The Development of Non-Homogeneous Flow Condition During Electro-Osmosis in a Saturated Clay Mineral[1]

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The possibility of the development of a non-homogeneous flow condition based on an analysis of the characteristics of the electro-osmotic system is discussed. The analysis indicates that, due to the unique characteristics of the hydrogen ion in aqueous solution, its electro-osmotic flow rate per unit of current may be less than that of other ions in the clay water system. The electro-osmotic flow rate per unit of current is presented for several homo-ionic modifications of North Carolina kaolin including hydrogen. The flow rate for the various cations is in accord with the following sequence: H < Fe < Ca < Na < Al. The change in the electro-osmotic flow rate during the transition from a hydrogen to a Ca clay is presented. Data are presented to show that the surface characteristics of an H clay saturated with distilled water change with time and that this change is indicated by a greatly increased electro-osmotic flow rate. The effect of various concentrations of $AlCl_3$ and $CaCl_2$ on the electro-osmotic flow rate of Al and Ca clays is shown.

These results show that a wide variation in the electro-osmotic flow rate can occur throughout the clay water system during electro-osmosis and that such conditions offer an explanation for such phenomena occurring during electro-osmosis such as the development of a moisture gradient, volume change, and changes in intergranular stresses and pore pressures. These data also imply that the electro-osmotic flow rate for a system may be limited to the flow rate for a hydrogen saturated material.

● THE utilization of electro-osmosis for draining and controlling the moisture in heavy clay structures appears to have some promise of success; however, a number of phenomena occurring during electro-osmosis must be more fully understood before its use can be placed on a sound basis.

Casagrande (*1*) has shown that during electro-osmosis, a redistribution of the moisture content at points between the cathode and anode occurs, resulting in a gradual decrease in the moisture content toward the cathode. This redistribution is a function of time and also a function of the potential gradient. The slope of the moisture distribution curve is maximum for low potential gradients and approaches zero when the potential gradient increases beyond bounds. Casagrande (*2*), as well as other investigators (*3*), has observed that pore water stresses and intergranular pressures develop during electro-osmosis and that shrinkage and cracking of the material occur. Various investigators (*2, 4, 5*) have observed that the combined application of a surcharge and electro-osmosis produces a volume decrease whose magnitude cannot be attained by either process acting separately.

This paper is an attempt to show that non-homogeneous flow conditions develop during electro-osmosis in clays due to the change in the surface characteristics of the material and that this condition of non-homogeneity

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may well form the basis for an explanation of some of the above observed phenomena.

SOME THEORETICAL CONSIDERATIONS

If several characteristics of the electro-osmotic system are analyzed qualitatively, the possibility of the development of a non-homogeneous flow condition in a clay water system during electro-osmosis becomes evident.

First, it must be recognized that for most electrodes used in electro-osmosis the concentration of hydrogen ions around the anode becomes much higher than in the remainder of the system. At the cathode, the concentration of hydroxyl ions is correspondingly increased. This results in the development of zones in the region between the anode and cathode each possessing different surface characteristics. In the immediate vicinity of the anode, a hydrogen saturated clay should tend to exist. At some distance from the anode, the clay will have properties similar to those of the original material. Between these two points will be a transition zone in which there should be a continuous change in the concentration of the hydrogen ions and the original ions adsorbed by the clay with distance from the hydrogen saturated zone. The length and position of these zones from the anode would, of course, be a function of time.

When the electrical field is applied to the saturated clay sample, the flow of water is proportional to the potential gradient. The velocity of flow is sometimes given by:

$$V = KeE \tag{1}$$

where V = quantity of liquid moved in unit time through a unit cross section
E = potential gradient (volts/cm)
Ke = electro-osmotic permeability (Cm/sec/volt/Cm)

The electro-osmotic flow could equally well be represented by the following formula:

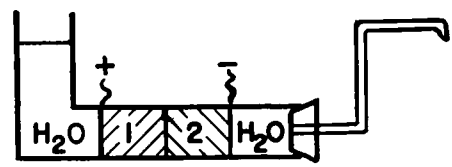
$$V = K_i i \tag{2}$$

where V = same as in equation (1)
i = current density (amps/Cm^2)
K_i = electro-osmotic permeability (Cm/sec/Amp/Cm^2)

For the purposes of this paper K_i will be used, and any future reference to electro-osmotic permeability will refer to this constant. The utility of K_i in this discussion will become evident.

