Specific anion effects on the swelling pressure of compacted Mx80 bentonite: experiments and modelling

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Outline

- Introduction
- Experiments and results
- Specific anion effects on the swelling pressure
- A physicochemical swelling pressure model
- Conclusions

Introduction

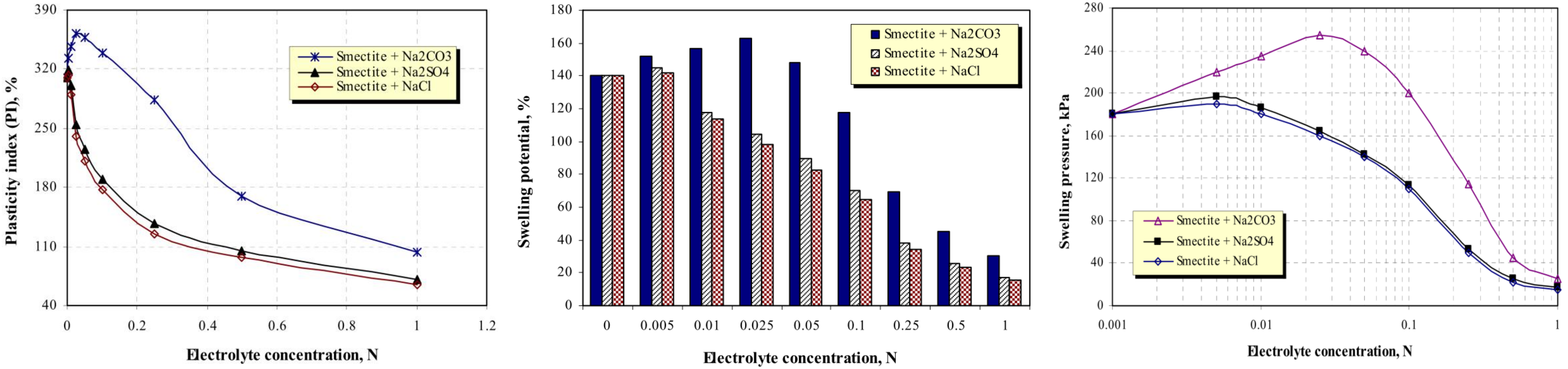
- Rich anions such as Cl-, SO_4^{2-}, HCO^{3-} and CO_3^{2-} exist in groundwater
- The role of anions was largely overlooked

Table 1 Chemical compositions of groundwater

	Meuse/Haute-Marne(MHM)	Beishan	Grimsel	Mont Terri	Yucca Mountain	Äspö
pH	7.5	7.2	9.7		8.0	7.4
Na^+	3.783	608	0.04	5610	63.6	1300
K^+	0.228	3.8	0.51	65.3	7.6	6.6
Ca^{2+}	1.014	90.2	20.89	570	46.1	990
Mg^{2+}	2.618	18.5	<0.32	344	11.5	65
Cl^-	1.411	621	1.52	10395	54.3	3820
HCO_3^- (TIC)	6.390	136	38.3	-	89.8	71
SO_4^{2-}	2.073	591	7.97	1251	50.4	106
NO_3^-	-	13.8	0.01	-	77.1	<0.01
F^-	0.237	1.4	21.3	0.77	11.6	1.3
Ref.	Linard et al. (2011)	Wu et al. (2024)	Konno et al. (2013)	Mazurek and Haller (2017)	Yang et al. (2003)	Smellie et al. (1995)
	mM/L	mg/L	mM/L	mg/L	mg/L	mg/L

Introduction

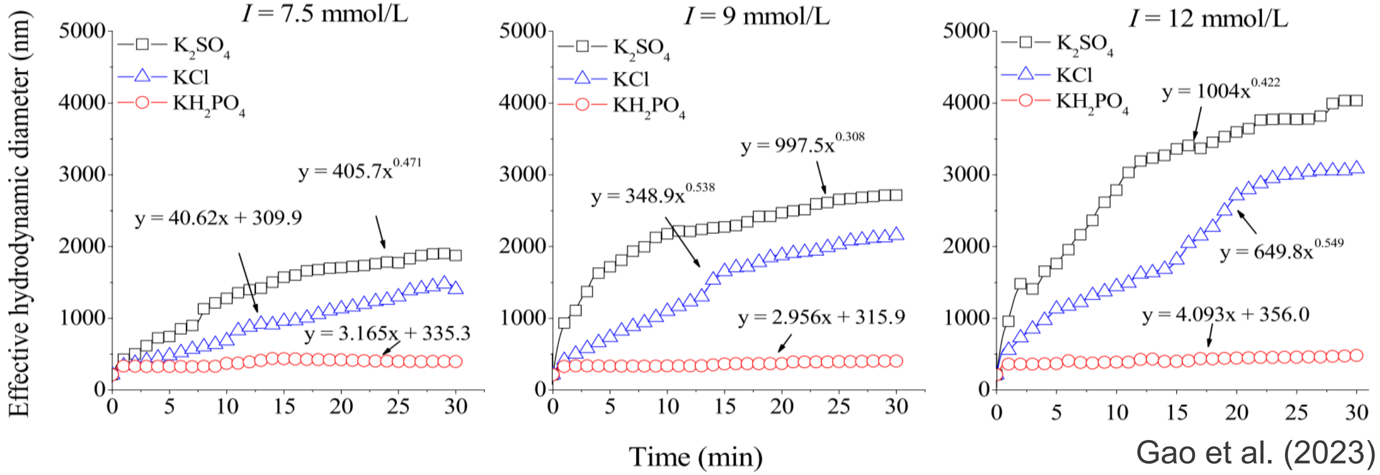
- The hydro-mechanical behaviours depend on both **concentration** and **anion type**
- Swelling ability: $CO_3^{2-} > SO_4^{2-} \approx Cl^-$



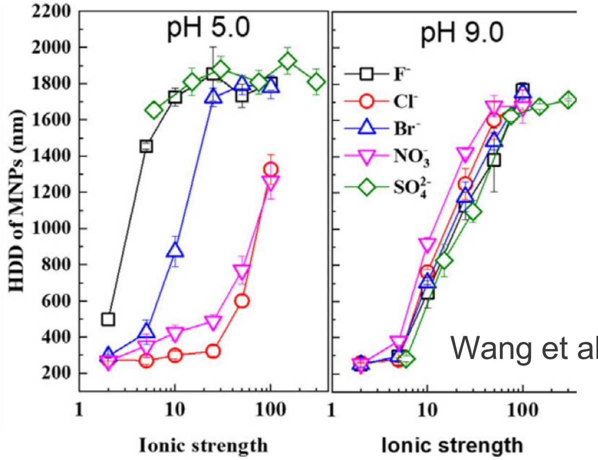
Goodarzi and Akbari (2014)

Introduction

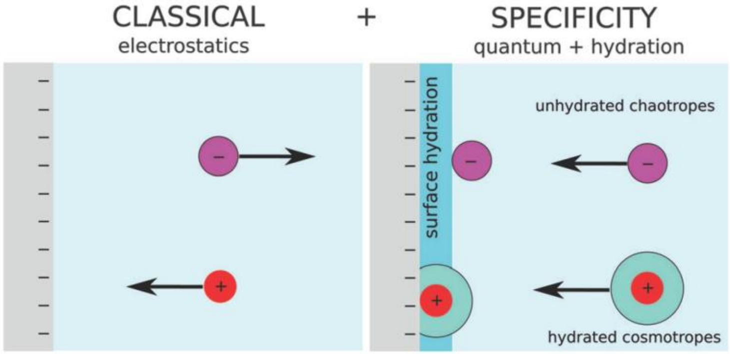
- Specific anion effects in inhibiting montmorillonite particle aggregation: $H_2PO_4^- > Cl^- > SO_4^{2-}$.
- Increase in **negative surface charge** due to **polarized anions** adsorbed onto the surface



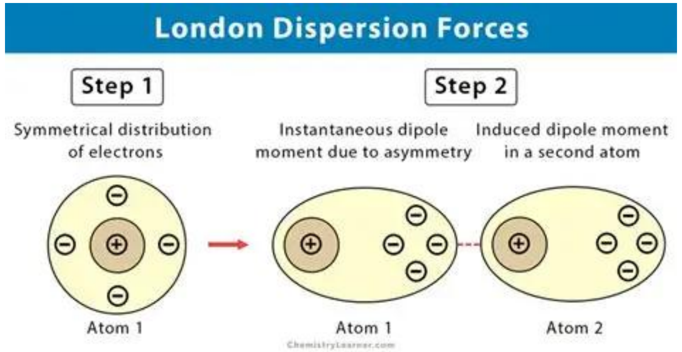
Gao et al. (2023)

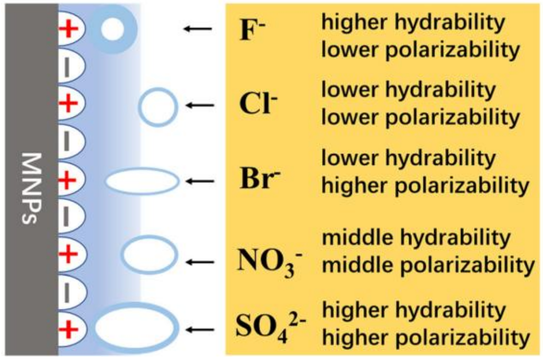


Wang et al. (2021)



Parsons et al. (2011)





Wang et al. (2021)

Introduction

- Specific anion effects can not be explained by traditional Gouy-Chapman double layer theory
- Mathematic difficulties in extend the traditional DDL theory to asymmetric electrolytes (1:2, 2:1, etc.)
- Objective of this study: to develop simpler interpretation and prediction of the specific anion effects

