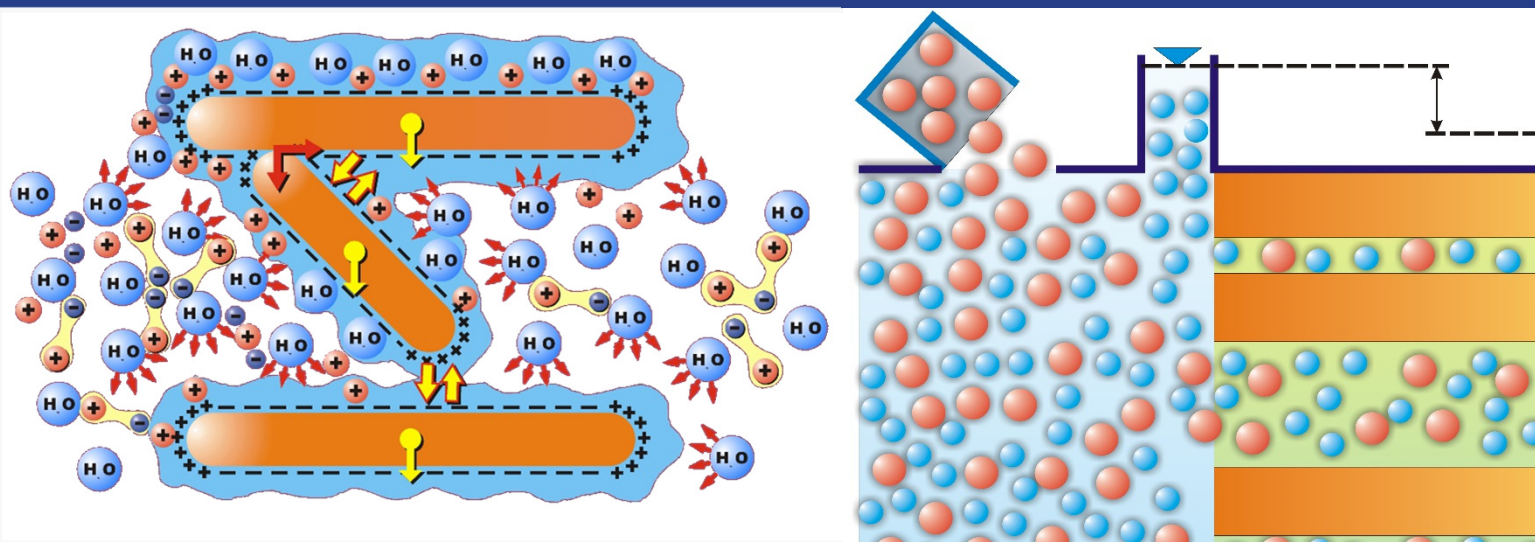




THE 27TH EUROPEAN YOUNG GEOTECHNICAL ENGINEERS' CONFERENCE (EYGEC) BODRUM, MUĞLA-TURKEY 26 - 27 SEPTEMBER 2019



CHEMICO-OSMOTIC EFFECTS IN BENTONITE-BASED BARRIERS FOR CONTAINMENT APPLICATIONS



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Politecnico di Torino

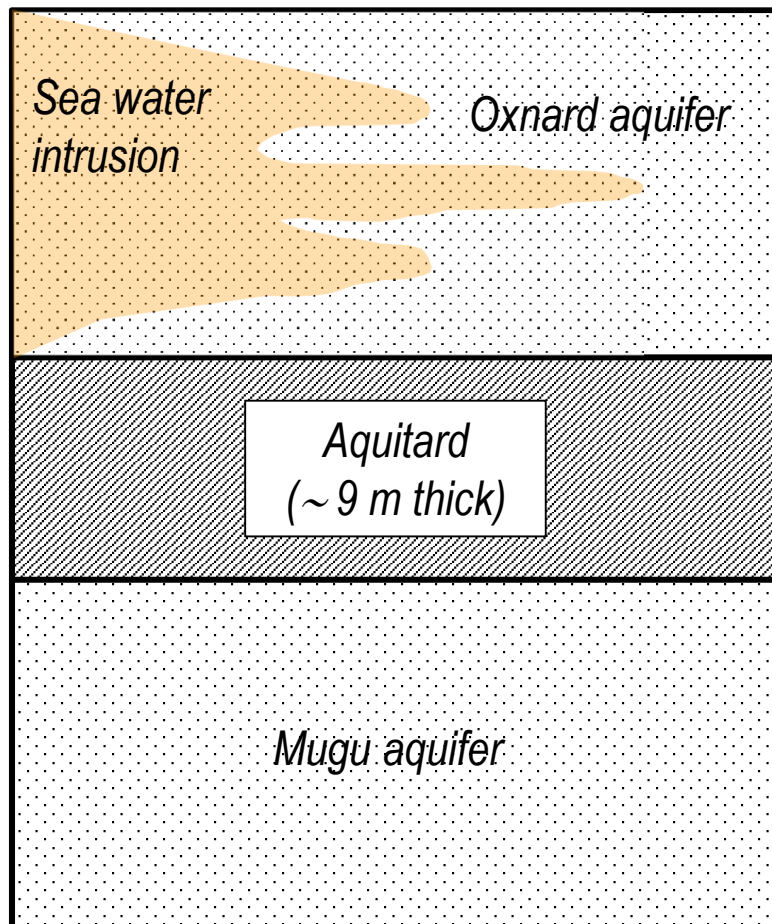
LECTURE OUTLINE

- ***BENTONITE-BASED BARRIERS FOR CONTAMINANT CONTAINMENT***
- ***THEORETICAL MODELLING OF CHEMICO-OSMOTIC EFFECTS***
- ***LABORATORY TESTS AND EXPERIMENTAL DATA***
- ***RELEVANCE OF OSMOTIC EFFECTS IN FIELD APPLICATIONS***



HISTORICAL NOTES

Pioneering studies on chemico-osmotic effects in fine grained soils were conducted in the field of geotechnical engineering by J. Mitchell in the 1970s.



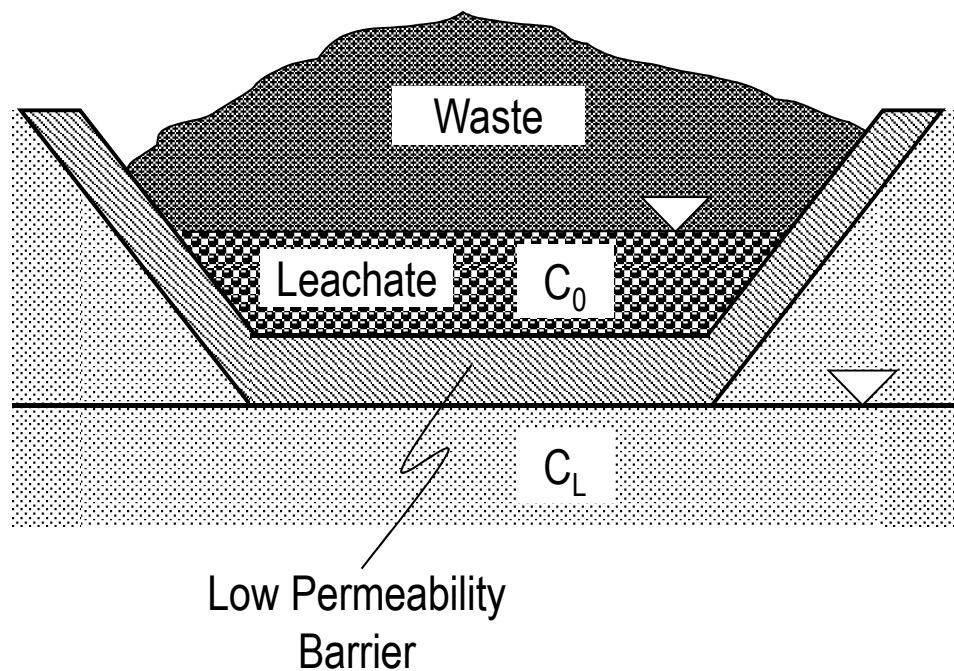
These studies were aimed at assessing the effects induced by salt intrusion into the Oxnard, California, groundwater basin:

- *consolidation settlement* of the underlying aquitard layer of fine grained soil;
- *NaCl migration* towards the uncontaminated Mugu aquifer.

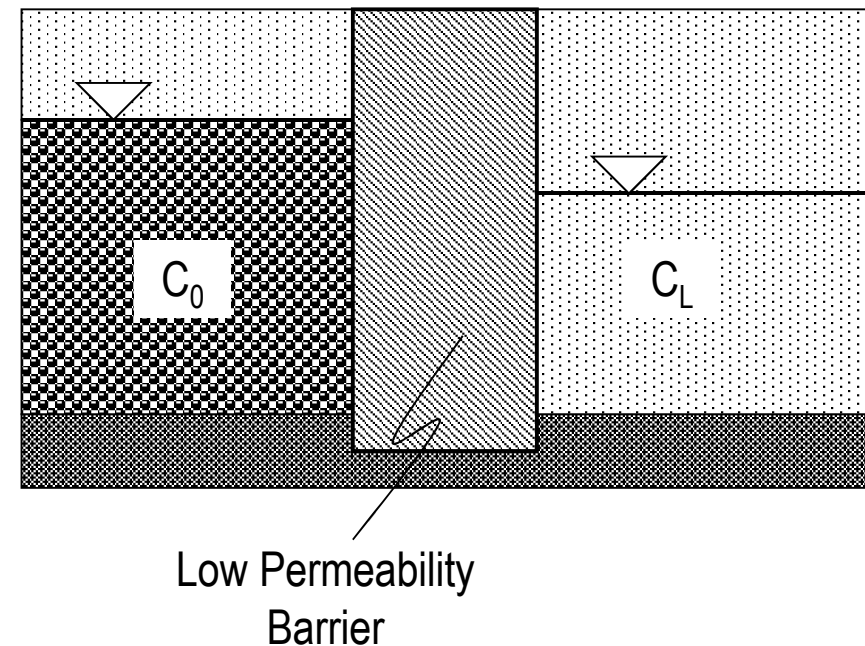


BARRIERS FOR CONTAINMENT APPLICATIONS

Bottom and Lateral Lining Systems
(Landfill Application)



Cut-off Walls for Encapsulation of
Contaminated Soils
(Soil Remediation Application)



BENTONITE BASED BARRIERS

The term '**bentonite**' is commonly used to indicate a clay soil with a high content (> 70%) of **montmorillonite**, a mineral of the smectite group.

Bentonite is used in hydraulic and contaminant barriers, because of its **low hydraulic conductivity**, k , to permeation with water and dilute aqueous solutions (k typically $\leq 3 \cdot 10^{-11}$ m/s).

Contaminant barriers constituted wholly or partially by bentonite include:

- soil-bentonite (SB) backfills for vertical cutoff walls;
- sand-bentonite mixture liners;
- bentonite amended natural clays that are used as compacted clay liners (CCLs)
- geosynthetic clay liners (GCLs).

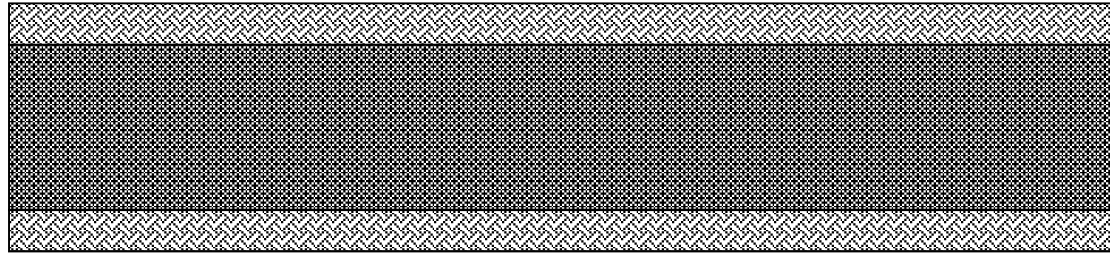


GEOSYNTHETIC CLAY LINERS

GEOTEXTILE

BENTONITE

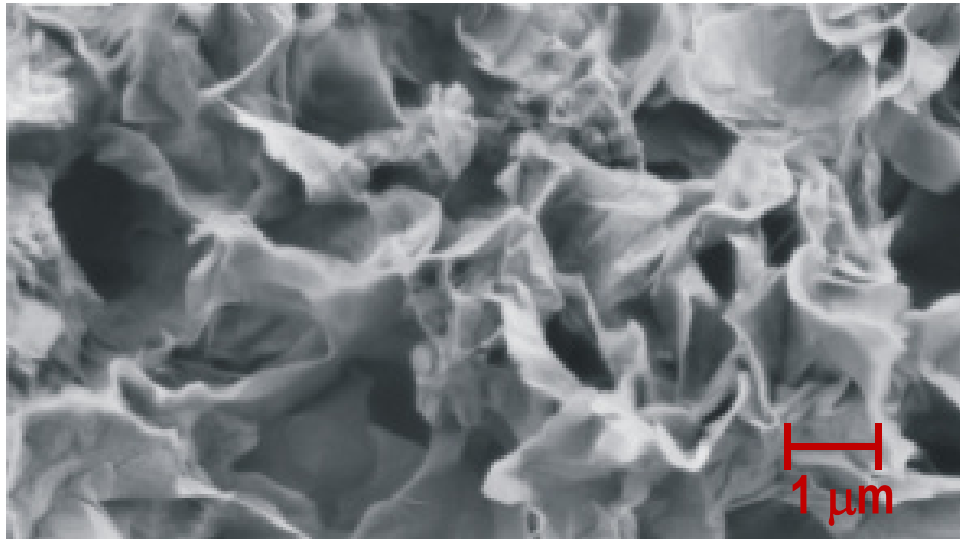
GEOTEXTILE



~ 6 mm
(initial, air
dried state)

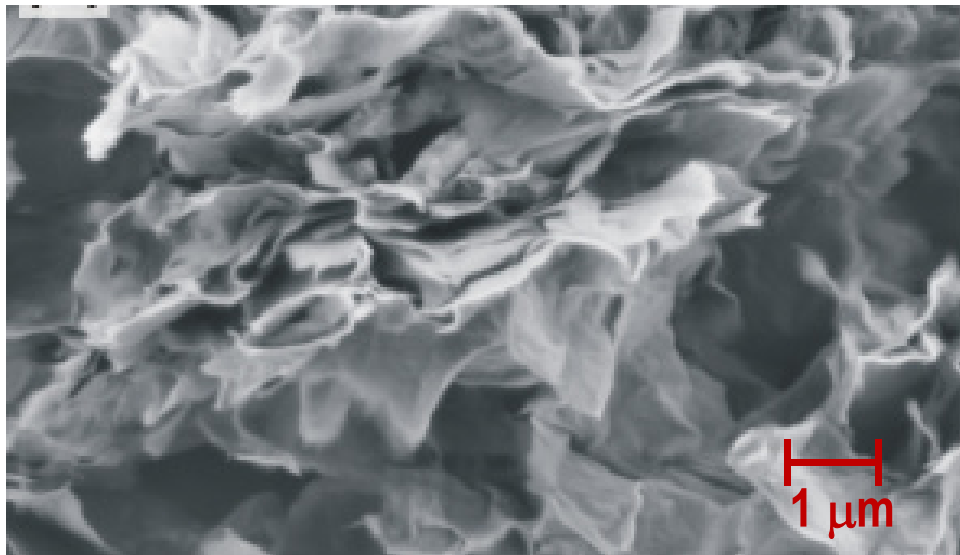


BENTONITE MICROSTRUCTURE



Bentonites properties:

