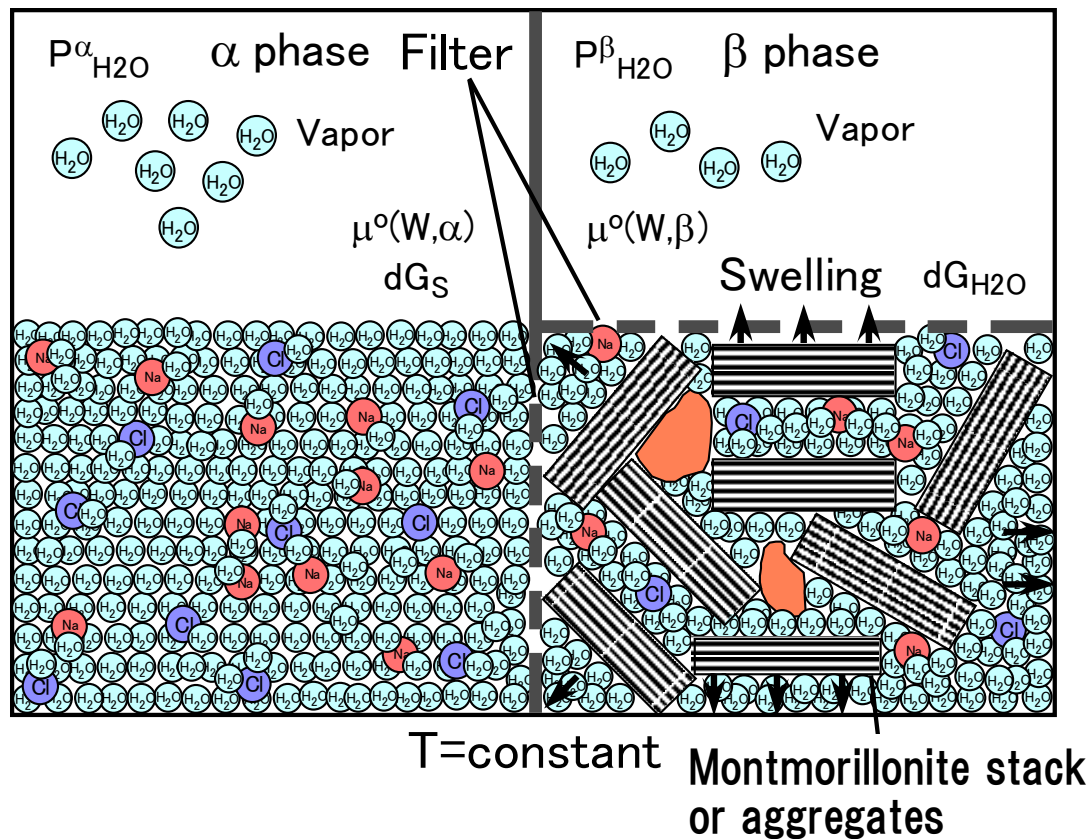
H. Sato:Proc. of 4th Japan-Korea Joint Workshop on Radioactive Waste Disposal 2008, pp.1-17 (2008b))

- Furthermore, we also developed **a thermodynamic model** which can calculate **the effect of temperature on the swelling stress** of bentonite, based on **the relative partial molar enthalpy** in recent studies **[e.g., Sato 2022]**.
- This talk introduces outline of **the thermodynamic model** and **thermodynamic data of interlayer water in montmorillonite** obtained so far. Additionally, we also introduce **the practicality of the model** by comparison with measured data of swelling stress.

A Thermodynamic Model of Swelling Stress (25°C)

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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



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.

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

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_{H_2O} .

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

A Thermodynamic Model of Swelling Stress (25°C)

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

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

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

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

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

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

Relation of swelling stress (dP_{ext}) with the Gibbs free energy changes ($dG = dG_S - dG_{H_2O}$) of waters in both phases

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

$$= \frac{dG_S - dG_{H_2O}}{V_w} \dots\dots (6)$$

dP_{ext} : swelling stress (Pa)

V_w : specific volume of water at 25°C
(18.0686cm³/mol)

$P_{H_2O}^\alpha$: vapor pressure in the α phase at 25°C (Pa)

$P_{H_2O}^\beta$: vapor pressure in the β phase at 25°C (Pa)

$P_{H_2O}^0$: vapor pressure of pure water at 25°C
(3.168kPa)

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

T : absolute temperature (K)

A Thermodynamic Model of Swelling Stress (effect of temp.)

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Basic equation which expresses the change in vapor pressure with respect to **temp. change** (Clausius-Clapeyron's equation)

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

Vapor pressures of waters in the α & the β phases at **arbitrary temperature (T)**

$$\int_{P_{H_2O}^\alpha}^{P^\alpha} \frac{dP}{P} = \int_{T_0}^T \frac{dH_v^0(H_2O)dT}{RT^2}$$

$$\therefore \ln \left(\frac{P^\alpha}{P_{H_2O}^\alpha} \right) = \frac{dH_v^0(H_2O)}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (8)$$

$$\int_{P_{H_2O}^\beta}^{P^\beta} \frac{dP}{P} = \int_{T_0}^T \frac{dH_v(s)dT}{RT^2}$$

$$\therefore \ln \left(\frac{P^\beta}{P_{H_2O}^\beta} \right) = \frac{dH_v(s)}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (9)$$

For Eq. (9)

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

$$\therefore \ln \left(\frac{P^\beta}{P_{H_2O}^0} \right) = \frac{dH_v(s)}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) + \ln \left(\frac{P_{H_2O}^\beta}{P_{H_2O}^0} \right) \quad (10)$$

$P_{H_2O}^\alpha$: vapor pressure in the α phase at 25°C (Pa)

$P_{H_2O}^\beta$: vapor pressure in the β phase at 25°C (Pa)

$P_{H_2O}^0$: vapor pressure of pure water at 25°C

P^α : vapor pressure in the α phase at arbitrary temperature (Pa)

P^β : vapor pressure in the β phase at arbitrary temperature (Pa)

$dH_v(s)$: enthalpy of vaporization of water in the β phase (J/mol)

$dH_v^0(H_2O)$: enthalpy of vaporization of pure water (44.0kJ/mol)

A Thermodynamic Model of Swelling Stress (effect of temp.)