Liu (2013)

$$\begin{cases} p = p_{\mathrm{CSS}}(h) + p_{\mathrm{DDL}}(h, c, v) - p_{\mathrm{vdW}}(h) \\ p_{\mathrm{CSS}} = k \exp\left(\frac{-h}{l}\right) \\ p_{\mathrm{DDL}} = 2cRT(\cosh \boxed{y^{\mathrm{m}}} - 1) \\ p_{\mathrm{vdW}} = \frac{A_{\mathrm{H}}}{6\pi}\left\{\frac{1}{h^3} - \frac{2}{(h+D_{\mathrm{p}})^3} + \frac{1}{(h+2D_{\mathrm{p}})^3}\right\} \end{cases}$$

Midplane potential

Reciprocal Debye length

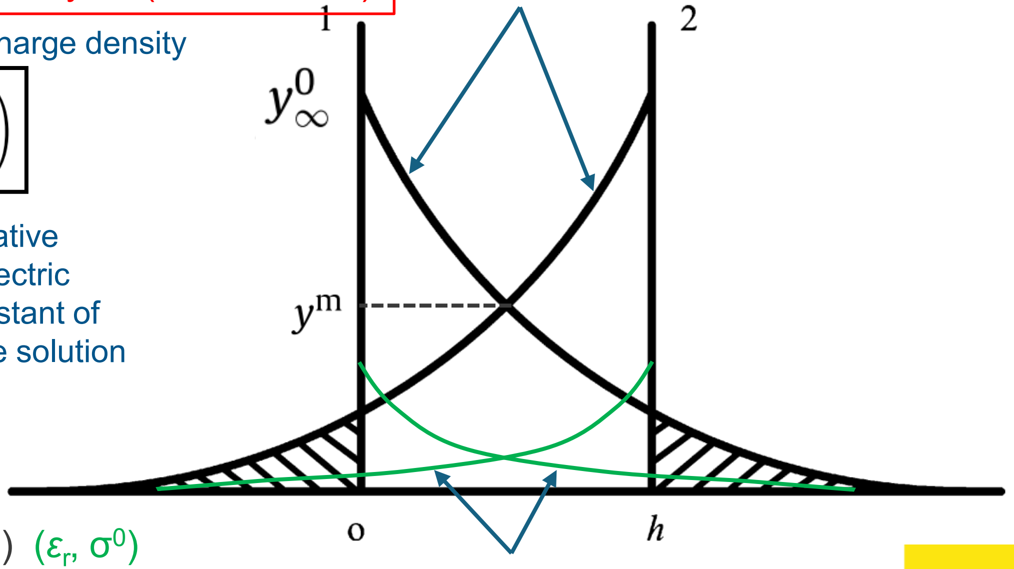
$$\kappa = \left(\frac{2\boxed{cv^2}F^2}{\varepsilon_0 \varepsilon_r RT}\right)^{1/2} \qquad y_\infty^0 = 2 \sinh^{-1}\left(\frac{vF\boxed{\sigma^0}}{2\varepsilon_0 \boxed{\varepsilon_r} \kappa RT}\right)$$

Surface potential

Surface charge density

Relative dielectric constant of pore solution

- Concentration and valency of cations and anions are not distinguished
- Only for dilute, symmetric electrolytes (1:1, 2:2, etc.)



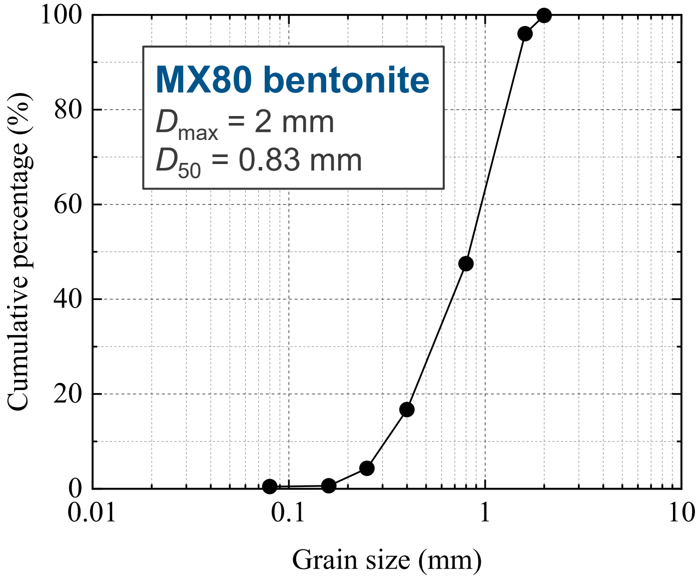
- Traditional DDL: y^{m} ~ electrostatic (c, v)
- Modified DDL: y^{m} ~ electrostatic (c, v) + dispersion (adsorption of polarized anions) (ε_r, σ^0)

- Complicated chemical reactions and calculations for the ε_r and σ^0

Materials and methods

Samples
- Height: 10 mm
- Diameter: 50 mm
- Dry density: **1.3 Mg/m³, 1.5 Mg/m³**

Tests
- Swelling pressure
- MIP



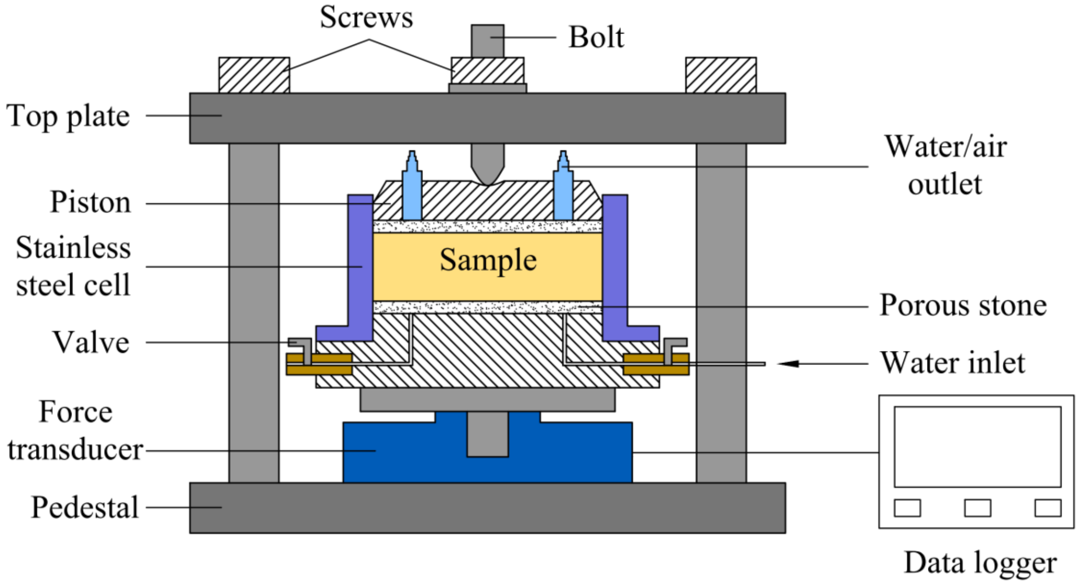


Table 2 Material properties

Properties	Values
Montmorillonite content (%)	86
CEC (meq/100 g)	80
Exchangeable cations (meq/100 g)	**Na^+ (67)**, Ca^{2+} (8), Mg^{2+} (4), K^+ (1)
Initial water content (%)	14.5

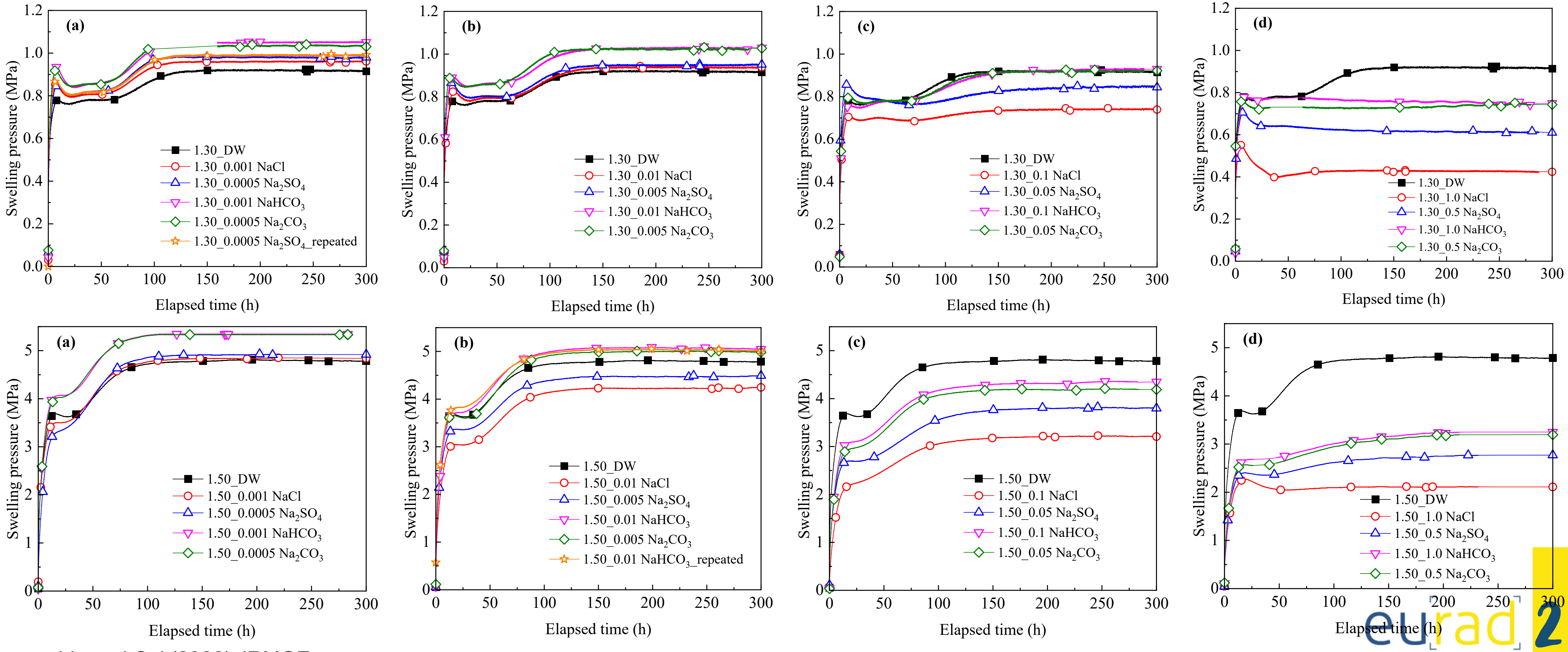
Table 3 Solution properties

Solutions	Concentrations (mol/L)
NaCl	0.001, 0.01, 0.1, 1.0
Na_2SO_4	0.0005, 0.005, 0.05, 0.5
$NaHCO_3$	0.001, 0.01, 0.1, 1.0
Na_2CO_3	0.0005, 0.005, 0.05, 0.5

