

# Chemico-Osmosis Versus Diffusion-Osmosis

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During the 1960s it became widely recognized that chemico-osmosis is a mechanism by which chemical gradients cause groundwater to move from dilute to more concentrated pore-fluid solutions and is most effective in densely compacted materials of high exchange capacity. Evidence has been accumulating since about 1970 that an additional mechanism may cause groundwater movement in response to chemical gradients and reactions. Some data show that the direction of soil-pore-fluid movement in response to a concentration gradient is opposite to that of chemico-osmosis. Other data suggest that chemically induced groundwater movement may be significant not only in densely compacted materials of high exchange capacity but also in poorly consolidated materials of low exchange capacity. Laboratory evidence is reviewed for the additional mechanism and include recent data on loosely compacted kaolinite and an undisturbed sample of claystone. The additional mechanism appears to be diffusion-osmosis (i.e., the convection, or drag, of bulk pore fluid by the diffusion of solute species). It is suggested that electro-osmosis is a special case of diffusion-osmosis where pore fluid moves in response to the migration of solute species caused by an externally imposed electrical potential gradient.

The term "osmosis" refers to nonhydraulic components of groundwater movement that arise from thermal, electrical, and chemical causes. This paper is concerned with osmosis having chemical causes and, more specifically, with the mechanisms by which chemical gradients cause groundwater movement.

Osmosis generated by naturally occurring chemical causes is referred to in the literature by different names, including osmosis (1-5), chemical osmosis (6), normal osmosis and chemico-osmosis (7), and natural electro-osmosis (8), suggesting that more than one mechanism is involved and that the characteristics of and differences among those mechanisms have yet to be clarified adequately.

One of those mechanisms, referred to as chemico-osmosis in this paper, became widely recognized during the 1960s as a possible source of anomalous pore-fluid pressures and a cause of groundwater movement from dilute to more concentrated pore-fluid solutions. Evidence has been accumulating since about 1970 that an additional mechanism, denoted here as "diffusion-osmosis," may cause groundwater movement in response to chemical gradients and reactions and that this mechanism drives soil-pore-fluid movement in the direction of decreasing solute concentrations, which is opposite to

that for chemico-osmosis. This paper reviews laboratory evidence for those mechanisms, including recent data on loosely compacted kaolinite and an undisturbed sample of claystone.

## CHEMICO-OSMOSIS

Here, chemico-osmosis is used to describe water movement from less concentrated to more concentrated solutions separated by a semipermeable membrane, which restricts solute flows but allows water flow. The driving force for chemico-osmosis is the chemical potential difference of the water phase between the two solutions, the more concentrated solution having the lower potential. In a perfect semipermeable membrane (i.e., a membrane that totally excludes the flow of solutes), the driving force equals the pressure difference that must be applied to the concentrated side to stop water flow. This chemico-osmotic pressure for a perfect semipermeable membrane is given by the well-known thermodynamic relation

$$\Delta\pi = \frac{RT}{V_w} \ln \frac{a_1}{a_2} \quad (1)$$

where

$\Delta\pi$  = chemical potential difference of water across membrane,

$R$  = gas constant,

$T$  = absolute temperature,

$V_w$  = molar volume of water,

$a_1$  = activity of water on the less concentrated side, and

$a_2$  = activity of water on the more concentrated side.

Flow of water through a perfect semipermeable membrane is governed by both the hydraulic pressure difference and the chemical potential difference in the water phase across the membrane.

$$q = k[\Delta P + \Delta\pi] \left[ \frac{1}{\gamma_w} \right] \quad (2)$$

where

$q$  = flow rate per unit cross-sectional area,

$k$  = hydraulic conductivity,

$\Delta P$  = hydraulic pressure difference across membrane,

$\Delta\pi$  = chemical potential difference of water across membrane, and

$\gamma_w$  = unit weight of water.

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The so-called "membrane properties" of clays result from charge deficiencies on the surfaces of clay particles balanced by a deficiency of anions compared with cations in the pore fluid adjacent to the particle surfaces. Because of this deficiency of anions, which is commonly referred to as "anion exclusion," the flow of solute is restricted relative to the flow of water. In consequence, clays behave, to some degree, like a semipermeable membrane and are commonly called imperfect or leaky membranes. Therefore, chemico-osmotic pressures and flows in argillaceous materials are generally some fraction of those predicted from Equations 1 and 2.

The degree to which clays exhibit membrane behavior has been characterized by terms such as "ideality" and "membrane efficiency" and is generally quantified by a parameter Staverman (9) introduced and named the "reflection coefficient." Some investigators of membrane behavior in geologic materials adopted both Staverman's parameter and the term reflection coefficient to describe it (5,10). Others, such as Kemper and Rollins (11), adopted Staverman's parameter but describe it with a different name, "osmotic efficiency coefficient." Staverman (9) defined this parameter  $\sigma$  as presented in Equation 3. Comparison with Equation 2 indicates that the reflection coefficient  $\sigma$  modifies the chemico-osmotic driving force for water flow through a perfect membrane  $\Delta\pi$ . Here,  $\sigma$  varies from zero to unity for membranes having efficiencies that vary from zero to 100 percent.

$$q = k[\Delta P + \sigma\Delta\pi] \left[ \frac{1}{\gamma_w} \right] \quad (3)$$

Similarly, the chemico-osmotic pressure difference that develops when flow is prevented is

$$\Delta P_{q=0} = \sigma\Delta\pi \quad (4)$$

where  $\Delta\pi$  is given by Equation 1.

