Chemical causes of groundwater movement

Harold W. Olsen
U.S. Geological Survey, Box 25046, M.S. 966, Denver, Colorado 80225, USA

Elliot N. Yearsley & Karl R. Nelson
Colorado School of Mines, Golden, Colorado 80401, USA

ABSTRACT It became widely recognized during the 1960's that chemico-osmosis is a mechanism by which chemical gradients cause groundwater to move from dilute to more concentrated pore-fluid solutions in densely compacted materials of high-exchange capacity in deep sedimentary basins. Since then, additional mechanisms have been identified that cause groundwater movement in response to chemical gradients and reactions, namely, diffusion-osmosis and electro-osmosis. Moreover, research concerning electro-osmosis, and landslides induced by chemically-driven electro-osmosis, suggest that chemical causes of groundwater movement may be of more importance in geomechanical processes than has yet been recognized. An experimental system has been developed to investigate the near-surface conditions where chemical causes of groundwater movement are significant. Preliminary data on a loosely compacted specimen of kaolinite, having a void ratio of 1.043 and a thickness of 2.55 cm, demonstrate diffusion-osmosis in terms of osmotic pressures on the order of 5 to 10 cm H_2O in response to diffusion of 1 M NaCl and 1 M CaCl_2 solutions through the specimen.

INTRODUCTION

Herein, "osmosis" refers to non-hydraulic components of groundwater movement generated by thermal, electrical, and chemical causes. Naturally occurring osmosis is recognized as a possible source of anomalous pore-fluid pressures which facilitate overthrust faulting (Hanshaw & Zen, 1965) and landsliding (Veder, 1981). It may be influencing the mechanics of groundwater systems (Greenberg et al., 1973; Marine, 1974; Marine & Fritz, 1978, 1981; Olsen, 1972), and it may be a cause of non-Darcy flow behavior in argillaceous materials observed in laboratory studies during the last three decades (Olsen, 1985).

These examples suggest that osmosis may be more important in geomechanical processes than has yet been recognized. However, an adequate basis for understanding the effects of osmosis in such processes has yet to be developed. In particular, there are fundamental gaps in our understanding of the mechanisms by which chemical conditions in nature can generate groundwater movement.
In this paper, the existing information concerning these mechanisms is reviewed, an experimental system developed to investigate the near-surface conditions in nature wherein chemical causes of groundwater movement are significant is described, and experimental information on osmosis caused by diffusion in a loosely compacted specimen of kaolinite is presented.

REVIEW OF EXISTING INFORMATION

During the 1960's it became widely recognized that groundwater moves from dilute to more concentrated pore-fluid solutions in densely compacted argillaceous materials of high-exchange capacity in deep sedimentary basins. This understanding evolved from both field and laboratory studies showing clays to exhibit chemico-osmotic behavior consistent with that of leaky semi-permeable membranes (Berry, 1959; Bredehoeft et al., 1963; Hanshaw & Hill, 1969; Hanshaw & Zen, 1965; Kemper, 1961; Kemper & Rollins, 1966; Young & Low, 1965). The fundamental cause of such pore-fluid movement is the free-energy gradient in the water phase of the solutions. The efficiency of this driving force is governed by the extent to which solutes are excluded from the pore space by the electrical double layers that extend into the pore space from the charged surfaces of the membrane material (Fritz, 1986; Graf, 1982).

Data published in the 1970's show discrepancies from the leaky membrane model. The fundamental finding is that the direction of soil pore-fluid movement in response to a solute concentration gradient is not always from the dilute solution to the more concentrated solution. Elrick et al. (1976) show the direction of pore-fluid movement generated by a solute concentration gradient in sodium montmorillonite can be reversed by short circuiting electrodes in contact with opposite sides of the test specimen. This also short-circuits the semi-permeable characteristic of the specimen. Kemper & Quirk (1972) showed reversals in the direction of pore-fluid movement also occur in systems having a low degree of ion exclusion. This occurs in materials of relatively low exchange capacity (kaolinite) and relatively high concentrations of solutes in the pore fluids. The mechanism revealed by these reversals is the convection, or drag, of bulk pore fluid by the diffusion of solute species. This mechanism is referred to below as diffusion-osmosis.