The second factor about the electro-osmotic system which must be recognized is that the current flowing through each of the zones previously mentioned is the same regardless of the surface characteristics of the clay in that zone. The hydrogen zone, the transition zone, and the original material may all have different resistances. But since they are connected in series, the current flowing through them will be the same; and the potential drop in each zone will be distributed according to Ohm's Law. It should be readily apparent that if the electro-osmotic permeability K_i or the flow for a given current density is a function of the surface characteristics of the clay, then a non-homogeneous flow condition could exist. To clarify this point further, consider Figure 1, which shows a hydrogen saturated clay adjacent to the anode and a calcium saturated clay adjacent to the cathode. The same current will flow through zone 1 as zone 2. If we assume (experimental results validate this assumption) that the flow of water per unit of current is greater for calcium clay than for the hydrogen clay, then a non-homogeneous condition could exist, and more water would flow out of zone 2 than flows into that zone. There would thus be a decrease of water in zone 2. Since the electro-osmotic flow is also a function of the moisture content, K_i for zone 2 will tend to decrease as its moisture content decreases until K_i for zone 2 equals K_i for zone 1. At this point, the moisture content of zone 2 will be less than that of zone 1, and K_i for zone 1 would have determined the flow rate for the system.

The third point which should be recognized is that the relationship between the hydrogen



1 = hydrogen saturated clay

2 = calcium saturated clay

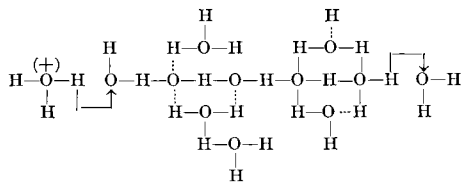
Figure 1.

ion and its environment in aqueous solution is completely different from that of other cations likely to be found in the clay water system. Gieseking (*6*), in discussing the nature of water in the clay water system, states as follows:

"The oxygen atom in water according to the work of Bernal and Fowler and of Cross tends to direct its attractive forces toward the four corners of a regular tetrahedron. In the water molecules, most of the attractive force of the oxygen atom will be directed toward the two corners of the tetrahedron where the hydrogen atoms will reside, but a small residual force will be directed toward the two other corners of the tetrahedron. The total positive attractive force on the two hydrogen atoms should exactly equal the total negative attractive force on the divalent oxygen atom. For steric reasons, according to Bernal and Fowler, the two hydrogens cannot exactly neutralize the four spots on the oxygen atoms so that the spots where the hydrogen atoms reside will carry a slight residual positive charge and the other two corners of the tetrahedron should carry an equally small residual negative charge. Water molecules, therefore, tend to attract or adsorb each other. In this way a molecule of water is subjected to less strain if the residual positive side of the molecule has its positive charge neutralized by the negative side of a neighboring molecule. This process, whereby residual positive hydrogen rich spots of one molecule neutralize residual negative spots in neighboring molecules is called hydrogen bonding. According to Bernal and Fowler, hydrogen bonding does not stop with the union of only two molecules of water in the liquid phase, but from X-ray diffraction patterns of water, Fowler and Bernal have concluded that a few tens or hundreds of water molecules tend to hydrogen bond. The oxygen ions in the surface of the clay mineral crystals, like the oxygen atoms in the water molecules, will also be weakly charged. These layers of oxygen atoms will direct most of their forces backward into the crystal towards the positive silicon or metallic ions in the interstitial spaces of the clay mineral crystal. Weak residual negative charges will result on the outside layer of oxygen atoms in the clay mineral crystals, which will be free to take part as donors in hydrogen bonding. Each oxygen if free from other adsorbed substances could attract the hydrogenated or positive side of a water molecule."