*Ions in Meuse/Haute-Marne groundwater (mol/L) (Linard et al., 2011): Na^+ (0.0038), Cl^- (0.0014), SO_4^{2-} (0.0021), HCO_3^- (0.0064)

Liu and Cui (2026) JRMGE

Results: swelling pressure development mode



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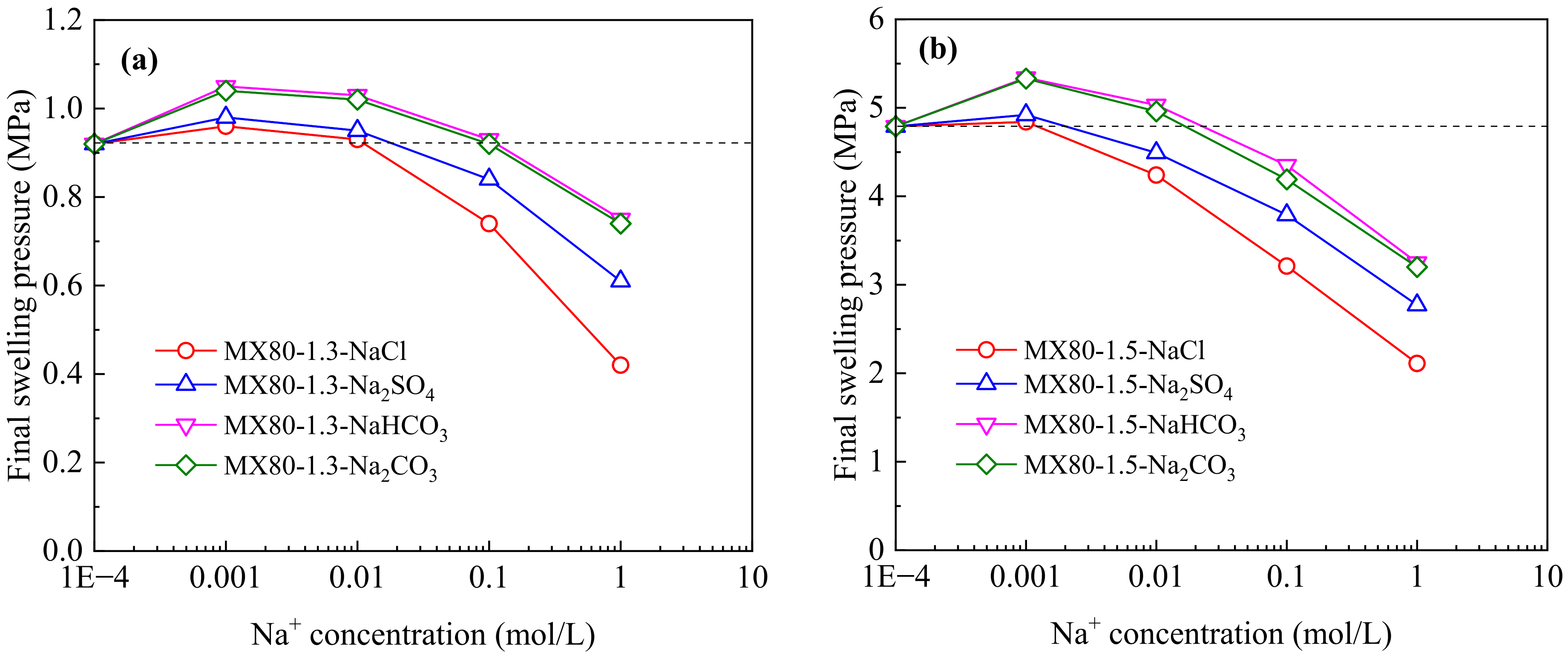
Results: swelling pressure vs. Na^+ concentration



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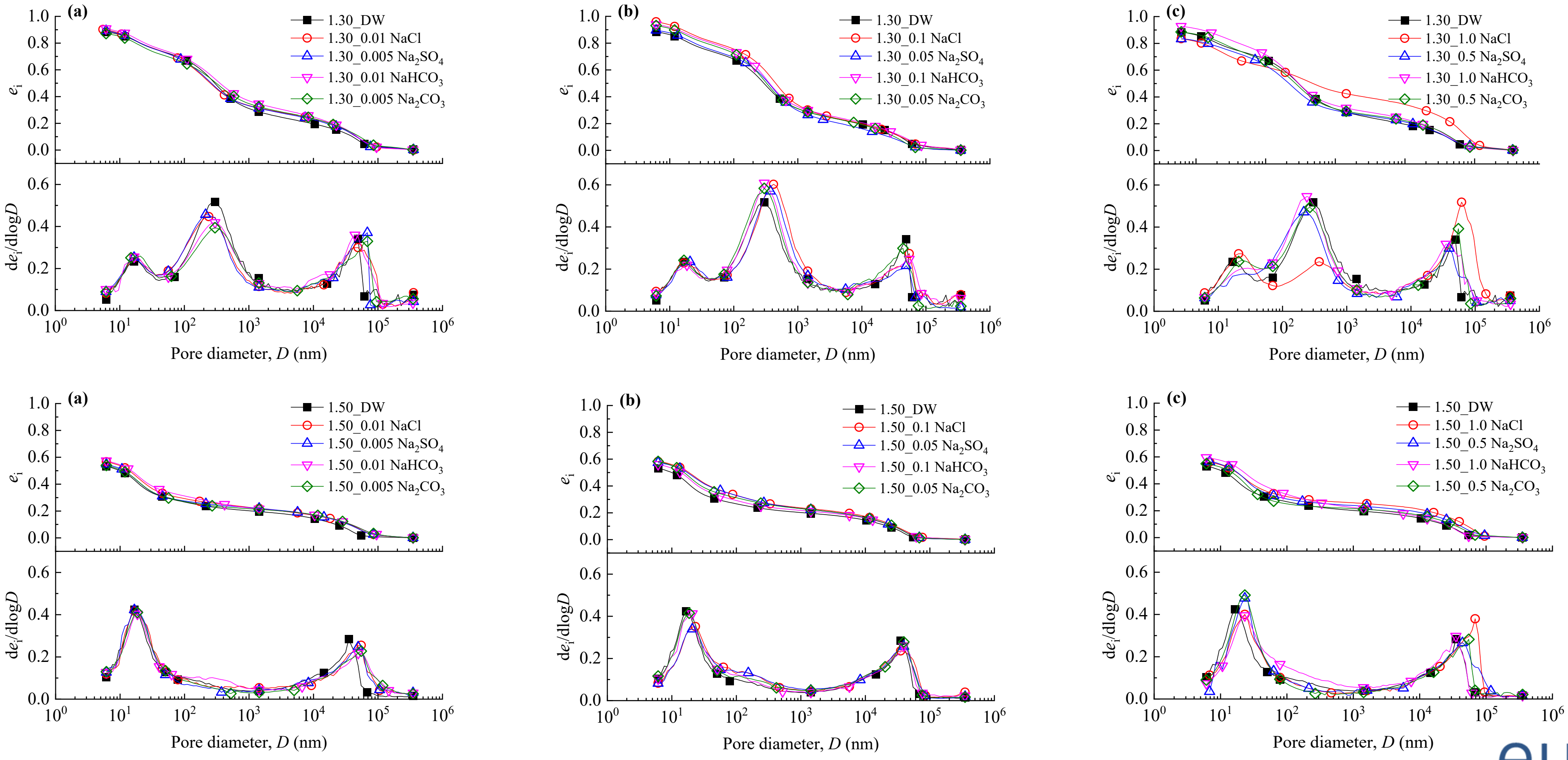
Results: pore size distributions



