

Semipermeable membrane behavior in clays – history, relevance, and limitations

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ABSTRACT: The ability of clays comprising high-activity clay minerals such as shales and bentonites to exhibit semipermeable membrane behavior resulting in the restriction of solute migration has been recognized for approximately a century. This period corresponds with that over which geotechnical engineering has been recognized as a formal discipline, the beginning of which can be traced to the publication of the first book on soil mechanics in 1925 by Karl Terzaghi. Over this period, semipermeable membrane behavior in clays has been studied in conjunction with (i) subsurface accumulation of brines and metal ores, (ii) anomalous pore-water pressures, (iii) deep geological deposition of waste, (iii) moisture migration to plant roots, (iv) consolidation, (v) non-Darcian flow, and, most recently, (vii) engineered bentonite-based barriers used for waste containment. After introducing the concepts of semipermeable membrane behavior and chemico-osmosis in porous media, an historical perspective on the study of semipermeable membrane behavior in clays pertaining to the aforementioned applications is presented. This history culminates in a brief overview of the results of extensive research conducted during the past approximate 25-30 years pertaining to evaluating the extent and magnitude of membrane behavior in a variety of engineered bentonite-based barriers used for liquid- and solid-waste containment. The relevance of semipermeable membrane behavior in geotechnical and geoenvironmental engineering applications is highlighted, and factors that work to limit the existence of semipermeable membrane behavior, such as pore-water chemistry and temperature, are described. The presentation provides a brief overview of the extensive history and current efforts on understanding the roles of semipermeable membrane behavior in clays for applications in a wide range of disciplines, including geotechnical and geoenvironmental engineering.

KEYWORDS: anion exclusion, bentonite, chemico-osmosis, clay, effective porosity, filtration, non-Darcian flow, semipermeable membrane, shale, solute restriction

1 INTRODUCTION

Semipermeable membrane behavior refers to the ability of a porous medium to restrict the migration of dissolved solutes or suspended colloids in liquids, such as aqueous solutions, while simultaneously allowing the passage of molecular water (H₂O). Thus, the membrane is permeable to water (Fig. 1a) but not to the solutes or colloids (Fig. 1b). The process of separating dissolved or suspended constituents from liquids such as aqueous solutions via semipermeable membranes is referred to as filtration (technical) or filtering (colloquial).

Filtration of solutes via a semipermeable membrane gives rise to the development of a chemical concentration difference across the membrane resulting in the process of chemical osmosis (chemico-osmosis), whereby the liquid (i.e., water) migrates through the membrane from a zone of lower solute concentration to a zone of higher solute concentration. This water migration causes an increase in pressure in the higher solute concentration zone and decrease in pressure in the lower solute concentration zone (Fig. 1b). The resulting flux of water through the membrane is referred to as the chemico-osmotic liquid flux (Shackelford & Scalia 2022). In reality, chemico-osmosis occurs because the chemical activity (potential) of H₂O in the lower solute concentration zone is higher than that in the higher solute concentration zone, such that water migrates in response to a gradient in the chemical activity of H₂O, from higher water activity to lower water activity (Fritz et al. 2000, 2025).

Solute filtration occurs when the sizes of the pores within the membrane are smaller than the sizes of the migrating solutes or colloids. Mackay (1946) noted that osmotic effects take place up to a maximum pore size of 0.5 μm, with impedance varying from pore sizes ranging from 1 μm at the lower limit of filtration to about 3 nm for the smallest solutes or colloids. When the sizes of all solutes or colloids in a liquid are not the same, a membrane with a uniform size of pores may filtrate some but not all solutes or colloids, such that the extent of filtration is dependent on a specific solute or colloid. Similarly, if the sizes of all the solutes or colloids are the same, but the sizes of the pores in the membrane vary, only some of the