Most physical chemists believe that the relationship of the hydrogen ion to this picture of liquid water provides a basis for an explanation of the high mobilities of the hydrogen ion in aqueous solution as compared with the mobilities of other ions. The mobilities of most ions in aqueous solution varies from about 3 to 8 $\times 10^{-4}$ Cm per sec, and the mobility of the hydrogen ion is about 3.6 $\times 10^{-3}$ Cm per sec. The mobility of the hydrogen ion is from five to seven times the mobility of cations likely to be found in the clay water system. An explanation of the abnormal mobility of the hydrogen, or more correctly the hydronium ion, is based on the associated structure of water as previously outlined, and is given by Kortum and Bockris (*7*) as follows:

"A given hydronium ion can be considered to be in equilibrium with a swarm consisting of a large number of water molecules, so that proton exchange could take place over a large distance, as shown in the following two dimensional project:



In the equilibrium state, this proton exchange occurs equally in all directions, but application of an external field causes the motion to have a preferred component in the direction of the field because the solution is being depleted of H_3O ions at the cathode."

According to this picture, a large part of the current carried by the hydronium ion is affected by proton transfer over a large distance and not by the ion moving continuously through the liquid. On the other hand, the various other cations of the clay water system move continuously through the system. Some of these ions may be hydrated, and some are believed not to be hydrated.

According to the Helmholtz theory, the electrical force acts on charges within the electrical double layer. The charged ions within this layer move as a consequence of this force. Water in the capillary pores in the vicinity of this layer are dragged along with the moving layer as a result of viscous friction. Winterkorn (*8*) presents evidence to show that the applied electric field potential acts on all molecules and ions within the sphere of influence of the electric field originating from the solid surface. He shows that these molecules move as a direct result of their electric state and the applied potential rather than as an indirect result of the transmission of momentum from a moving layer adjacent to the solid surface, as indicated by the Helm-

holtz theory. In view of the unique conducting mechanism suggested for the hydronium ion and with due consideration of the above concepts of electro-osmotic flow, it seems entirely probable that the flow rate for a hydrogen clay per unit of current will be considerably less than other cations associated with the clay water system. If this concept is correct non-homogeneous flow conditions in the electro-osmotic system are an immediate consequence.

EXPERIMENTAL MATERIALS AND METHOD OF PREPARING HOMO-IONIC CLAYS

A North Carolina kaolin was the clay used in these experiments. Differential thermal analysis curves for this material are shown in Figure 2. The cation exchange capacity of the material, as determined by the barium acetate method, was around 15 milliequivalents per hundred grams of clay.

Various investigators such as Paver and Marshall (*9*), Mukherjee and his co-workers (*10*) have shown that so-called H clays prepared by electrodialisis or by treatment with dilute acids contain both H and Al as exchangeable cations and that the proportions of Al cations are usually large. Wiklander (*11*) has demonstrated both theoretically and experimentally that true hydrogen clays can be prepared by treatment with hydrogen saturated exchange resins. He states as follows:

" By mixing an M saturated exchanger of low exchange capacity and acidoid strength with an appropriate amount of an H saturated one of high capacity and acidoid strength, the M ions will be practically completely adsorbed on the latter exchanger. Systems of that kind are soils and exchange resins of the type used here. From experiments it appeared that a resin/soil weight ratio of 1 (for mineral soils) and a reaction time of 2 to 4 hours are sufficient for this purpose."

In these experiments, hydrogen saturated clays were prepared by using exchange resin Amberlite IR120. Enough clay was mixed with water to form approximately a 5 percent solution. Resin in amount to give at least a resin to soil ratio of 1 was added to the system and stirred thoroughly. The resin and clay were allowed to stand for approximately 24 hours during which time they were periodically mixed. Al, Ca, Na, Fe modifications were prepared by mixing an excess of the appropriate cation saturated resin with H clay. The

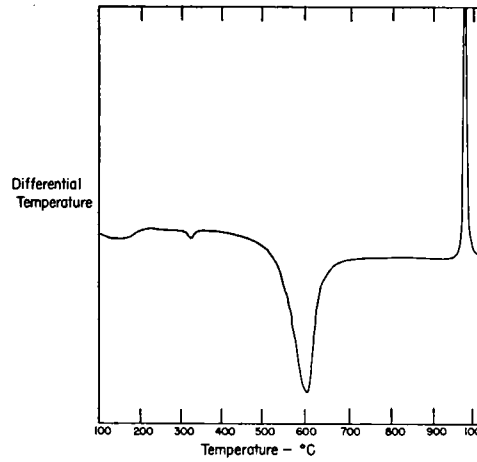


Figure 2. Differential thermal analysis for North Carolina kaolin.

exchange resin was separated from the clay by passing the mixture through a silk cloth of appropriate pore size. Excess water was sucked out of the clay, using a double-walled auto irrigator pot. By using this procedure, relatively large amounts of the homo-ionic clay mineral could be prepared.