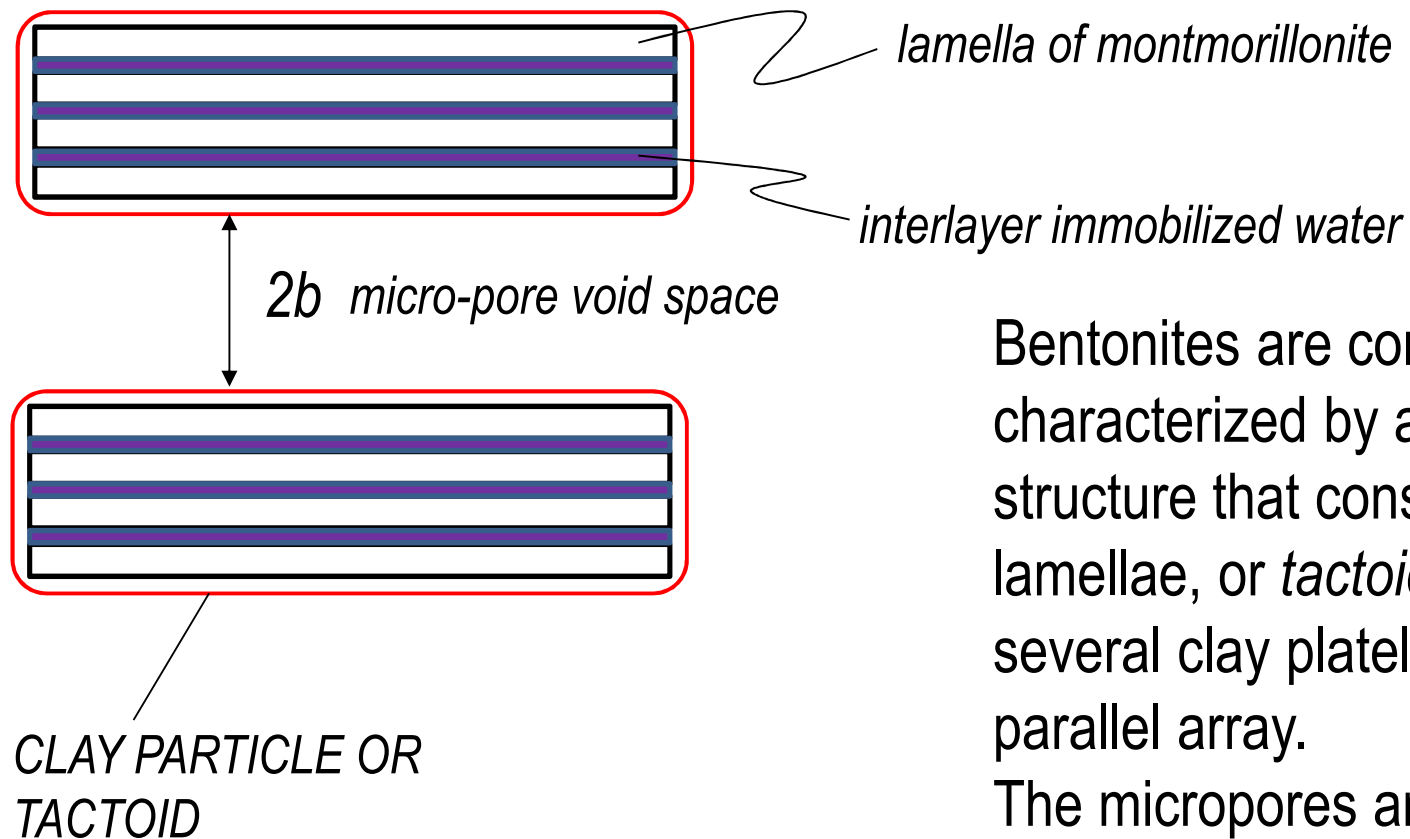
- > 70% montmorillonite content
- high total specific surface ($S = 760 \text{ m}^2/\text{g}$)
- negative surface electric charge ($\sigma = 0.114 \text{ C/m}^2$)
- non-uniform lamellar micro-structure



Field Emission Scanning Electron Microscopy (FESEM) micrographs (magnification 10000x) (Viola et al., 2005)



BENTONITE MICROSTRUCTURE

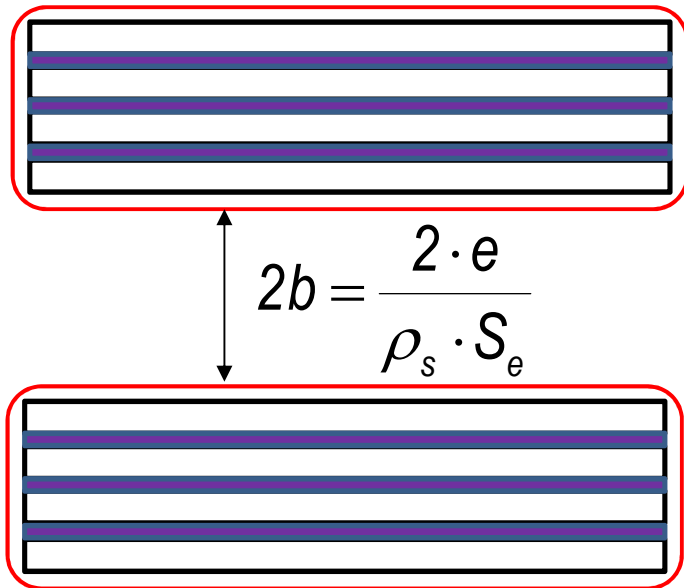


Bentonites are commonly characterized by an aggregated structure that consists of packets of lamellae, or *tactoids*, within which several clay platelets are in a parallel array.

The micropores are the conductive pores, as opposed to the interlayer spaces within the aggregates, which are not accessible for solvent and solute transport.



BENTONITE MICROSTRUCTURE



e = void ratio of bentonite

ρ_s = unit weight of solid particles

The effective specific surface, S_e , of the bentonite can be determined as follows:

$$S_e = S / N_l$$

where N_l is the average number of lamellae per tactoid.

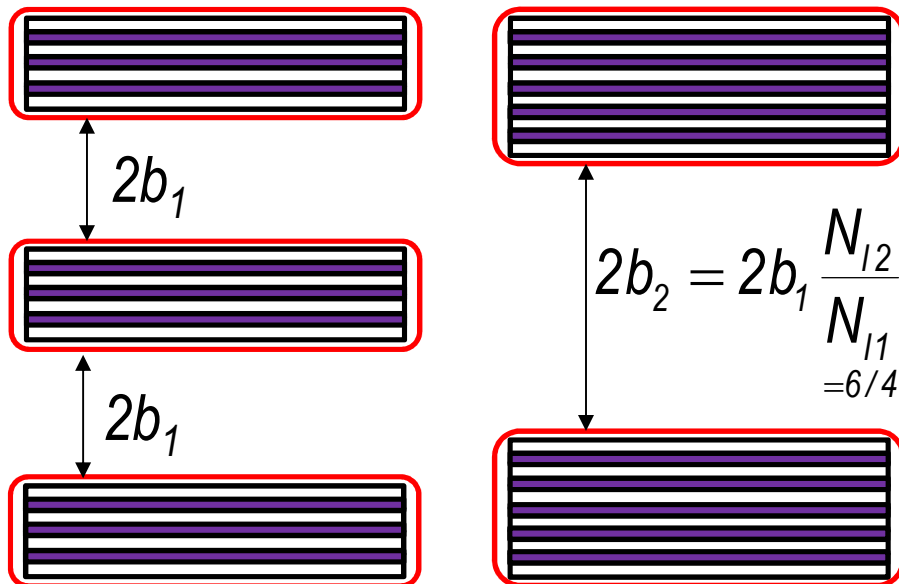
The micropores size is inversely proportional to the S_e .



BENTONITE MICROSTRUCTURE

$$N_{I1} = 4$$

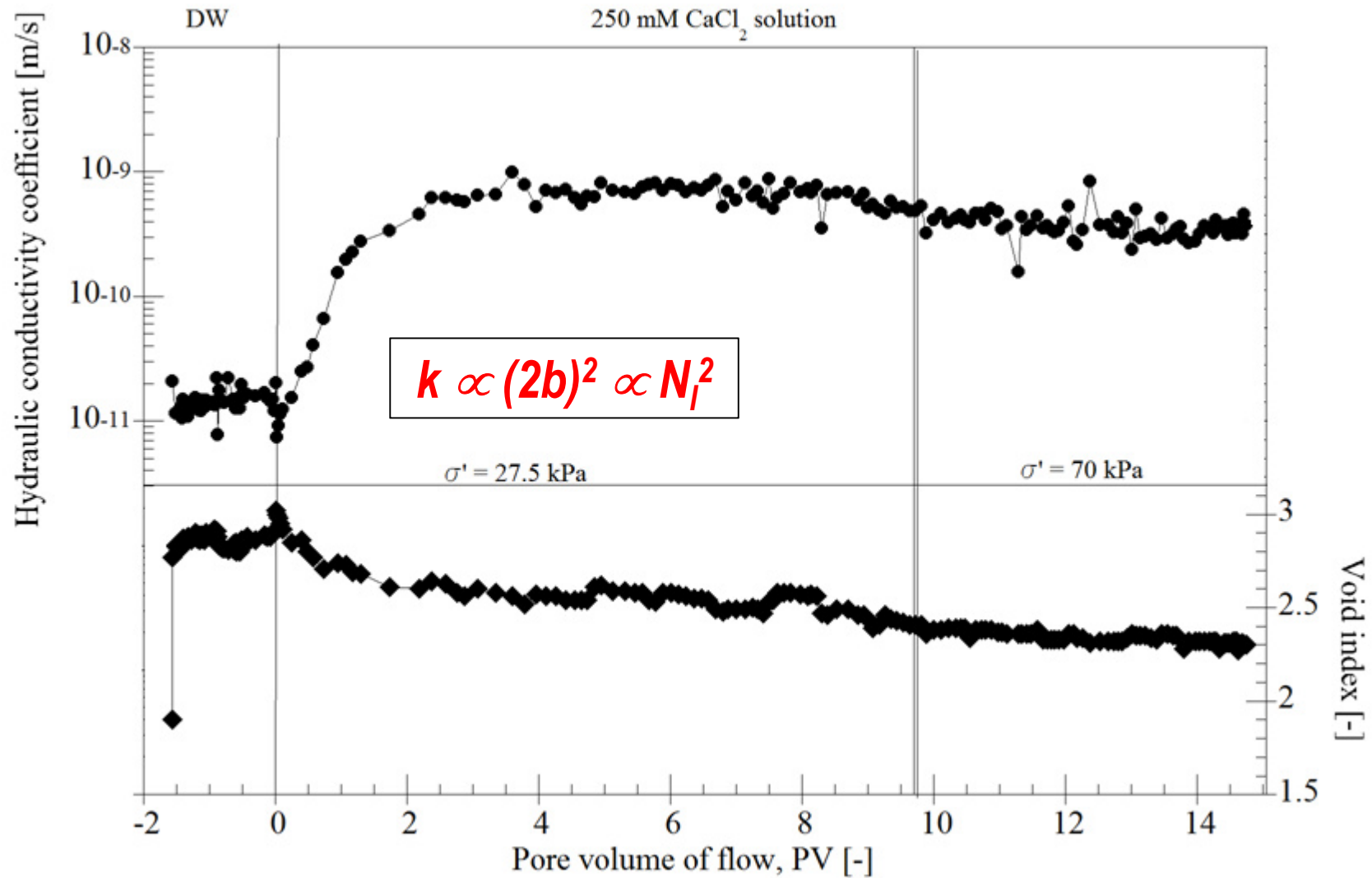
$$N_{I2} = 6$$



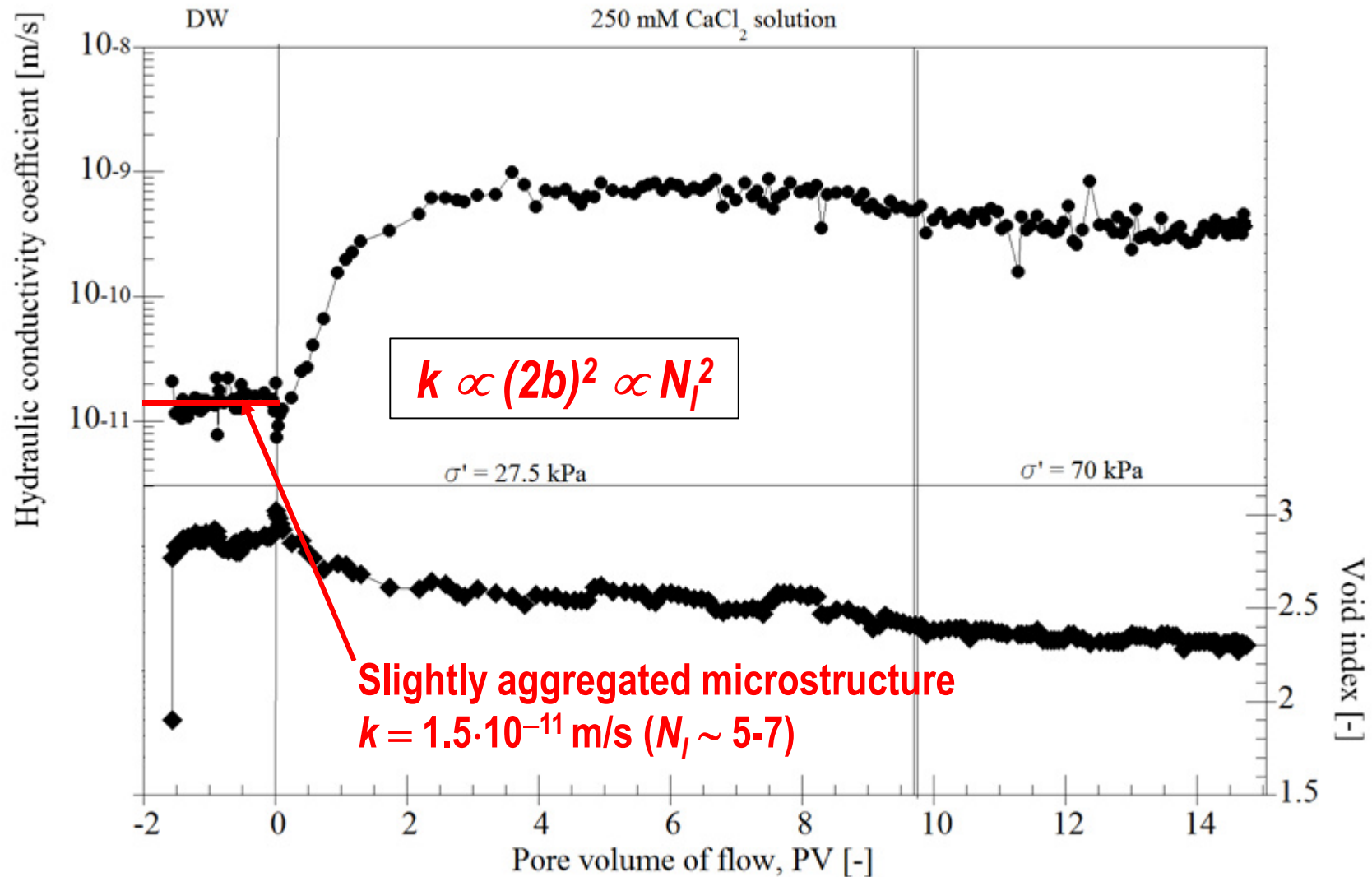
The *aggregation process*, i.e. the increase in the number of lamellae per tactoid is determined by a reduction in the electrical repulsive forces among the clay particles, which is mainly induced by an *increase in the salt concentration* (or a decrease in the solvent dielectric constant of the pore solution for liquids different from water).