A more useful form of Equation 3 is obtained for this paper by separating the osmotic and hydraulic components of flow and then by defining separate hydraulic and chemico-osmotic conductivities, as follows.

$$q_t = q_h + q_{co} \quad (5)$$

$$q_h = k_h \Delta P \left[ \frac{1}{\gamma_w} \right] \quad (6)$$

$$q_{co} = k_{co} \Delta\pi \left[ \frac{1}{\gamma_w} \right] \quad (7)$$

$$\sigma = -\frac{k_{co}}{k_h} \quad (8)$$

where

- $q_t$  = total flow rate per unit cross-sectional area,
- $q_h$  = hydraulic flow rate per unit cross-sectional area,
- $q_{co}$  = chemico-osmotic flow rate per unit cross-sectional area,
- $k_h$  = hydraulic conductivity, and
- $k_{co}$  = chemico-osmotic conductivity.

Figure 1 illustrates the experimental system used by Kemper (12) and data he obtained to demonstrate chemico-osmotic

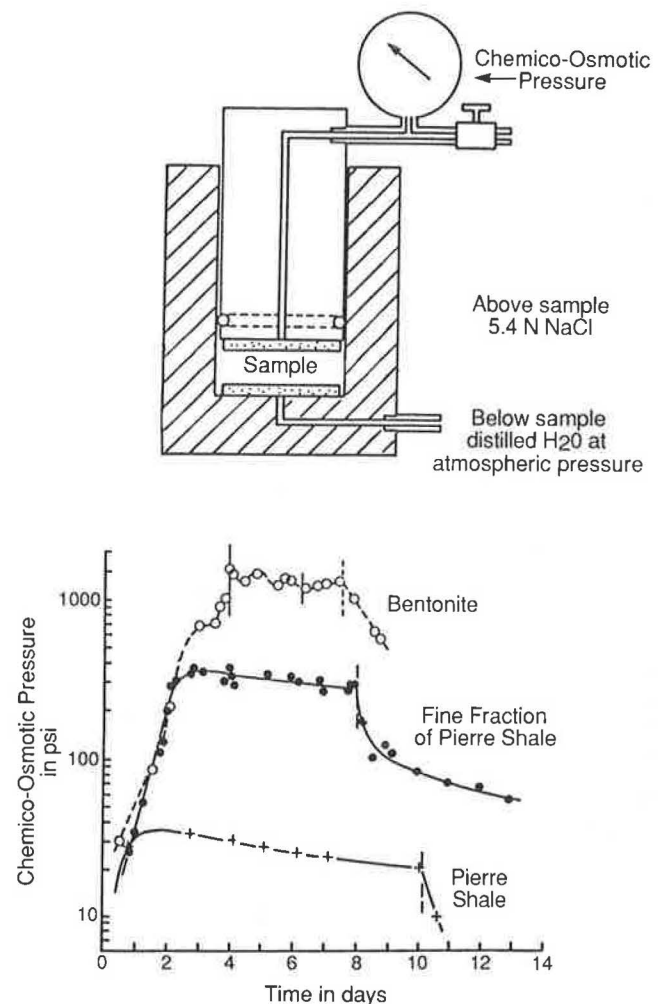


FIGURE 1 Kemper's test cell and data (12).

pressures across compacted clay specimens in response to a 5.4 N NaCl solution above the specimen and distilled water below the specimen. Figure 2 illustrates the experimental system used by Young and Low (13) and the data they obtained to demonstrate chemico-osmotic flow of water in two siltstone samples (A and B in Figure 2) composed of 8 to 12 percent of clay-size material of which 40 to 50 percent was illite, 30 to 40 percent kaolinite, and the remainder was montmorillonite or mixed-layer clays. The Kemper and the Young and Low studies are two of the earliest studies that demonstrate chemico-osmotic pressures and flow in argillaceous earth materials.

Various investigators have demonstrated that the chemico-osmotic efficiency coefficient  $\sigma$  increases with the cation exchange capacity of an argillaceous material, increases with its degree of compaction, and decreases with increasing concentration of dissolved solutes in the pore fluid of the material (5,11,14). Figure 3 illustrates the Kemper and Rollins (11) test cell and some of the classic data they obtained on bentonite that illustrate the variation of chemico-osmotic efficiency with the degree of compaction, as reflected in the moisture content of the clay, and with pore-fluid solute concentration, which is reflected in the average normality of the solutions on either side of the clay specimen.