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Relative partial molar Gibbs free energies in both phases at arbitrary temperature

$$\begin{aligned} dG^\alpha &= RT \ln \left(\frac{P^\alpha}{P_{H_2O}^0} \right) \\ &= dH_v^0(H_2O) \left(\frac{T}{T_0} - 1 \right) \end{aligned} \quad (11)$$

$$\begin{aligned} dG^\beta &= RT \ln \left(\frac{P^\beta}{P_{H_2O}^0} \right) \\ &= dH_v(s) \left(\frac{T}{T_0} - 1 \right) + RT \ln \left(\frac{P_{H_2O}^\beta}{P_{H_2O}^0} \right) \end{aligned} \quad (12)$$

Chemical potentials (μ^0) of waters in both phases when both phases reached equilibrium by penetration of the α phase to the β phase at arbitrary temperature

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

$$\begin{aligned} \mu(W, \beta) &= dG^\beta + \int_{P_{ext}^0}^{P_{ext}} V_w dP \\ &= dH_v(s) \left(\frac{T}{T_0} - 1 \right) + \ln \left(\frac{P_{H_2O}^\beta}{P_{H_2O}^0} \right) \\ &\quad + \int_{P_{ext}^0}^{P_{ext}} V_w dP \end{aligned} \quad (14)$$

Swelling stress (dP_{ext}) derived from the balance of chemical potentials of waters in both phases in equilibrium state

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

dG^α : relative partial molar Gibbs free energy of water in the α phase at arbitrary temp.

dG^β : relative partial molar Gibbs free energy of water in the β phase at arbitrary temp.

dH_{H_2O} : relative partial molar enthalpy
($= dH_v^0(H_2O) - dH_v(s)$)

Examples of Measurements of $a_{\text{H}_2\text{O}}$ & $dG_{\text{H}_2\text{O}}$ of Water

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Relation of thermodynamic parameter with relative humidity (RH)

Activity of water

$$a_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}^{\beta}}{P_{\text{H}_2\text{O}}^{\circ}} \quad (16)$$

Relative partial molar Gibbs free energy

$$\begin{aligned} dG_{\text{H}_2\text{O}} &= RT \ln \left(\frac{P_{\text{H}_2\text{O}}^{\beta}}{P_{\text{H}_2\text{O}}^{\circ}} \right) \\ &= RT \ln(a_{\text{H}_2\text{O}}) \end{aligned} \quad (17)$$

Relation of activity of water with RH

$$a_{\text{H}_2\text{O}} = \frac{\text{RH}}{100} \quad (18)$$

Relation of relative partial molar Gibbs free energy with RH

$$dG_{\text{H}_2\text{O}} = RT \ln \left(\frac{\text{RH}}{100} \right) \quad (19)$$

$a_{\text{H}_2\text{O}}$: activity of water

$dG_{\text{H}_2\text{O}}$: relative partial molar Gibbs free energy

$P_{\text{H}_2\text{O}}^{\beta}$: vapor pressure of water in the β phase at 25°C

$P_{\text{H}_2\text{O}}^{\circ}$: saturated vapor pressure of water at 25°C (3.168kPa)

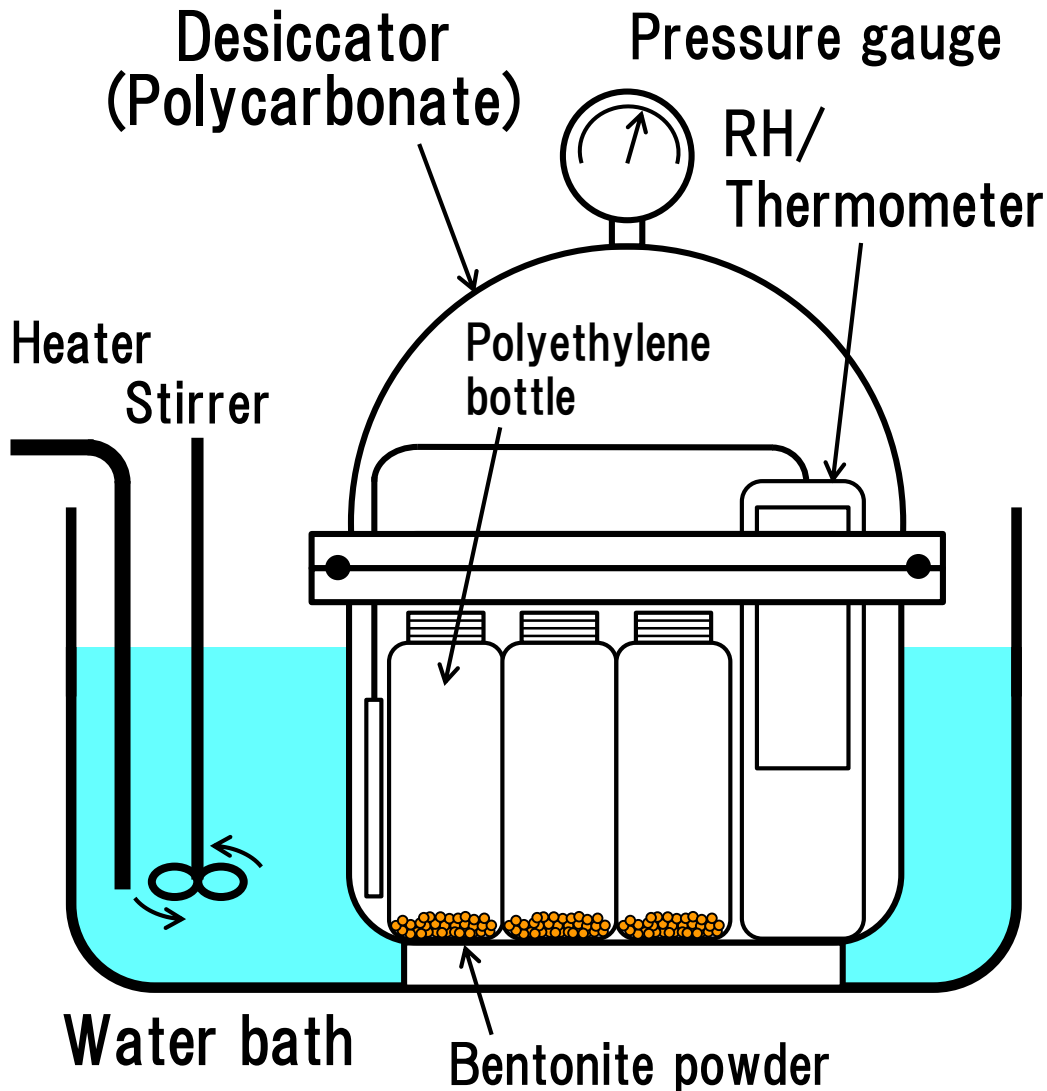
RH: relative humidity at 25°C (%)

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

T: absolute temperature (K)

Examples of Measurements of $a_{\text{H}_2\text{O}}$ & $dG_{\text{H}_2\text{O}}$ of Water