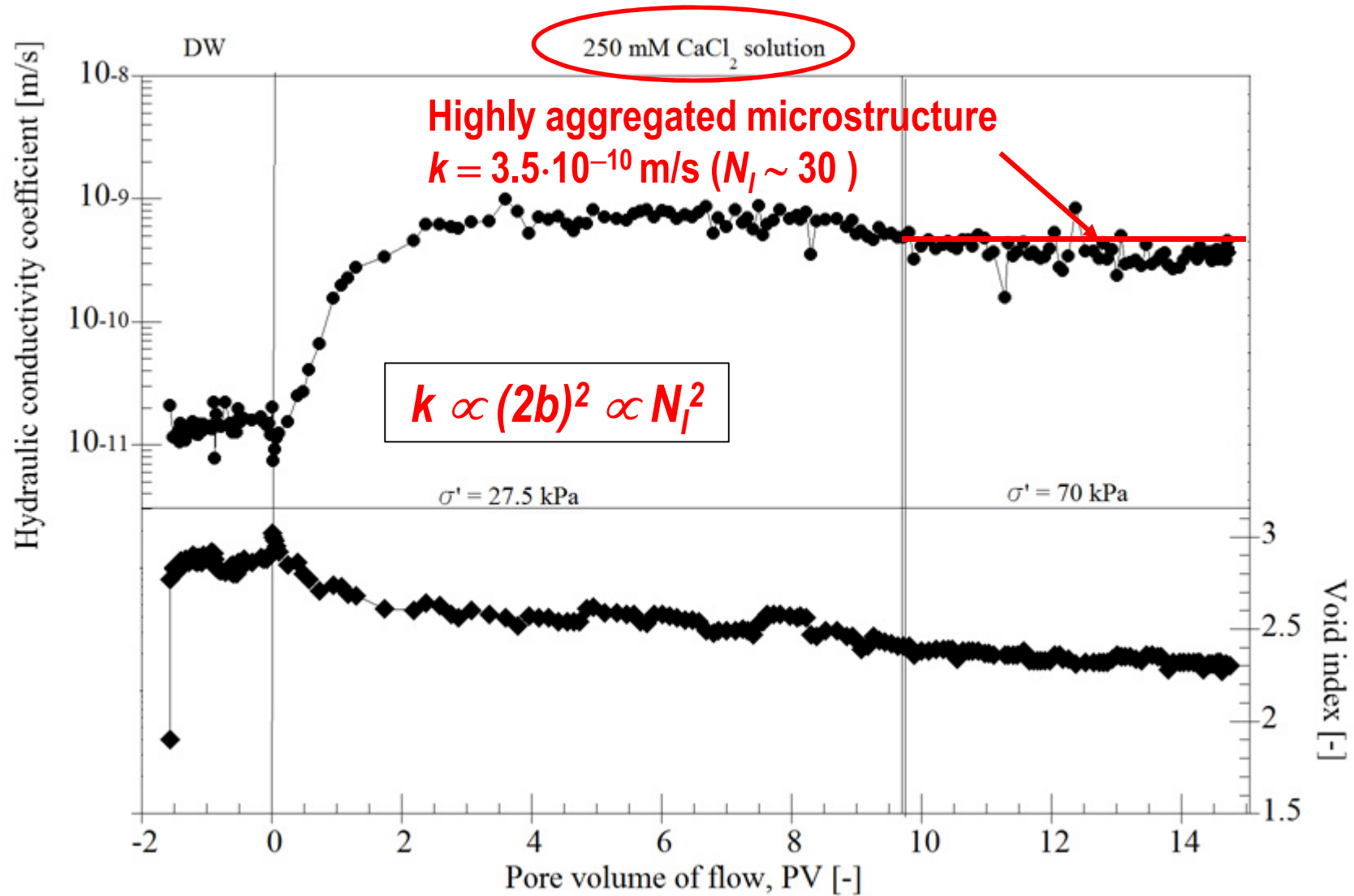
BENTONITE MICROSTRUCTURE



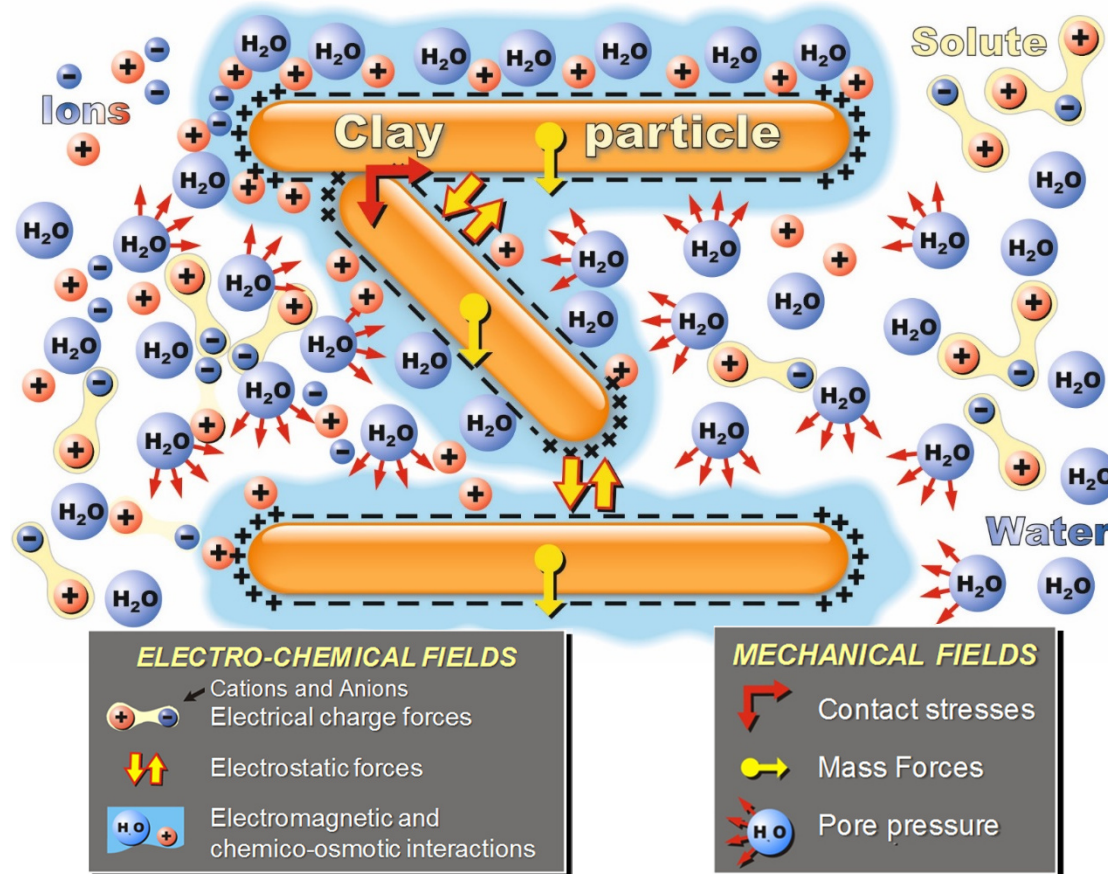
BENTONITE MICROSTRUCTURE



BENTONITE MICROSTRUCTURE



BENTONITE BEHAVIOUR



Features of bentonite behaviour:

- the surface forces of electric nature prevail on the self-weight forces;
- the negative electric charge of the solid skeleton (clay particles) interact with the charged ions that are contained in the pore solution;

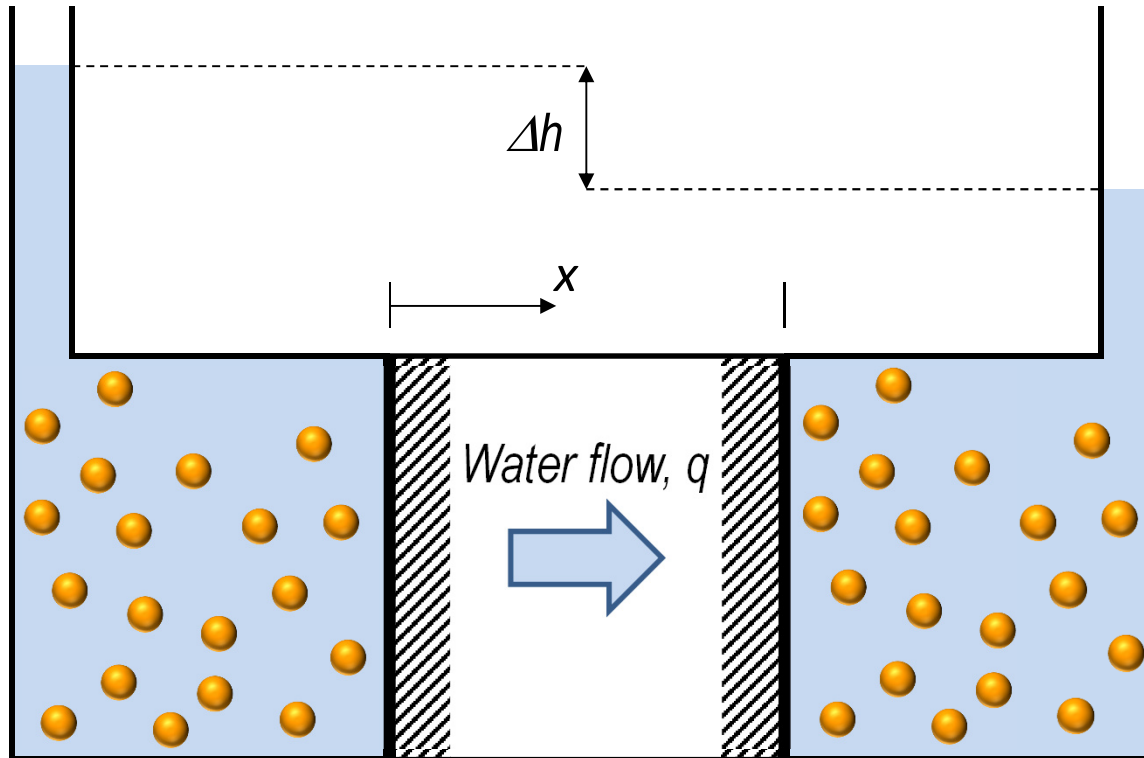
- Changes in the electrical repulsive forces among the clay particles can determine a modification of the microscopic structure, with consequent variation in the macroscopic transport parameters (e.g. after permeation with solutions that are characterized by a high salt concentration).

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WATER FLOW



$$q = k \cdot \left(-\frac{\partial h}{\partial x} \right)$$

$k = \text{hydraulic conductivity}$

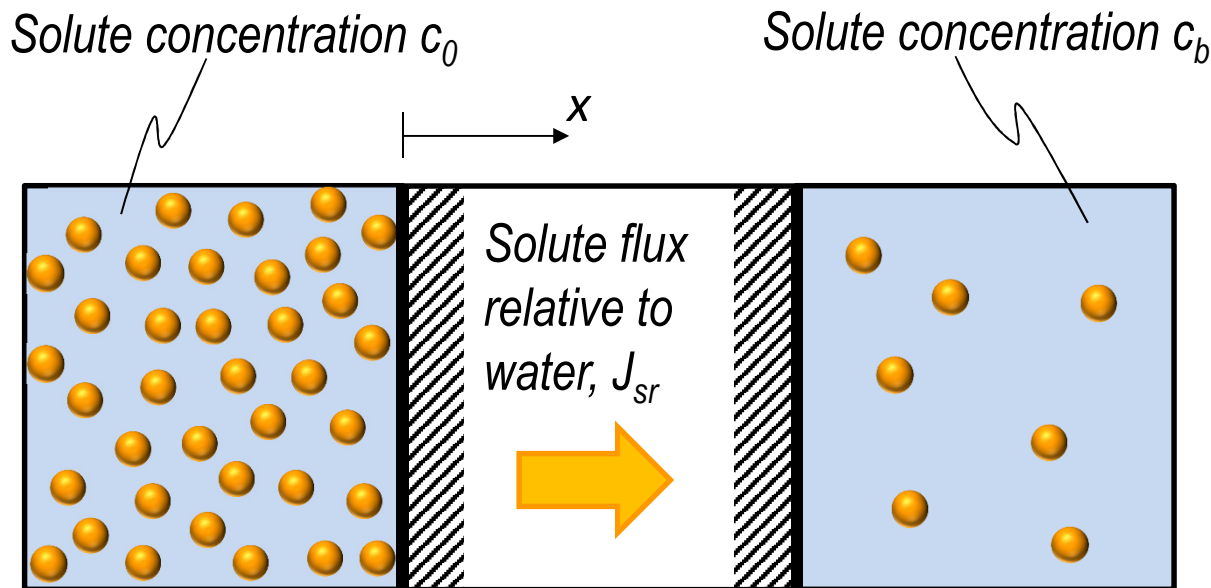


Water (i.e. electrolyte solution)



Solute particle (i.e. ion in solution)

SOLUTE DIFFUSIVE TRANSPORT



$$J_{sr} = n \cdot D_s^* \cdot \left(-\frac{\partial c}{\partial x} \right)$$

$n = \text{porosity}$

$D_s^* = \text{effective diffusion coefficient}$



Water (i.e. electrolyte solution)



Solute particle (i.e. ion in solution)

ADVECTIVE-DIFFUSIVE TRANSPORT THEORY

Advective flux:

$$J_{s,adv} = q \cdot c$$

Solute flux relative to water:

$$J_{sr} = -n \cdot D_s^* \left(-\frac{\partial c}{\partial x} \right)$$

Mass solute flux:

$$J_s = J_{s,adv} + J_{sr} = q \cdot c - n \cdot D_s^* \cdot \frac{\partial c}{\partial x}$$