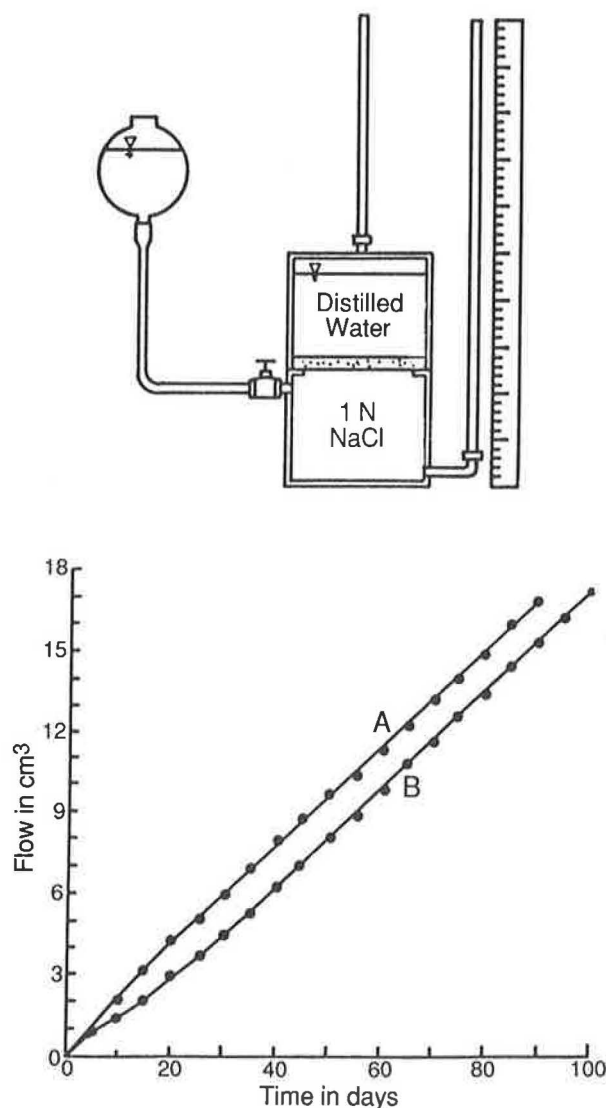


FIGURE 2 Young and Low's experimental system and data (13) on two siltstone samples.

#### DISCREPANCIES FROM CHEMICO-OSMOSIS

In 1972, Kemper and Quirk (15) published the data in Figures 4 to 6 that expanded the scope of Kemper and Rollins' (11) 1966 investigation (illustrated in Figure 3) in three ways: (a) Ag-AgCl electrodes were used to measure the electric potential differences induced by solute concentration differences across the clay sample, (b) data were obtained over a larger range of average solute concentrations, and (c) data were obtained not only on bentonite but also on illite and kaolinite.

Those data show that the direction of soil-pore-fluid movement in response to solute concentration gradients is often opposite to that for chemico-osmosis. This is reflected in osmotic efficiency coefficients having negative values. Kemper and Quirk describe this discrepancy from chemico-osmosis as "negative osmosis," and they suggest the mechanism to be electro-osmosis, as follows: "The osmotic flow was often from the high salt to low salt concentration side and was generally

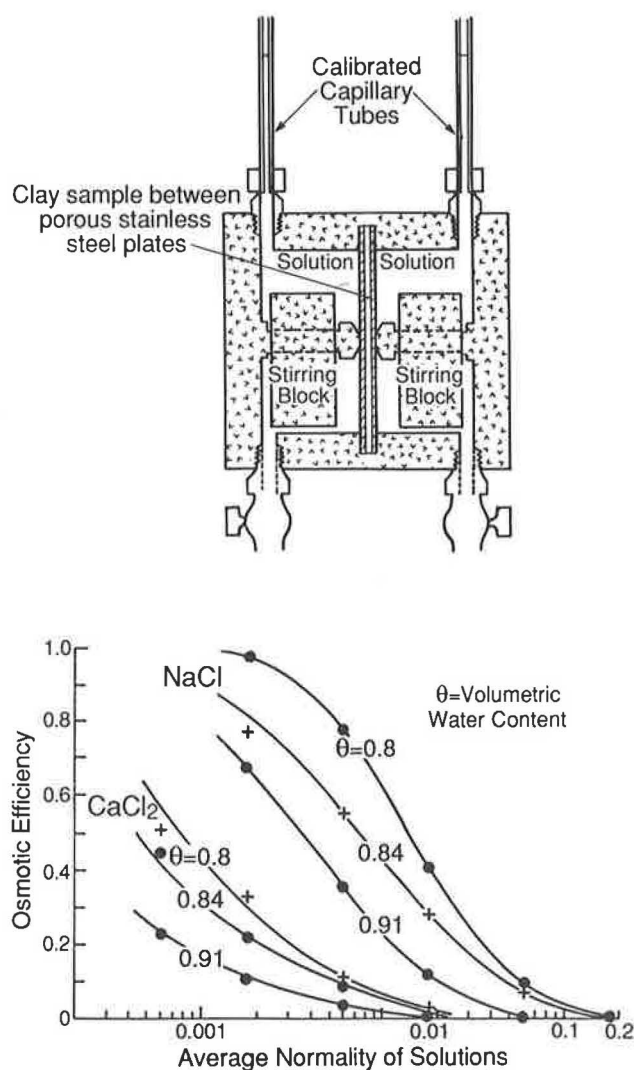
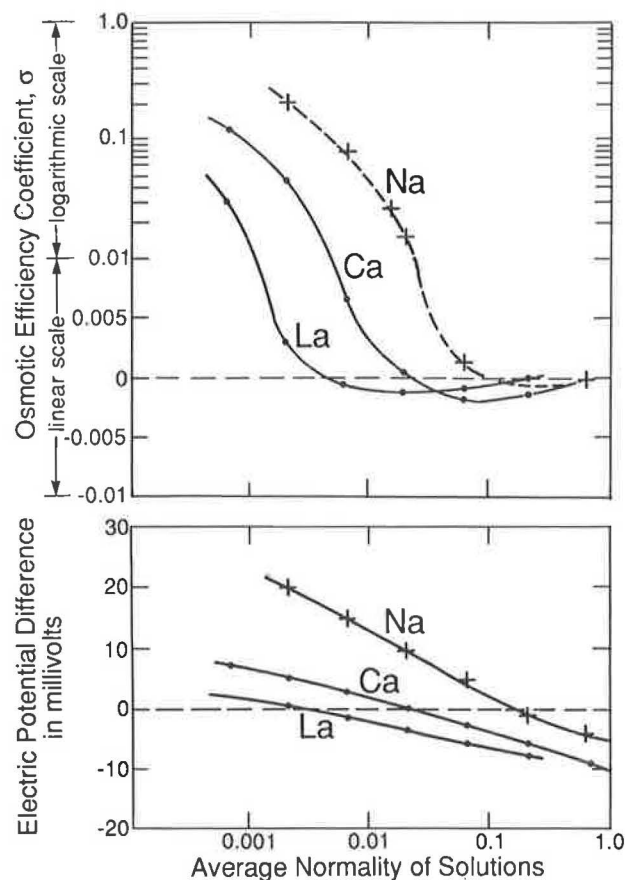