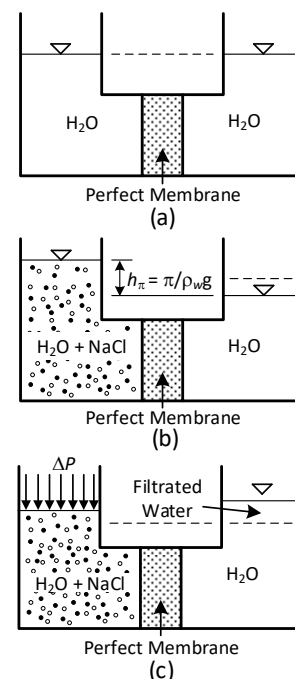


Figure 1. Schematic scenarios of adjacent reservoirs separated by a perfect semipermeable membrane: (a) pure water (H₂O) at equilibrium in both reservoirs; (b) chemico-osmotic pressure (π) and pressure head (h_{π}) developed by inclusion of a salt (NaCl) in left reservoir; (c) salt filtration via reverse-osmosis (ultrafiltration) by application of an applied pressure difference (ΔP). Note: ρ_w = density of water; g = gravitational acceleration.

solute or colloid may be filtered. When all solutes are filtered, the membrane is referred to as an ‘ideal’ or ‘perfect’ membrane, as shown in Fig. 1, whereas the membrane is ‘non-ideal’ or ‘imperfect’ when only some solutes or colloids are filtered. In the case of a perfect membrane, the maximum chemico-osmotic

pressure will be developed (π in Fig. 1b), whereas for an imperfect membrane, the chemico-osmotic pressure developed will be less than the maximum. The magnitude of the maximum chemico-osmotic pressure for a perfect membrane is a function of two variables, viz., the difference in water (H_2O) activity across the membrane, which is a function of the solute (salt) concentrations in the solutions on either side of the membrane, and temperature (Fritz et al. 2020, 2025).

Semipermeable membranes are used to filter unwanted solutes or colloids from liquids, such as the use of manufactured (e.g., polymer) membranes for desalination of saltwater via reverse osmosis or ultrafiltration. Reverse osmosis is facilitated by applying pressure to the liquid on the higher solute concentration side of the membrane to force the liquid through the membrane to the lower solute concentration side, thereby filtering the unwanted solutes from the liquid (Fig. 1c). Although both reverse osmosis and ultrafiltration refer to this process, reverse osmosis, also known as hyperfiltration, negative osmosis (Russell 1933), and exosmosis (Mackay 1946), refers to membranes with smaller pores that filtrate the liquid to a greater degree of purity but at the expense of greater energy consumption, whereas ultrafiltration refers to membranes with larger pores that filtrate liquids to a lesser degree of purity but consume lesser energy.

2 HISTORICAL PERSPECTIVE

The study of semipermeable membrane behavior is founded in physical chemistry, and the origin of this study can be traced to the mid-19th century for applications that were largely related to filtration for medical purposes, such as dialysis for filtrating harmful substances from blood (Ferry 1936). According to Ferry (1936), the first time the term ‘ultrafiltration’ was used was in 1906 by the German chemist Jakob Bechhold (1866-1937), who worked with colloids in medicine.

The earliest publications documenting semipermeable membrane behavior in clays appear to date to the early 20th century, or about a century ago, which corresponds with the advent of the formal discipline of geotechnical engineering circa 1925 as represented by the publication of Terzaghi’s book on soil mechanics (Terzaghi 1925). Berry (1969) presents a good review of the literature on the semipermeability of clays and shales prior to 1969 that includes publications dated to 1933 (e.g., Russell 1933; Schlumberger et al. 1933). The focus of many studies has been on clays that comprise an appreciable amount of high swelling smectite (montmorillonite) clay mineral, such as shales and bentonites. Some studies have evaluated the membrane behavior of lower activity clays such as kaolinite clay (kaolin) (Olsen 1969; Mazzieri et al. 2003; Heister et al. 2006) and mudstones (Takeda et al. 2014; Takeda & Manaka 2018), as well as mixtures of soils, typically comprising bentonite mixed with lower activity clays such as kaolin (e.g., Zheng et al. 2022) or natural soils (e.g., Tang et al. 2014), or bentonite-sand mixtures (e.g., Saindon & Whitworth 2005; Meier & Shackelford 2017). Although saturated soil conditions have been assumed for most studies, some studies have evaluated membrane behavior under unsaturated conditions (Bresler 1973; Allred 2007; Allred et al. 2007; Sample-Lord & Shackelford 2014, 2017, 2018). Finally, the membrane behavior of chemically modified bentonites also has been evaluated. Examples include bentonites modified with propylene carbonate (Mazzieri et al. 2010) and with polyacrylic acid (Bohnhoff et al. 2014).