UNCOUPLED TRANSPORT THEORY

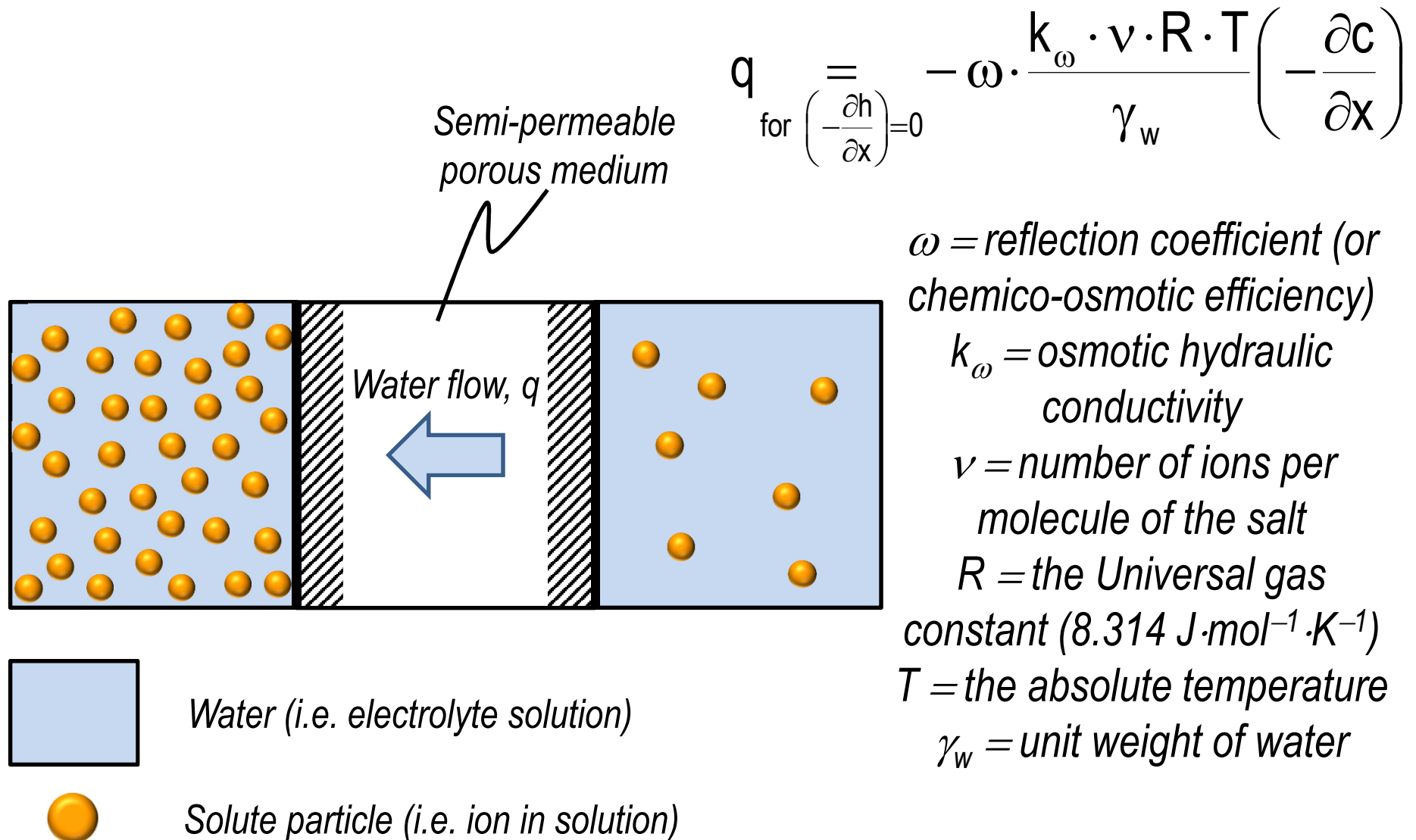
$$\begin{Bmatrix} q \\ J_{sr} \end{Bmatrix} = \begin{bmatrix} k & 0 \\ 0 & n \cdot D_s^* \end{bmatrix} \cdot \begin{Bmatrix} (-\partial h / \partial x) \\ (-\partial c / \partial x) \end{Bmatrix}$$



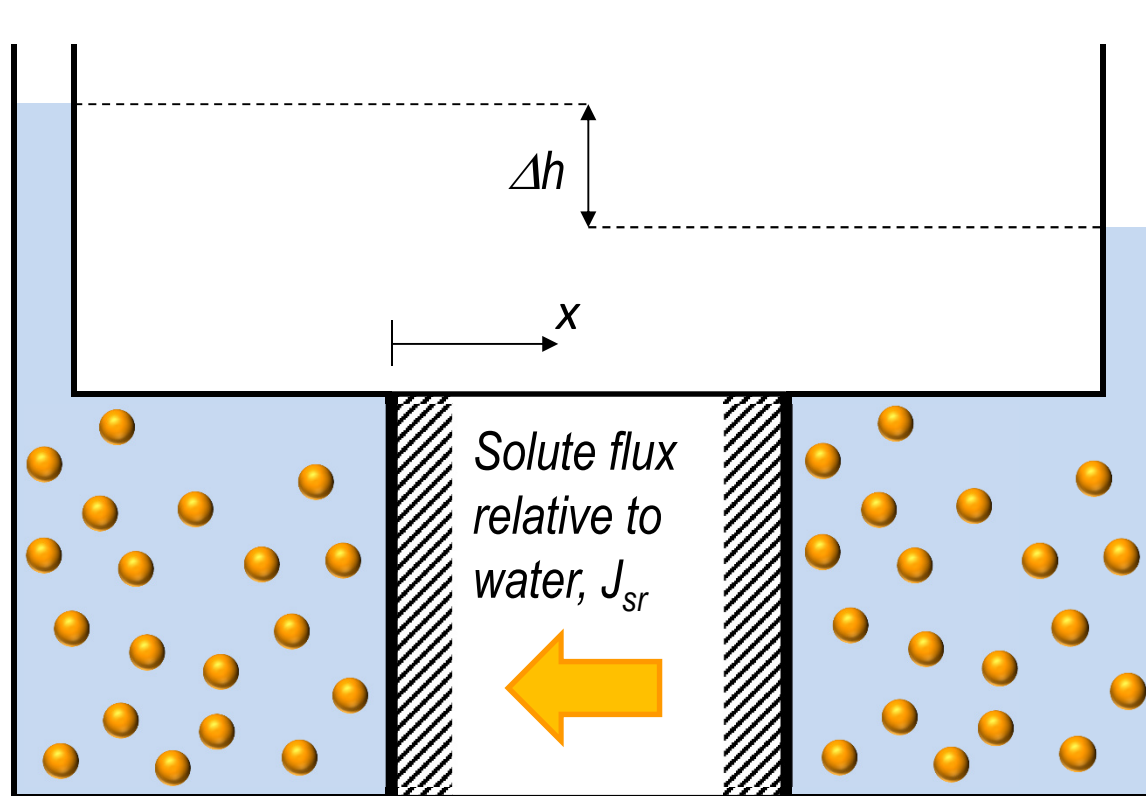
*Uncoupled matrix of
phenomenological coefficients*



CHEMICO-OSMOTIC WATER FLOW



CHEMICO-OSMOTIC SOLUTE FLUX



$$J_{sr} = -\omega' \cdot q \cdot c =$$

$$\text{for } \left(-\frac{\partial c}{\partial x} \right) = 0 \quad = -\omega' \cdot c \cdot k_{\omega} \left(-\frac{\partial h}{\partial x} \right)$$

ω' = second reflection coefficient



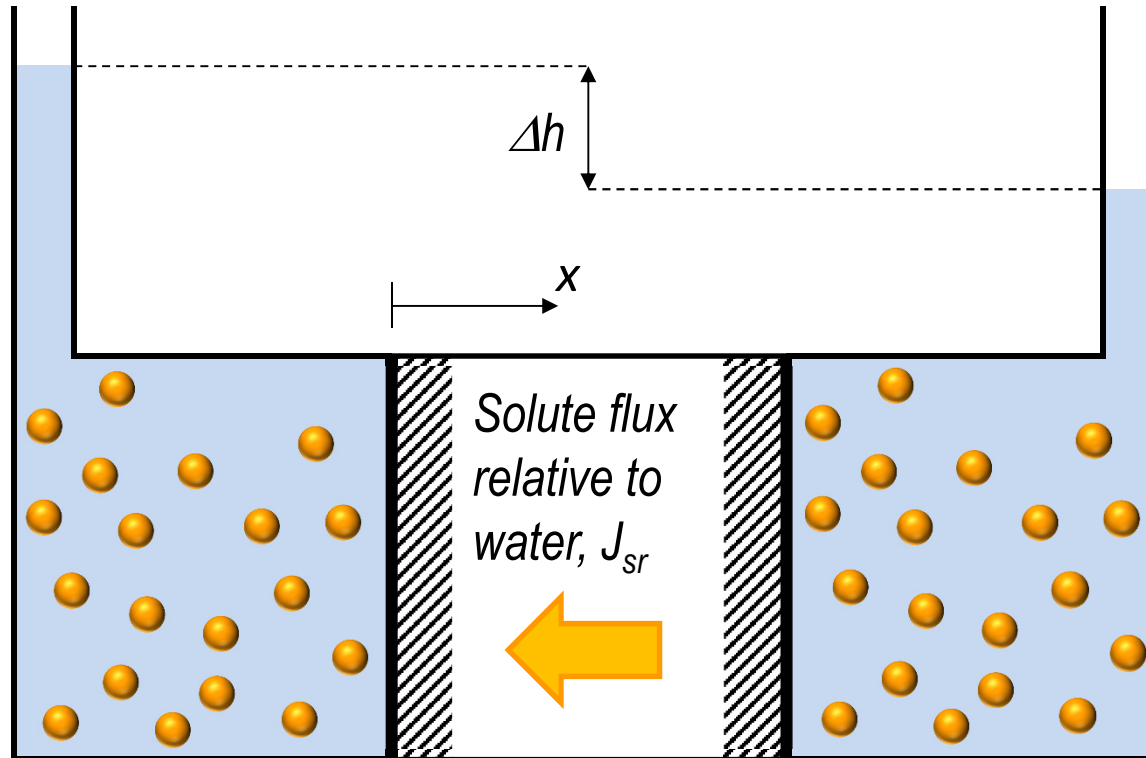
Water (i.e. electrolyte solution)



Solute particle (i.e. ion in solution)



CHEMICO-OSMOTIC SOLUTE FLUX



Water (i.e. electrolyte solution)



Solute particle (i.e. ion in solution)

When $\omega' = 1$

$$J_{sr} = -q \cdot c$$

Since $J_{adv} = q \cdot c$,
the total salt flux
is given by

$$J_s = J_{adv} + J_{sr} = 0$$

COUPLED FLOW THEORY

$$\begin{Bmatrix} q \\ J_{sr} \end{Bmatrix} = \begin{bmatrix} k_{\omega} & -\omega \cdot \frac{k_{\omega} \cdot v \cdot R \cdot T}{\gamma_w} \\ -\omega' \cdot k_{\omega} \cdot c & n \cdot D_{\omega}^* + \omega' \cdot \omega \cdot \frac{k_{\omega} \cdot v \cdot R \cdot T}{\gamma_w} \cdot c \end{bmatrix} \cdot \begin{Bmatrix} (-\partial h / \partial x) \\ (-\partial c / \partial x) \end{Bmatrix}$$

*Coupled matrix of
phenomenological coefficients*



COUPLED FLOW THEORY

$$\begin{Bmatrix} q \\ J_{sr} \end{Bmatrix} = \begin{bmatrix} k_{\omega} & -\omega \cdot \frac{k_{\omega} \cdot v \cdot R \cdot T}{\gamma_w} \\ -\omega' \cdot k_{\omega} \cdot c & n \cdot D_{\omega}^* + \omega' \cdot \omega \cdot \frac{k_{\omega} \cdot v \cdot R \cdot T}{\gamma_w} \cdot c \end{bmatrix} \cdot \begin{Bmatrix} (-\partial h / \partial x) \\ (-\partial c / \partial x) \end{Bmatrix}$$

Phenomenological coefficients:

k_{ω} = osmotic hydraulic conductivity

ω = reflection coefficient

ω' = second reflection coefficient

D_{ω}^* = osmotic effective diffusion coefficient



COUPLED FLOW THEORY

On the basis of:

- Experimental evidence
- Onsager's law of thermodynamics of irreversible processes (close to equilibrium)
- Mixture theory law that states that the sum of the momentum transferred among all the components is equal to zero

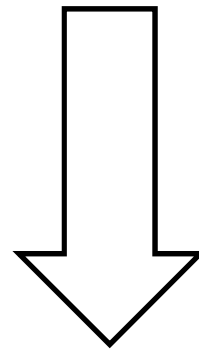
$$\omega = \omega'$$



COUPLED FLOW THEORY

$$q = k_{\omega} \cdot \left[\left(-\frac{\partial h}{\partial x} \right) - \omega \cdot \frac{v \cdot R \cdot T}{\gamma_w} \left(-\frac{\partial c}{\partial x} \right) \right]$$

$$J_s = (1 - \omega) \cdot q \cdot c + n \cdot D_{\omega}^* \left(-\frac{\partial c}{\partial x} \right)$$



$$k_{\omega} = k$$

$$D_{\omega}^* = D_s^*$$

$$\omega = 0$$

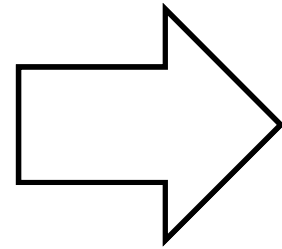
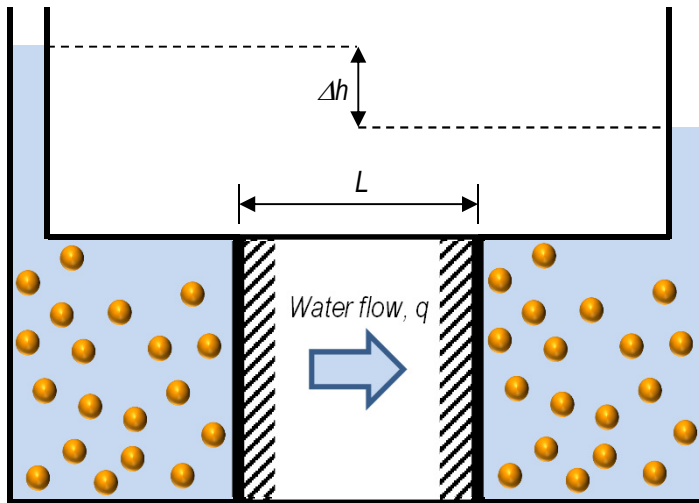
*For a porous medium
without semipermeable
properties*

$$q = k \cdot \left(-\frac{\partial h}{\partial x} \right)$$

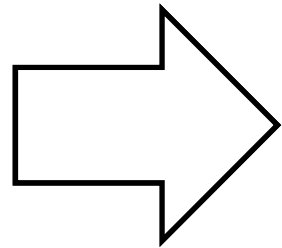
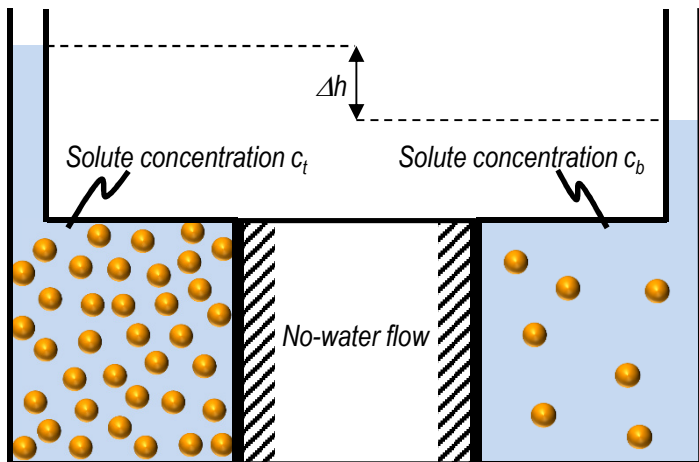
$$J_s = q \cdot c + n \cdot D_s^* \left(-\frac{\partial c}{\partial x} \right)$$



