Experimental study on the effects of pore fluid chemistry on the swelling behavior of MX-80 and BCV bentonite

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Abstract:

Compacted bentonite is a critical component in the design of Engineered Barrier Systems (EBS) and seals for deep geological repositories intended for the isolation of high-level nuclear waste (HLW) and spent nuclear fuel (SNF). Its exceptional swelling and water-retention properties make it ideal for these applications. This research investigates the chemo-mechanical behavior of compacted bentonites subjected to different pore fluids. The study evaluates the swelling pressure and strain of two bentonites: MX80 (Na^+ dominated) and BCV (Ca^{2+}/Mg^{2+} dominated). A detailed study of the bentonites is presented, with mineralogical analysis using X-ray diffraction (XRD). The results suggested that the osmotic pressure generated by the type and concentration of electrolytes in the pore fluids reduces swelling pressures and strains. The XRD analyses support the macroscopic observation, indicating that salinity impacts crystalline swelling as demonstrated by the reduction of basal spacing of clay minerals when the osmotic suction increases.

Introduction

The EBS is subjected to complex thermo-hydro-mechanical-chemical (THMC) interactions driven by multiple factors: heat generated from HLW and SNF, hydration from infiltrating groundwater, stress increments caused by the progressive wetting and swelling of compacted bentonite under highly confined conditions, and chemical interactions with surrounding materials. This study, therefore, focuses on the swelling behavior of compacted bentonite, with particular emphasis on the influence of pore fluid composition on the swelling pressures (SWP) developed during hydration.

Previous research has demonstrated that the nature of exchangeable cations in bentonite significantly affects its hydro-mechanical response. Studies [1][2] examined various bentonite types, including those dominated by monovalent cations (e.g., MX-80) and divalent cations (e.g., FEBEX). These studies found that, under identical matric suction conditions, bentonites enriched with divalent cations retain more water than bentonites enriched with monovalent cations. This behavior is attributed to the lower tendency of exchangeable Ca^{2+} ions to dehydrate compared to Na^{+} ions. Consequently, calcium-rich bentonites exhibit a greater capacity to retain water at high matric suction levels [2]. No comprehensive study has specifically focused on comparing the effects of **osmotic suction** in bentonites dominated by different exchangeable cations.

The dominant exchangeable cation in the bentonite highly influences both the crystalline and osmotic swelling mechanisms observed in the expansive clays [3]. Crystalline swelling occurs in the interlayer spacing of clays, typically between 10 and 22 Å[2], and it is driven by the adsorption of water molecules into the interlayers of smectite. Osmotic swelling, on the other hand, takes place at larger interparticle distances—generally beyond 22 Å—because of repulsive forces associated with the development of diffuse double layers (DDL). In Na-dominated clay, both swelling mechanisms—osmotic and crystalline—play a significant role in determining the swelling pressure. In contrast, Ca-bentonite is primarily influenced by crystalline swelling. This is because the number of flakes per stack is considerably higher in Ca-montmorillonite than in Na-montmorillonite, resulting in a significantly smaller number of electrical double layers per unit volume (weaker DDL).

The experimental investigations include both macroscopic and microscopic scales. The macroscopic tests consist of both swelling pressure (SWP) and swelling strain under constant stress experiments of compacted bentonite saturated with solutions prepared with water and different types of salts and concentrations. The microscopic study is based on XRD analysis of postmortem samples from the tests mentioned above.

Materials

Two different materials were used in this work. The first material is MX-80 bentonite, sourced from Wyoming, USA, and supplied by Cetco. The second material is BCV (Bentonite Černý Vrch) from deposits in the České Středohoří Mountains in the Czech Republic.

Table 1. Major properties of MX-80 [4]and BCV bentonite[5].

Properties	MX-80	BCV
Montmorillonite content (%)	70	69.7
CEC (meq/100g)	90	60.9
Dominant cation	Na^{+}	Mg^{2+} and Ca^{2+}

Experimental methods

Swelling Pressure tests

The system used to perform the SWP tests is a constant-volume cell comprised of the following components (Figure 1a): a cell to hold the sample, a rigid frame to maintain a constant global dry density throughout the tests, a load cell to measure stress evolution during hydration, and a dial gauge to detect any potential movement of the steel frame. The samples had a cylindrical shape (63.5 mm in diameter and 20 mm in height), and they were statically compacted by applying vertical stress to achieve a dry density of ρd = 1.48±0.02 Mg/m^3 from powder with hygroscopic water content (w_c=10±2%). The compaction stress was maintained for 24 hours to ensure material uniformity and minimize rebound effects. Finally, the samples were placed between two porous stones in the swelling pressure cells.