Clay membranes have been studied as a potential cause of subsurface accumulation of salt brines (e.g., Russell 1933) and metal ores (Mackay 1946), anomalous pore-water pressures in sedimentary formations such as shales (e.g., Neuzil 2000;

Neuzil & Provost 2009), water and nutrient migration to plant roots in soils (e.g., Kemper & Rollins 1969; Kemper & Quirk 1972), well-bore stability (Sherwood & Craster 2000), consolidation (Mitchell et al. 1973; Barbour & Fredlund 1989), apparent causes of non-Darcian flow (Olsen 1985), and waste isolation using natural and engineered clay barriers (e.g., Hanshaw 1972; Shackelford et al. 2001; Takeda et al. 2014; Bourg 2018).

2.1 *Subsurface accumulation of brine and metal ores*

Russell (1933) postulated osmosis resulting from the existence of semipermeable membrane behavior in clays and shales as a possible mechanism for the observation of chloride brines more concentrated than sea water at subsurface horizons not closely associated with sea water. However, he concluded that too little was known at that time about the effects of osmosis in sedimentary rocks to justify any positive statement.

Mackay (1946) described the factors affecting the ability of natural geological barriers, such as shales, to restrict the passage of metals ores in solutions. Evidence was presented for the existence of these geological barriers at several locations around the world, including Solvenia, Italy, Cyprus, Canada (Quebec), Tanganyika (Tanzania), and Nigeria.

McKelvey & Milne (1960) evaluated salt filtering via permeation of NaCl solutions through highly compacted specimens of Wyoming bentonite and a disaggregated shale. They observed a buildup of salt concentration on the inflow side of the specimens that exceeded the source liquid concentration and a decrease in salt concentration on the outflow side of the specimens, with ratios of inflow-to-outflow concentrations ranging from 1.7 to 8 for the bentonite specimens and 1.3 to 1.7 for the shale specimens. They hypothesized that the salt filtering phenomenon could be responsible for the accumulation of brines within the subsurface and concluded that this was probable for similar shales in subsurface systems.

Chemico-osmosis also has been proposed as a process to enhance the recovery of oil from oil-bearing shales with high salinity (Fakcharoenphol et al. 2015; Uzun & Kazemi 2021). The concept involves injecting low salinity water adjacent to the oil-bearing shale that behaves as a semipermeable membrane, resulting in a buildup of osmotic pressure within the shale that decreases the effective stress causing swell, and producing a counter flow of oil from the shale.

2.2 *Anomalous pore-water pressures*

The aforementioned accumulation of salts associated with shales also has been postulated as the reason for anonymously high pore-water pressures in subsurface systems relative to hydrostatic pore-water pressures due to chemico-osmosis, such as illustrated in Fig. 1b (Hanshaw & Zen 1965). For example, Marine & Fritz (1981) proposed an osmotic model to explain the elevated pressure heads observed in two wells located in an underlying basin with elevated salt concentrations relative to the pressures observed in the overlying, freshwater coastal plain aquifer. Their analysis indicated that the heads in each well were close to the osmotic equilibrium heads of 80 m (788 kPa) and 132 m (1298 kPa) calculated from the solution concentration of water (i.e., water activity) in each well.

Neuzil (2000) describes the results of a nine-year field study conducted in the Pierre Shale located in South Dakota, USA, involving measurements of liquid pressures and solute concentrations in four boreholes drilled in the shale. The results of the field experiment indicated the possibility of shales similar to the Pierre Shale generating osmotic pressures as high as ~20 MPa. Neuzil & Provost (2009) concluded that some argillaceous formations that behave as semipermeable membranes have the capability to generate osmotic pressures

exceeding 30 MPa (3 km of head) at porosities as high as ~ 0.1 and 10 MPa at porosities as high as ~ 0.2 .