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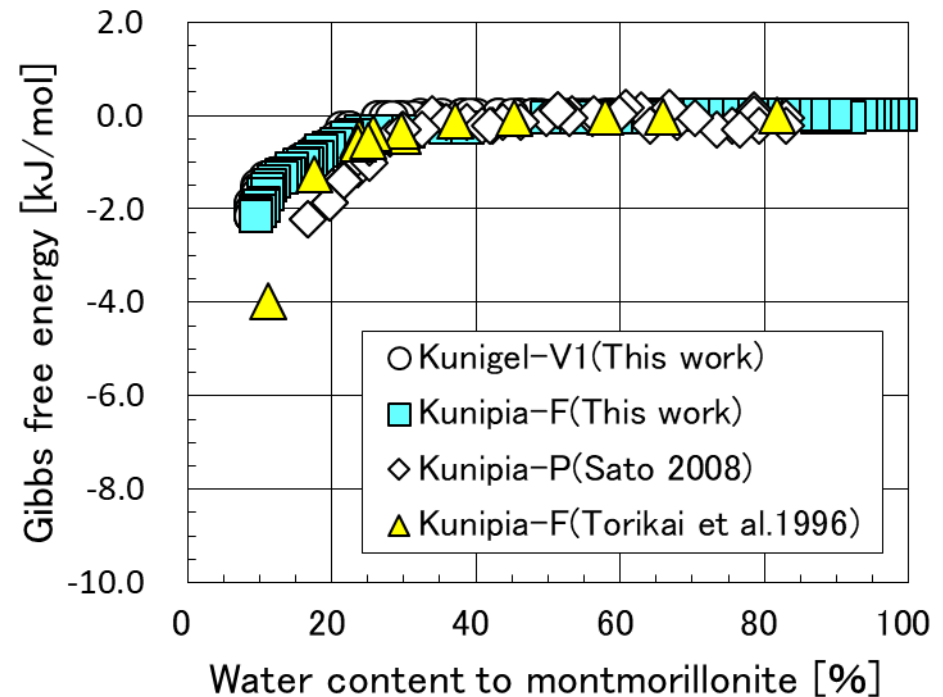
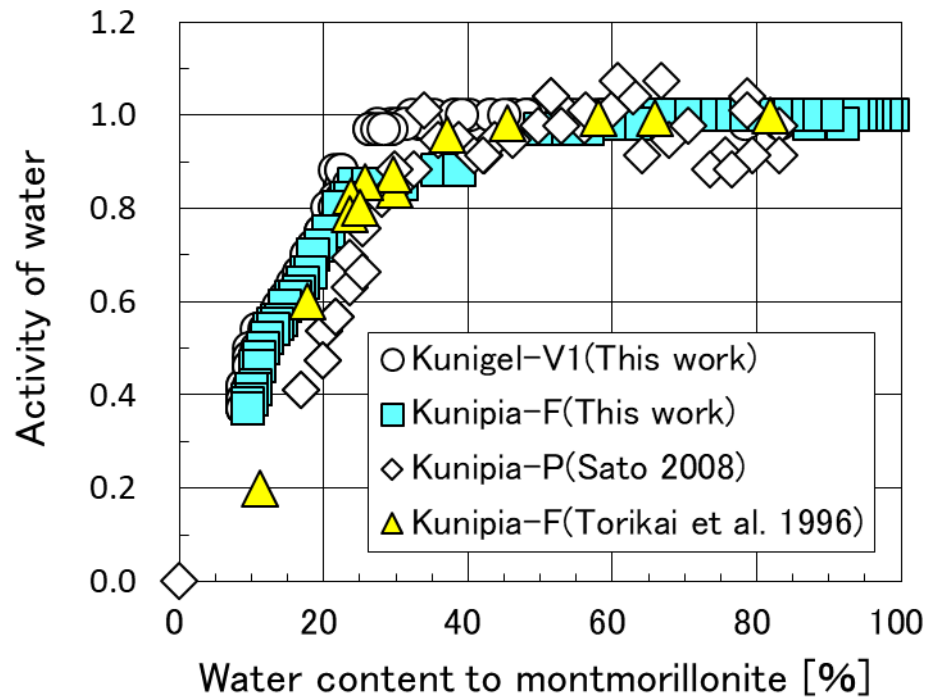
Concept of measurement of water vapor pressure by RH method

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 & temp. (-101.3kPa, 18-42°C, 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%)

An Example of $a_{\text{H}_2\text{O}}$ & $dG_{\text{H}_2\text{O}}$ versus Water Content

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

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

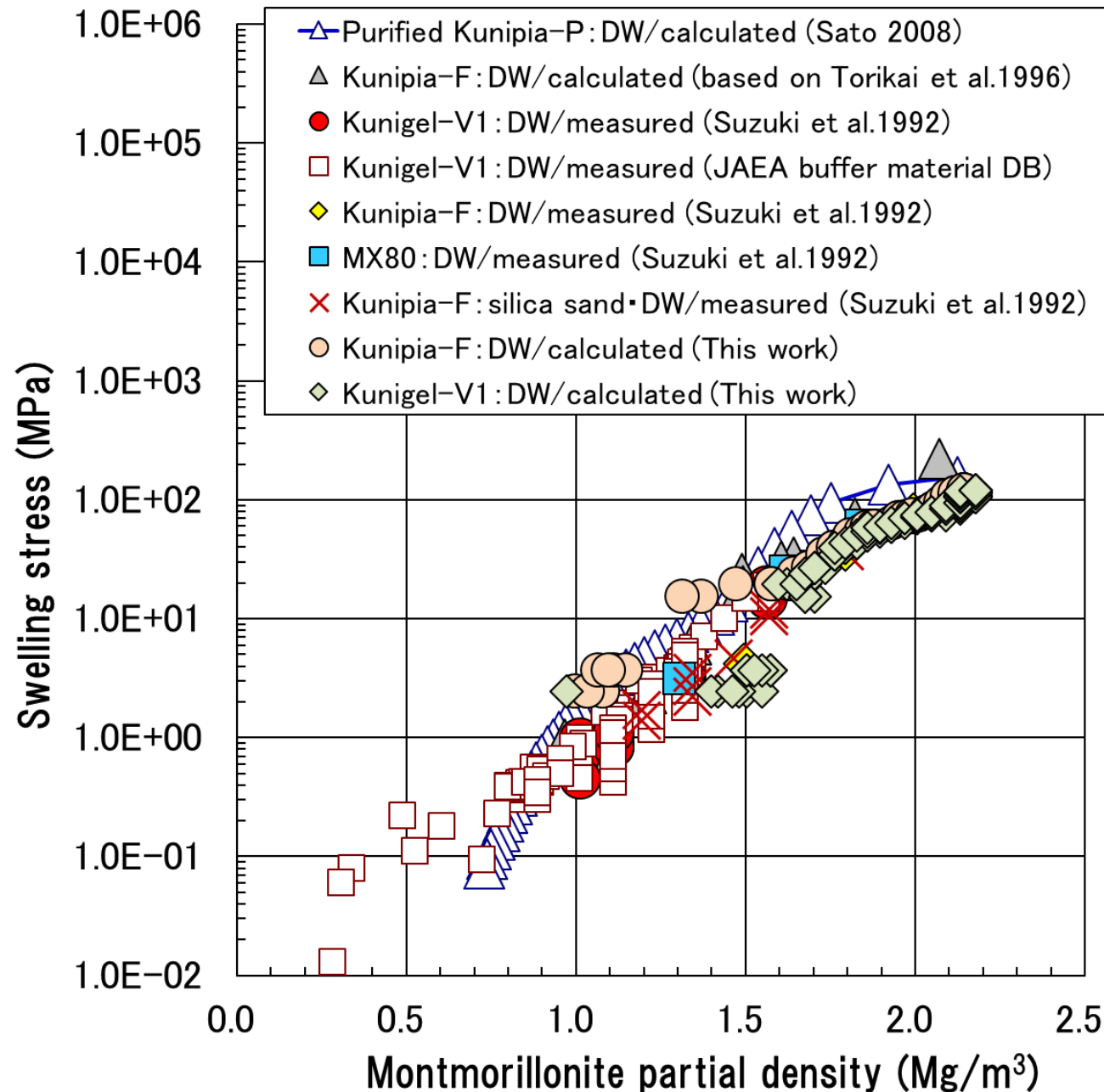
Montmorillonite content in bentonite

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]