FIGURE 3 Kemper and Rollins' test cell and data on bentonite (11).

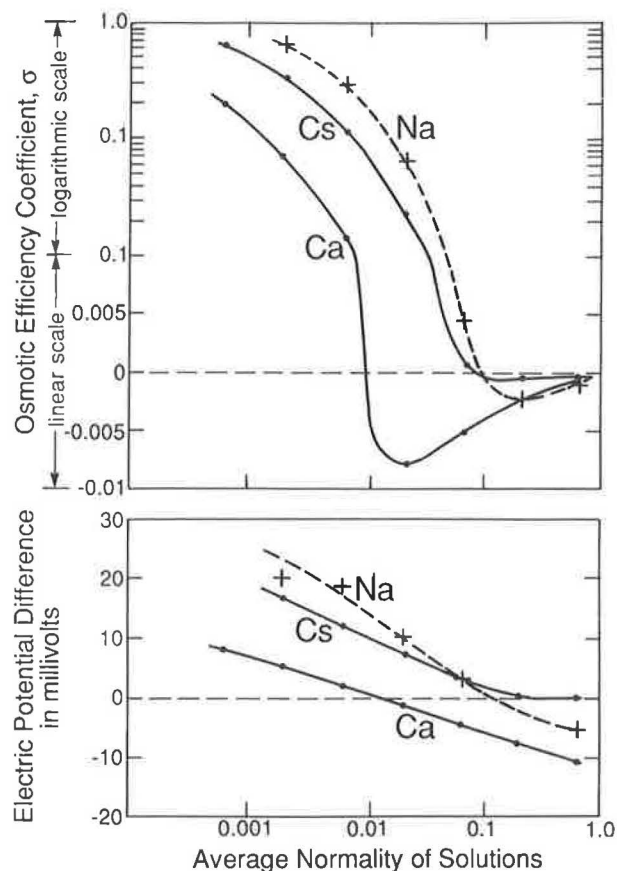
in the direction of more negative [electric] potential, indicating electro-osmosis as the mechanism involved in osmotic flow." Negative osmosis occurred primarily where the average solute concentrations were very high and became increasingly pronounced in illite and kaolinite when compared with bentonite. Under such conditions the chemico-osmotic efficiency of the clay samples is low because anion exclusion and, hence, the degree of restriction to the solute flux, is low, as is noted previously.

In 1976, Elrick et al. (16) reported data on osmotic pressures and electrical potentials caused by concentration gradients across homo-ionic montmorillonite by using the test cell illustrated in Figure 7 (top). Their data, also in Figure 7 (bottom), show dramatic changes can be caused by short circuiting the reversible Ag-AgCl electrodes on either side of the clay specimen. The rate of transfer of salt increases, and the direction of the osmotic pressure is reversed.

The explanation given by Elrick et al. for those changes is illustrated in Figure 8. The top half of Figure 8 illustrates the



**FIGURE 4** Kemper and Quirk's (15) data presenting variations in osmotic efficiency and chemically induced electrical potential differences across bentonite with average normality of external solutions and exchangeable cations.



**FIGURE 5** Kemper and Quirk's (15) data presenting variations in osmotic efficiency and chemically induced electrical potential differences across Fithian illite with average normality of external solutions and exchangeable cations.

case when the potential difference between the electrodes is being measured with a high-impedance voltmeter, or potentiometer. The clay sample behaves like a membrane because anions are excluded from the pore space and thus are prevented from migrating across the clay. Electroneutrality restrains the cations, and, hence, the flux of solute through the clay is prevented. Water migrates toward the chamber having the high solute concentration and thus generates a chemico-osmotic pressure gradient needed to stop water movement.

In contrast, the bottom half of Figure 8 illustrates the case when the electrodes are short circuited. The Ag-AgCl electrodes provide a mechanism for chlorine ions in the left chamber to become attached to the electrode in the left chamber and release their electrons to the interconnecting wire. Those electrons can flow through the wire and combine with chlorine atoms attached to the electrode in the right chamber, which converts the chlorine atoms into ions and releases them from the electrode into the adjacent solution. Electroneutrality allows cations to flow through the clay, consistent with the rate at which anions are adsorbed and released at the electrodes in the left and right chambers, respectively. The cation flow exerts drag on the water in the direction opposite to the direction of flow in chemico-osmosis. Because short circuiting

reversed the direction of the osmotic pressure, the tendency for water flow induced by cation diffusion was considerably greater than that induced by chemico-osmosis.