However, Tremosa et al. (2012) presented the results of analyses indicating that the actual osmotic pressures developed in the field are likely to be significantly lower than those postulated by Neuzil (2000) and Neuzil & Provost (2009) for two reasons. First, natural pore waters vary in terms of types of salts present, and the presence of even low percentages of divalent cations such as calcium (Ca^{2+}) can significantly reduce the salt filtering capabilities of shales that behave as semipermeable membranes relative to those determined in the laboratory using simple salt solutions, such as sodium chloride, (NaCl). Second, osmotic pore-water pressures based on steady-state conditions as previously assumed tend to be overpredicted relative to those based on transient conditions, which are more prevalent in field scenarios.

2.3 Deep geological deposition of waste

Hanshaw (1972) discusses the role of membrane behavior in the context of subsurface liquid waste emplacement in locations where sedimentary rocks such as argillaceous shales exist, and describes a scenario where lack of understanding and consideration of membrane behavior in the shale can result in hydraulic fracturing that leads to contamination of potable water resources. Semipermeable membrane behavior also has been considered in the context of deep geological disposal of high-level radioactive waste (HLRW), in terms of both natural argillaceous rock surrounding the disposal cells (e.g., Heister et al. 2006), and the highly compacted bentonite buffers used to contain the HLRW in the cells (Chen et al. 2007; Rousseau-Gueutin et al. 2008; Baechler et al. 2012).

2.4 Moisture migration to plant roots

Kemper & Rollins (1966) and Kemper & Quirk (1972) studied semipermeable membrane behavior and chemico-osmosis in clays in the context of the migration of water and nutrients to plant roots. They evaluated osmotic or membrane efficiency coefficients reflecting the degree of solute restriction for several clay mineral soils, including bentonite, illite, and kaolin. Their conclusions were consistent with expected clay soil behavior on the basis of electrostatic or diffuse double layer (DDL) theory in that a greater degree of solute restriction was favored for conditions that included lower versus higher salt concentrations and monovalent salts such as NaCl (e.g., $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$) versus divalent salts such as calcium chloride (i.e., $\text{CaCl}_2 \rightarrow \text{Ca}^{2+} + 2\text{Cl}^-$). They also found that solute restriction was greater for clays comprising higher activity clay minerals (e.g., sodium bentonite) versus lower activity clay minerals (e.g., illite, kaolin), because of the greater prominence of DDLs in the behavior of higher activity clay minerals.

2.5 Consolidation

Mitchell et al. (1973) described laboratory experiments focused on determining the extent of consolidation in five fine-grained soils due to chemico-osmosis. Specimens consolidated to an initial effective stress of 98 Pa were subjected to a high-concentration boundary salt solution to induce chemico-osmosis from within the specimens to the boundary, resulting in consolidation. The results indicated that chemico-osmotic consolidation was detectable only for a highly compressible bentonite.

Greenberg et al. (1973) developed a numerical model to evaluate coupled salt and water flows through a series of unconfined and confined aquifers separated by silt and clay aquitards comprising the groundwater regime in the Oxnard coastal basin in California. The aquitards were considered to behave as semipermeable membranes, and a primary concern

was land subsidence due to consolidation of the upper most aquitard resulting from chemo-osmotic water flow from the aquitard to the overlying Oxnard unconfined aquifer with high salt concentration due to seawater intrusion. They found that land subsidence resulting from chemico-osmotic consolidation was minor relative to that resulting from pumping the underlying Mugu confined aquifer.

Barbour & Fredlund (1989) identified two mechanisms causing osmotic consolidation in clays termed 'osmotically induced consolidation' and 'osmotic consolidation' (Musso et al. 2017; Shackelford et al. 2019). Osmotically induced consolidation results when chemico-osmotic flow of water occurs from the clay to a surrounding zone of higher salt concentration, such as imposed by Mitchell et al. (1973). Osmotic consolidation occurs simultaneously as solutes diffuse from the zone of higher concentration into the clay pores, resulting in a compression of the DDLs and an increase in effective stress. Laboratory tests were conducted on two clay soils exposed to concentrated NaCl solutions and the dominant mechanism was found to be osmotic consolidation.