Model Analysis of Swelling Stress of Bentonite (25°C)

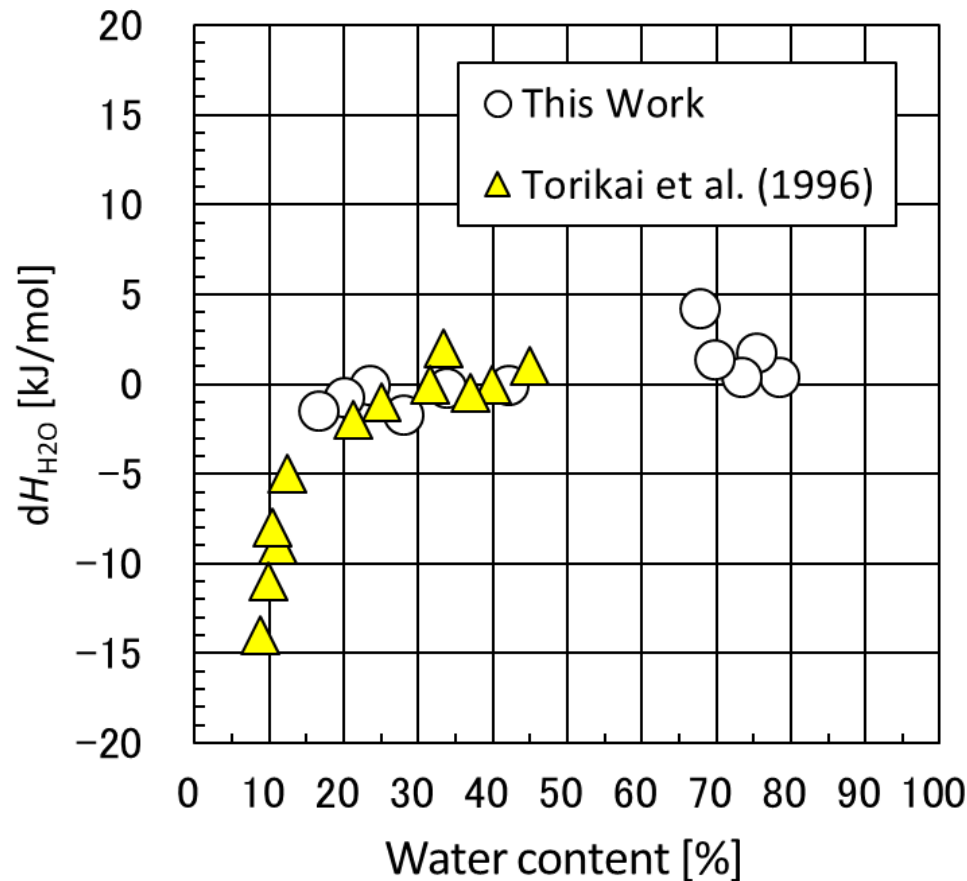
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- The analyzed results of the swelling stress of bentonite are generally in good agreement with the measured data over the montmorillonite partial density for both bentonites (Kunigel-V1 (montmorillonite content approx. 50 %) & Kunipia-F (montmorillonite content over 99%))
- Thermodynamic model is practical for the analysis of the swelling stress of bentonite

Relative Partial Molar Enthalpy (dH_{H_2O}) vs. Water Content

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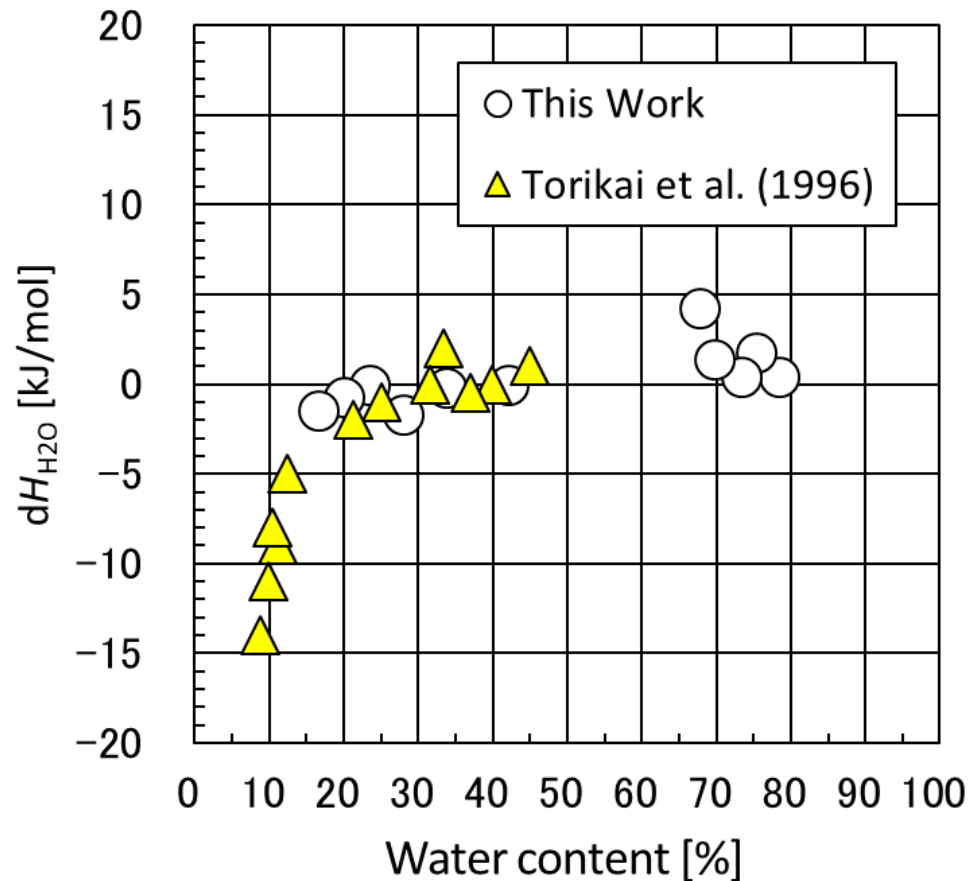


- The relative partial molar enthalpy (dH_{H_2O}) of interlayer water decreased with decreasing water content in water contents lower than about 40% [Sato 2022] (same trend was obtained also in the past studies [Ohashi 1996, Torikai et al. 1996])

→ This indicates that the swelling stress of bentonite decreases with increasing temperature in montmorillonite partial densities higher than about 1.25 Mg/m^3

Relative partial molar enthalpy (dH_{H_2O}) of interlayer water in Na-montmorillonite (Kunipia-F) vs. water content

(Fig. H. Ohashi:PNC-TJ1600-96-004 (1996), Y. Torikai et al.:Nucl. Technol. 115 (1996), H. Sato:MRS Advances Vol.7, Issue 7-8 (2022))



- Analysis & comparison of swelling stresses at 298.15K (25°C) & 333.15K (60°C)

Calculated results

Water content %	Partial density (Mg/m ³)	dH _{H₂O} (kJ/mol)	dP _{ext} (MPa) (25°C)	dP _{ext} (MPa) (60°C)	Remarks
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
16.8	1.85	-1.56	122.0	111.9	This work
12.4	2.02	-5	147.6	115.1	Literature

- The degree of decrease in swelling stress is approx. 10% at montmorillonite partial density 1.26Mg/m³, 15% at 1.6Mg/m³ and 20% at 2.0 Mg/m³, and the effect of temp. is small
- Considering design density of buffer material, it can be said that it is the density range where we needn't consider the effect of temp.