The discrepancies from chemico-osmosis in the Kemper and Quirk (Figures 4 to 6) data are identical to those in the Elrick et al. data (Figure 7) in that the discrepancies appear when solutes are able to migrate through the clay pores in response to externally imposed solute concentration gradients. There are two differences between the systems. One difference is that cations and anions migrate together through the Kemper and Quirk samples whereas only cations migrate through the Elrick et al. sample. The other difference is that solute migration rates in the Kemper and Quirk data vary with the composition of the samples and their pore fluids whereas in the Elrick et al. sample the solute migration rate is externally controlled with reversible Ag-AgCl electrodes. Nevertheless, the fundamental mechanism causing discrepancies from chemico-osmosis appears to be the same in both studies (i.e., solute migration). In other words, solute diffusion in response to a concentration gradient imposes drag on, or momentum transfer to, the pore fluid and thus tends to move the pore fluid in the direction of decreasing solute concentration, which is opposite to the direction of pore-fluid movement in chemico-osmosis.

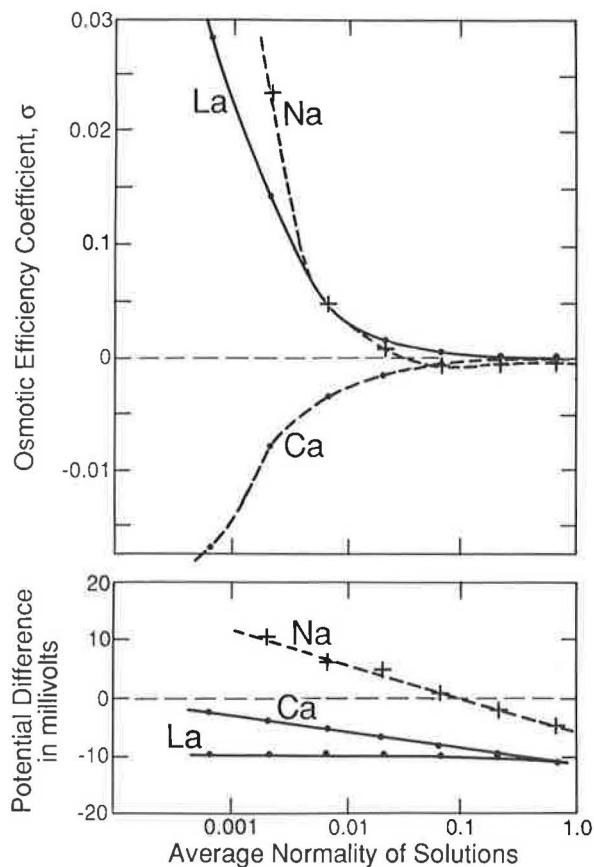


FIGURE 6 Kemper and Quirk's (15) data presenting variations in osmotic efficiency and chemically induced electrical potential differences across kaolinite with average normality of external solutions and exchangeable cations.

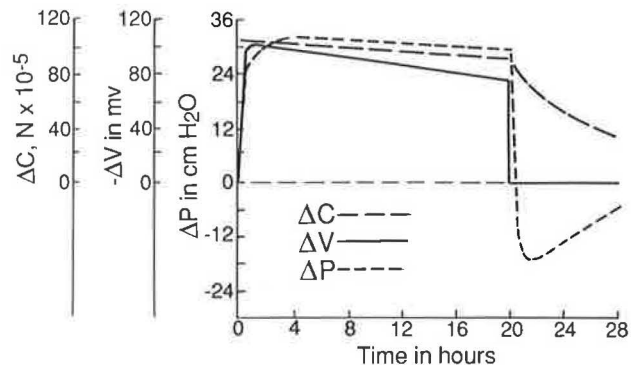
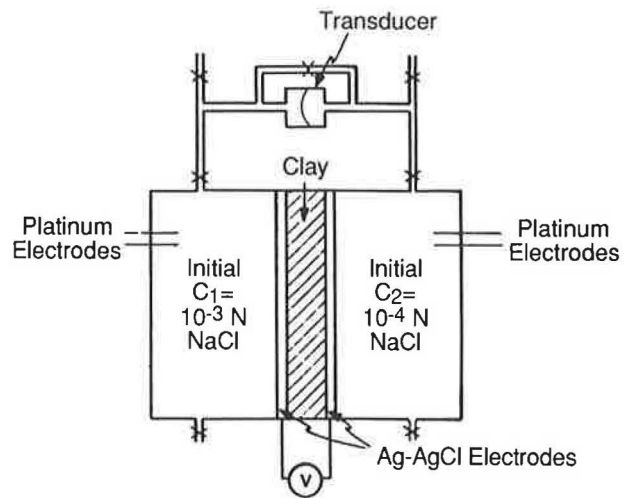


FIGURE 7 Elrick et al.'s test cell and data (16).

## DIFFUSION-OSMOSIS

Olsen et al. (17) introduced the term "diffusion-osmosis" to describe the transport of water in response to diffusion of dissolved solutes. They demonstrated this process on a loosely compacted specimen of kaolinite mounted in a triaxial system.