Di Maio (1996) conducted oedometer tests on specimens of a sodium bentonite subjected to distilled water and saturated electrolyte solutions comprising one of three salts, viz. NaCl, KCl, and CaCl_2 . The results indicated that exposure to any of the electrolyte solutions produced consolidation, which was attributed to osmotic consolidation due to inward diffusion of salt ions and collapse of the DDLs.

2.6 Non-Darcian flow

Olsen (1985) cited previously published evidence supporting the hypothesis that osmosis is a mechanism that causes non-Darcian flow (seepage) behavior in fine-grained soils, where non-Darcian flow behavior is represented in a plot of flow rate versus head difference by a non-zero head difference at zero flow rate, and by non-zero flow rate at zero head loss. However, Olsen (1965) noted that this behavior could be attributed to chemico-osmosis and/or electro-osmosis.

Fox et al. (2000) measured the hydraulic conductivity of specimens of two bentonite-based geosynthetic clay liners (GCLs) and showed that plots of discharge (Darcy) velocity versus total head difference were linear but indicated non-zero (positive) discharge velocities at zero head difference. They noted that the observed linear but non-proportional behavior was consistent with that described by Olsen (1985) and could be attributed to flow driven by a combination of hydraulic and chemical concentration gradients. Although not explicitly stated as a conclusion, the results in Fox et al. (2000) are likely the first published indication of the existence of semipermeable membrane behavior in bentonite-based GCLs.

2.7 Bentonite-based containment barriers

The results of the aforementioned studies indicate that semipermeable membrane behavior can be significant for high activity clays such as sodium bentonites. Accordingly, considerable study has occurred over the past approximate 25-30 years focused on evaluating the extent of membrane behavior in bentonite-based waste containment barriers (e.g., Shackelford 2012, 2013; Medved & Černey 2013).

For example, Malusis & Shackelford (2002) measured the extent of solute restriction (membrane efficiency) of specimens of a GCL when exposed to electrolyte solutions with different concentrations of KCl, and showed that their results were comparable to those reported by Kemper & Rollins (1966) for a sodium bentonite exposed to NaCl solutions (see Fig. 2). They concluded that the GCL acts as a semipermeable membrane in the presence of the KCl solutions, with membrane efficiencies

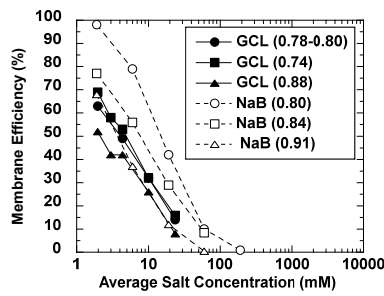


Figure 2. Comparison of measured membrane efficiencies for a GCL from Malusis & Shackelford (2002) versus those for a sodium bentonite (NaB) from Kemper & Rollins (1966) Note: number(s) in parentheses represents porosity.

ranging from 69 to 8% as the KCl concentrations ranged from 3.9 to 47 mM, respectively, and that membrane efficiency decreased with increasing salt concentration and increasing porosity.

Numerous studies have evaluated the membrane efficiencies of other bentonite-based containment barriers, including compacted bentonites (Dominijanni et al. 2013, 2018; Su et al. 2023), soil-bentonite backfills for slurred cutoff walls (Evans et al. 2008; Ni et al. 2022), bentonite-amended compacted clay (Kang & Shackelford 2010; Tang et al. 2014, 2015), and a compacted sand-bentonite mixture (Meier & Shackelford 2017). A primary outcome of these studies is that bentonite-based containment barriers can exhibit significant semipermeable membrane behavior, but the bentonite component of these barriers is essential to the existence of membrane behavior. Natural clays that may be suitable as compacted clay barriers on the basis of low hydraulic conductivity but are lacking in high activity clay minerals are unlikely to exhibit appreciable membrane behavior (Kang & Shackelford 2010).