- We developed a thermodynamic model which can calculate the swelling stress of bentonite as a buffer material composing engineered barrier in the HLW disposal, and also obtained some thermodynamic data ($a_{\text{H}_2\text{O}}$, $dG_{\text{H}_2\text{O}}$, $dH_{\text{H}_2\text{O}}$) of interlayer water in Na-montmorillonite which is the major component of Na-bentonite so far.
- The analyzed results of swelling stress by the thermodynamic model were in good agreement with the measured data. Therefore, the thermodynamic model is practical for the analysis of the swelling stress of bentonite.
- The effect of temp. on the swelling stress of bentonite depended on the relative partial molar enthalpy ($dH_{\text{H}_2\text{O}}$), and it was considered that swelling stress decreased with increasing temp. in the range of montmorillonite partial density higher than $\text{ca. } 1.25\text{Mg/m}^3$ from relation with water content.
- The degree of decrease in swelling stress to temp. is considered small to be 10-20% in the comparison between 298.15K (25°C) and 333.15K (60°C).

Thank you very much for your attention

- 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 author would like to thank all organizations for financially supporting.

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APPENDIX

Summary of the Nature of Bentonite

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Buffer material (reference case)

- Material which was compacted a mixture of bentonite (main component is Na-montmorillonite) and a silica sand content of 30wt.% with a dry density of 1.6Mg/m^3

Nature of buffer material

- Low permeability (hydraulic coefficient: 10^{-12} - 10^{-11}m/s)

→ Movement restraint of groundwater

→ Mass transfer is dominated by diffusion

Swelling

→ Bentonite swells by absorbing water and fills the gap

Mechanical buffering

→ Control the swelling stress by absorbing or desorbing water (hydration & dehydration)

Chemical buffering

→ Control the pH and porewater chemistry by dissolution of soluble minerals such as calcite

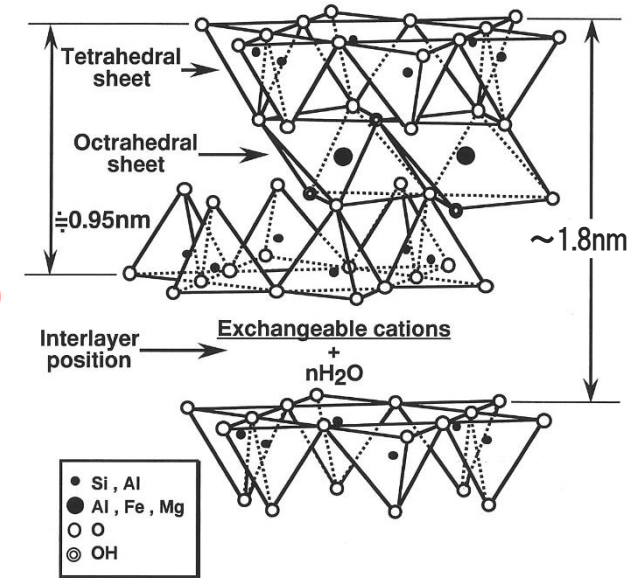
Retardation of radionuclide migration

→ High sorption due to high cation exchange capacity (CEC of montmorillonite: ca.100meq/100g)

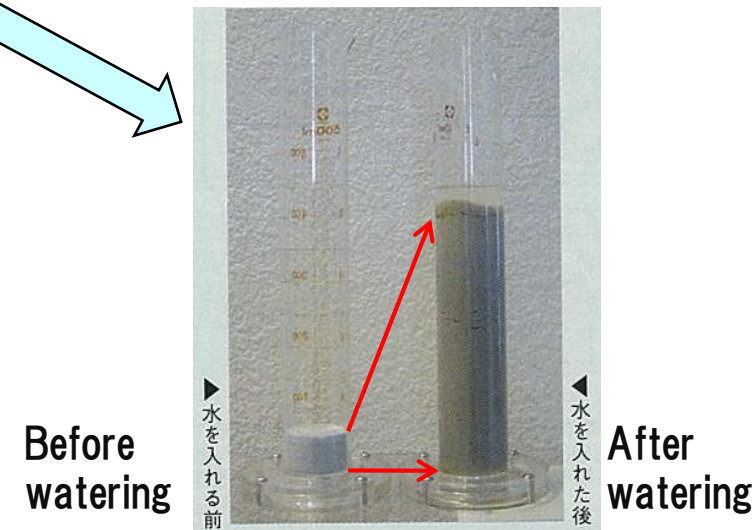
Narrow path

→ Filtration of colloids, organic matter and microbes

Structural formula of Na-montmorillonite:



Crystal Structure of Montmorillonite

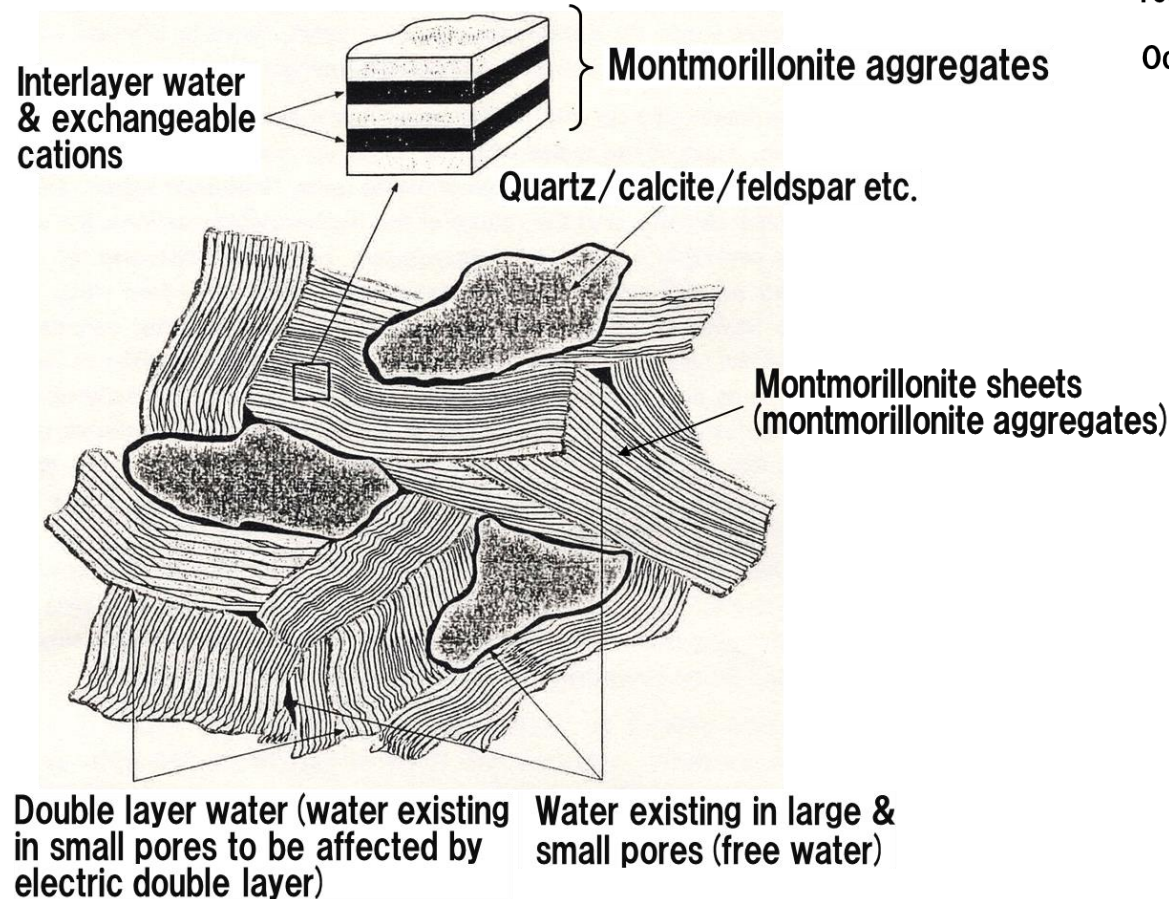


Swelling of Bentonite (Kunigel-V1: montmorillonite content 50wt.%+water)

Principle of Swelling of Bentonite

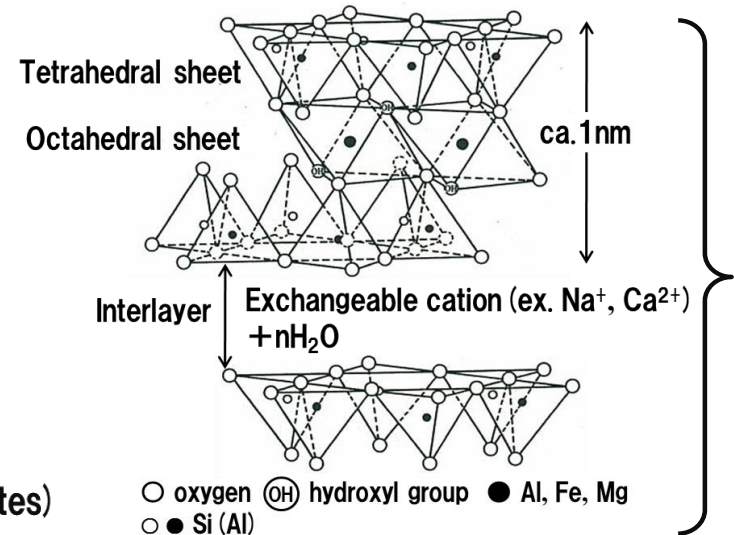
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Water (porewater) Existing in Bentonite

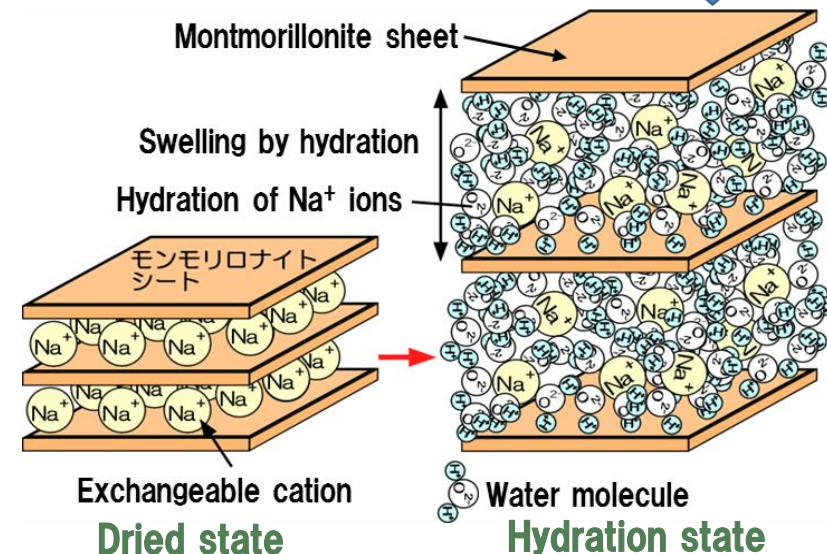


(Bradbury et al.:PSI Bericht Nr. 02-10, 2002)

Bentonite swells by hydration of interlayer cations existing between montmorillonite sheets



