Hydro-chemical effects on clay permeability for nuclear waste disposal

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Abstract: A geological disposal facility (GDF) is globally recognised as a sustainable solution for managing nuclear waste. Bentonite clay, with its low permeability and self-sealing capabilities, is the leading candidate for engineered barriers in GDFs. However, groundwater salinity presents significant challenges by suppressing the bentonite's swelling behaviour, potentially compromising the barrier functionality. As swelling is closely linked to the movement and distribution of moisture within the bentonite's dual-porosity structure, this study investigates the effects of salinity on its saturated and unsaturated hydraulic behaviour. A modified Kozeny-Carman (K-C) equation is proposed, incorporating salinity effects through changes in macroporosity and effective specific surface area. The model predictions align with experimental data, revealing an increased permeability under saline conditions due to a reduction in microstructural swelling. The proposed modifications are implemented within a fully coupled thermo-hydro-mechanical (THM) numerical framework to simulate hydro-chemical interactions. The model allows for prediction of bentonite performance under saline conditions, offering valuable insights for ensuring the long-term reliability of GDFs in diverse geological environments.

Introduction

Compacted bentonite clay is widely regarded as the lead candidate for engineered barriers in geological disposal facilities (GDFs) for high level waste and spent nuclear fuel due to its favourable properties such as low permeability, high swelling capacity, and self-sealing abilities. These characteristics enable it to isolate nuclear waste, minimise container corrosion and retard radionuclide migration. However, its long-term performance is governed by complex thermal, hydraulic, mechanical, and chemical (THMC) interactions, especially in saline groundwater conditions. This can be a concern in geological environments rich in soluble carbonates or evaporites, where salinity can exceed seawater concentrations (>35,000 mg/L). While bentonite's behaviour in freshwater is well-studied, its performance under saline conditions remains less understood. This knowledge gap is critical, as salinity significantly diminishes swelling capacity, a property essential for the reliability of the barrier in GDFs.

The main challenge in modelling bentonite's behaviour under complex THMC boundary conditions is its complex pore structure, consistng of microstructure (interlayer spaces between unit layers, occupied by exchangeable cations and water) and macrostructure (pore spaces between aggregates and between particles [1]), as shown in Figure 1. This dual-porosity structure plays a central role in governing its hydraulic and mechanical properties, which are inherently coupled and sensitive to environmental changes.

Bentonite, primarily composed of montmorillonite, exhibits swelling governed by two key mechanisms: crystalline swelling and osmotic swelling [2]. The former occurs as montmorillonite's charged surfaces attract water into interlayer spaces, while the latter arises from concentration gradients between interlayer and external water, driving water migration into the interlayers. Both mechanisms are microstructural phenomena that are closely related to changes in its hydraulic properties, where the distribution and movement of water within the pore structure dictate the expansion and shrinkage of clay.
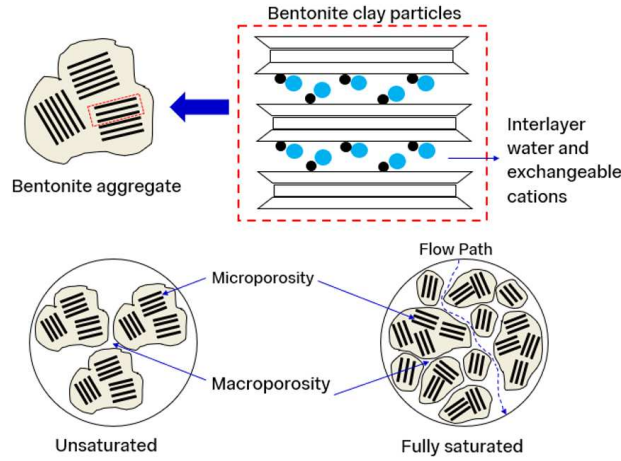

Figure 1: Schematic of the dual pore structure of compacted bentonite (adapted from [3]).