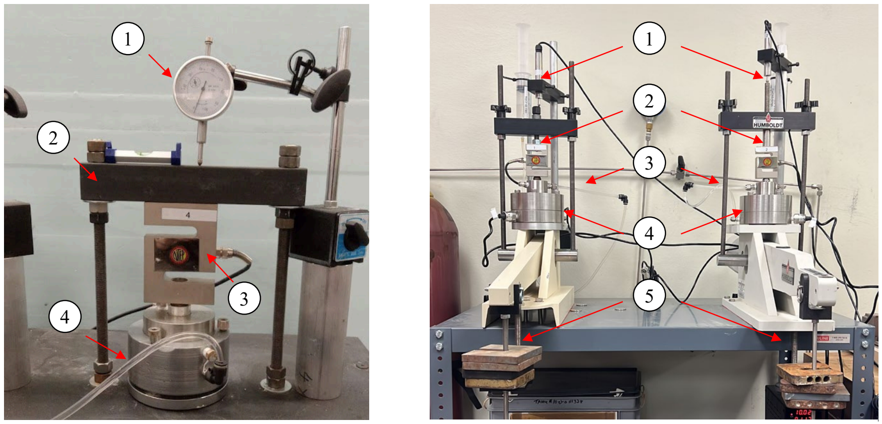
The samples were saturated by inundating them with pore fluid. The pore fluids adopted in this study included distilled water (DW), and either NaCl or $CaCl_2$ solution at the same osmotic suction; all were prepared at room temperature (T = 22°C). A total of six SWP tests were conducted, which included two samples that were saturated using distilled water and four samples inundated with saline solutions with an osmotic suction equal to 2.36 MPa. The osmotic suction (so) of the solutions was determined using the following formula, and its value was selected to approach the seawater salinity.

$$s_o = -10^{-6}\frac{RT}{M_w}\ln(a_w) \quad (MPa) \tag{1}$$

where R is gas constant (8.3143 J/ (mol K)), a_w is the activity of the water, T is the temperature in Kelvin (K), and M_w is the molecular mass of the water (18 g/mol). The water activity depends on the concentration of dissolved salts in the solution. This variable was computed using the Pitzer model from the computer program PHREEQC Version 3[6]. A chilled mirrored-point psychrometer (WP4-T, Decagon Devices, Pullman, Washington) was used to check the osmotic suction of the solutions. Water content measurements and XRD patterns were performed for each experiment as part of postmortem analyses.

Swelling strain tests under constant stress

The swelling strain under constant stress was measured in oedometers cells as shown in Figure 1b. Six swelling strain tests were carried out for MX-80 and BCV. The samples were saturated using distilled water and NaCl and $CaCl_2$ solutions at the same osmotic suction (s_o = 2.36 MPa). The samples were flooded at constant vertical effective stress σ'_v = 100 kPa. The swelling strains were recorded until they reached equilibrium conditions.



a) 1. Dial gauge, 2. Steel frame, 3. Load cell, 4. Constant volume swelling pressure cell.

b) 1. Linear strain conversion transducer (LSCT), 2. Load cell, 3. Consolidation frame, 4. 1D consolidation cell, 5. Dead weights.

Figure 1. Details of experimental devices. a) swelling pressure cell, and b) oedometer set-ups.

X-ray diffraction

The d_{001} spacing of the smectite mineral in the BCV bentonite was measured after the competition of the SWP test. The diffraction patterns were recorded on the Advance Bruker D8 X-ray powder diffractometer using a point detector (Sol-X). The machine used CuKα radiation (Wavelength=1.54060) with a dwell time of 3s/step and a step size of 0.05°. The X-ray tube operated at 40 kV and 40 mA. The basal spacing of MX 80 samples were measured on a D8 FOCUS X-ray powder diffractometer using a LYNXEYE detector. The machine also used CuKα radiation but with time step of 0.1s and step size of 0.02°.

The samples were cut into rectangular pieces of approximately 1.5 cm x 1.5 cm x 2 mm. They were placed in X-ray powder holders and flatted from the top by applying hand pressure with a glass slide. 0.25mil Mylar film was located between the sample and the glass slide to get a smooth surface and to prevent water evaporation during sample preparation and the X-ray analyses. The sample was sealed with the Mylar film and with the help of a rubber band in the holder's boundaries. An internal standard of Muscovite powder was sprinkled on top of the sample. The internal standard helped to correct sample displacement by using the d_{001} peak of muscovite compared to its ideal position.