3 RELEVANCE

As has been illustrated, semipermeable membrane behavior in clays is a multidisciplinary concept that is relevant to the disciplines of geology, soil science, geotechnical engineering, and geoenvironmental engineering. In many of these studies, clay membrane behavior was evaluated as a possible explanation for observed behavior either in the laboratory or the field that was unusual or unexpected. In terms of practical applications related to geotechnical and geoenvironmental engineering, the study by Greenberg et al. (1973) to evaluate the potential for land subsidence due to chemico-osmotic consolidation resulting from an aquitard behaving as a semipermeable membrane represents a good example. Also, the existence of semipermeable behavior in bentonite-based solid- and liquid-waste containment barriers may offer a benefit for enhanced restriction of contaminant transport through the barrier and, therefore, improved containment performance.

For example, as illustrated in Fig. 3, the relative solute flux at steady state, defined as the solute flux at any membrane efficiency relative to the solute flux at zero membrane efficiency, through a 1-m-thick barrier is shown to decrease with increasing membrane efficiency of the barrier. The hydraulic gradient, where $i_h = 0$ represents the pure diffusion case and $i_h > 0$ represents coupled advective-diffusive transport, is shown to have little effect on the overall trend, primarily due to the low hydraulic conductivity values for the barrier (1.33×10^{-11} to 2.06×10^{-11} m/s), which significantly reduced the advective component of solute transport. The overall effect is that the solute flux through the barrier approaches zero as the

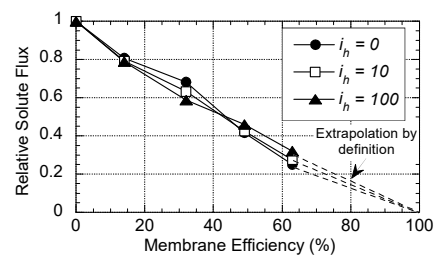


Figure 3. Relative solute flux at steady state through a 1-m-thick clay barrier as a function of membrane efficiency and hydraulic gradient (i_h). Data from Malusis & Shackelford (2004).

membrane efficiency approaches 100% (Manassero & Dominijanni 2003). Thus, taking advantage of the existence of semipermeable membrane behavior in these bentonite-based containment barriers can significantly improve the performance of the barriers, although there are limitations and challenges associated with implementing the concept of solute restriction.

4 LIMITATIONS AND CHALLENGES

As previously noted, the existence of semipermeable membrane behavior in clays is consistent with DDL theory (e.g. Cey et al. 2001). This correlation results because clays behave as charged membranes due to the negative surface charge of clay particles (platelets) resulting primarily from isomorphous substitution. The resulting negative surface potential emanates from the particle (platelet) surface into the pore, and dissipates in magnitude with distance away from the surface (Shackelford & Scalia 2022). When adjacent particles (platelets) are sufficiently close such that the negative surface potentials overlap, the net potential within the pore is negative, such that negatively charged ions (anions) such as chloride (Cl^-) are repelled from entering the pore, and the associated cation (e.g., K^+) is repelled due to the requirement for charge equilibrium in the pore water. The repulsion of the anion often is referred to as 'anion exclusion' (e.g., Bresler 1973; Van Loon et al. 2007; Tournassat & Appelo 2011), and the overall effect of anion exclusion leads to a reduction in the pore space effective for solute migration resulting in an 'effective porosity' that is less than the total porosity (e.g., Manassero & Dominijanni 2003).