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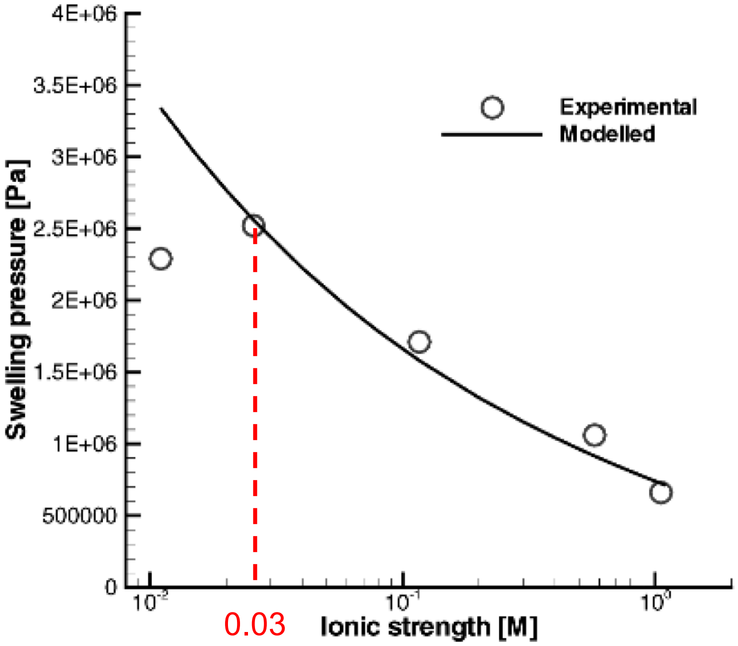
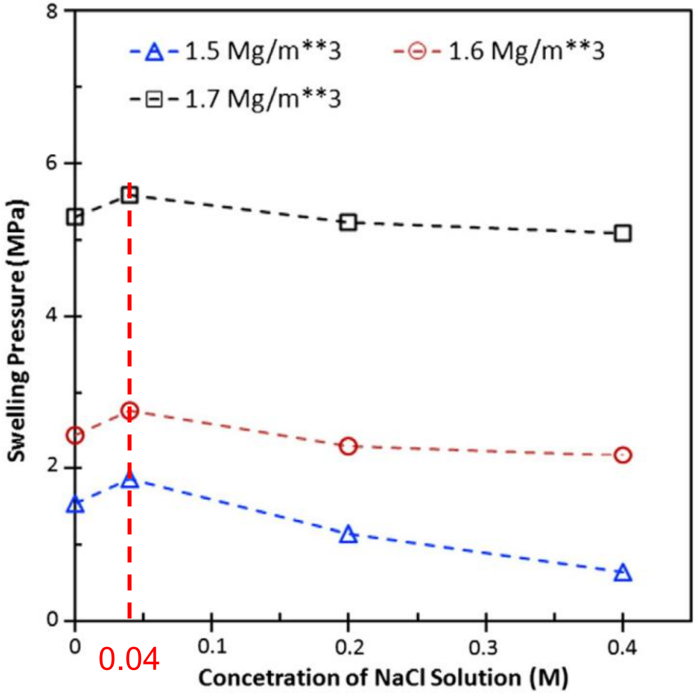
Similar results in literature



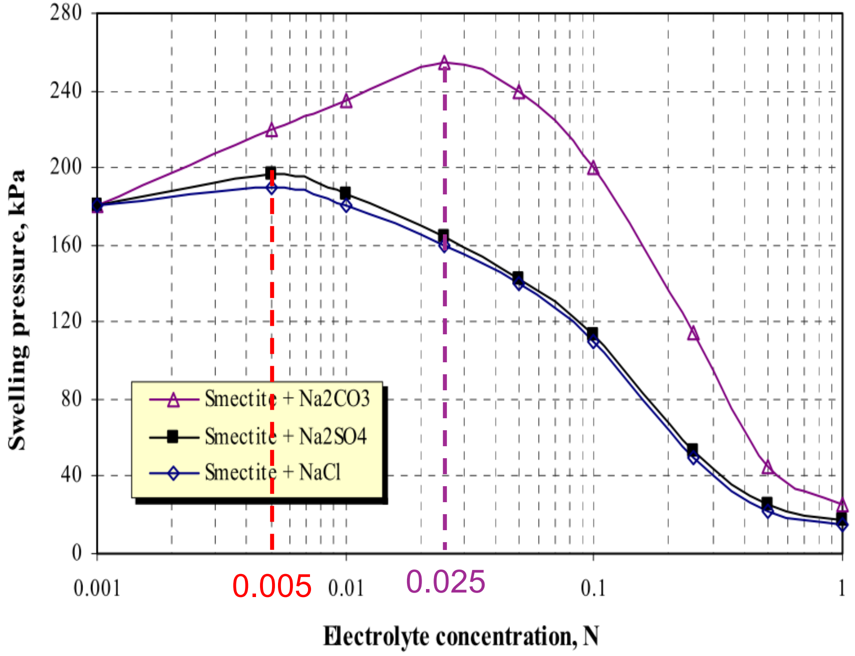
MX80 Na-bentonite + NaCl

Xie et al. (2007)



Kyeongju Ca-bentonite + NaCl

Lee et al. (2012)

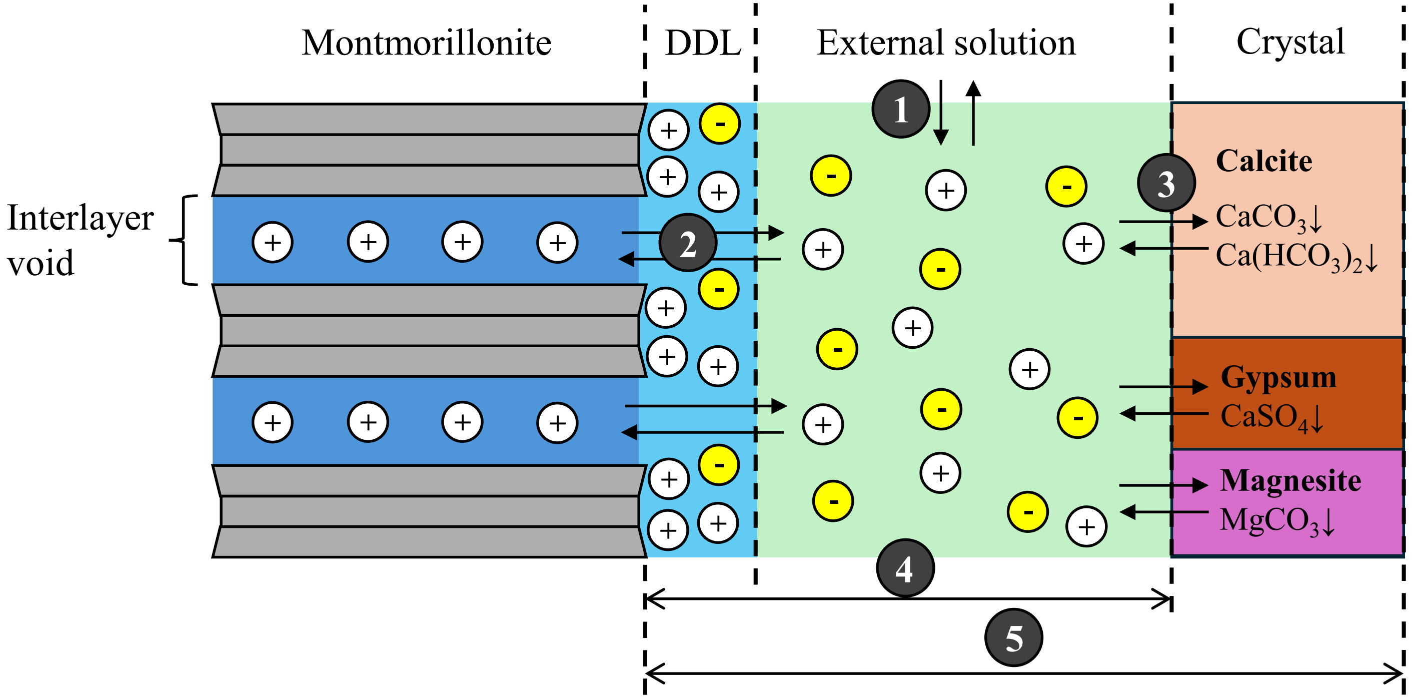


Na-smectite + NaCl/Na_2SO_4/Na_2CO_3

Goodarzi and Akbari (2014)

Main physicochemical reactions in bentonite/salt system

- **Salinity increase (SI):** increase of internal solution concentration ⇨ **Osmotic swelling ↓**
- **Cation exchange (CE):** exchange of interlayer and external cations ⇨ **Crystalline swelling ↑**
- **Salt precipitation (SP):** precipitation of low solubility salts ⇨ **Dry density ↑**



⊕ Cations (Na^+, K^+, Ca^{2+} and Mg^{2+})

⊖ Anion (Cl^-, SO_4^{2-}, HCO_3^- or CO_3^{2-})

1. Inflow/outflow of external solution
2. Exchange of interlayer and external cations
3. Precipitation/dissolution of low solubility salts
4. Reduced interparticle void by precipitated crystals
5. Initial interparticle void without precipitated crystals

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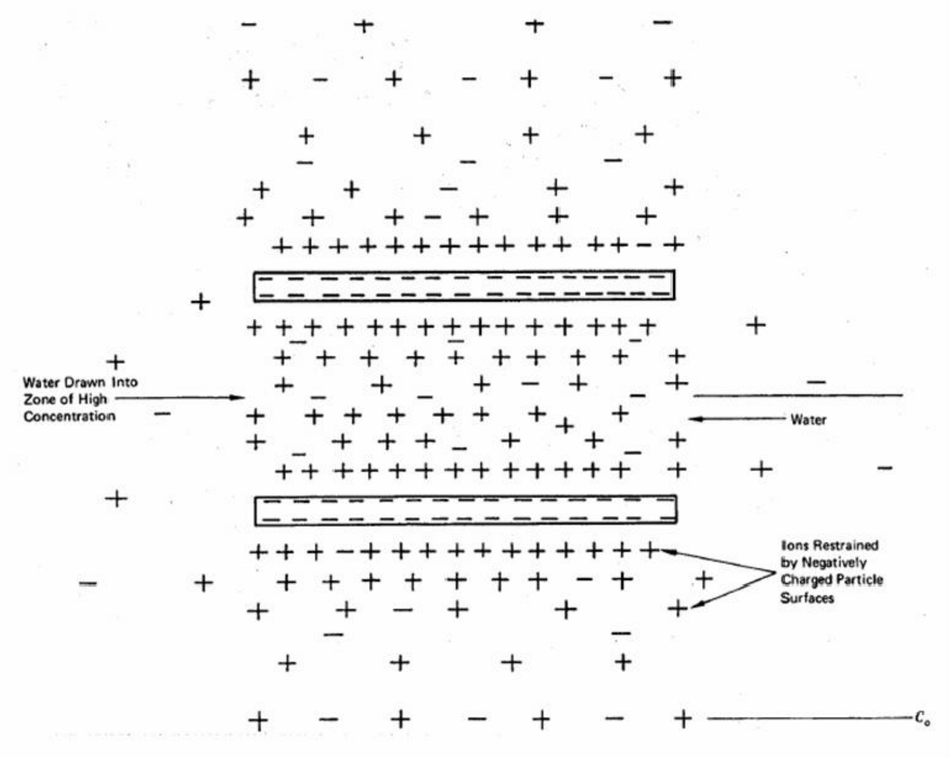
Impact of salinity increase (SI): reducing the osmotic swelling