Developing robust models to capture this coupling under high-salinity conditions is therefore critical. This paper is part of a study aimed at addressing this knowledge gap by developing predictive models that explicitly account for the effects of salinity on bentonite's hydraulic behaviour. The permeability model proposed here incorporates the dual-porosity structure of bentonite, where salinity-induced changes at micro- and macrostructural level are reflected in the permeability calculations.

Literature Review

Salinity effects on bentonite behaviour

Recent experimental investigations show that subjecting bentonite clay to salinity leads to alteration of its mechanical, hydraulic and thermal properties. Swelling is noticeably suppressed with increasing concentration of total dissolved solids, TDS, while saturated permeability increases with increasing TDS (e.g [4]). However, increasing the dry density of bentonite seems

to counteract these effects [5], as higher dry density leads to increased swelling (due to greater swelling clay content per unit volume) and reduced permeability (from compaction of clay particles) (Figures 2a and 2b, respectively).

<div align="center">(a)</div>
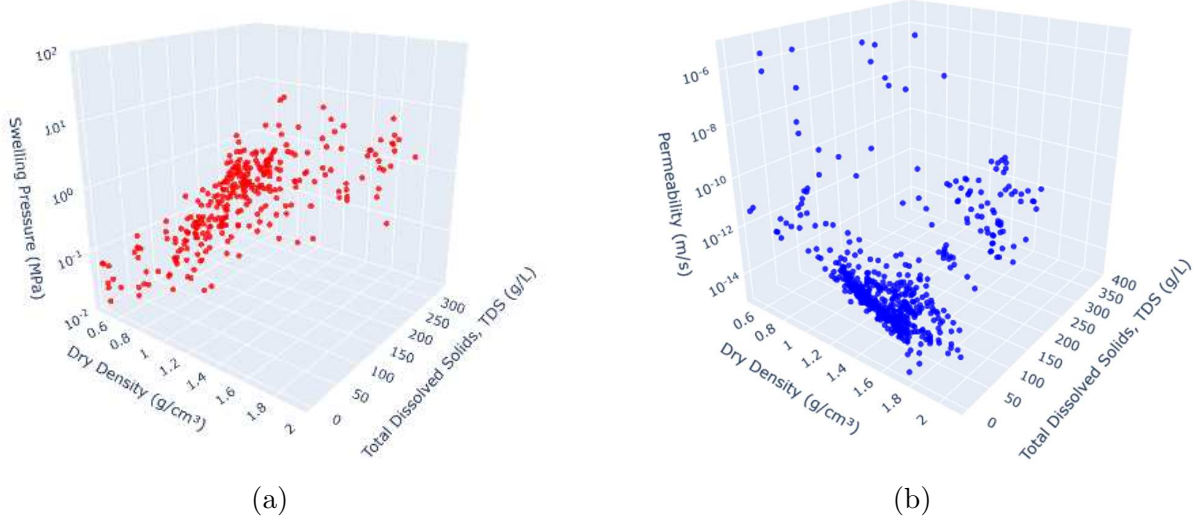

<div align="center">(b)</div>

Figure 2: Relationship of (a) swelling pressure and (b) saturated permeability of various types of compacted bentonite with dry density and total dissolved solids of pore fluid.

Salinity suppresses swelling by reducing both crystalline and osmotic swelling. Higher ion concentration in pore water lowers the chemical potential gradient, reducing interlayer water uptake. Besides, salt ions neutralize the negative charges on montmorillonite surfaces, reducing the Double Diffuse Layer (DDL) thickness and decreasing overall swelling. With reduced invasion of micropores into the macropore space, the volume of macropores available for water flow increases, leading to higher permeability.

Most studies focus on salinity's impact on saturated permeability, with limited attention to its effects on the suction related permeability. Salinity-induced pore structure changes are likely to affect this relationship, critical for moisture movement and swelling pressure development as bentonite saturates in GDFs. This underscores the need for further investigation in this area.