Thus, naturally occurring osmosis may be caused by factors in addition to the simple solute-concentration gradients that characterize the chemical cause of pore-fluid movement in semi-permeable membranes. Diffusion-osmosis differs from chemico-osmosis in that the convection of pore fluid by diffusion depends not only on the concentration gradient of the dissolved species but also on its hydrated radius, which varies with its composition. In addition, it appears reasonable to expect osmosis to be generated by electrical potential gradients that arise from naturally occurring geochemical reactions. This follows because electro-osmosis, fundamentally, is a variation of diffusion-osmosis where electric fields, rather than concentration gradients, provide the driving forces on the solute species which...
carry bulk pore fluid with them as they migrate through a porous medium.

The question arises whether naturally occurring osmosis is significant in natural environments other than those containing densely compacted materials of high-exchange capacity that exhibit semi-permeable membrane behavior. An affirmative answer is suggested by evidence that electro-osmosis is most efficient in unconsolidated argillaceous materials of low-exchange capacity that are abundant in near-surface environments (Mitchell, 1976). In this regard, Veder (1981) claims electro-osmosis is generated by oxidizing and reducing reactions that occur above and below the weathering front in near-surface materials. He further claims that excess pore pressures are thus at the weathering front, that such excess pore pressures are a common source of landslides in natural terrain, and, finally, that such landslides can be stabilized by short circuiting the electrical potential gradient across the weathering front with iron rods.

EXPERIMENTAL SYSTEM

Figure 1 presents a photographic view and a scheme of the experimental system which consists of (a) a triaxial cell, (b) a single-channel flow pump, (c) a dual-channel flow pump, (d) two differential pressure transducers, (e) a permeant composition exchange system, and (f) a manifold that interconnects the above elements with the permeant lines leading to the base pedestal and top cap for a specimen. Many of these capabilities have previously been introduced and integrated to provide a versatile, flexible-wall permeameter (Olsen et al., 1985; Olsen et al., 1988). The new capabilities of this system are illustrated in the scheme. First, the specimen volume is controlled by the single-channel flow pump. Second, the dual-channel flow pump enables the specimen volume to be maintained constant during leaching, and also during exchange of permeant at one or both ends of the specimen. These capabilities provide volumetric control of a specimen, in contrast to previous flexible-wall systems where the effective stress in the test specimen is externally controlled. One advantage of specimen-volume control is that the tendency for specimen-volume change can be readily measured in terms of effective stress changes. In comparison, seepage-induced volume changes cannot be measured in most stress-controlled, flexible-wall permeameters. Another advantage of specimen-volume control is that, during leaching, the effect of changes in the pore-fluid chemistry on the fabric and the volume of a specimen can be measured separately. These effects cannot be distinguished in stress-controlled systems.

SAMPLE PREPARATION, TESTING, AND RESULTS

The data presented in this paper were obtained on a specimen of Standard Air Floated (SAF) clay that is marketed by the Georgia Kaolin Company. The specimen was molded from a slurry having a water content of about 110%. The slurry was prepared by letting distilled and deaired water be absorbed by dry clay powder under
Fig. 1 Photograph of the experimental system and scheme of the triaxial cell (TC), the differential pressure transducers (DPT), the single-channel flow pump (SFP) and the dual-channel flow pump (DFP).

vacuum in a dessicator. To form the specimen, the slurry was poured into a cylinder, 5.08-cm dia. x 10-cm long, whose base was capped by a porous stone and submerged under water in a bucket. A porous stone and piston were placed on the slurry at the top end of the cylinder. The entire assembly was mounted in a loading press, where the sample was consolidated very slowly at a constant rate of deformation to a predetermined volume that would yield a loosely consolidated specimen with sufficient strength to be trimmed and mounted in a triaxial cell. Finally, the material was extruded from the cylinder, cut to a convenient length, jacketed with an impermeable membrane, and mounted in the triaxial cell between the base pedestal and the top cap.