(Mitchell, 1993)

Change of osmotic pressure with salinity increase (Van't Hoff equation):

$$\Delta p_{\mathrm{si}} = 0.001\zeta RT(c_{\mathrm{int}} - c_{\mathrm{ext}}) = 0.001\zeta RTc_{\mathrm{ext}}(\Xi - 1)$$

- Only for ideal, dilute solutions
- For parallel montmorillonite layers

Change of osmotic pressure with salinity increase (Empirical equation):

$$\Delta p_{\mathrm{si}} = \left[A\exp(B\rho_{\mathrm{d0}}) + \Delta p_{\max}\right]\left\{\exp\left[-(c_{\mathrm{Na^+}}/m)^{\omega}\right] - 1\right\}$$

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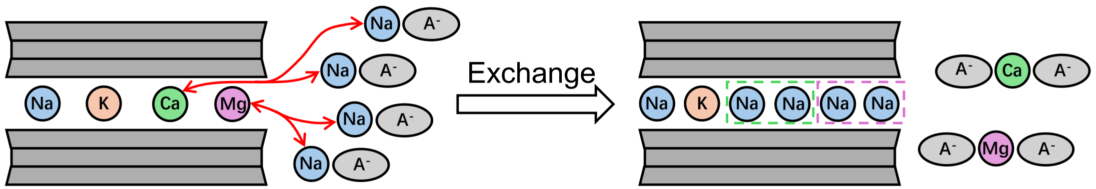
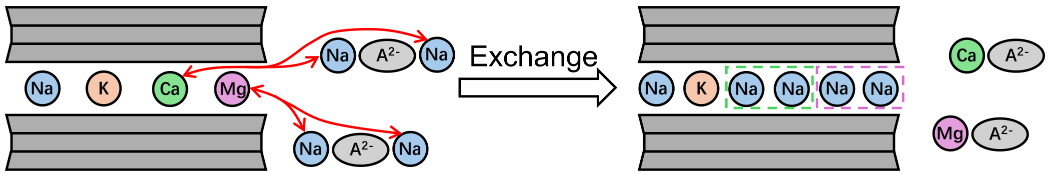
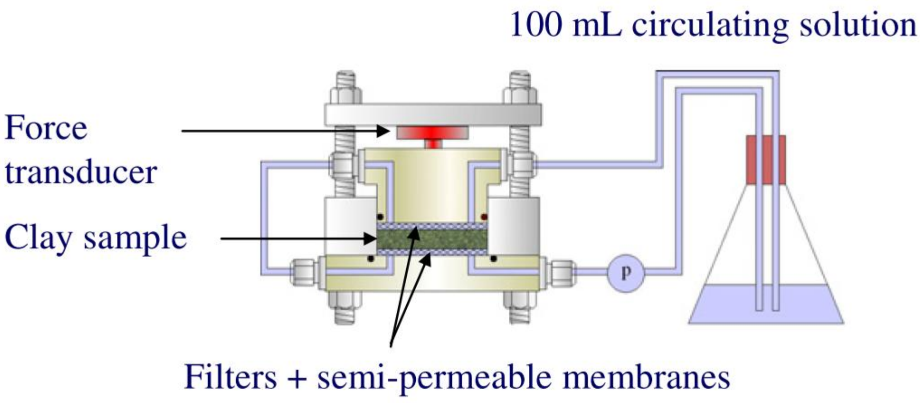
Cation exchange (CE)

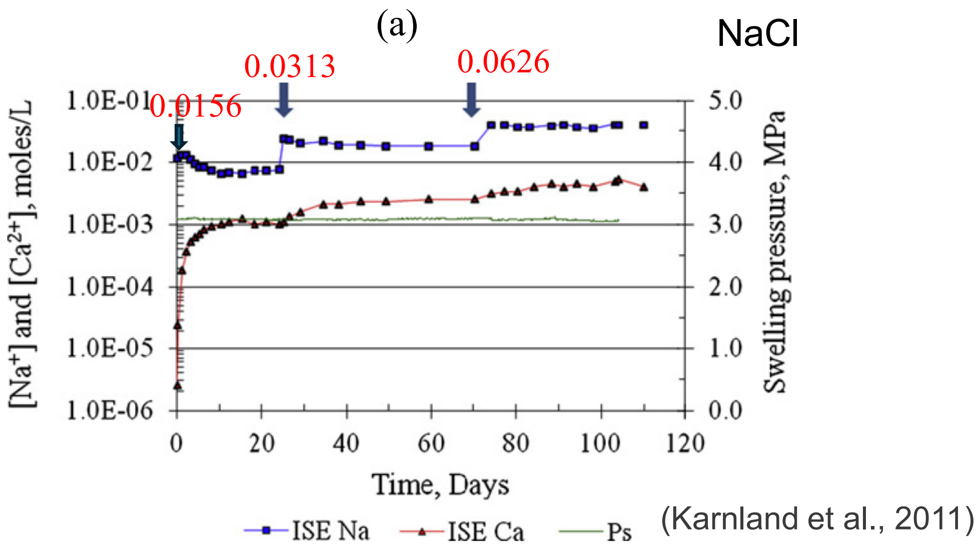
(a) 1:1 electrolyte (e.g., NaCl, $NaHCO_3$)



(b) 1:2 electrolyte (e.g., Na_2SO_4, Na_2CO_3)







(Karnland et al., 2011)

- General exchange selectivity: $K^+ > Ca^{2+} \approx Mg^{2+} > Na^+$ (Birgersson and Karnland, 2009)
- But Ca^{2+} and Mg^{2+} can be replaced by Na^+, given sufficient Na^+ concentration (Wersin et al., 2004)

- c_{Na+} decreased while c_{Ca2+} increased with time, suggesting exchange of interlayer Ca^{2+} by external Na^+.
- With increasing c_{Na+}, higher c_{Ca2+} was detected, indicating increase in degree of cation exchange with c_{Na+}.

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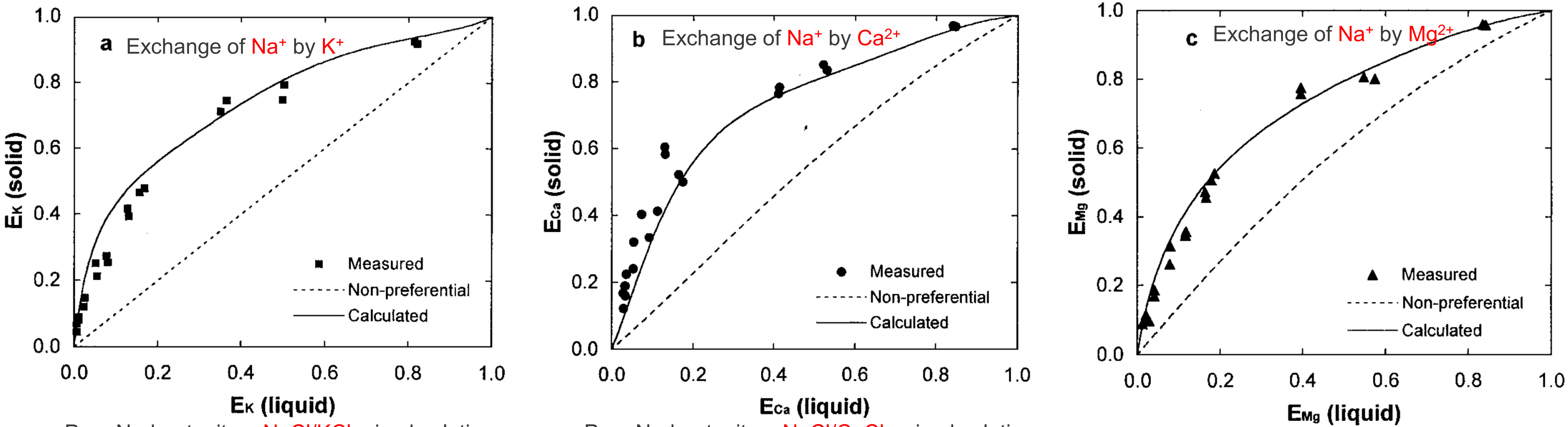
Cation exchange (CE): experimental evidence



Pure Na-bentonite + NaCl/KCl mixed solution
Pure Na-bentonite + NaCl/$CaCl_2$ mixed solution
Pure Na-bentonite + NaCl/$MgCl_2$ mixed solution

E_k (solid): equivalent fraction of exchangeable K^+ in initial pure Na-bentonite treated by NaCl/KCl mixed solution = **degree of cation exchange** of Na by K.
E_k (liquid): equivalent fraction of K^+ in external NaCl/KCl solution.

Huertas et al. (2001)

Degree of cation exchange:

$$\eta_i = 100\% \left[1 - \frac{1}{1+(\alpha c_{K^+})^{\tau}} \right]$$

c_{K+}: external K^+ concentration.