Results

Swelling pressure test

Figure 2 presents the evolution of swelling pressure (SWP) in compacted MX-80 and BCV bentonite samples during hydration with different pore fluids. The results demonstrate a clear reduction in SWP with increasing osmotic suction of the pore fluids.

As shown in Figure 2a, the effect of pore fluid chemistry is more pronounced in the sodium-dominated bentonite (MX-80). Saturation with NaCl resulted in a greater reduction in SWP compared to saturation with $CaCl_2$, with reductions of approximately 45% and 30%, respectively. This indicates that MX-80 is more sensitive to the type of ions present in the pore fluid.

Figure 2b shows that the swelling behavior of the calcium/magnesium-dominated bentonite (BCV) is also influenced by osmotic suction and ion concentration. However, the specific chemical nature of the pore fluid had a less significant impact compared to MX-80, with a SWP reduction of approximately 38%, regardless of whether NaCl or $CaCl_2$ was used.

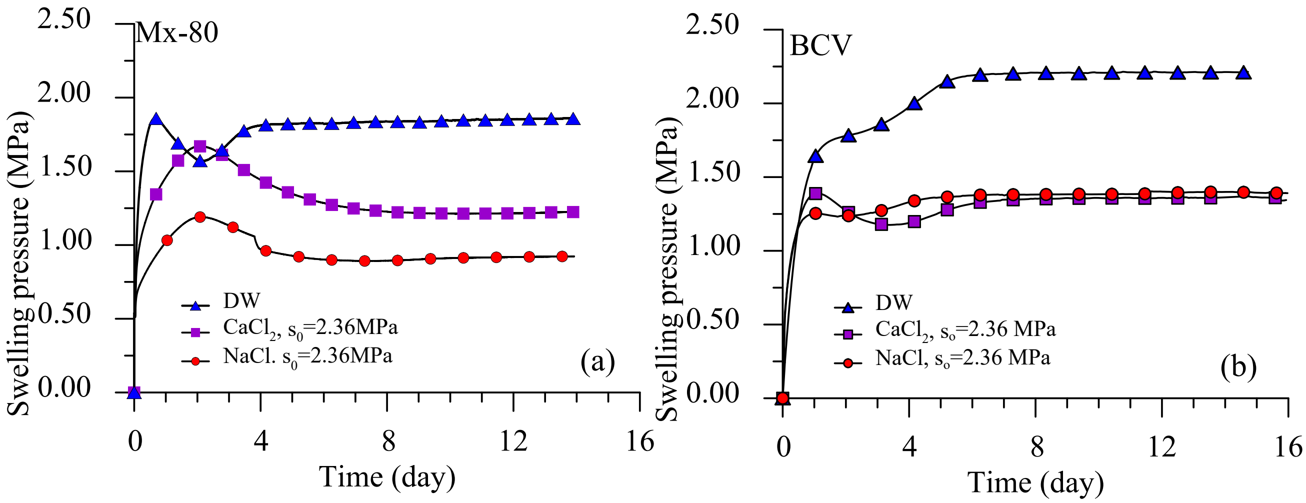


Figure 2: Time evolution of swelling pressures for samples hydrated with distilled water, sodium chloride (NaCl), and calcium chloride ($CaCl_2$) solutions for two different bentonites: (a) MX-80 (monovalent bentonite) and (b) BCV (divalent bentonite).

Swelling strain tests under constant stress

All tests were conducted starting from the same initial water content and under a constant vertical effective stress of $\sigma'_v = 100$ kPa. The samples were saturated using different pore fluids, including distilled water, NaCl, and $CaCl_2$ solutions at various concentrations, corresponding to an osmotic suction of $s_o = 2.36$ MPa.

Figure 3a presents the time evolution of swelling strains in MX-80 samples, plotted against normalized time, defined as the ratio of actual time to the final time required to reach equilibrium for each sample. The results show that samples saturated with saline solutions exhibited lower swelling strains compared to those saturated with distilled water. The trend in swelling strain closely follows the behavior observed in swelling pressure.

Similarly, Figure 3b illustrates the time evolution of swelling strains in BCV samples under the same conditions. The results indicate a smaller effect of salinity on swelling strain compared to MX-80, although a slight reduction is still observed with increased salt concentration.