Prediction of saturated permeability for clay soils

The Kozeny-Carman (K-C) expression [6] (Equation 1) is a well-known and established relationship of the permeability of porous media with respect to their porosity, specific surface area (SSA) and tortuosity. The equation is based on the Poiseuille's law, which describes water flow through an assembly of capillary tubes [7].

$$k_{\mathrm{sat}} = \frac{\gamma_w}{\mu_w} \cdot \frac{C_s}{\tau^2 A_{\mathrm{total}}^2 \rho_d^2} \cdot \frac{n_{\mathrm{total}}^3}{(1 - n_{\mathrm{total}})^2} \tag{1}$$

where γ_{w} is the unit weight of water (N/m^3); μ_{w} is the dynamic viscosity of water (N·s/m^2); C_s is a shape constant, where a typical value of 0.2 for soils is adopted [8]; τ refers to the

<div align="center">3</div>

tortuosity of saturated clay; n_{total} is the total porosity; A_{total} is the total specific surface area (m^2/g); and ρ_{d} is the dry density of the soil (g/cm^3).

The K-C equation is generally recognised to work well for coarse-grained soils but not so for fine-grained soils like bentonite [8]. In bentonite, not all pores within the clay fabric are available for fluid flow, as they are either too small or disconnected [3]. Additionally, micropores usually contribute minimally to water flow as they mainly contain immobile adsorbed water [9].

The abundant literature discusses the modification of the K-C equation for application to clay soils. The two main parameters to redefine are the SSA and porosity. The SSA should refer to the contact area between the pore fluid and soil particles, while the porosity is the pore space available for water flow. Based on this, a modified K-C equation [3] is proposed in Equation 2:

$$k_{\text{sat}} = \frac{\gamma_w}{\mu_w} \cdot \frac{C_s}{\tau_{\text{macro}}^2 A_{\text{eff}}^2 \rho_d^2} \cdot \frac{n_{\text{macro}}^3}{(1 - n_{\text{macro}})^2} \tag{2}$$

where τ_{macro} refers to the tortuosity of saturated macropores; n_{macro} is the macroporosity; and A_{eff} is the effective specific surface area (m^2/g).

Many studies agree that instead of total porosity, only macroporosity should be considered, e.g. [3], since the fluid's movement in micropores is limited. Generally, macropores are pore volume excluding the interlayer pore volume. There is a multiplicity of approaches to determine the interlayer pore volume, such as the solid solution model [1] and saturated basal spacing [10]. Other studies define macropores as the pore space excluding the immobile adsorbed water (e.g. [11]), or as calculated from experiments using Mercury Intrusion Porosimetry (MIP) [7].

For defining A_{eff}, many studies suggest using only the external SSA, A_{ext} [3], which can be experimentally measured through gas adsorption methods, or calculated based on empirical models [3]. Some studies provided a more theoretical approach in determining A_{eff}, such as calculating the surface area of clay particles with adsorbed water [11]. Finally, some studies [7] suggest that A_{eff} which excludes any blind, unconnected or small pores can be measured experimentally via MIP combined with the freeze-drying method.

There are limited studies exploring how salinity effects can be incorporated into the K-C equation. Achari et al. [12] proposed a cluster model to predict permeability by correcting the K-C equation based on microporosity and the number of clay particles per cluster, N, with an empirical relationship linking N to solute concentration. While effective for low ion concentrations, the model's accuracy diminishes at higher salinity levels.

Unsaturated permeability function for unsaturated soils

For unsaturated soils, permeability is a function of its suction [13]. Direct measurement of permeability via laboratory methods can be expensive and time consuming, hence a practical approach is to estimate it indirectly. Mualem [14] proposed an approach where the unsaturated permeability is related to its saturated and relative parts (Equation 3 and 4).

$$k_{\text{unsat}} = k_{\text{r}} k_{\text{sat}} \tag{3}$$

$$k_{\mathrm{r}} = \left(\frac{\theta - \theta_{\mathrm{res}}}{\theta_{\mathrm{sat}} - \theta_{\mathrm{res}}} \right)^{\alpha} \tag{4}$$

where θ_{sat} and θ_{res} refer to the saturated and residual volumetric water content respectively, while α is a constant. However, Chen et al. [3] argued that only water flow within the macropore space contributes significantly to overall permeability. They proposed modifying Equation 4 to evaluate the permeability function based on the degree of saturation in the macroporosity, as shown in Equation 5.