EXPERIMENTAL DETERMINATION



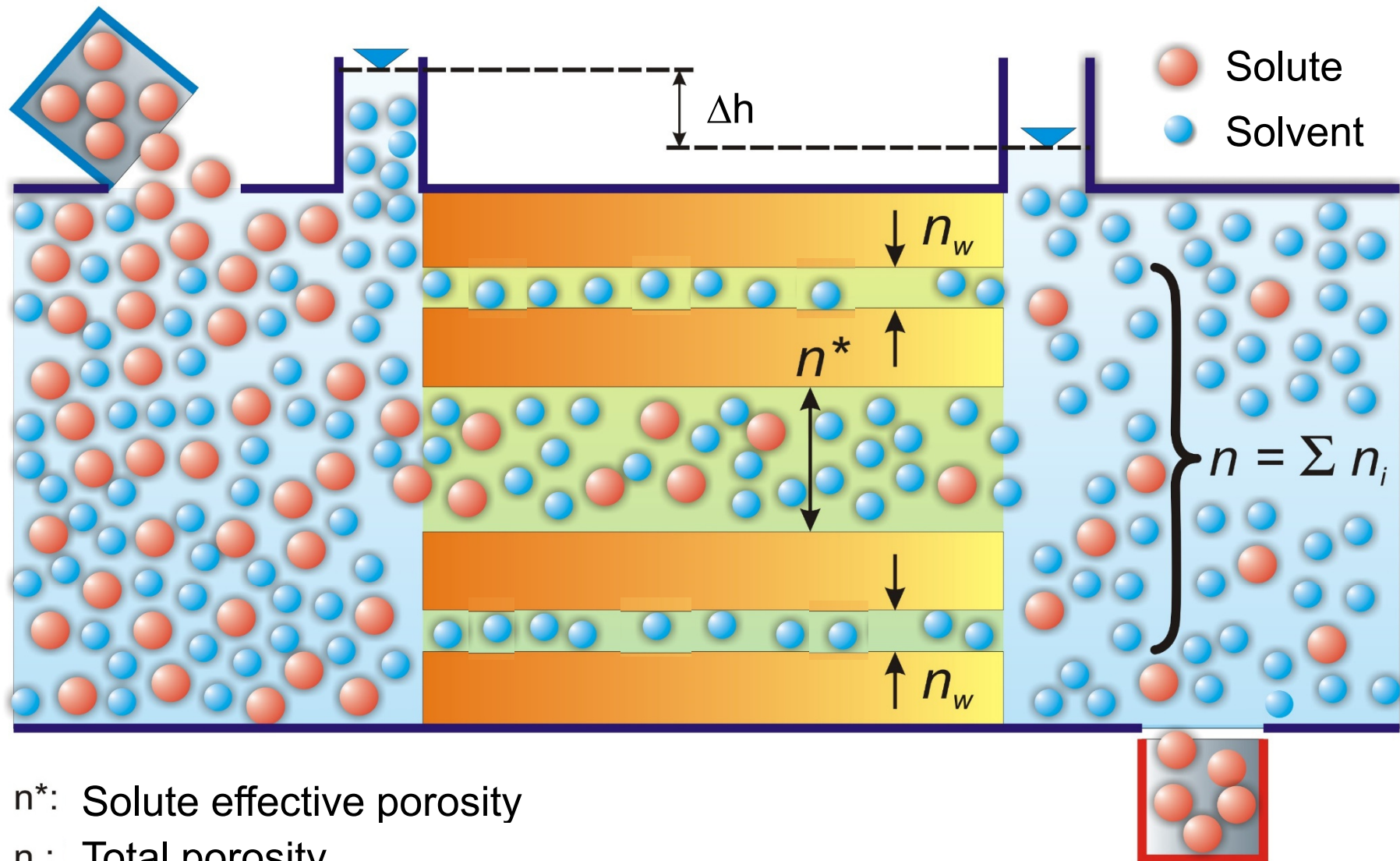
$$k_{\omega} = \left(\frac{q}{\Delta h} \right)_{\Delta c=0} \cdot L$$



$$\omega = \left(\frac{\Delta h}{\gamma_w \cdot v \cdot R \cdot T \cdot \Delta c} \right)_{q=0}$$

$$D_{\omega}^* = \left(\frac{J_s}{\Delta c} \right)_{q=0} \cdot \frac{L}{n}$$

PHYSICAL INTERPRETATION: MODEL 1



PHYSICAL INTERPRETATION: MODEL 1

Phenomenological coefficients interpretation:

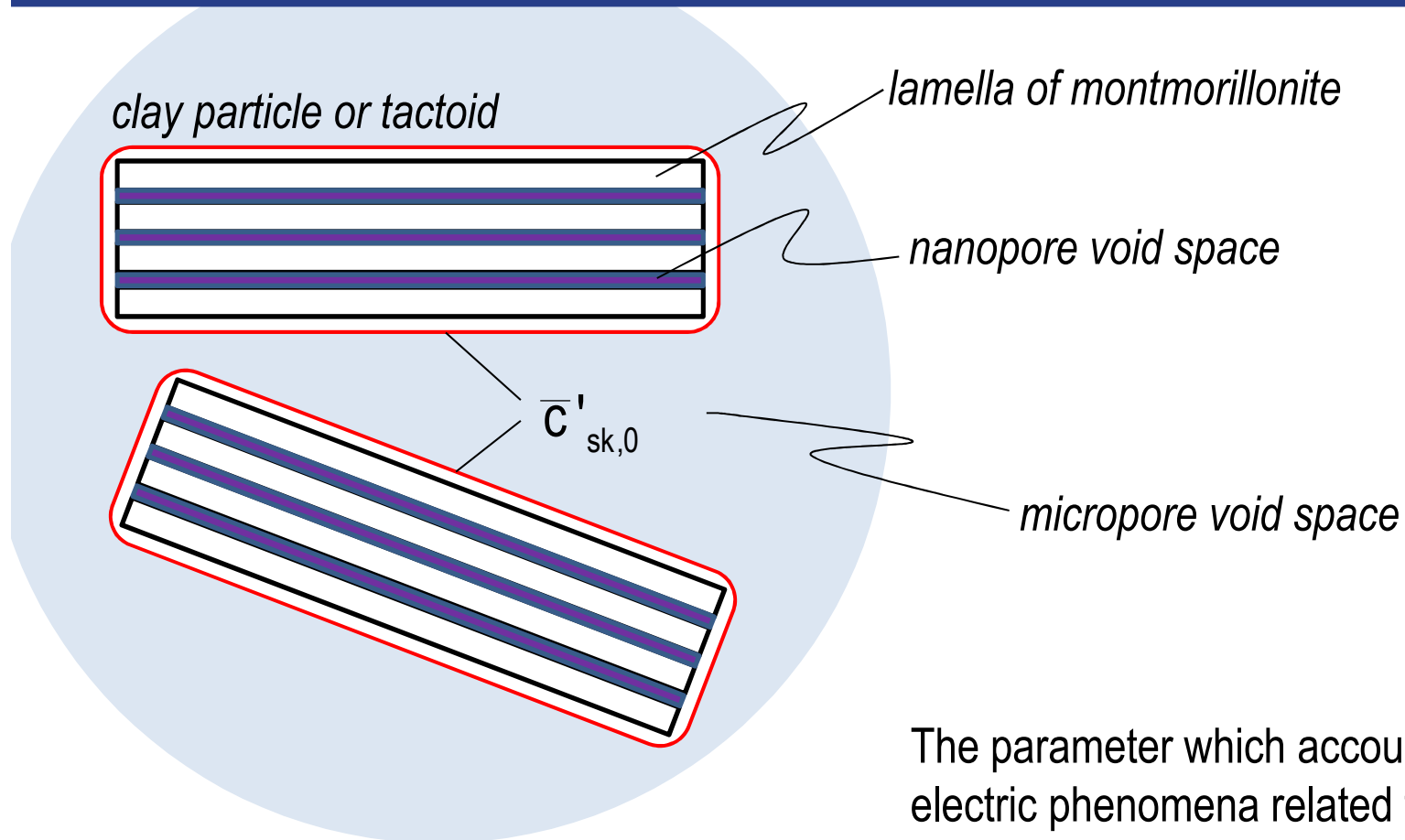
$$k_{\omega} = k$$

$$\omega = \omega' = 1 - \frac{n^*}{n}$$

$$D_{\omega}^* = \frac{n^*}{n} \cdot D_s^* = (1 - \omega) \cdot D_s^*$$



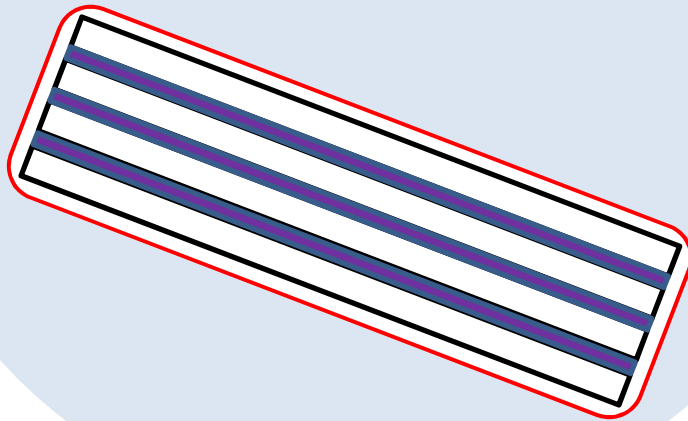
PHYSICAL INTERPRETATION: MODEL 2



The parameter which accounts for the electric phenomena related to the solid skeleton charge is the concentration (referred to solid volume) of the solid skeleton electric charge, $\bar{c}'_{sk,0}$.

PHYSICAL INTERPRETATION: MODEL 2

clay particle or tactoid



Introducing the following quantities:

e_m = micro-void ratio

N_l = average number of lamellae per clay particle

the solid skeleton electric charge concentration can be related to the basic physical properties of clay lamellae as follows:

$$\bar{c}'_{sk,0} = \frac{(1 - f_{Stern}) \cdot \sigma}{F} \cdot \rho_{sk} \cdot \frac{S}{N_l} \cdot \frac{e}{e_m}$$

F = Farady's constant (96,485 C·mol⁻¹);

f_{Stern} = fraction of surface electric charge compensated by the cations specifically adsorbed in the Stern layer (50-90 %)

σ = electric surface charge of montmorillonite lamellae (0.114 C·m⁻²);

ρ_{sk} = density of solid phase (2.65 g·cm⁻³);

S = total specific surface of montmorillonite lamellae (760 m²/g).



PHYSICAL INTERPRETATION: MODEL 2

Osmotic hydraulic conductivity

$$k_{\omega} = \frac{\tau_m}{3 \cdot \left[\mu_w + \underbrace{\mu_e(\bar{c}'_{0,sk})}_{\text{electroviscosity}} \right]} \frac{e^3}{(1+e)} \frac{\gamma_w}{(\rho_{sk} \cdot S_e)^2}$$

Reflection coefficient (chemico-osmotic efficiency coefficient)

$$\omega = \omega' = 1 - \frac{1}{\sqrt{\left(\frac{\bar{c}'_{sk,0}}{2 \cdot e \cdot c} \right)^2 + 1 + (2 \cdot t_1 - 1) \left(\frac{\bar{c}'_{sk,0}}{2 \cdot e \cdot c} \right)}} \quad t_1 = \frac{D_{0,1}}{D_{0,1} + D_{0,2}}$$

Osmotic effective diffusion coefficient

$$D_{\omega}^* = \frac{D_s^*}{\sqrt{\left(\frac{\bar{c}'_{sk,0}}{2 \cdot e \cdot c} \right)^2 + 1 + (2 \cdot t_1 - 1) \left(\frac{\bar{c}'_{sk,0}}{2 \cdot e \cdot c} \right)}} = (1 - \omega) \cdot D_s^*$$