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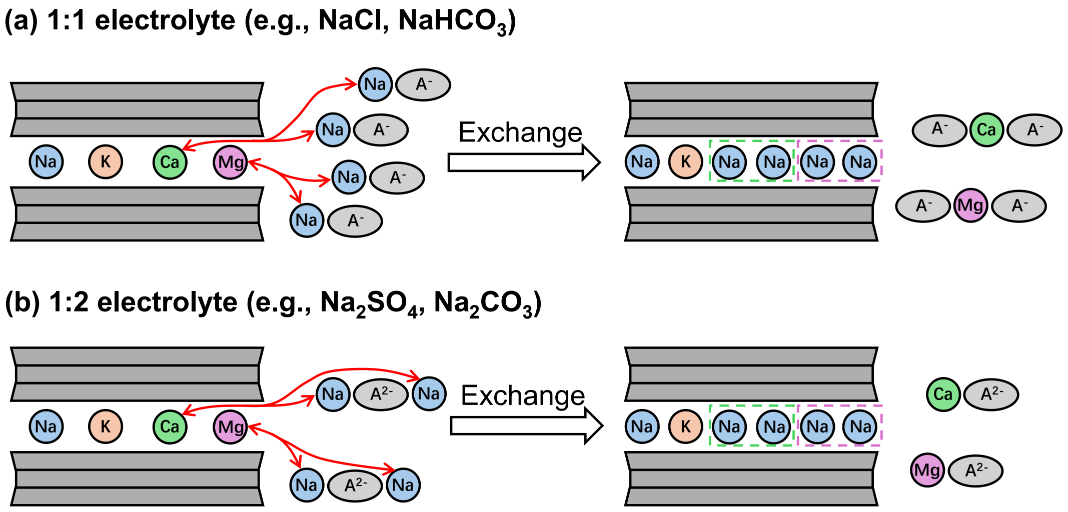
Role of cation exchange (CE): enhancing the crystalline swelling



Enhancement of swelling pressure due to CE:

$$\Delta p_{ce} = \Delta p_{max}\eta_i = \Delta p_{max}\left[1 - \frac{1}{1+(\alpha c_{Na^+})^{\tau}}\right]$$

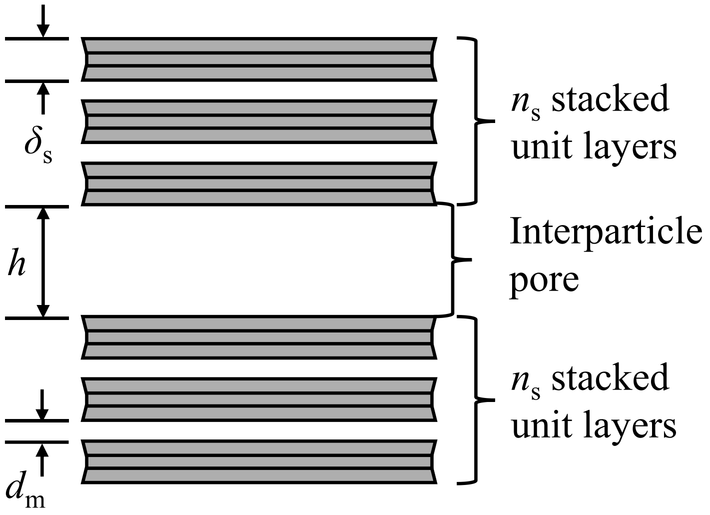
Where, Δp_{max} is the maximum swelling pressure increase induced by CE.

Maximum layer number of interlayer water (Liu, 2013):

- Na^+: 4
- K^+: 2
- Ca^{2+}: 3
- Mg^{2+}: 3

Liu and Cui (2026) JRMGE

Salt precipitation (SP): theoretical calculations



Interparticle concentration of cation *i*:

$$c_i = \frac{0.01 EXC_i \eta_i}{v_i} \cdot \frac{1}{1/\rho_{d0} - 1/\rho_s - \dfrac{(n_s - 1) d_m C_b C_m}{n_s \delta_s \rho_m}}$$

EXC_i: exchangeable capacity of cation *i*
v_i: valence of cation *i*
ρ_{d0}: initial dry density
ρ_s: solid density of bentonite

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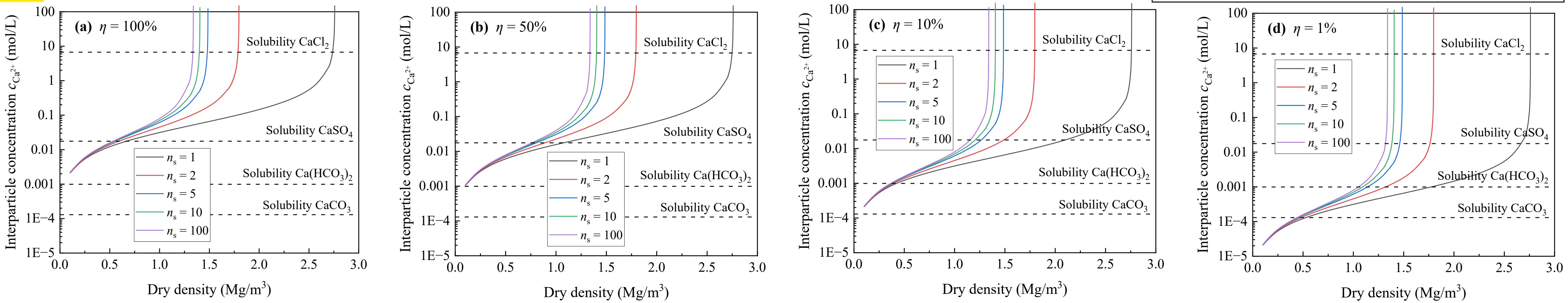
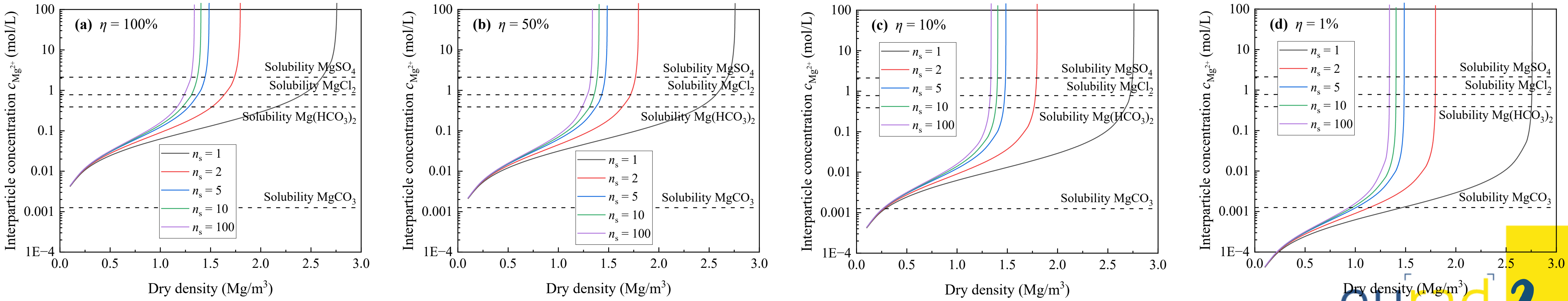
Salt precipitation (SP): theoretical calculations

Salts to precipitate (for $c \leq 0.1$ mol/L, $\rho_d \leq 2.0$ Mg/m^3):

- $CaCO_3$
- $Ca(HCO_3)_2$
- $CaSO_4$
- $MgCO_3$





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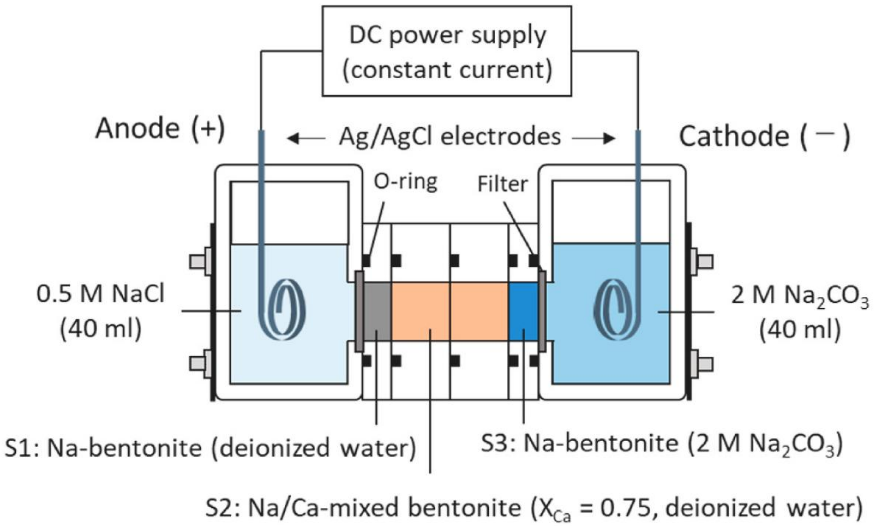
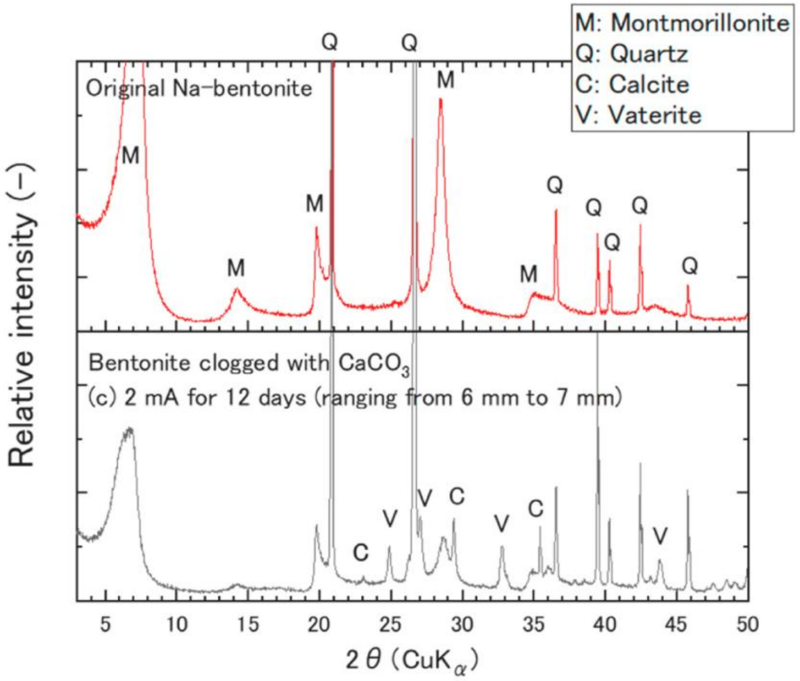
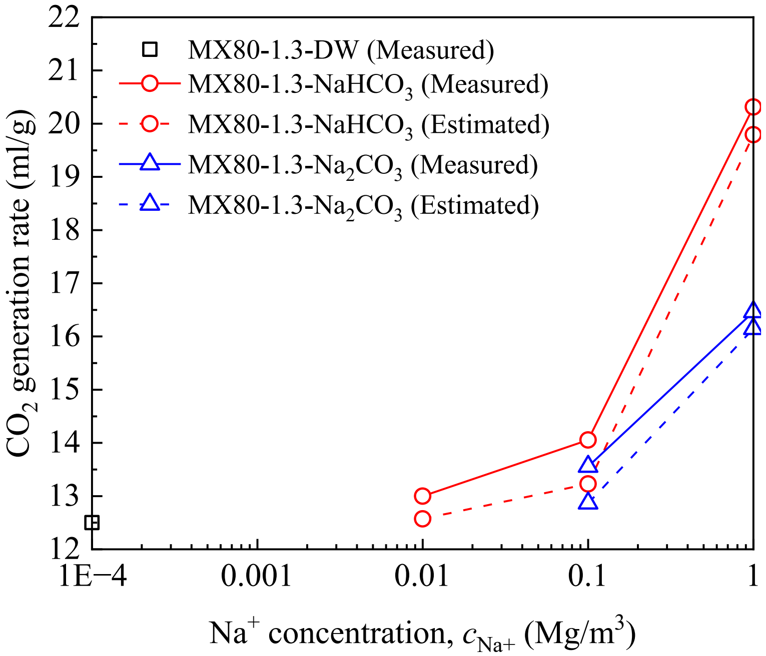
Salt precipitation (SP): experimental evidences