ELECTRO-OSMOTIC APPARATUS AND TEST PROCEDURE

An apparatus utilizing the symmetry principle of Briggs was used in these experiments and is shown schematically in Figure 3. This apparatus was made from Plexiglass, and the construction was similar to that of an apparatus described by Winterkorn (*8*). The Plexiglas ring containing the sample was 5 cm. inside diameter and 4 cm. long. Reversible silver-silver chloride electrodes were utilized to

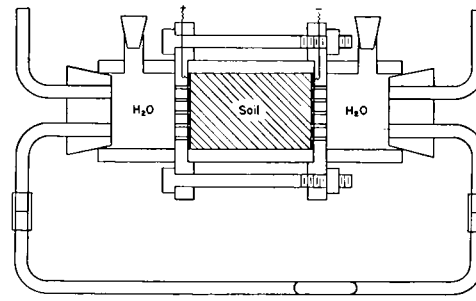


Figure 3. A schematic diagram of electro-osmotic apparatus.

TABLE 1
THE ELECTRO-OSMOTIC FLOW RATE OF H KAOLINITE SATURATED WITH VARIOUS IONS

Adsorbed Cation	Volts	Milli-Amps	Time for 0.25 Ml Flow
			sec.
H	9	10	80
Al	60	10	15
Ca	35	10	30
Na	35	10	22
Fe	20	10	42

prevent difficulties associated with evolution of gases at the electrodes, which occurs when using platinum or other type electrodes. The electrodes were made from silverplate 1/32 of an inch and were perforated with holes approximately 1/16 of an inch in diameter. The electrodes were chloridized essentially according to procedures described by Hepburn (*12*) and Biefer and Mason (*13*). This procedure consisted of placing the silverplate, which was cleaned thoroughly in nitric acid, in the apparatus filled with 0.1N HCl. A current of approximately 50 milliamps was allowed to flow for between two and three hours. The silverplate was charged positively, and a perforated carbon electrode served as the cathode during the chloridization process.

In phase three, hydrogen-saturated clays were prepared by mixing the clay with resin for 3 and 24 hours, respectively. After the clay was separated from the resin, it was allowed to stand in distilled water. Periodically, the water was sucked out and the electro-osmotic flow rate determined.

In phase four, Al and Ca kaolinite modifications were prepared and allowed to dry. Various concentrations of $AlCl_3$ and $CaCl_2$ were mixed with the appropriate modification to bring the moisture content to approximately 75 percent, after which the electro-osmotic flow rate was determined.

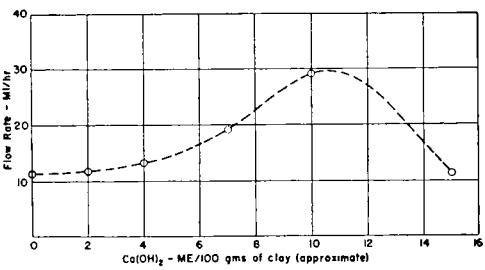


Figure 4. The relationship between the electro-osmotic flow rate and calcium hydroxide added to H kaolinite.

TEST RESULTS

Table 1 shows a summary of the experimental results of the electro-osmotic flow rate and applied potentials. It will be observed from these data that the order of the flow rate per unit of current is H < Fe < Ca < Na < Al while the order for the applied potential is H < Fe < Ca = Na < Al. It will be noted that all of the four bases have a considerably greater flow rate per unit of current than hydrogen, and the ratio of the flow rate of the base ion to hydrogen ion varies from approximately 2 for iron to 5 for aluminum.

Figure 4 shows the change in the flow rate per unit of current during the transition from an H to a Ca kaolinite. It is noted that the flow rate for Ca clay is nearly 2.5 times the flow rate for H clay. At approximately 15 milliequivalents of $Ca(OH)_2$, the flow rate has dropped back to essentially the flow rate for H clay. This reduction probably occurs because the clay is saturated with calcium, and there is excess electrolyte in the system.