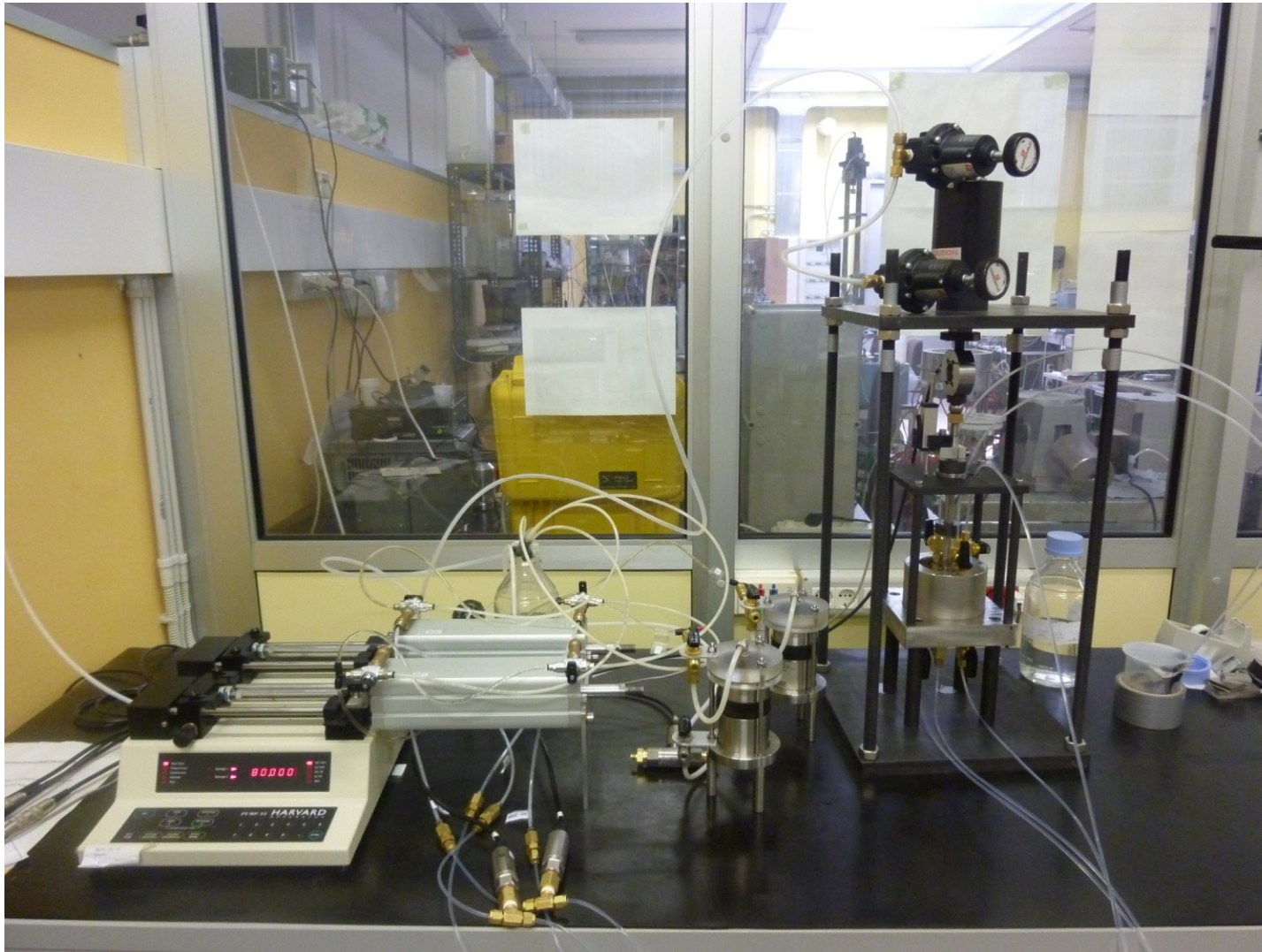


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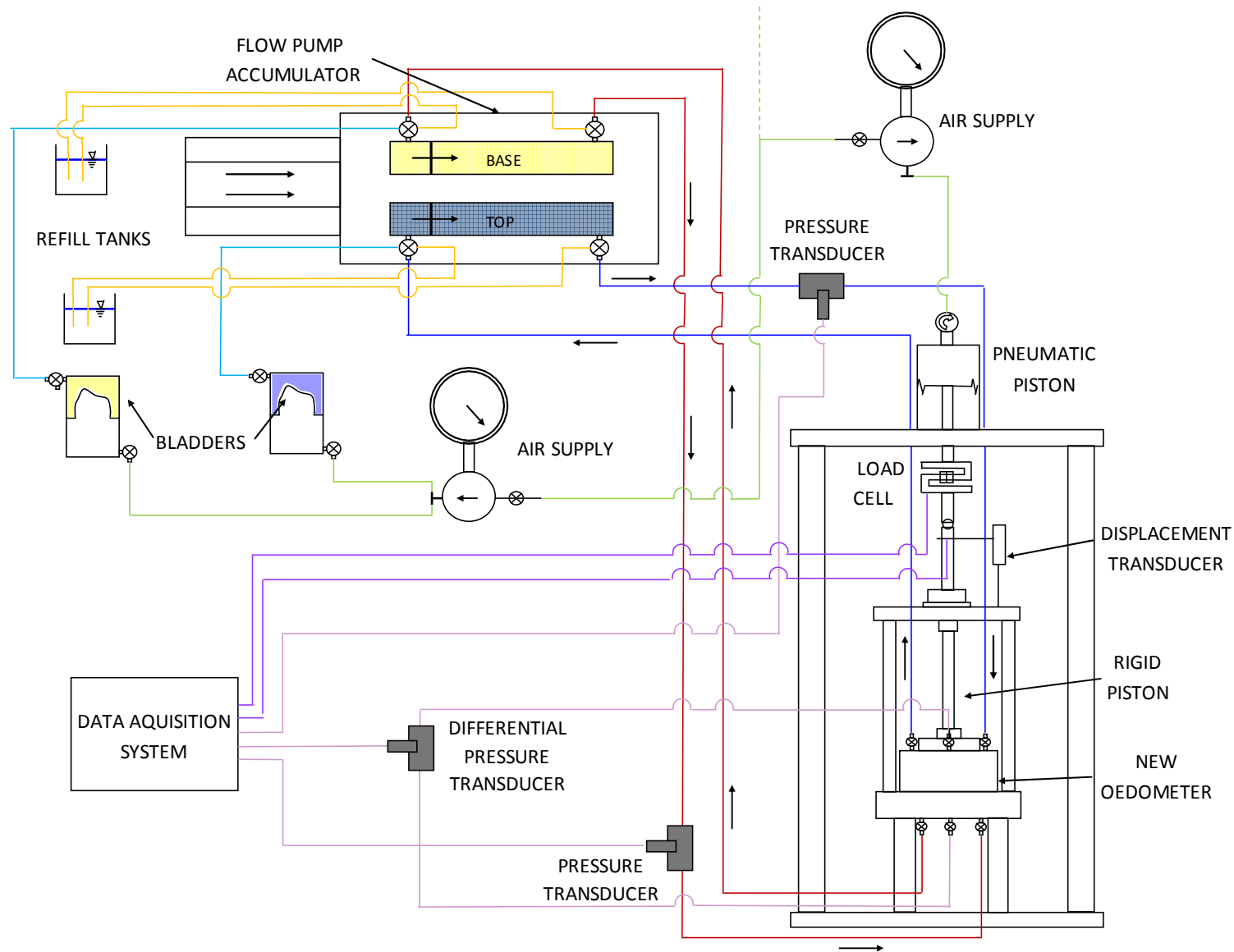


LABORATORY APPARATUS

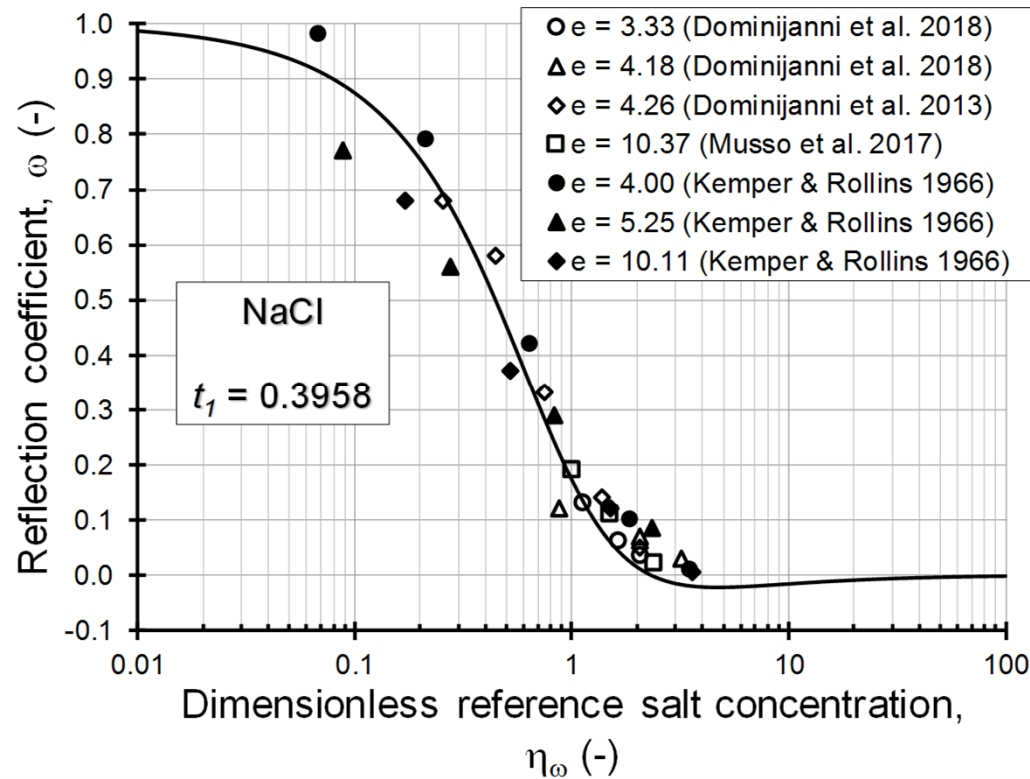


A. Dominijanni – 27th EYGEC, 26-27 September 2019, Bodrum, Turkey

LABORATORY APPARATUS



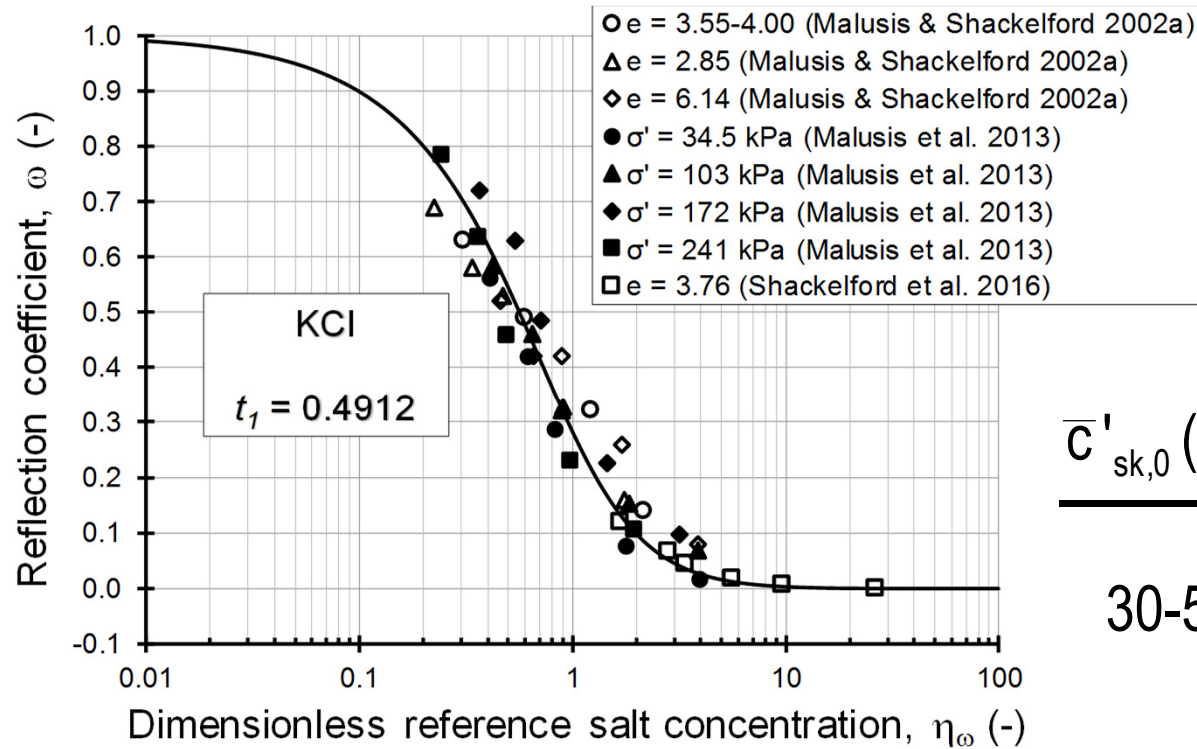
EXPERIMENTAL RESULTS



$\bar{c}'_{sk,0}$ (mM)	Sample	Ref.
80-110	Initially dry bentonite	Dominijanni et al. (2013) and (2018) Musso et al. (2017)
225	Consolidated slurry	Kemper and Rollins (1966)



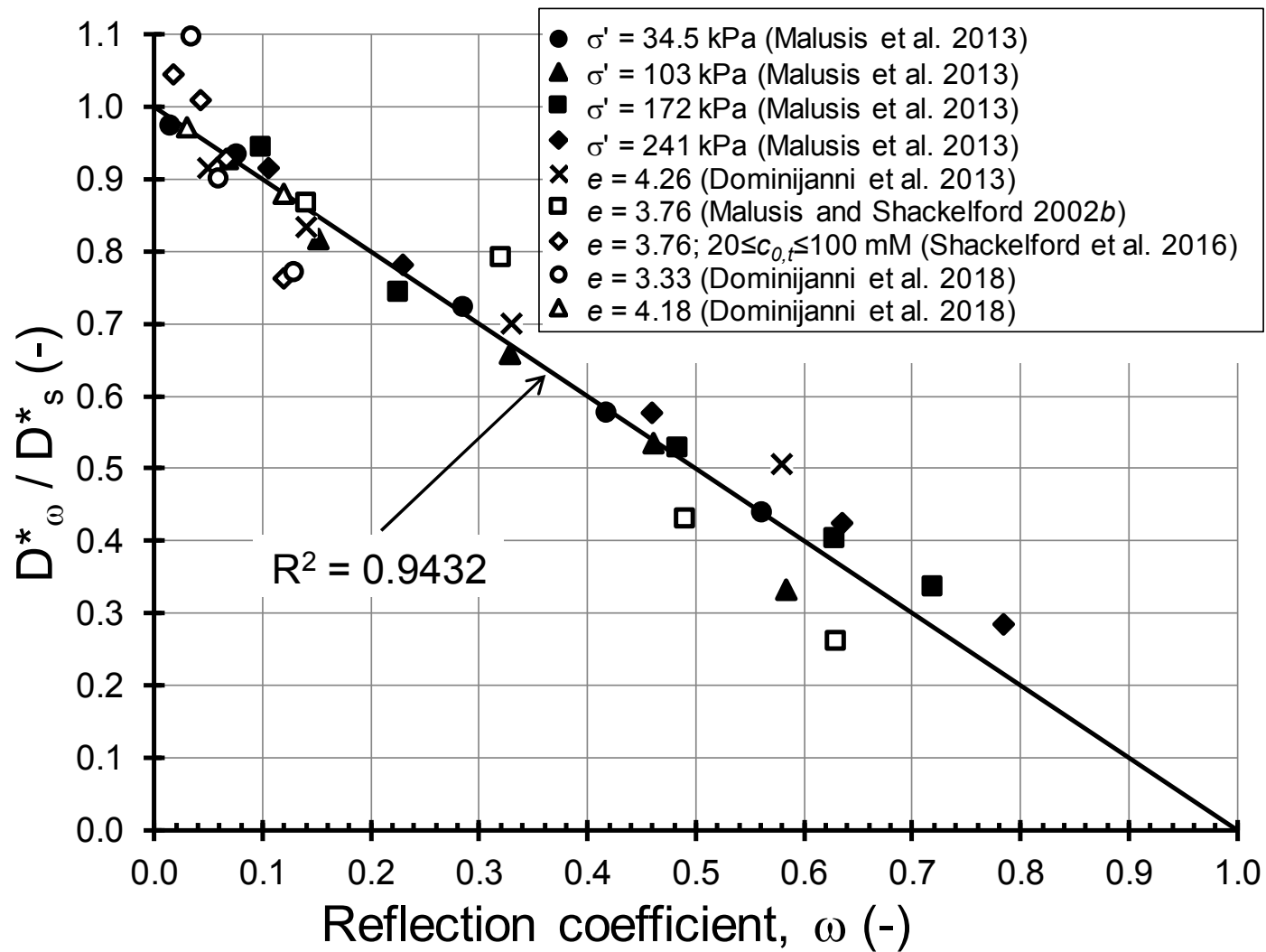
EXPERIMENTAL RESULTS



$\bar{c}'_{sk,0}$ (mM)	Sample	Ref.
30-50	Needle-punched GCL	Malusis and Shackelford (2002), Malusis et al. (2013), Shackelford (2016)