$$k_{\mathrm{r}} = \left(\frac{\theta_{\mathrm{macro}} - \theta_{\mathrm{macro,res}}}{\phi_{\mathrm{macro}} - \theta_{\mathrm{macro,res}}} \right)^{\alpha} \tag{5}$$

where θ_{macro} is the volumteric water content of the macroporosity, calculated by subtracting the microporosity, ϕ_{micro}, from the total volumetric water content, θ_{total}, and $\theta_{\mathrm{macro,res}}$ refers to the residual volumetric water content of the macroporosity. This modified equation more accurately estimates how permeability changes with suction, as the conventional equation (Equation 4) tends to overestimate it by considering total porosity for flow.

Theory

Modified Kozeny-Carman equation with salinity considerations

The study in this paper builds on the insights from the literature, by explicitly incorporating salinity effects into Equation 2. This modified K-C equation with salinity considerations reflects the salinity-induced changes in the microporosity, macroporosity, and A_{eff}.

The presence of salinity can be expressed via osmotic suction. Experimental evidence by [15] has shown how the number of stacks of unit layers per clay particles, n, changes with total suction (summation of matric suction and osmotic suction). Since $A_{ext} = A_{total}/n$ [3], the increase in salinity (osmotic suction) would cause an increase in n and thus a decrease in A_{ext}. However, this empirical model is developed based on hydration and dehydration tests, which may differ physically from salinisation and desalinisation of clay, introducing inaccuracy in the predicted saturated permeability, especially for the saline case.

Kobayashi et al. [11] defined porosity and A_{eff} based on the two-layer hydration state, with the corresponding water content, w^{*}, determined by X-ray diffraction (XRD) analysis. Micro-voids are calculated as $e_{micro} = w^{*} \cdot G_{s}$. It is hypothesised that absorbed water in the microstructure decreases as salinity increases, thus reducing w^{*}. This reduction leads to a decrease in e_{micro} and A_{eff}. Incorporating these effects into the K-C equation allows for a more accurate description of the observed increase in saturated permeability with salinity, providing a framework to quantify the impact of chemical interactions on hydraulic properties.

Unsaturated permeability function with salinity considerations

Limited studies have examined the effects of salinity on the permeability of bentonite. However, Chen et al. [3] introduced a modified unsaturated permeability function that isolates the macroporosity component, excluding the microstructural contribution where flow is negligible.

The usefulness of this approach lies in its ability to reflect salinity effects when coupled with a saturated permeability model that accounts for changes in micro- and macroporosity under varying salinity conditions. This approach effectively captures salinity-induced changes in water flow by linking pore structure evolution to permeability.

Methodology

The finite element (FE) software ICFEP (Imperial College Finite Element Program) [16, 17] is employed for the numerical analyses in this study. The software has a fully coupled THM formulation for saturated [18] and unsaturated [19] soils. A dual-porosity constitutive model, the Imperial College Double Structure Model (ICDSM) [20] is employed for modelling bentonite clays. For the permeability model, saturated values were obtained from the modified K-C equation with salinity considerations. This means that the values of n_{macro} and A_{eff} are calculated based on w^*, which is evaluated using the equations introduced in [11], with experimental values obtained from XRD analyses for different types of bentonite. w^* is a function of the bentonite dry density and montmorillonite content, χ_{mnt}, as shown in Table 1.

Table 1: Derived equations for two-layer hydration water content based on XRD analyses.

Material	Equation
Na-bentonite	$w^* = 0.01\chi_{mnt}/(0.052+3.8\times10^{-6}\chi_{mnt}\rho_d^{12.1\chi_{mnt}})$
Ca-bentonite	$w^* = 0.01\chi_{mnt}/(0.066+2.6\times10^{-7}\chi_{mnt}\rho_d^{15.16\chi_{mnt}})$

For saline case, it is hypothesised that the hydration layer would transition from two layer to one layer, hence, based on the different dry densities and montmorillonite content, the value of w^* would decrease with TDS, and is halved at high TDS of around 350 g/L.