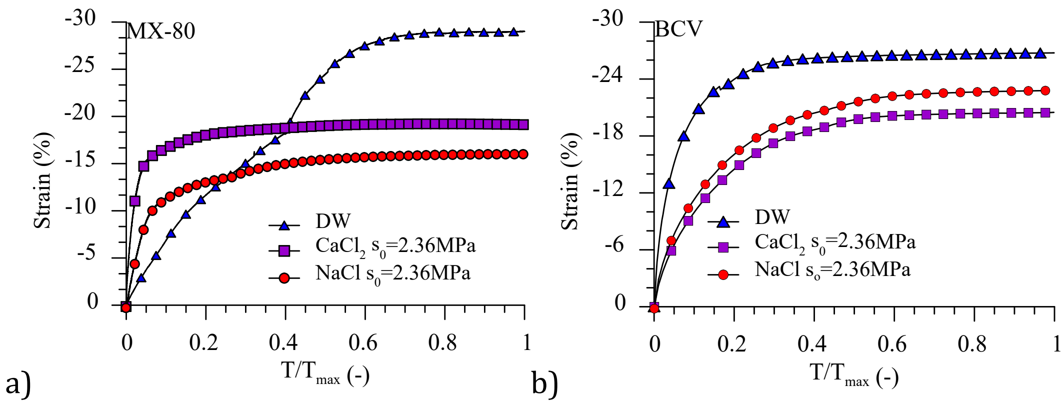


Figure 3. Evolution of swelling strains in the samples under 100 kPa, with distilled water, sodium chloride (NaCl), and calcium chloride ($CaCl_2$) solutions for two different bentonites: (a) MX-80 (monovalent bentonite) and (b) BCV (divalent bentonite).

X-ray diffraction

Figures 4 and 5 show the diffraction patterns and the characteristic peaks for some of the crystalline phases in the MX-80 and BCV samples, including smectite (Sm), muscovite (Ms), and Quartz (Qz). The Mylar film contributed a broad peak in the range of 20 to 30° 2theta. Figure 4 illustrates that the peak shift is more pronounced in the MX 80 samples (from 18.63 Å to 15.69 Å). As seen in Figure 5, the Sm peak shifts slightly to the right in the BCV samples exposed to saline solutions. Although the changes are minimal, the shift in the d_{001} spacing of expansive clay was observed (from 19.27 Å to 18.9 Å). The variation on d_{001} suggests that the exposure to saline solutions reduces basal spacing; These findings are consistent with previous studies [7]. This observation aligns with the macroscopic observation from the swelling pressure tests.

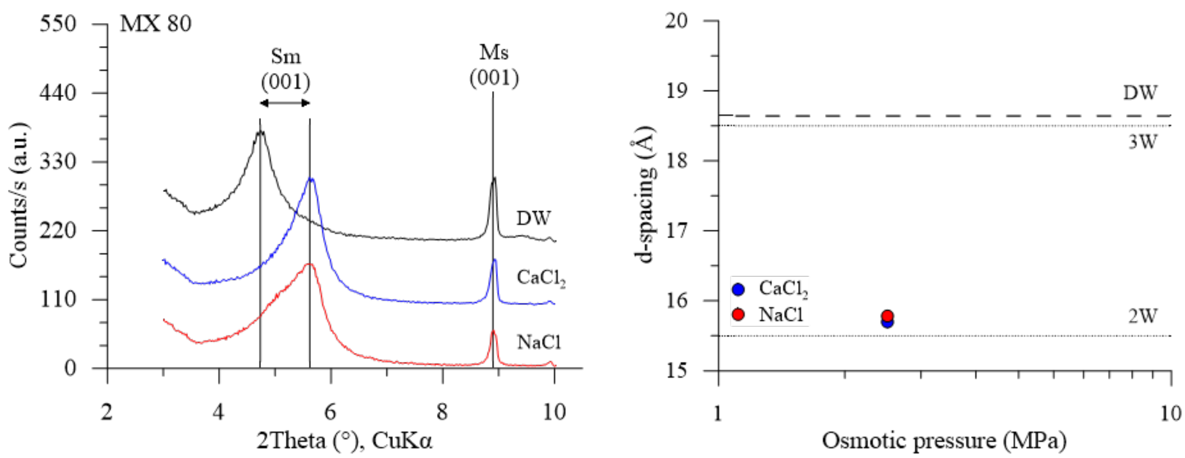


Figure 4. Diffraction patterns and basal spacing of smectite in the MX 80 samples. Continuous lines show the characteristic peak of the lattice plane of Sm, Ms and Qz. The dashed line illustrates the Sm d_{001} of the sample saturated with DW. Dotted lines correspond to the 3W and 2W states.