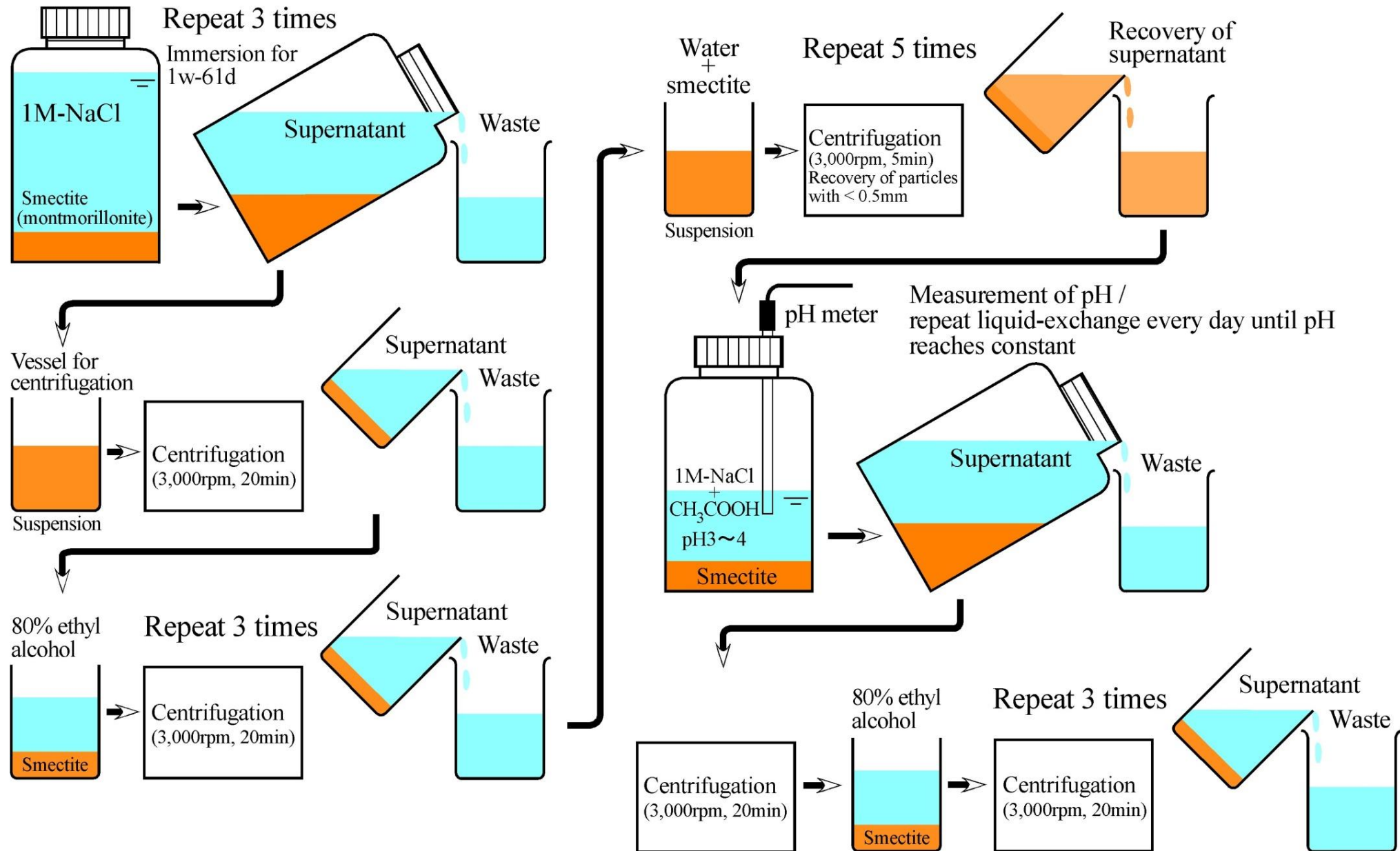
Crystal Structure of Montmorillonite



Swelling of montmorillonite by hydration of interlayer

Preparation of Na-Montmorillonite (Purification)

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Measurements of Water Vapor Pressure by RH Method

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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)

Measurements of Water Vapor Pressure by RH Method

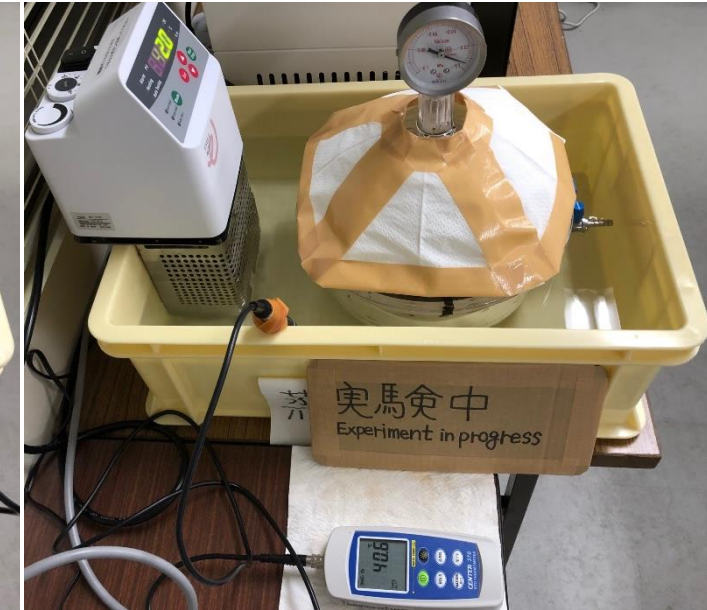
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Adsorption of vapor to samples (-99.5kPa, ~9 months)

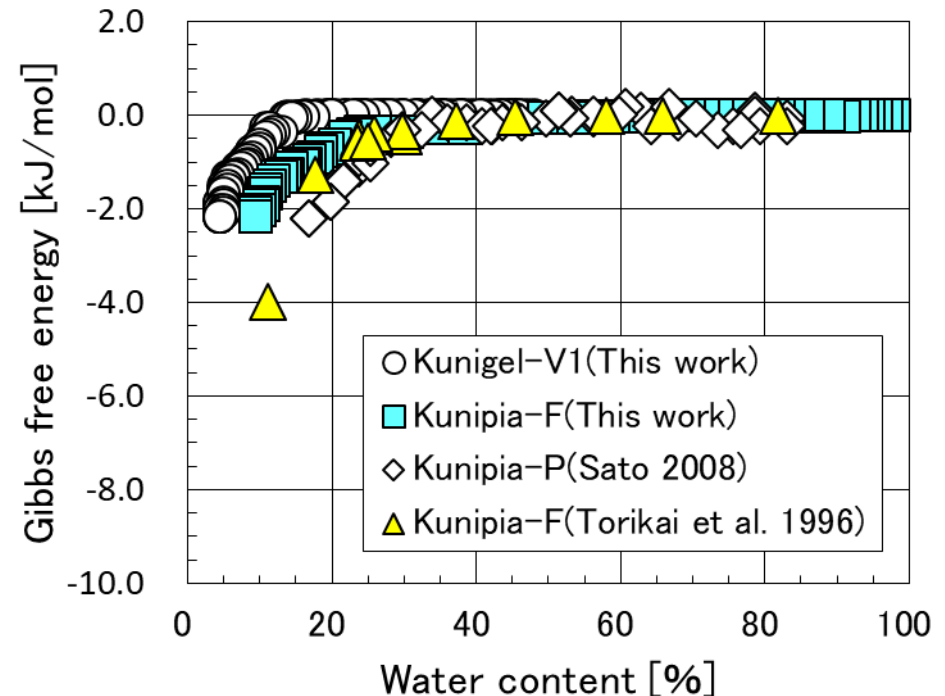
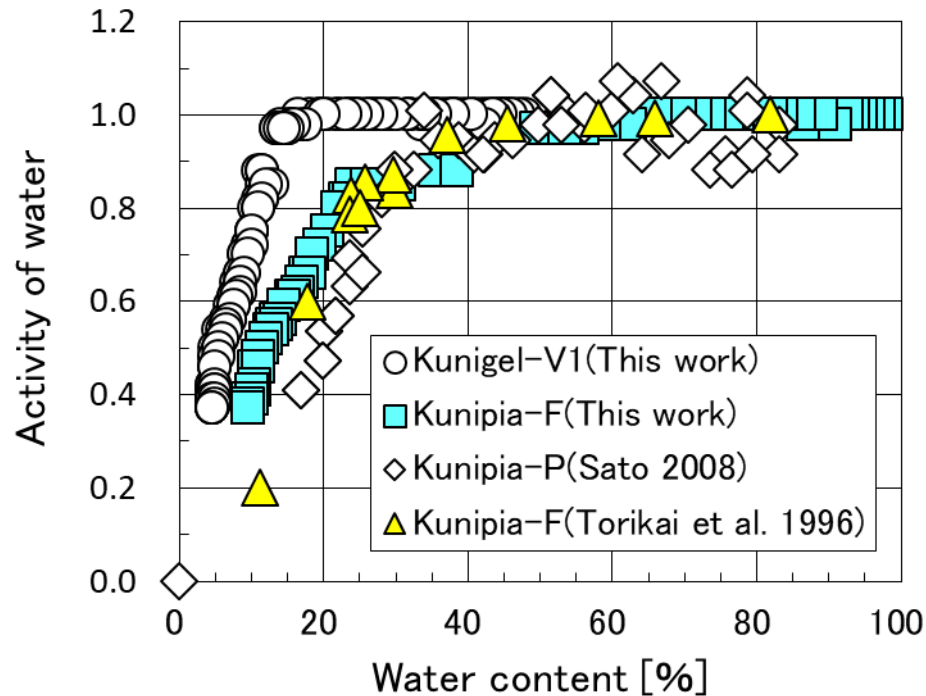