The experimental program consisted of two phases. The first phase demonstrated that the experimental system enables constant-flow hydraulic conductivity and continuous-loading compressibility measurements on a specimen mounted in a triaxial cell. The data obtained during this phase will be reported elsewhere. Figure 2 presents the data obtained in the second phase of the experimental program after the sample had been consolidated to about 90 psi and subsequently rebounded to 20 psi. The horizontal axis describes
**Chemical causes of groundwater movement**

![Graphs and data](image)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIST H₂O</td>
<td>DISTILLED H₂O adjusted to pH 10 with NaOH</td>
</tr>
<tr>
<td>IM NaCl</td>
<td>0.5 M CaCl₂</td>
</tr>
</tbody>
</table>

Fig. 2. Experimental data on a kaolinite specimen.
the sequence of circulation and leaching periods conducted with
the dual-channel flow pump, and also the corresponding cumulative
volume of permeant that was either circulated through the porous
discs at the ends of the specimen or leached upward through the
specimen. The circulation and leaching volumes can readily be
converted to equivalent pore volumes because the void volume of
the specimen was approximately 25 cm$^3$.

The void ratio of the specimen was maintained constant
throughout the second phase of the experimental program, with the
following exception. After the initial period when distilled
water was circulated through the porous discs in the top cap and
the base pedestal, pore fluid was infused into the specimen with
the single-channel flow pump in order to reduce the effective
stress back to about 20 psi. The effective-stress plot shows this
event as a vertical discontinuity and also shows the void ratio of
the specimen before and after this event.

The data of principal interest are those in the lowest graph
immediately above the description of the circulation and leaching
periods. This graph shows the head difference across the specimen
when flow through the specimen was prevented. Under this
condition, the head difference across the specimen is the osmotic
pressure.

During the initial period of circulation through the porous
stones in the top cap and base pedestal, there is no head
difference or osmotic pressure across the specimen. However, when
1 M NaCl was circulated through the porous stone 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 during this phase of the experimental program. In this
case, the higher pore pressure was at the top of the sample, which
is designated in the plot by showing head-difference values above
the zero axis. Hence, the solute concentration difference is
tending to drive pore-fluid movement from a high concentration to
a low concentration, which is consistent with diffusion-osmosis
but inconsistent with chemico-osmosis in a semi-permeable
membrane.

Subsequently, as the 1 M NaCl solution was leached upward
through the specimen, the magnitude of the osmotic pressure
diminished substantially after leaching about 50 to 75 cm$^3$ upward
through the sample. Because this quantity of flow is equivalent
to 2 to 3 pore volumes of the specimen, the decrease in the
osmotic pressure is to be expected as the solute concentration
increases in the porous stone in the top cap and thereby
diminished the solute concentration difference across the
specimen.

In the next period, distilled water was alternatively
circulated through the porous disc in the base pedestal and
leached upward through the specimen. The higher pressure is now
at the base, because the higher solute concentration is at the
top, and the direction of solute diffusion is downward through the
sample. As 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, 1 M 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 1 M CaCl₂ solution through the porous disc of the top cap.

The other data in Figure 4 provide information on the magnitudes of the permeability and effective stress of the specimen during the osmotic pressure measurements, and also their variations during the periods of circulation and leaching. During each period of leaching that resulted in a change in the pore-fluid composition in the specimen, the permeability decreased and its variation with time reflects the progress of leaching. Consideration of the magnitudes of the induced permeability changes is beyond the scope of this paper except to note that the permeability changes occurred while the specimen void ratio was maintained constant, and hence the permeability changes must have been caused by chemically-induced changes in the clay fabric.

The effective stress variations during circulation and leaching are more complex. The overall rising trend of effective stress may reflect the gradual dissolution of a small amount of undissolved air in the specimen, whose presence is suggested by the values for $\bar{E}$ that are less than unity. Nevertheless, a chemical effect on the effective stress corresponding to that on the permeability is clearly evident for the period when the composition of the pore fluid in the specimen was changed from 1 M NaCl to distilled water having a pH of 10. Similar chemical effects of lesser magnitude during other leaching periods, if present, are obscured by the data scatter in the overall rising trend of effective stress noted above.

CONCLUSIONS

An experimental system has been developed to investigate the near-surface conditions where chemical causes of groundwater movement are significant. Preliminary data on a loosely compacted specimen of kaolinite, having a void ratio of 1.043 and a thickness of 2.55 cm, demonstrate diffusion-osmosis in terms of osmotic pressures on the order of 5 to 10 cm H₂O in response to diffusion of 1 M NaCl and 1 M CaCl₂ solutions through the specimen.

REFERENCES