EXPERIMENTAL RESULTS

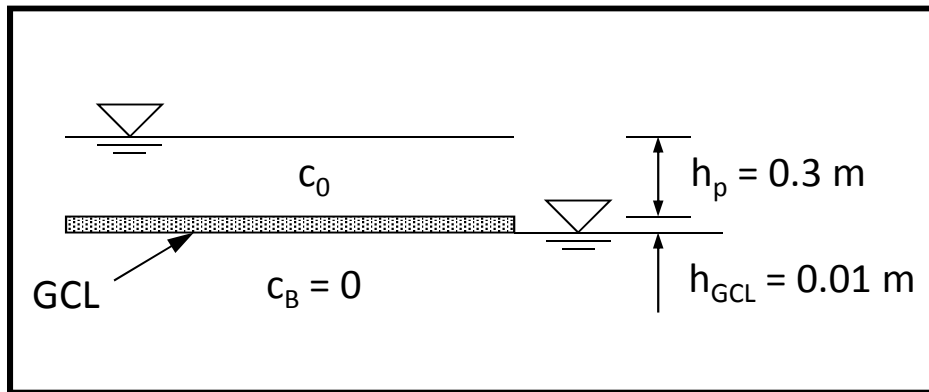


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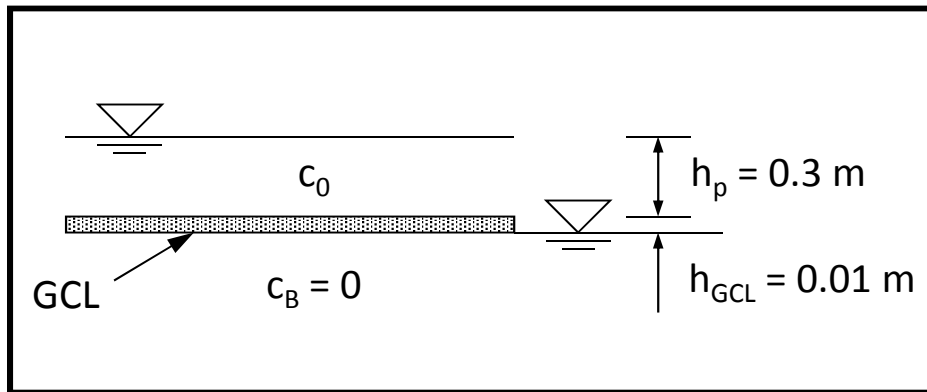
GEOSYNTHETIC CLAY LINER



$$\Delta h = h_p + L_{\text{GCL}} = 0.31 \text{ m}$$

$$i_h = \frac{\Delta h}{L} = 31$$

GEOSYNTHETIC CLAY LINER



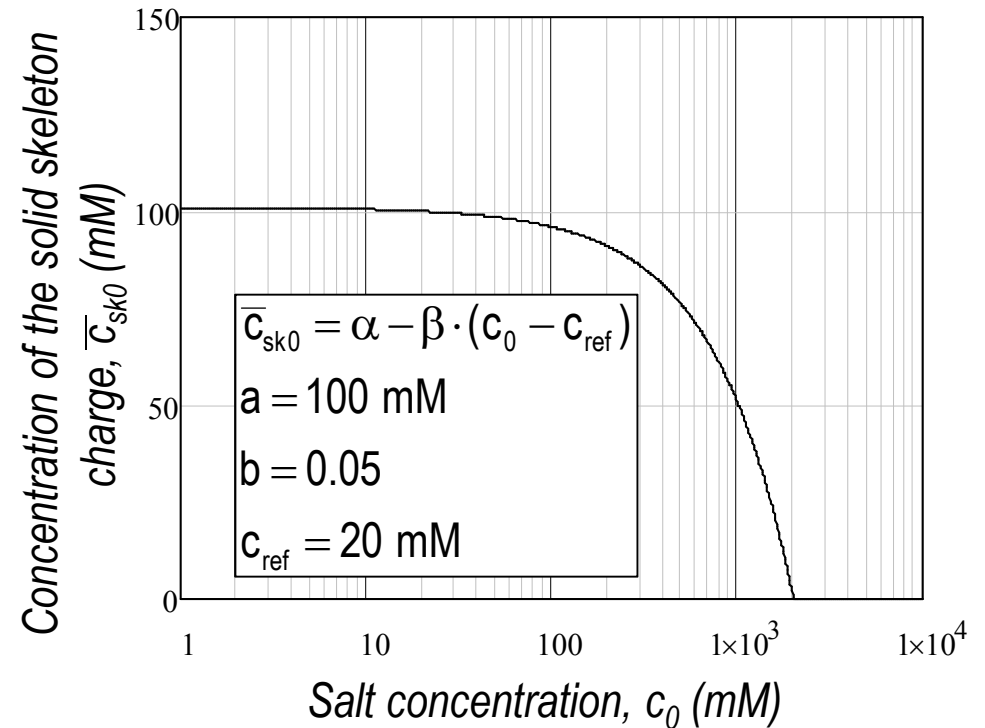
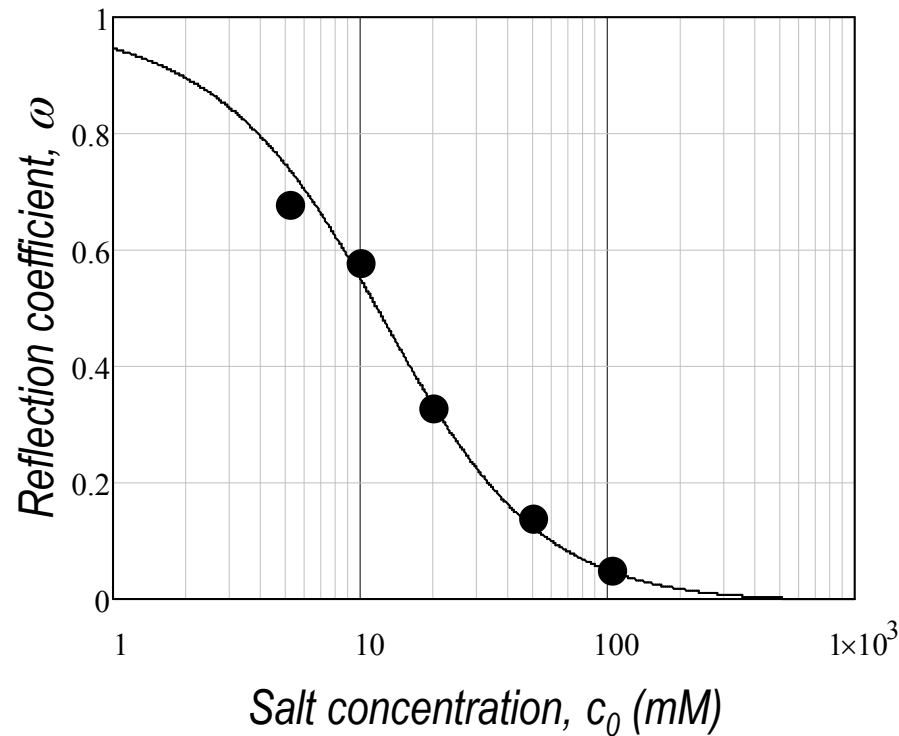
$$\Delta h = h_p + L_{GCL} = 0.31 \text{ m}$$

$$i_h = \frac{\Delta h}{L} = 31$$

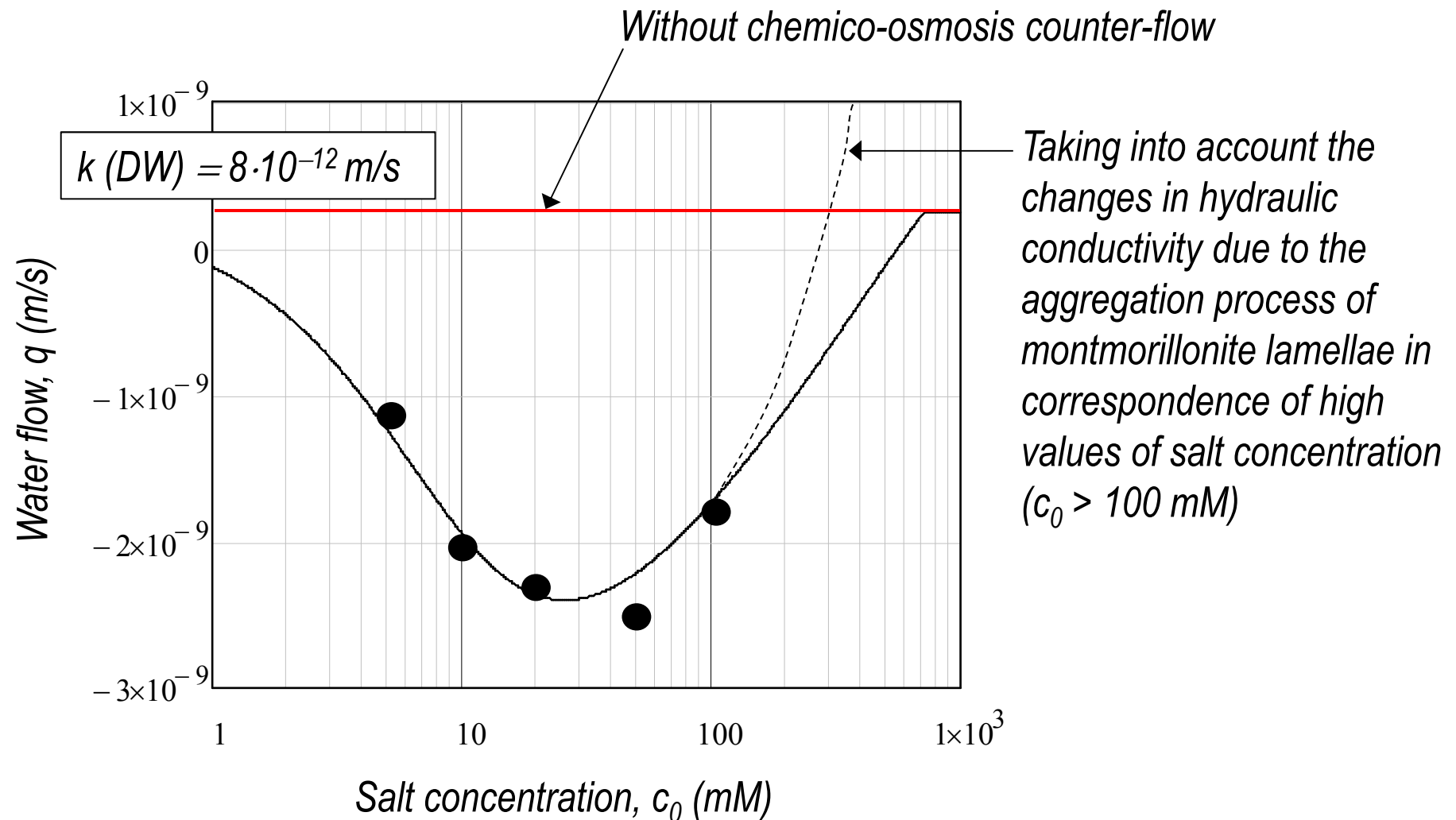
c_0 (mM) (NaCl)	ω Dominijanni et al. (2013)	$\Delta h = -\omega \frac{vRTc_0}{\gamma_w}$ (m) <i>Equivalent</i>	$i_\pi = -\omega \frac{vRTc_0}{\gamma_w \cdot L}$
5 (5.14)	0.68	-1.74	-174
10 (9.94)	0.58	-2.86	-286
20 (19.58)	0.33	-3.21	-321
50 (49.67)	0.14	-3.45	-345
100 (103.24)	0.05	-2.56	-256