Measurements of Vapor Pressure (temperature is controlled in a water bath / periodic measurement of moisture weight)



Activity & Gibbs Free Energy vs. Water Content

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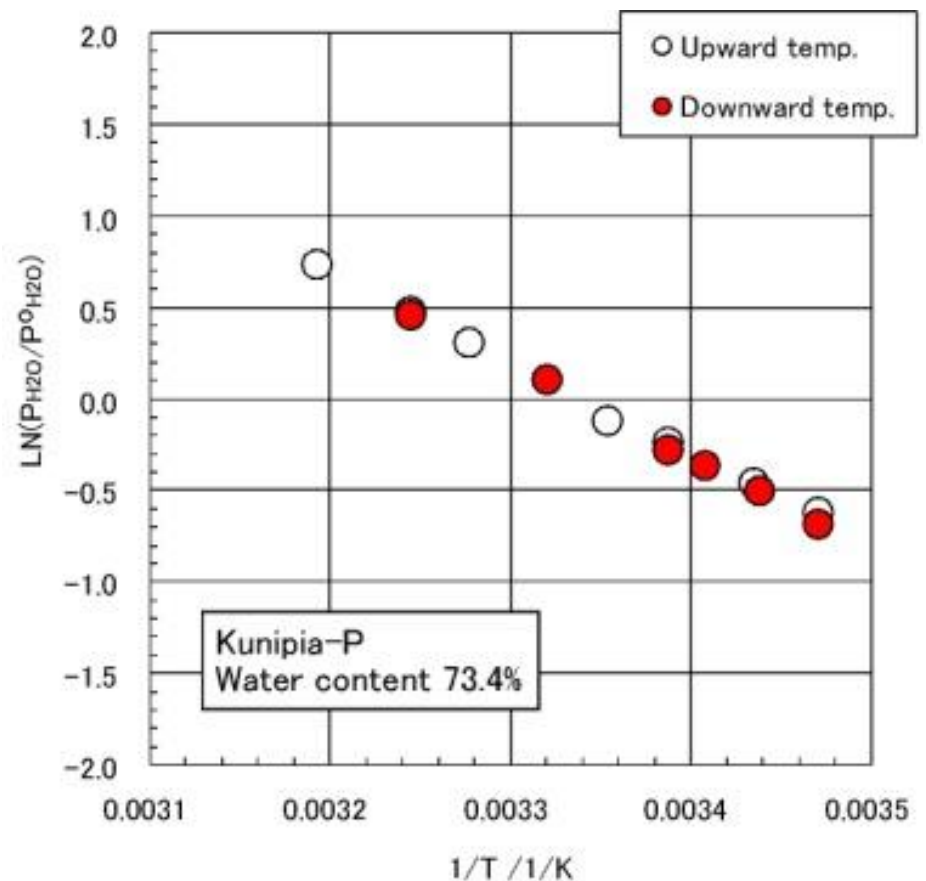
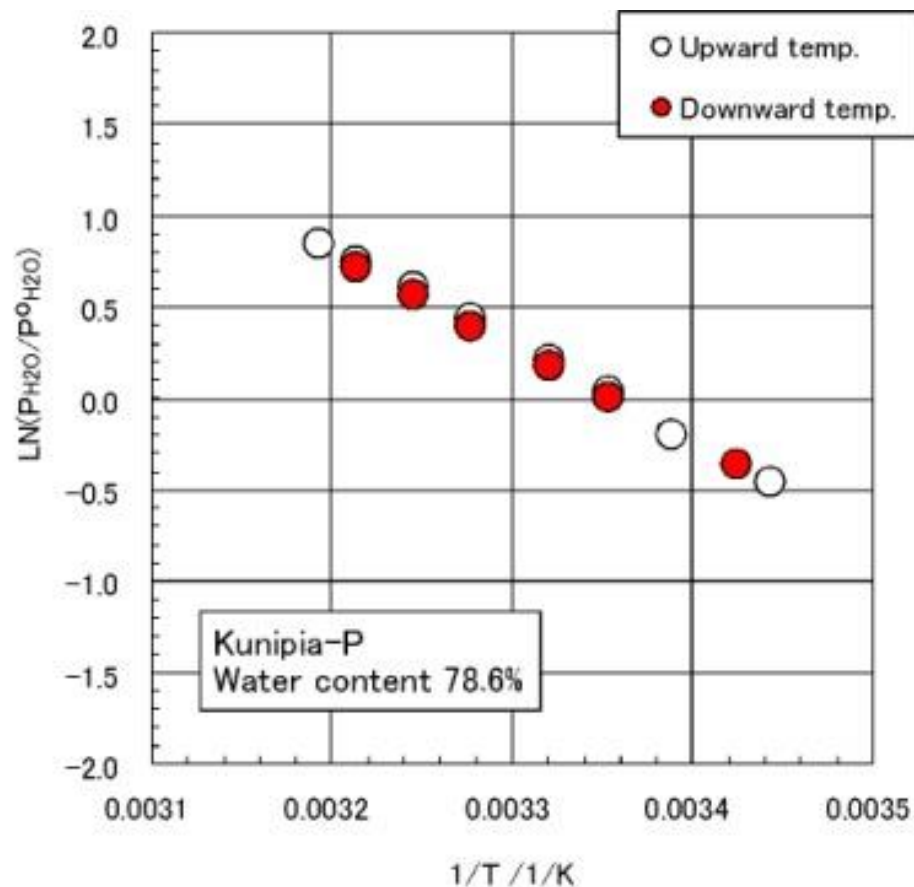


Activity of water ($a_{\text{H}_2\text{O}}^0$) (left) & relative partial molar Gibbs free energy ($dG_{\text{H}_2\text{O}}^\beta$) (right) vs. water content of bentonite (W_c)

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

- 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]

Examples of the Measured Results of Vapor Pressures 27



Examples of $\text{LN}(P_{\text{H}_2\text{O}}/P^0_{\text{H}_2\text{O}})$ vs. $1/T$ (water content : 78.6% & 73.4%)

- ❑ Water vapor pressures to upward & downward temperatures are in good agreement
- ➡ obtained water vapor pressures are in equilibrium state