To model the unsaturated nature of the problem, the modified permeability function (Equation 5) was used, while for the retention behaviour, a simple van Genutchen type non-hysteretic model was employed, with derived parameters obtained from [20].

Numerical Analyses and discussion

In this study, FE analyses simulated constant volume swelling tests on unsaturated compacted FEBEX bentonite [21] ($\rho_d = 1.65\ g/cm^3$, $\chi_{mnt} = 0.92$) and MX80 bentonite [22] ($\rho_d = 1.60\ g/cm^3$, $\chi_{mnt} = 0.85$) under saline conditions were performed. Swelling pressure reduction due to salinity was modelled by adjusting the microstructural compressibility parameter, κ_m, in the ICDSM [20]. The FE meshes and boundary conditions for the analyses are shown in Figure 3.

Modified Kozeny-Carman equation with salinity considerations

The results from the FE model using the modified K-C equation with salinity considerations ('Model') are compared with measurements in Figures 4a and 4b, as evolution of swelling pressure with time. For both FEBEX and MX80 bentonite, the time to reach a peak swelling pressure is shown to reduce with increased salinity of the pore water. This behaviour is attributed
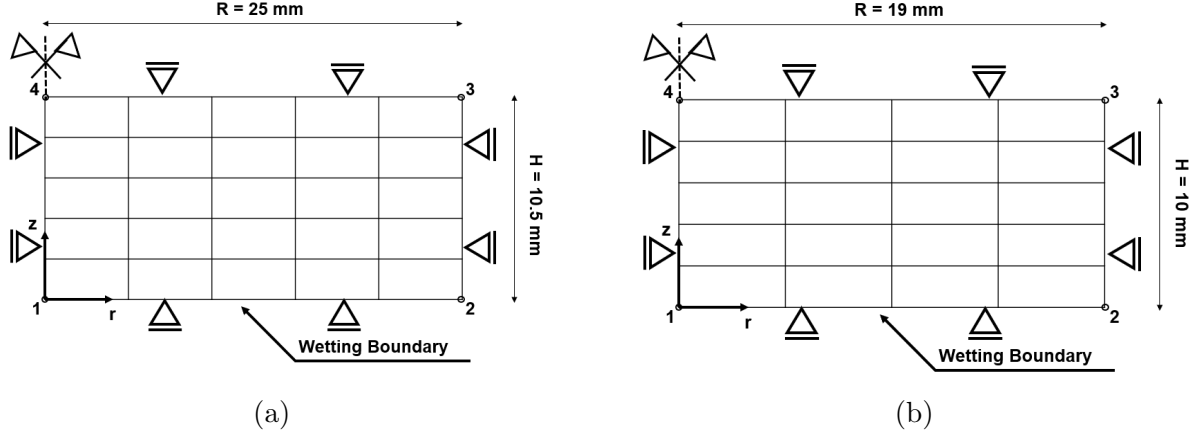
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Figure 3: FE mesh for (a) FEBEX and (b) MX80 bentonite.

to increased permeability under increasing salinity. The modified K-C equation with salinity considerations captures this increase in permeability with reasonable accuracy. To demonstrate the effect of using n_{total} and A_{total} as in the original K-C equation, Figure 5 compares the predicted swelling pressures just for the distilled water case from Figure 4a. It is evident that the original K-C function overestimates saturated permeability, causing the predicted swelling curve to peak much earlier than observed experimentally or in the 'Model' prediction. Furthermore, under constant-volume swelling experiments, where total porosity remains unchanged, the original K-C equation is unable to account for salinity effects, underscoring the necessity of the modifications introduced.