The triaxial system, illustrated in Figure 9, consists of a triaxial cell (A), two differential pressure transducers (C and D), a single-syringe flow pump (E), and a dual-syringe flow pump (F). The differential pressure transducers monitor the effective stress in, and the pressure difference across, the specimen (B). The single-syringe flow pump controls the volume of the specimen. The dual-syringe flow pump controls pore-fluid movement in either direction through the specimen without changing its volume and provides a means to exchange the permeant solution at either end of the specimen without changing its volume or its effective stress.

Figure 10 illustrates diffusion-osmotic pressures measured on a 5.08-cm diameter by 2.55-cm high specimen at a void ratio of 1.03 after having been consolidated to 90 psi and subsequently rebounded to 20 psi. The graph shows head difference ( $\Delta h$ ) values across the specimen when flow through the specimen is prevented. Positive values (values above the zero axis) indicate higher pore pressure at the top of the sample than at its base.

During the initial period, while distilled water was circulated through porous discs in the top cap and base pedestal, no head difference or osmotic pressure developed across the specimen. However, when 1 M NaCl was circulated through the porous disc in the base pedestal, an osmotic pressure of a few centimeters of water developed, which is on the order of the 2.55-cm height of the specimen. In this case, the higher pore pressure was at the top of the sample. Hence, the solute concentration difference tends to drive pore-fluid movement from a high concentration to a low concentration. This is consistent with diffusion-osmosis but inconsistent with chemico-osmosis.

Subsequently, as the 1 M NaCl solution leached upward through the specimen, the magnitude of the osmotic pressure diminished substantially after leaching about 50 to 75 cm<sup>3</sup> upward through the sample. Because this quantity of flow is equivalent to 2 to 3 pore volumes of the specimen, solute should have migrated upward through the specimen and into the porous stone in the top cap. In consequence, a decrease in the solute concentration difference across the specimen, and a corresponding decrease in osmotic pressure, are to be expected.

In the next period, distilled water was alternately circulated through the porous disc in the base pedestal and leached upward through the specimen. The higher pressure is now at



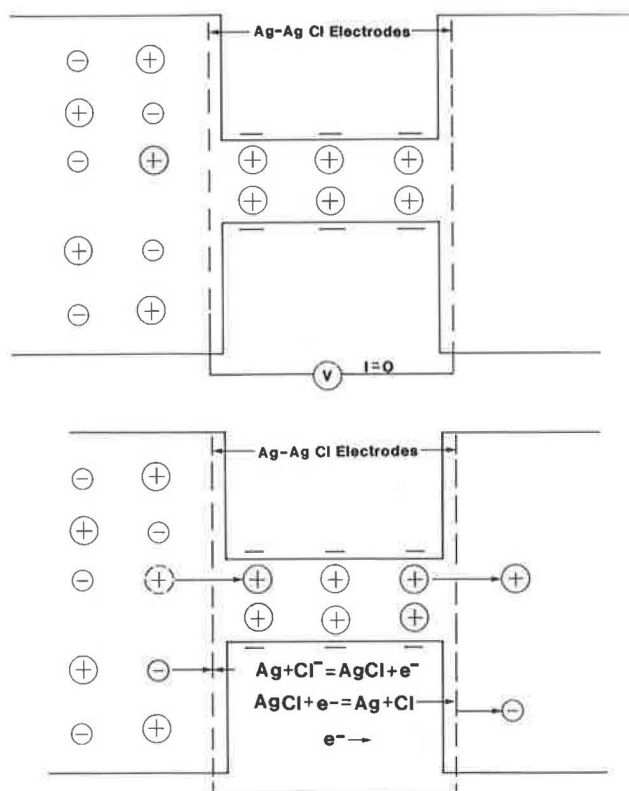


FIGURE 8 Models of the mechanisms involved in Elrick et al.'s (16) experimental data (Figure 7) when the electrodes were connected to a high-impedance voltmeter (top) and when they were short circuited (bottom).

the base, because the higher solute concentration is at the top, and the direction of solute diffusion is downward through the sample. While leaching takes place, the osmotic pressure decreases as the solute concentration in the porous disc in the top cap is diluted.

In the final period, 0.5 M  $\text{CaCl}_2$  was first circulated through the porous disc of the base pedestal. The ensuing osmotic pressure is similar qualitatively in both direction and magnitude to that generated by the 1 M NaCl solution. Subsequently, the osmotic pressure was eliminated by circulating the same 0.5 M  $\text{CaCl}_2$  solution through the porous disc in the top cap.

More recently, Yearsley (18) measured osmotic pressures in response to solute concentration gradients on undisturbed core samples from the Salton Sea Geothermal System in southern California. Those measurements were conducted in a one-dimensional consolidation test cell illustrated in Figure 11. The cylindrical sample (S) is epoxied within the sample holder (H) and confined axially by pistons (P) and laterally by a cylindrical sleeve (CS). Axial load is applied to the sample through the pistons by means of a hydraulic press (not shown). A dual-syringe flow pump (DFP) provides a means to exchange the pore fluid at either end of the specimen and to generate pore-fluid movement in either direction through the specimen. A differential pressure transducer (DPT) monitors the pressure difference across the specimen.