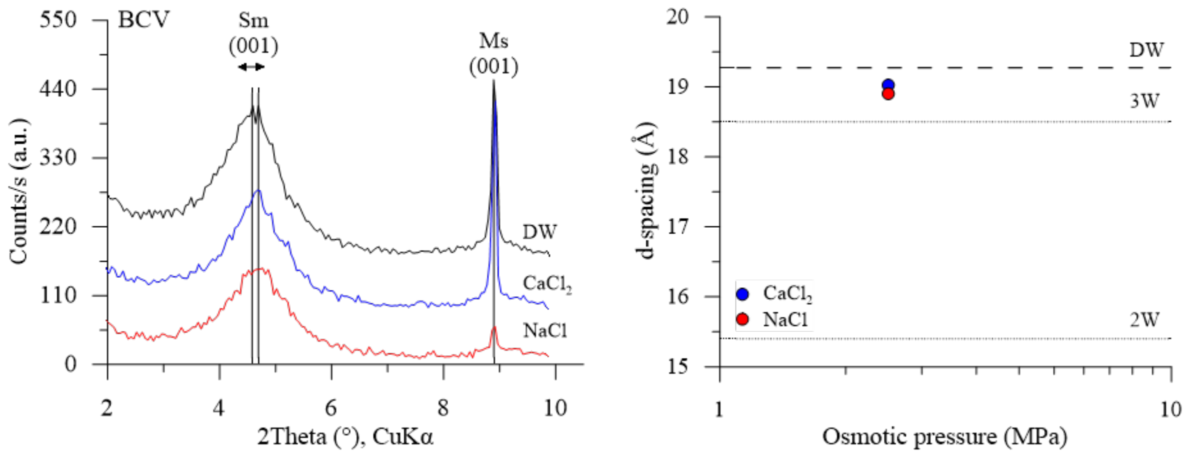


Figure 5. Diffraction patterns and basal spacing of smectite in the BCV samples. Continuous lines show the characteristic peak of the lattice plane of Sm, Ms, and Q. The dashed line illustrates the Sm d_{001} of the sample saturated with DW. Dotted lines correspond to the 3W and 2W states.

Conclusions

This study summarizes the swelling behavior of different compacted bentonites subjected to various pore fluids. The results indicate that both the initial exchangeable cation composition and the chemistry of the pore fluids play a significant role in determining the final swelling pressures and swelling strains. Higher osmotic suction, induced by higher salt concentrations, reduced both swelling pressure and swelling strain. The macroscopic observations align with the microscopic findings, suggesting that the swelling behavior of MX-80 bentonite is more susceptible to the osmotic suction and the chemistry of the pore fluid. Although this work does not study the reasons for exposing the difference in crystalline behavior, it is important to consider that the crystalline swelling of montmorillonite not only depends on the type of counter ions but also the layer charge density, opening opportunities for future investigations.

Acknowledgments

The financial support from NEUP-DOE, USA, Award DE-NE0009291 (Project #22-27240) is acknowledged. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC (NTESS), a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration (DOE/NNSA) under contract DE-NA0003525. This work is authored and owned by an employee of NTESS and is responsible for its contents. Any subjective views or opinions expressed in the written work do not necessarily represent the views of the U.S. Government. The publisher acknowledges the U.S. Government license to provide public access under the DOE Public Access Plan.

References

[1] M. V. Villar, “Water retention of two natural compacted bentonites,” *Clays Clay Miner*, vol. 55, no. 3, pp. 311–322, Jun. 2007, doi: 10.1346/CCMN.2007.0550307.

[2] N. Saiyouri, D. Tessier, and P. Y. Hicher, “Experimental study of swelling in unsaturated compacted clays,” *Clay Miner*, vol. 39, no. 4, pp. 469–479, Dec. 2004, doi: 10.1180/0009855043940148.

[3] K. Norrish, “The swelling of montmorillonite,” *Discuss Faraday Soc*, vol. 18, p. 120, 1954, doi: 10.1039/df9541800120.

[4] M. Victoria Villar, “MX-80 Bentonite. Thermo-Hydro-Mechanical Characterisation Performed at CIEMAT in the Context of the Prototype Project,” 2018. [Online]. Available: https://www.researchgate.net/publication/267413378

[5] F. Laufek *et al.*, “Mineralogical, geochemical and geotechnical study of bcv 2017 bentonite—the initial state and the state following thermal treatment at 200 ∘ c,” *Minerals*, vol. 11, no. 8, Aug. 2021, doi: 10.3390/min11080871.

[6] D. L. Parkhurst and C. A. J. Appelo, “Description of input and examples for PHREEQC version 3—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations,” *US geological survey techniques and methods*, vol. 6, no. A43, p. 497, 2013.

[7] Slade, P. G., J. P. Quirk, and K. Norrish. "Crystalline swelling of smectite samples in concentrated NaCl solutions in relation to layer charge." *Clays and Clay Minerals* 39.3 (1991): 234-238.