(Tanaka, 2022)



(Tanaka, 2022)



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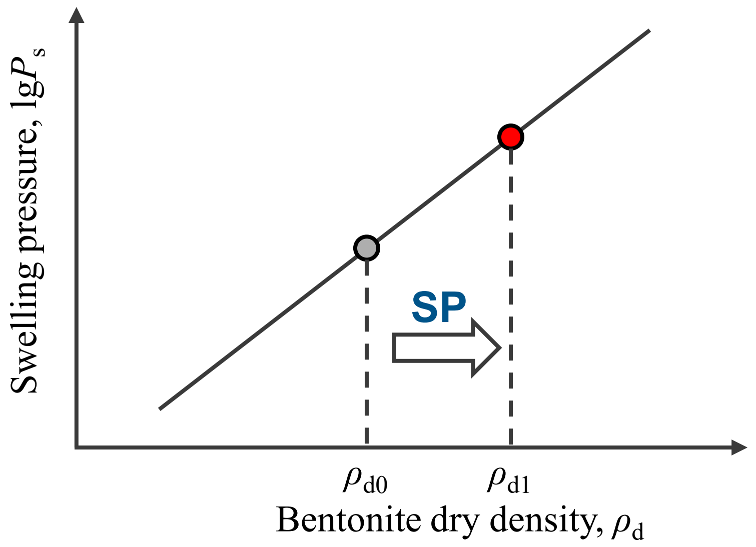
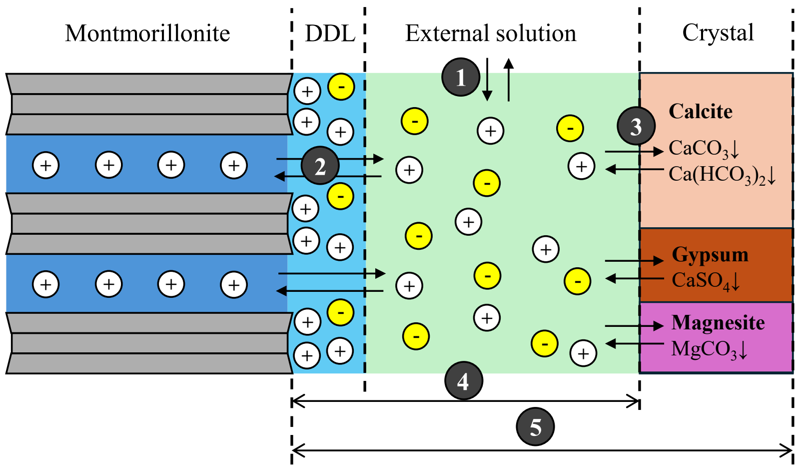
Role of salt precipitation (SP): increasing the dry density



Relationship between swelling pressure and dry density:

$$p_{sp} = A\exp(B\rho_d)$$



Effect of salt precipitation on dry density:

$$\rho_d = \rho_{d0}\left[1 + 0.001e_0(1-\chi)\boxed{\sum_i V_{M\_i}\mathrm{ReLU}(c_i - c_{s\_i})}\right]$$

i = $CaCO_3$, $Ca(HCO_3)_2$, $CaSO_4$, $MgCO_3$, etc.
V_{M_i}: molar volume of salt crystal i
c_i: interparticle concentration of salt i
c_{s_i}: solubility of salt i

Total volume of the precipitated salt crystals

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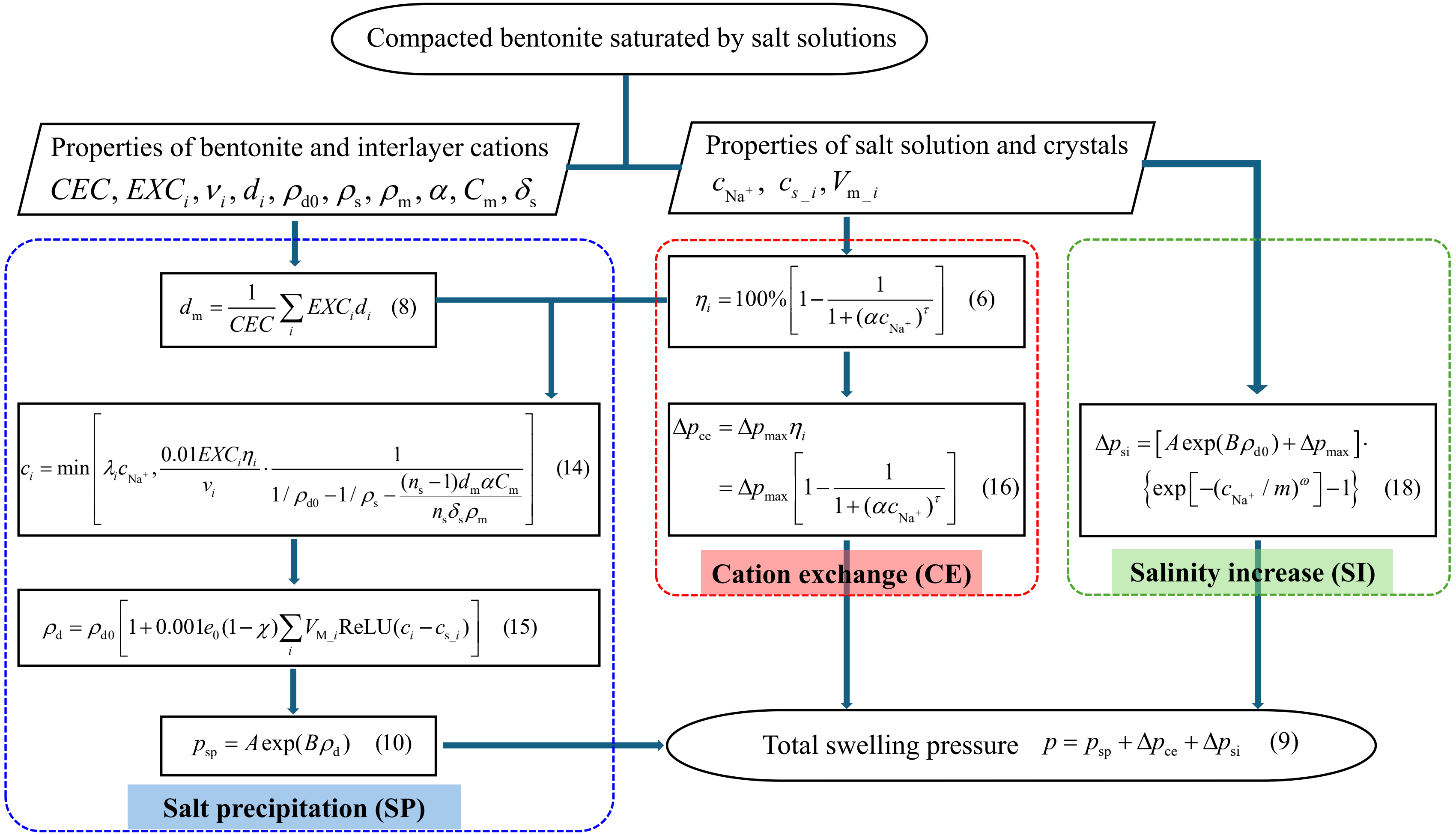
A physicochemical swelling pressure model