Figure 12 illustrates data Yearsley obtained on a light gray-green silty shale sample from a depth of 6,037 ft, having a

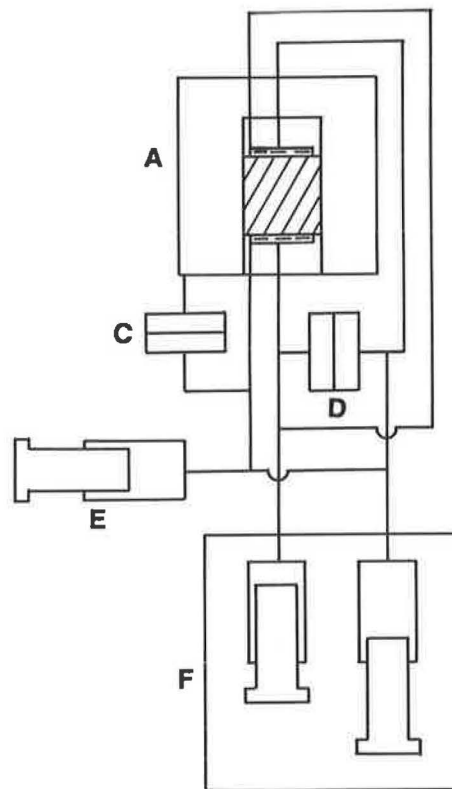


FIGURE 9 Scheme of triaxial cell (A) and permeant system.

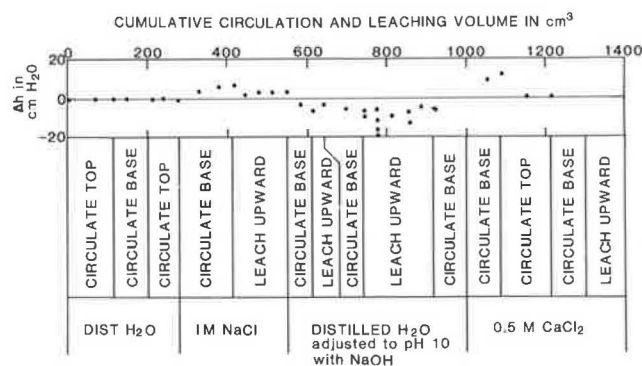


FIGURE 10 Data illustrating diffusion-osmosis in a kaolinite specimen obtained with the triaxial system illustrated in Figure 9.

porosity of 2 percent, where the dominant clay minerals were illite and chlorite. The sample was saturated and tested with solutions that have a range of solute concentrations but the same chemical composition, which was designed to simulate the chemistry of the in situ interstitial fluids. The pore-fluid solute concentration is shown on the horizontal axis in terms of weight percent of total dissolved solids (TDS). The vertical axis shows the head difference ( $\Delta h$ ) across the specimen while flow through the specimen is prevented. Positive values designate cases where the direction of the head difference is

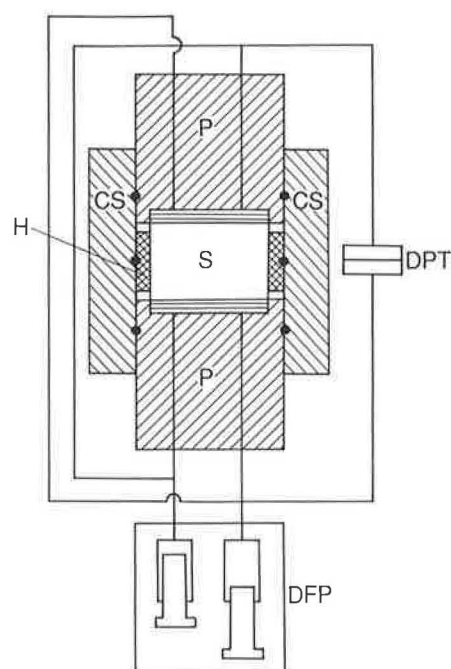


FIGURE 11 Scheme of a one-dimensional consolidation test cell and permeant system (11).

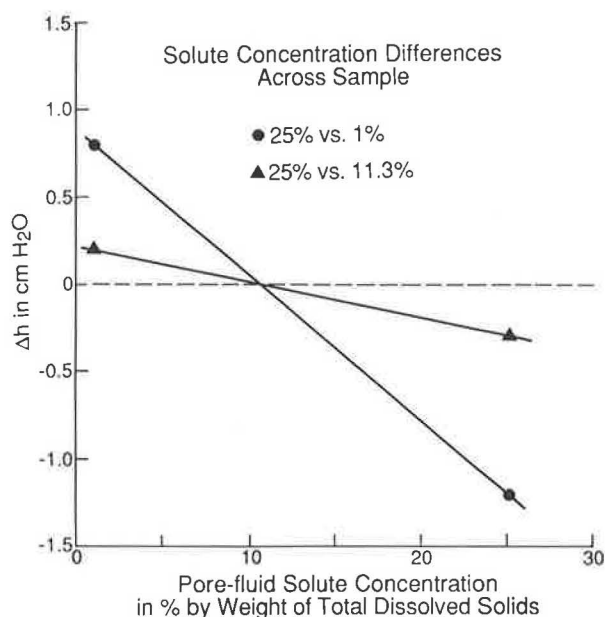


FIGURE 12 Hydraulic head differences ( $\Delta h$ ) induced by solute concentration differences across a silty shale specimen.

consistent with chemico-osmosis. Conversely, negative values designate cases consistent with diffusion-osmosis.