Table 2 shows the change in flow rate of an H kaolinite on standing in distilled water. It is noted that the flow rate at the end of 21 days is greater than that for any cation except Al. It is obvious that a change in the surface characteristics of the clay has occurred. The nature of the changes in the flow rate per unit current and the applied potential lead one to suspect that Al is acting as an exchangeable cation. A number of experiments similar to the one described here have been carried out. In some of them the change in the surface charac-

TABLE 2
THE CHANGE IN THE ELECTRO-OSMOTIC FLOW RATE OF H KAOLINITE AFTER STANDING IN DISTILLED WATER

Resin-Clay Mixing Time	Time After Separation	Volts	Milli-Amps	Time for 0.25 Ml Flow
				sec.
3 hours	3 hrs.	10	10	73
	96 hrs.	10	10	73
	21 days	48	10	21
	After drying	48	10	21
24 hours	3 hrs.	8	10	80
	72 hrs.	8	10	80
	21 days	38	10	26
	After drying	45	10	21

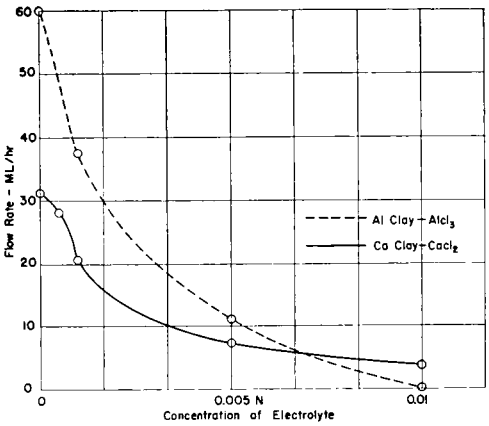


Figure 5. The relationship between the electro-osmotic flow rate and added electrolyte for a kaolinite clay.

teristics occurred in a much shorter time. In one such experiment the flow rate of an H clay changed to essentially that for a Al clay in less than three days. In another experiment, a clay was allowed to dry at approximately 40°C after which the electro-osmotic flow rate per unit current was determined. The flow rate and the applied voltage were essentially that of an Al clay. Based on the observation of a number of experiments of the type described above, there seems to be some indication that the maximum change in the surface characteristics of an H clay occurs when a small amount of some cation such as calcium remains adsorbed on the clay. More evidence is necessary, however, to substantiate this view.

Figure 5 shows the effect that excess electrolytic content has on the flow rate. It is observed from these curves that the flow rate corresponding to 0.01N $CaCl_2$ is only about a $1/10$ of the original flow rate for a Ca clay, while for an Al clay the flow rate corresponding to 0.01N drops to zero. Concentrations of $AlCl_2$ greater than 0.01N $AlCl_3$ actually produce a reversal of the flow.

DISCUSSION OF RESULTS AND CONCLUSION

The above results demonstrate the wide range in the electro-osmotic flow per unit of current which may occur during electro-osmosis. The change in the electro-osmotic flow rate during the transition from a Ca to an H clay demonstrates that the flow rate per unit of current during electro-osmosis at a given point in the clay mass changes continuously with time until a fully saturated H clay is obtained. In systems in which water is taken in at the anode and is discharged at the cathode, at a wellpoint, for example, this continuously changing flow rate throughout the system could very well produce the changes in intergranular stresses and pore pressures observed by other investigators.

The change in the surface characteristics of an H clay on standing in water solution further complicates the flow conditions. Since H ions are continuously produced at the anode and their concentration remains high at this point during electro-osmosis, a basis is established for believing that the clay at that point will remain H saturated. It thus appears possible that the flow for the entire system could be limited by the flow rate for the H saturated clay. Since the flow rate per unit of current for H kaolinite is much less than for the other ions normally found in the clay water system, a moisture content decrease in the direction of the cathode should occur as the system tends toward a steady state. The rate at which this moisture gradient would occur should depend on the cations normally associated with the clay. If the original clay contained soluble salts to any extent, a moisture decrease toward the cathode may never occur. If the salt concentration were of the right magnitude, the flow rate for the H saturated zone may exceed the rest of the system, and hydrostatic pressures could develop in the zone near the anode.

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