Figure 4: Model prediction of swelling pressure evolution with time at different pore fluid salinities for (a) FEBEX bentonite and (b) MX80 bentonite
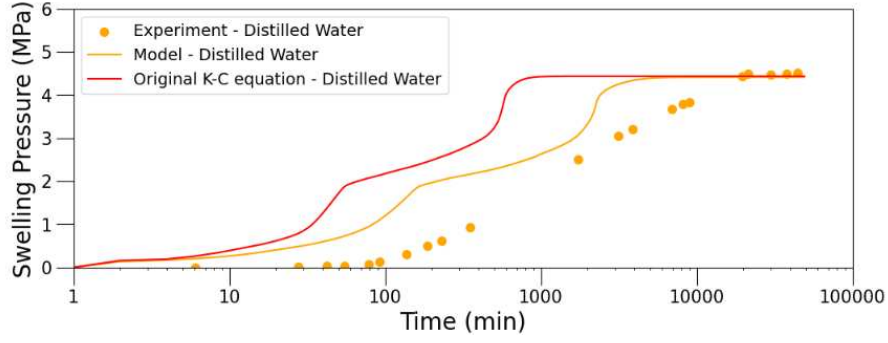
Figure 5: Model prediction of swelling pressure evolution with time using original and modified K-C equation with salinity considerations for FEBEX bentonite subjected to distilled water.

Unsaturated permeability function with salinity considerations

By excluding the contribution of microporosity toward water flow, the unsaturated permeability of bentonite is governed solely by the macroporosity. This approach results in a lower unsaturated permeability for FEBEX bentonite compared to the conventional model that considers total porosity at any given suction (Figure 6b). Consequently, the prediction of the evolution of the swelling pressure is improved using the modified unsaturated permeability function (Figure 6a). To enhance the framework, coupling with a SWR model that incorporates bentonite's dual-porosity structure could better capture the interactions between salinity, suction, and pore structure evolution.
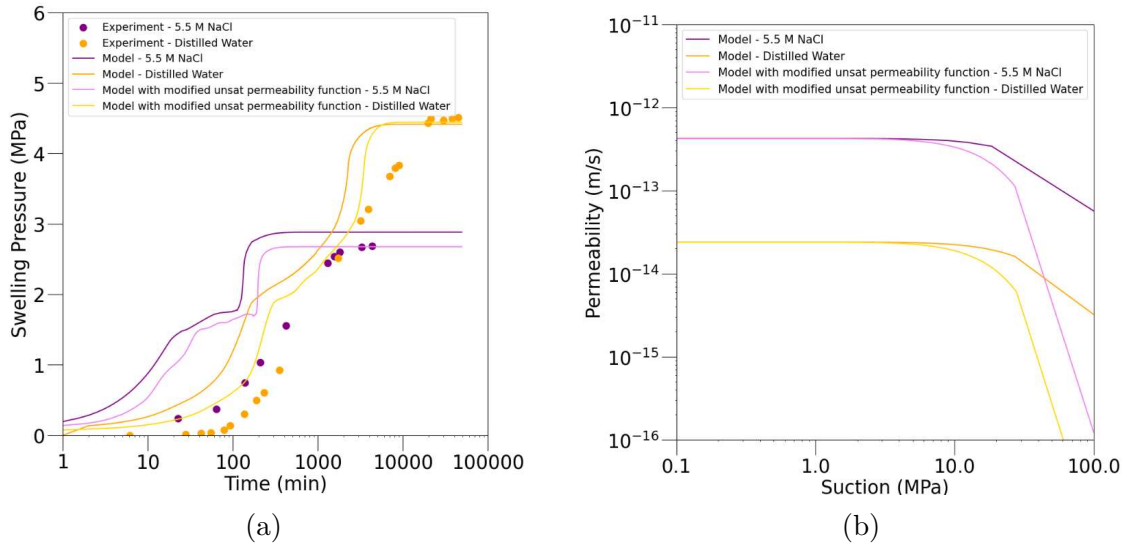

(a) (b)

Figure 6: FEBEX Bentonite: (a) Prediction of swelling pressure evolution using the modified permeability function and (b) comparison of conventional and modified permeability function,

Conclusion

This study highlights the impact of salinity on bentonite's hydro-mechanical properties, showing that modelling of saturated permeability crucially depends on how the flow-relevant pore space and the effective specific surface area are defined. Representing the permeability function using macroporosity offers a better reflection of hydraulic behaviour changes under salinity. Future work will integrate this model with a dual-porosity retention framework to achieve a more comprehensive hydro-chemical coupling for unsaturated clays.

Acknowledgements

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