The primary factors affecting the existence and magnitude of membrane behavior in clays include the pore-water chemistry, clay mineralogy, and porosity (Shackelford & Scalia 2022). In terms of pore-water chemistry, membrane efficiency in clays generally decreases with increasing salt concentration (Fig. 2) and is only significant at lower salt concentrations. In addition, most of the studies conducted to date on the membrane behavior in clays have involved simple monovalent salts (KCl, NaCl), and considerable evidence indicates that single salt solutions with divalent metals, such as CaCl_2 , and solutions with mixtures of multivalent metals deteriorate membrane behavior (Tremosa et al. 2012; Zhang et al. 2024). These results are consistent with the correlation between ionic strength of the chemical solution (pore water), $I (= \sum C_i z_i^2)$, where C_i = molar concentration and z_i = charge (valence) of a specific ion in solution, and \sum = summation of all ions in solution), and the thickness of the DDLs, with increasing I correlating with decreasing thickness of the DDL and decreasing solute restriction, and vice versa.

Clay mineralogy plays an important role in that clays comprising higher activity clay minerals such as smectite tend to correlate with smaller particle sizes and higher surface areas, such that the DDLs play a greater role in the behavior of these clays. This predominance of DDLs is the reason that semipermeable membrane behavior is greater in bentonites than

other clays with lower amounts of smectites (e.g., shales) and/or clays that comprise predominantly lower activity clay minerals such as illite and kaolinite.

As illustrated in Fig. 2, for the same clay, an increase in porosity results in a decrease in membrane efficiency, because increase in porosity results in larger pore sizes. For this reason, increasing the applied stress on a clay membrane can decrease the porosity and increase the membrane efficiency (e.g., Olsen 1969; Kang & Shackelford 2011).

Degree of water saturation also plays a role in membrane behavior, with decreasing water saturation correlating with increasing membrane efficiency (e.g., Sample-Lord & Shackelford 2018). The reason for this trend is that, as the degree of water saturation decreases, an increasing amount of water in the pores is displaced by air, which forces solutes to migrate closer to adjacent particle surfaces where the DDLs are prevalent, and reduces the cross-sectional area of water available for solute migration.

Recent evidence also indicates that higher temperatures can significantly deteriorate membrane behavior (Fig. 4), which raises doubt about the significance of membrane behavior in clay barriers involving elevated temperatures, such as solid waste landfills and bentonite buffers for HLRW containment.

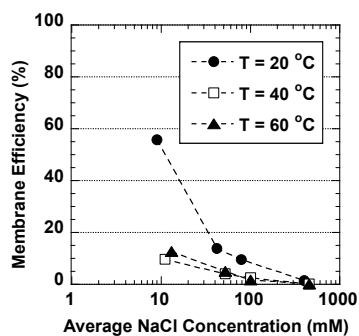


Figure 4. Effect of temperature (T) on the membrane efficiency of highly compacted GMZ bentonite. Data from Su et al. (2023).

Since many practical applications involve elevated concentrations, pore waters with complex chemistries, and/or elevated temperatures, overcoming these limitations to employ membrane behavior for improved containment barrier design remains a challenge. Nonetheless, knowledge of the potential existence of semipermeable membrane behavior can assist in explaining unexpected behavior in clays, such as the observation of non-Darcian flow and the existence of anonymously high or low pore-water pressures in clays.

5 SUMMARY

The existence of semipermeable membrane behavior in clays has been recognized for approximately a century. Membrane behavior may be relevant in clays that comprise higher activity smectites (montmorillonites), such as shales and bentonites. Membrane behavior results in solute restriction which leads to chemico-osmosis, or the flow of water from a zone of lower solute concentration (higher H₂O activity) to a zone of higher solute concentration (lower H₂O activity), and the development of chemico-osmotic pressure. Membrane behavior in shales can lead to subsurface accumulation of brines and metal ores, and osmotic pressures that exceed hydrostatic pore-water pressures. Membrane behavior also can lead to chemico-osmotic consolidation and non-Darcian flow, especially in high activity bentonites. The potential for significant membrane behavior in engineered bentonite-based barriers can enhance the containment function of these barriers due to solute

(contaminant) restriction. However, the effectiveness of membrane behavior is a function of pore-water chemistry, with membrane efficiency decreasing with increasing ionic strength. Elevated temperatures also have been shown to decrease membrane efficiency of bentonite. The challenge for the future will be in determining the relevance of semipermeable membrane behavior in practical applications of geotechnical and geoenvironmental engineering.

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