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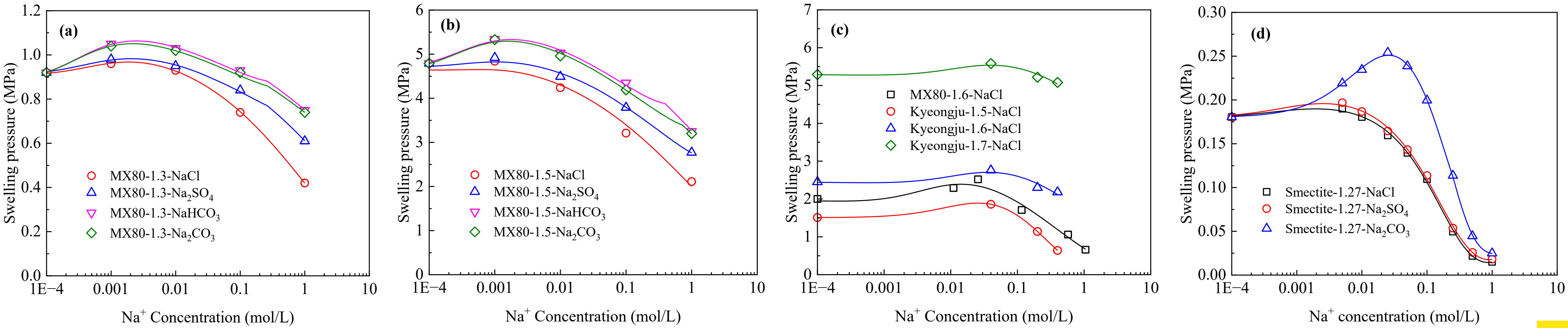
Model calibration

Table 4 Material parameters of bentonite used for model verification.

Bentonite	C_m (%)	ρ_s (Mg/m^3)	CEC (meq/100 g)	ρ_{d0} (g/cm^3)	Solution	Na^+ concentration (mol/L)	Data source
MX80 Na-bentonite	86	2.77	80: **Na^+ (67),** Ca^{2+} (8), Mg^{2+} (4), K^+ (1)	1.3, 1.5	$NaCl$, Na_2SO_4, $NaHCO_3$, Na_2CO_3	0, 0.001, 0.01, 0.1, 1.0	This study
MX80 Na-bentonite	86	2.77	80: **Na^+ (67),** Ca^{2+} (8), Mg^{2+} (4), K^+ (1)	1.6	$NaCl$	0.011, 0.0256, 0.116, 0.575, 1.053	Xie et al. (2007)
Kyeongju Ca-bentonite	70	2.75	57.6: Na^+ (6.6), **Ca^{2+} (46),** Mg^{2+} (4), K^+ (1)	1.5, 1.6, 1.7	$NaCl$	0, 0.04, 0.2, 0.4	Lee et al. (2012)
Na-smectite	77	2.81	81.5: **Na^+ (68.5),** Ca^{2+} (8), Mg^{2+} (4), K^+ (1)	1.27	$NaCl$, Na_2SO_4,Na_2CO_3	0, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5,1.0	Goodarzi and Akbari (2014)



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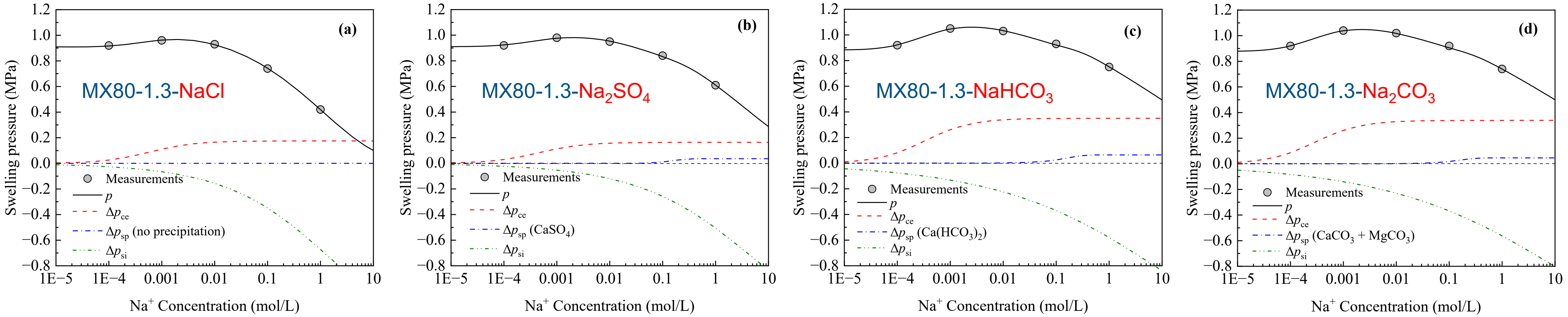
Model calibration

Individual contribution of cation exchange, salt precipitation and salinity increase to swelling pressure



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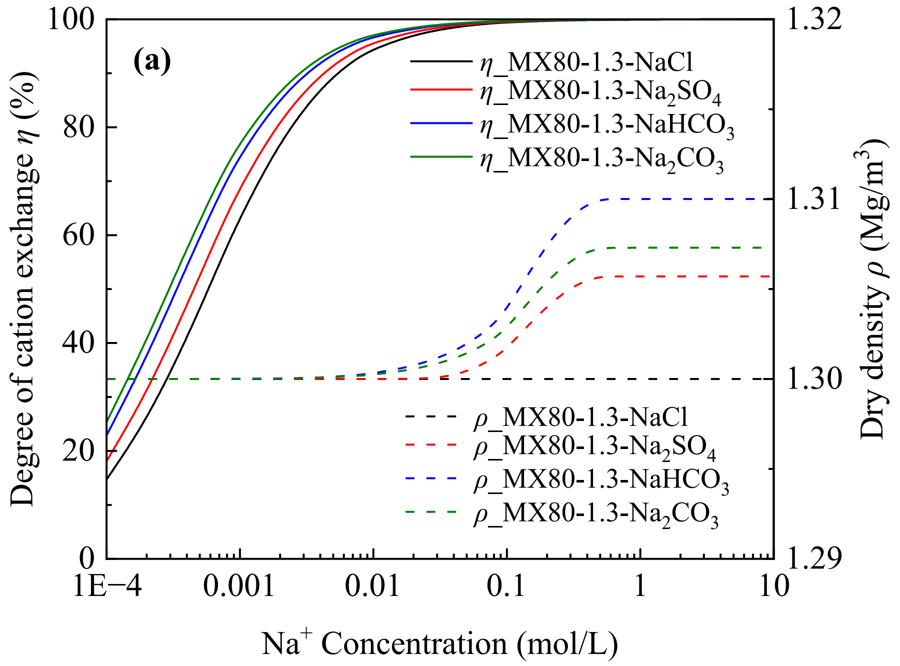
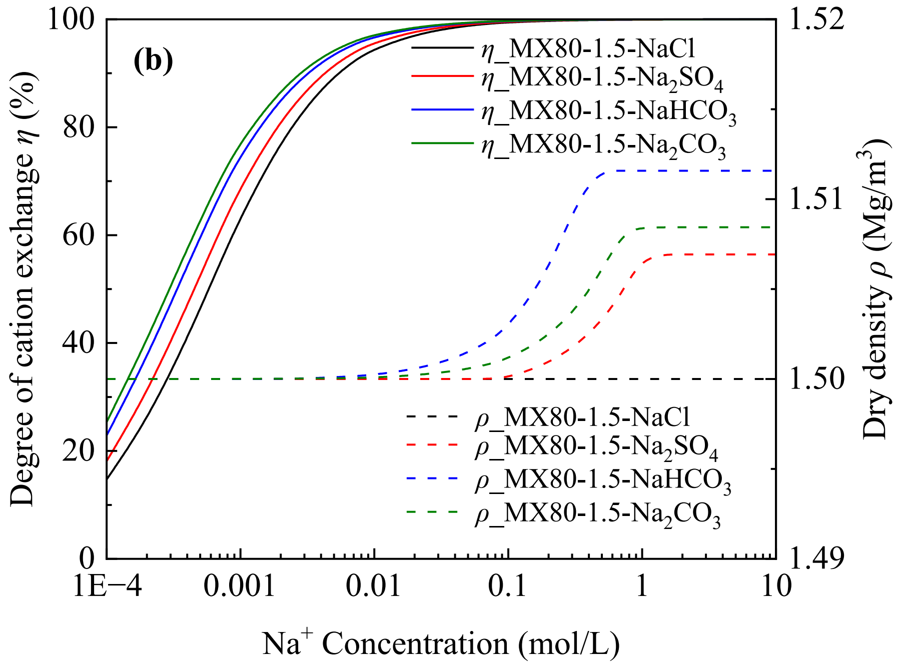
Model calibration

- Degree of cation exchange: $CO_3^{2-} > HCO_3^- > SO_4^{2-} > Cl^-$
- Dry density increase: $HCO_3^- > CO_3^{2-} > SO_4^{2-} > Cl^-$





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Conclusions

- The swelling pressure firstly increased then decreased as the Na^+ concentration increased from 0 to 1.0 mol/L, with a peak value at a Na^+ concentration of about 0.001 mol/L.
- The swelling pressure follows an order: $NaHCO_3 \approx Na_2CO_3 > Na_2SO_4 > NaCl$.
- The swelling pressure depends on specific anion effects, including **cation exchange (CE)**, **salt precipitation (SP)** and **salinity increase (SI)**.
- A **physicochemical model** incorporating the contributions of CE, SP and SI was developed and validated against experimental data of various bentonite treated by different salt solutions.

Acknowledgements

Publications

- Liu, Z.R.*, Cui, Y.J., 2026. Specific anion effects on swelling pressure of compacted MX80 bentonite: experiment and modelling. ***J. Rock Mech. Geotech. Eng.*** ().

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ANCHORS

THANK YOU

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