The sample was initially saturated by elevating the pressure in the permeant system and by leaching with a permeant having a 1 percent concentration of dissolved solutes (1 percent by weight of TDS). Then, the 1 percent solution in the upper porous disc was replaced sequentially with 11.3 percent and 25 percent solutions, which induced osmotic head

differences of 0.2 and 0.8 cm H<sub>2</sub>O, consistent with chemico-osmosis. Next, the pore fluid solute concentration was increased by leaching to 25 percent. Thereafter, the 25 percent solution in the upper porous disc was replaced sequentially with 11.3 percent and 1 percent solutions, which induced osmotic head differences of 0.3 and 1.2 cm H<sub>2</sub>O, consistent with diffusion-osmosis.

Finally, the lines connecting measurements with solute concentration differences of 25 percent versus 1 percent and 25 percent versus 11.3 percent both intersect the  $\Delta h = 0$  line at the same pore-fluid solute concentration. Those data indicate that chemico-osmosis and diffusion-osmosis progress simultaneously in the specimen, that their relative magnitudes vary with pore-fluid solute concentration, and that their magnitudes may be equal and opposite for a pore-fluid solute concentration of approximately 10 percent (by weight of TDS).

## DISCUSSION OF RESULTS

The question arises whether electro-osmosis is an additional mechanism involved in chemically driven groundwater movement. Kemper and Quirk (15) suggested that electro-osmosis was the mechanism involved in the osmotic flows they observed in the direction of decreasing solute concentration because the flow was generally in the direction of more negative potential. Also, Veder (8) uses the term "natural electro-osmosis" to describe his view that the pore water in argillaceous materials migrates in response to electrical potentials generated by weathering reactions.

To examine this question, it needs to be recognized that the term "electro-osmosis" is commonly used from a phenomenological point of view to describe soil-pore-fluid movement in response to an electric potential gradient that is externally imposed through electrodes. The potential gradient generates a current between the electrodes, and the current causes movement of the bulk pore fluid. The mechanisms involved include chemical reactions that transfer charge between the electrodes and the soil pore fluid. The mechanisms also include fluxes of, and interactions among, charged solute species and water. The number and complexity of the mechanisms involved vary with the magnitude of the electric potential imposed and the composition of the electrodes, the soil, and its pore fluid.

In contrast, Kemper and Quirk (15) refer to "electro-osmosis" as a specific mechanism that can be driven by externally imposed chemical gradients and reactions. This use of the term differs from the other in that this use focuses on a single mechanism (i.e., the coupling of an electrical gradient or current with bulk pore-fluid movement). In the simplest case, consistent with Kemper and Quirk's experimental system, the electrical gradient generates a current by driving positive ions to the cathode and negative ions to the anode. Ion fluxes are coupled with bulk fluid through viscous drag. Because of the relative sizes and distributions of cations and anions in soil pores, the amount of fluid carried by cations toward the cathode generally exceeds the amount of fluid carried toward the anode.

A fundamental problem with Kemper and Quirk's definition of "electro-osmosis" is that no current flows through the clay specimen. Another difficulty is that the measured elec-

trical potentials are not generating a current. Rather, they are well-known consequences of the diffusion of charged solutes through porous media in response to solute concentration gradients. The potentials are induced to counteract the tendency for ions of one charge to diffuse more rapidly than do ions of the opposite charge. In other words, the induced potentials equalize the fluxes of oppositely charged species and thus prevent current flow through the specimen.

Therefore, Kemper and Quirk's (15) use of the term "electroosmosis" may be inappropriate and that "diffusion-osmosis" is both adequate and more appropriate to describe the mechanism involved in the osmotic flows they observed in the direction of decreasing solute concentration gradients. In addition, electro-osmosis can be understood more clearly as a special case of diffusion-osmosis. In both mechanisms, bulk fluid movement is driven by the diffusion of solute species. Electro-osmosis differs from diffusion-osmosis only in that an externally applied electrical gradient controls the fluxes of the solute species.

The forgoing also has implications concerning the mechanism Veder (8) introduced and described with the term "natural electro-osmosis." In Veder's mechanism, geochemical weathering reactions generate electric potentials that drive electro-osmosis. One unknown is whether such electrical potentials cause currents by driving fluxes of cations and anions or whether they are induced for a different reason, such as the potentials that arise from diffusion in response to concentration gradients. Another unknown is whether chemical reactions in nature can drive diffusion-osmosis without the aid of electric potentials and currents. Those questions have yet to be clarified.

## CONCLUSIONS

A review of laboratory evidence demonstrates two mechanisms by which chemical gradients cause groundwater movement. Chemico-osmosis, widely recognized since the 1960s, causes soil-pore-fluid movement from dilute to more concentrated solutions and is most effective in densely compacted clays of high exchange capacity and low soil-pore-fluid solute concentration. Evidence has been accumulating since about 1970 for an additional mechanism for which the term "diffusion-osmosis" was recently introduced. In contrast with chemico-osmosis, diffusion-osmosis causes soil-pore-fluid movement from concentrated to dilute solutions, and it has been observed in argillaceous materials of low exchange capacity and high soil-pore-fluid solute concentrations. It is suggested that electro-osmosis is a special case of diffusion-osmosis where soil pore fluid moves in response to the migration of solute species when an externally imposed electrical gradient controls the migration of the solute species.

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