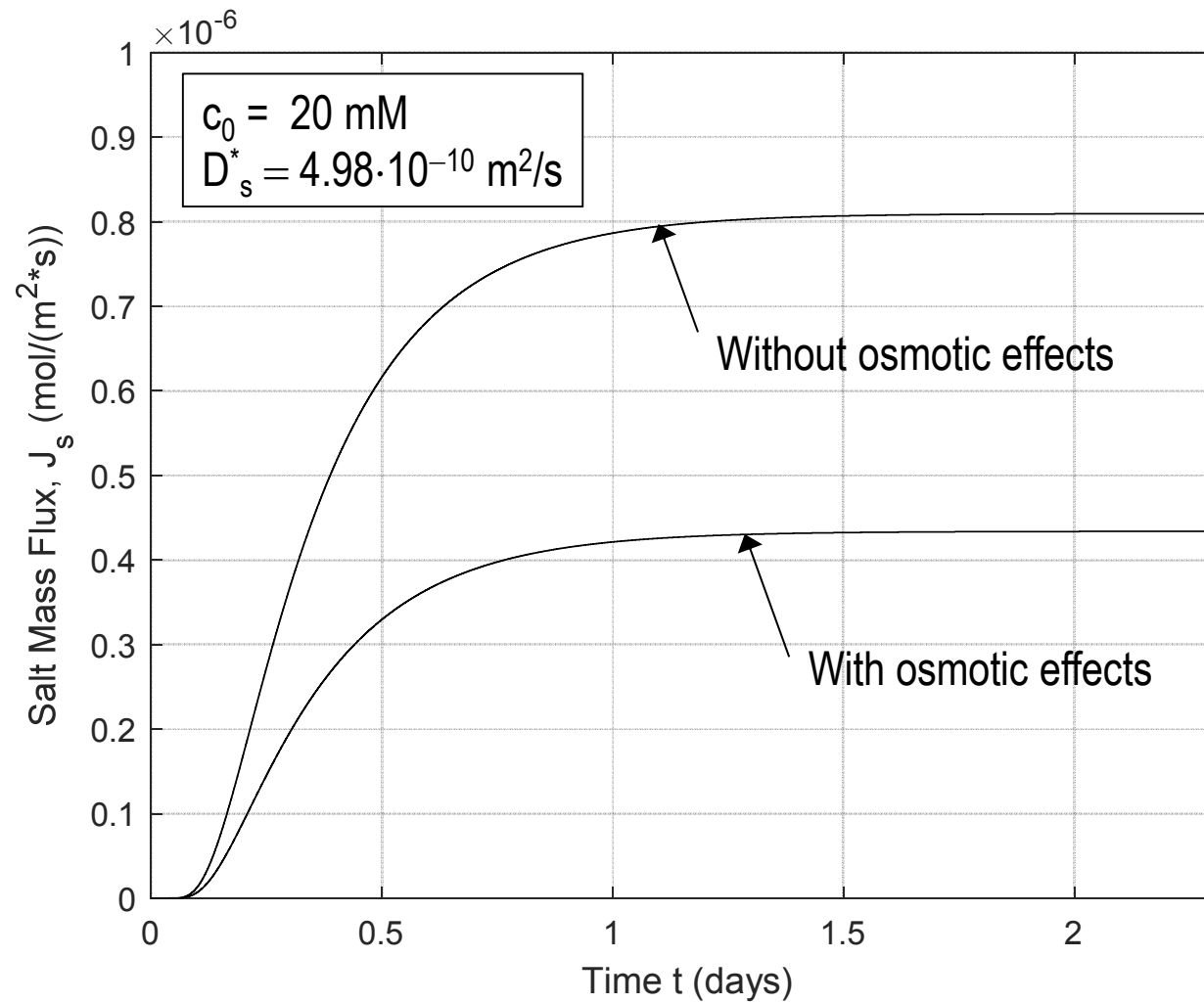
GEOSYNTHETIC CLAY LINER



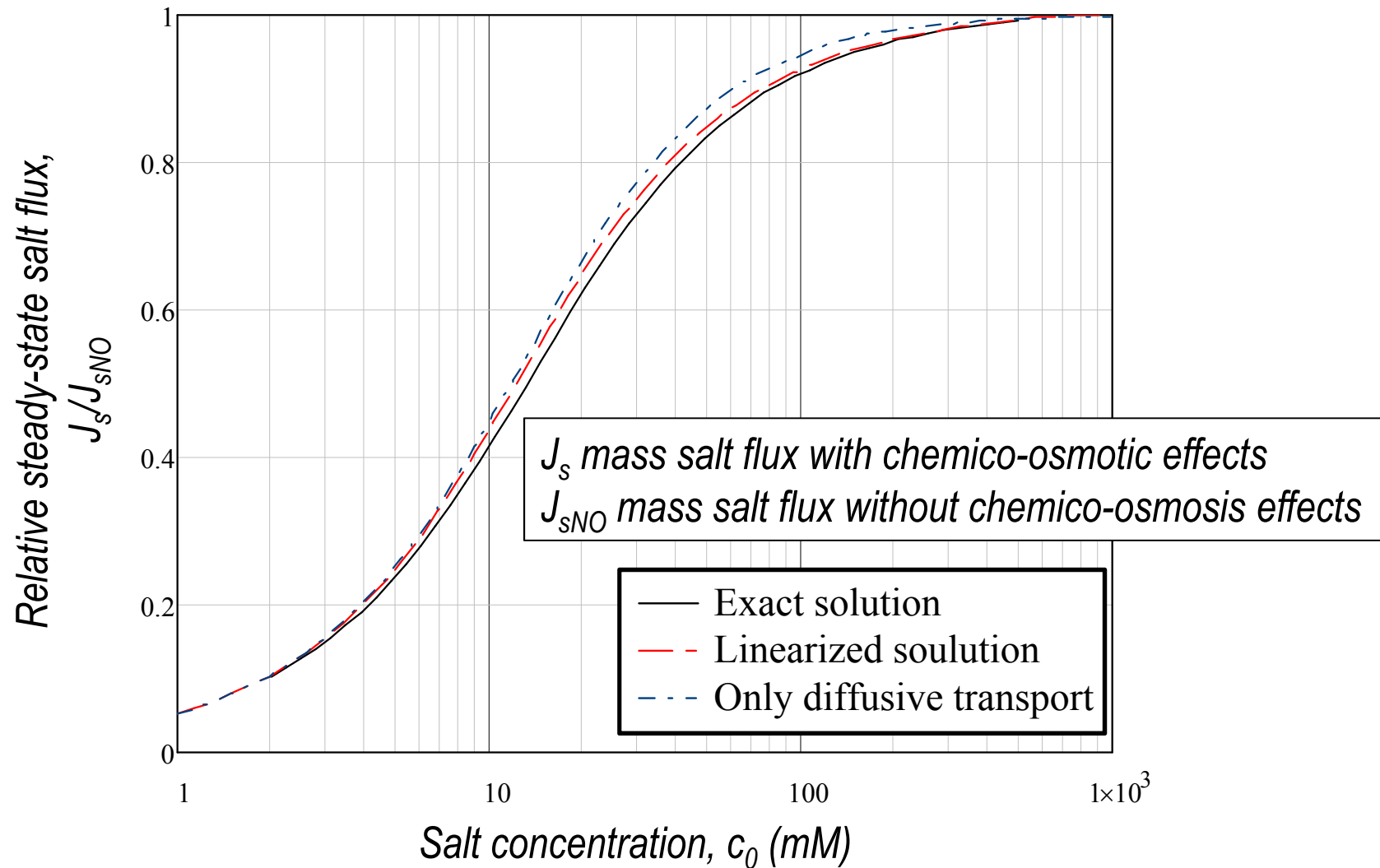
GEOSYNTHETIC CLAY LINER



GEOSYNTHETIC CLAY LINER



GEOSYNTHETIC CLAY LINER

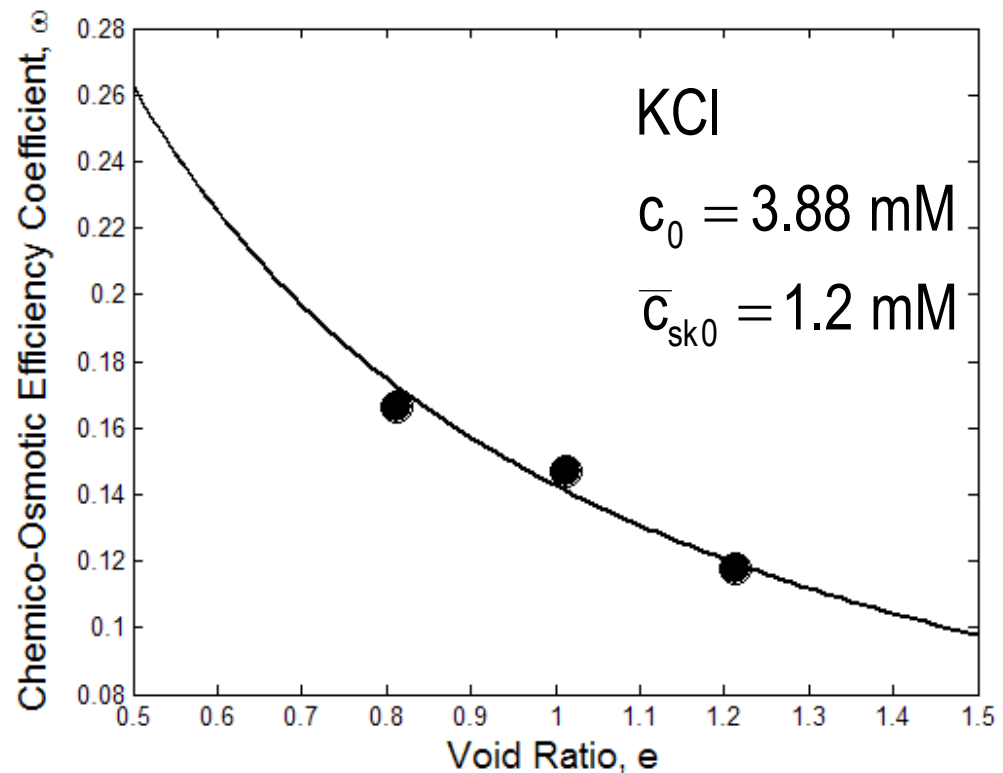


CUTOFF WALL

Data from: Yeo, Shackelford and Evans (2005). Membrane Behavior of Model Soil–Bentonite Backfills, *Journal of Geotechnical and Geoenvironmental Engineering*, 131(4), 418-429.

Sand-bentonite back-fill mixture: mixture of sand with 5% by weight of dry sodium bentonite.

Specimens of the base soil were mixed with a sufficient amount of bentonite-water slurry to correspond to 100-mm slump in accordance with standard practice for SB vertical cutoff walls.

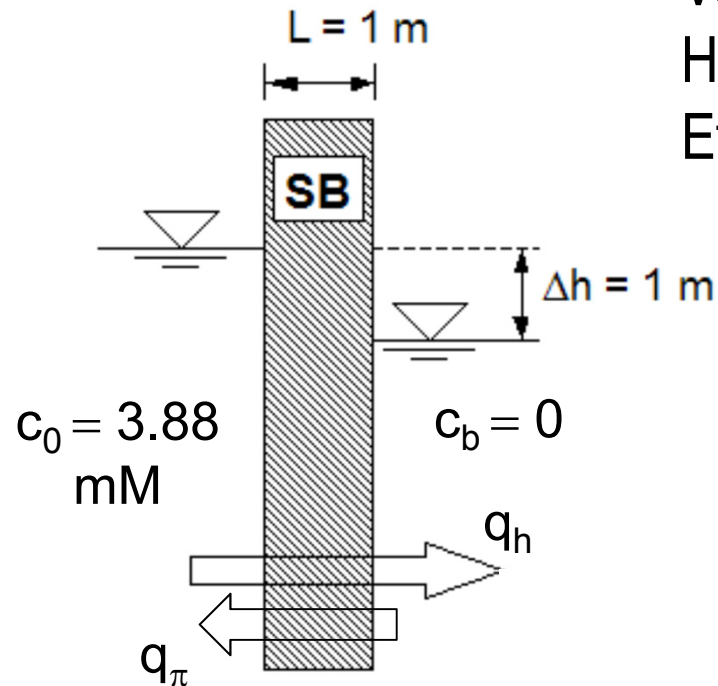


CUTOFF WALL

Void ratio, $e = 1$

Hydraulic conductivity $k = 1.5 \cdot 10^{-10} \text{ m/s}$

Effective diffusion coefficient $D_s^* = 2.7 \cdot 10^{-10} \text{ m}^2/\text{s}$



$$q_h = k \cdot \frac{\Delta h}{L} = 1.5 \cdot 10^{-10} \frac{\text{m}}{\text{s}}$$

$$q_\pi = -\omega \cdot \frac{k \cdot v \cdot R \cdot T \cdot c_0}{\gamma_w \cdot L} = -4.1 \cdot 10^{-11} \frac{\text{m}}{\text{s}}$$

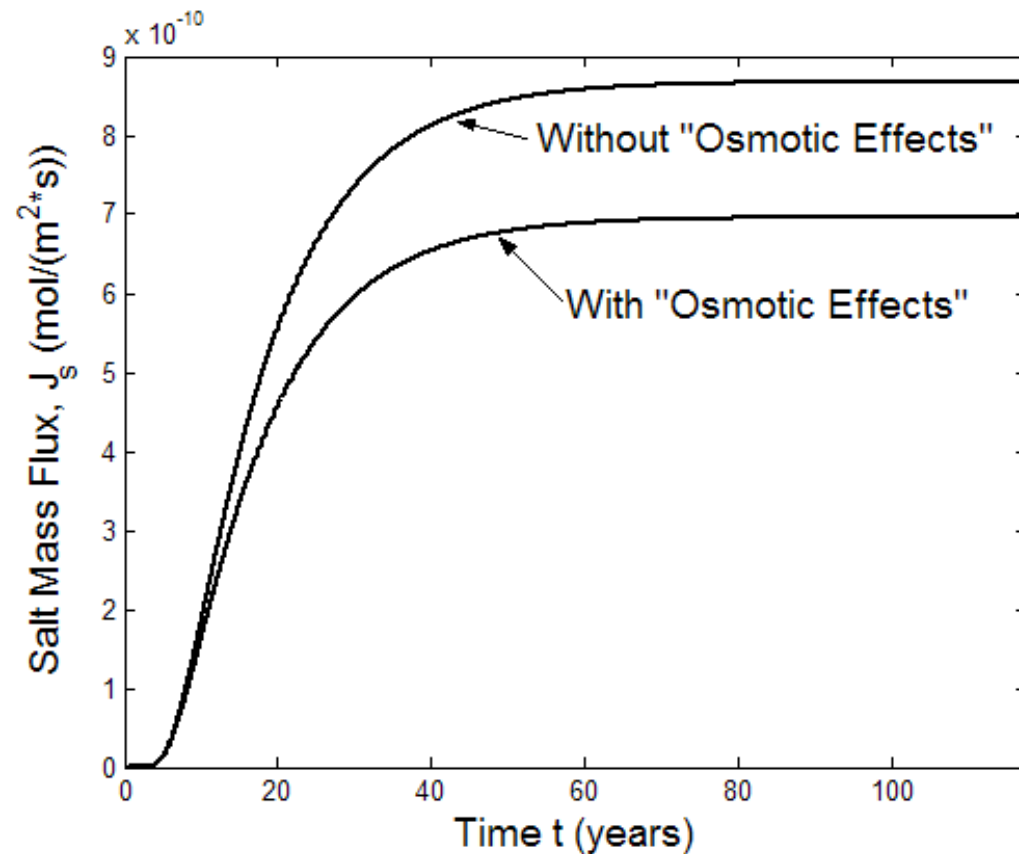
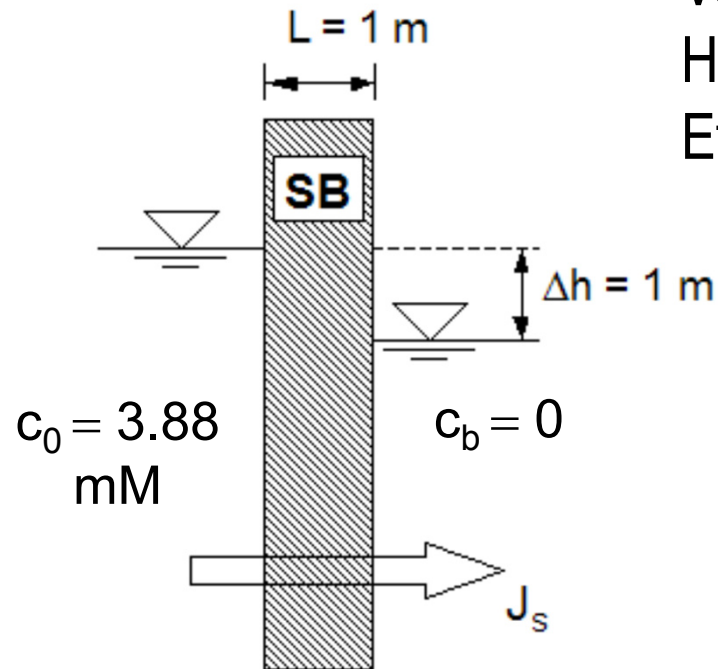


CUTOFF WALL

Void ratio, $e = 1$

Hydraulic conductivity $k = 1.5 \cdot 10^{-10}$ m/s

Effective diffusion coefficient $D_s^* = 2.7 \cdot 10^{-10}$ m²/s



CONCLUSIONS

- Bentonites are characterized by a microscopic lamellar structure with a high specific surface, which is indicative of the prevalence of the surface forces of electric nature with respect to the self-weight forces.
- Solute restriction, which is determined by the interaction of the charged ions with the negatively charged clay particles, produces the so-called chemico-osmotic phenomena at the macroscopic scale.
- To model such phenomena the standard advective-diffusion transport theory is not sufficient and we need to develop a coupled flow theory.
- The phenomenological parameters of the coupled flow theory have to be measured with macroscopic experimental tests and can be interpreted through physically-based models.



CONCLUSIONS

- An advanced model has been developed in order to relate the phenomenological parameters to the basic physical and chemical properties of the bentonite.
- In this model the electric phenomena at the micropore-scale are taken into account via a single parameter, $\bar{c}'_{sk,0}$, that represents the concentration of the solid skeleton electric charge.
- $\bar{c}'_{sk,0}$ may be determined by fitting the experimental values of the reflection coefficient as a function of the salt concentration or the void ratio.
- Based on the experimental data available and the related theoretical interpretations, the chemico-osmotic effects are shown to play a very significant role in the assessment of the performance of the bentonite-based barriers for the contaminant containment.



Chemico-Osmotic Effects in Bentonite-Based Barriers for Containment Applications

***THANK YOU VERY MUCH
FOR YOUR ATTENTION***

