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## Effect of Calcium on the Continuity of Electroosmotic Flow Rate

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**Introductory Remarks by the Chairman:** Large-scale use of the electroosmotic phenomenon appears to have been mainly in the drainage of fine-grained natural soils. For this, relatively low electric potentials are employed, and interference by chemical and polarization phenomena has been reported to be practically negligible. Chemical phenomena, however, have been utilized in electroosmotic stabilization of friction pile systems and have been observed in laboratory studies on soils in which the exchange ions were varied.

Much experimental work with chemically well-defined soils and employing a wide range of electric potentials remains to be done before electroosmosis can become a dependable tool in soil stabilization. It is gratifying, therefore, that the Engineering Experiment Station of Iowa State College has attacked this problem on a wide front and that Rollins is presenting us with the first results of this attack on the effect of calcium on the continuity of the electroosmotic flow rate.

● THE bearing capacity of a subgrade is a function of moisture content. A large number of pavement failures can be attributed to the loss in subgrade support which takes place when excess moisture accumulates. It follows that any method of controlling or reducing this accumulated moisture falls into the category of soil stabilization.

A number of investigators have shown that moisture content beneath pavements fluctuates throughout the year, increasing during the cold months and decreasing during the warm periods.

The most-critical time, so far as subgrade bearing support is concerned, is during the thawing period in the early spring. If some means were available for removing the excess moisture at that time, it seems reasonable to expect that the performance of the pavement would be considerably improved.

One possible means of removing this excess moisture which appears to have some possibilities is electroosmosis, or the movement of moisture by an electrical-potential gradient.

### PREVIOUS WORK IN ELECTROOSMOSIS IN SOILS

Space does not permit the inclusion of a complete review of all previous investigations in electroosmosis of soils; however Casagrande (2) has reviewed the subject in a recent publication. Unfortunately, in many cases too little attention has been paid to the physicochemical characteristics of the soil, and that makes it impossible to project the results to other areas.

Winterkorn (6) has presented data showing the relative electroosmotic permeabilities for homoionic modifications of a soil involving the usual cations likely to be associated with the electroosmosis of soils. The flow of water for constant amperage was very slow for Ca, Na, and K and contained a high percentage of suspended colloids. Mg and Fe soils gave a regular and clear flow up to approximately one hour, while the current density had to be reduced for Al and H systems early in the experiment when the resistance of the sample became so large that the power sup-

TABLE 1  
PHYSICOCHEMICAL PROPERTIES OF THE SOILS

Sample No.	Cat. Exch. Cap. M. E./100g	pH	Ca. and Mg. Expressed as CaCO <sub>3</sub> %	Conductivity of Sat. Ext. Millimhos/cm	Organic Matter
1	40.2	7.95	3.0	0.386	
2	24.4	6.7	1.6	0.277	0.37
3	18.2	7.0	1.9	0.342	0.18
4	30.4	6.25	1.6	0.145	
5	11.2	8.4	10.3	1.21	0.24
7	39.6	7.0	3.0	0.347	
8	23.0	7.75	9.8	1.09	

Sample No.	Atterberg Limits			Mechanical Analysis		
	L. L.	P. L.	P. I.	% Sand	% Silt	Clay % <sup>a</sup>
1	71.5	24.5	47	2.11	27.89	70
2	51.9	18.5	33.4	0.7	60.2	39.4
3	39.4	26.9	12.5	2.0	70.6	27.4
4	70.6	21.9	48.7	8.2	31.0	60.8
5	29.6	27.3	2.3	4	82.6	13.4
7	70	36	34	19	26	55
8	55	23	32	24	30	45

<sup>a</sup> Less than 5 microns.

ply was insufficient to maintain it. Economic yields were lowest for Ca, K, and Na modifications, medium for Mg systems, and greatest for H and Al soils.

Casagrande (1), who has been a prolific writer with respect to electroösmosis and electrochemical hardening in soils, summarizes his experience as to the continuity of flow in systems in which the electrodes are in contact with the soil as follows: "The rate of discharge of water at the cathode, continuous for many weeks at an almost constant rate, finally drops off gradually with a corresponding decrease in the electric current."

Winterkorn (7), using the Schmidt concept for micro systems, has developed equations relating electroösmotic permeability to porosity. He presents data to show that in general the experimental curves are quite similar to the theoretical curves; however in the expanding lattice type clays, such as bentonite, the electroösmotic permeability porosity relationship is affected by hydration of the clay micelles.

This paper represents the initial phase of a broad program of research having to

do with electroösmosis in soils. Specifically this paper shows the effect of calcium and magnesium on the continuity of the electroösmotic-flow rate. An attempt is made to show the reason for this effect as well as to suggest a possible use of natural calcium and magnesium in soils as stabilizing agents.

#### TECHNICAL REQUIREMENTS FOR ELECTROÖSMOTIC DRAINAGE

The following three general questions associated with electroösmotic drainage must be answered before the technical feasibility of such an operation can be clearly defined, but it is not believed that they have been fully answered up to the present:

1. Under what conditions is it possible to remove moisture from a saturated soil by electroösmosis, and what pre-testing procedures need be adopted? Involved in this question are such things as: (1) What is the relative ability of the common soil cations themselves to transmit water in electroösmosis as differentiated from the

effect they have on hydration and swelling? (2) What is the effect of hydration and swelling on electroosmotic permeability? (3) What is the influence of the type of clay mineral on electroosmotic flow? (4) How do various types and quantities of soluble salts affect the movement of moisture in electroosmosis? (5) How does the electroosmotic-flow rate vary with the porosity?

2. Assuming that water can initially be removed from soil, is it possible to continue this removal over an extended period of time? This question is not completely independent of the first one, for it involves in addition a consideration of electrode reactions and over-potentials, type and kind of electrodes and the positioning of the electrodes. Solubilities of the various com-

were clays with the exception of two, which were silts. Physico-chemical data for these soils are presented in Table 1. The combined calcium and magnesium was determined by leaching the samples with 1.5N HCl and titrating with versinate. The results are expressed in equivalent calcium carbonate. Based on actual determination of exchangeable cations for some of the soils and a comparison of the calcium versus magnesium content previously determined by other investigators for soils found in similar areas, it is believed that the calcium content was considerably greater than the magnesium content for these soils.

It is observed that all soils have considerably more than enough calcium and

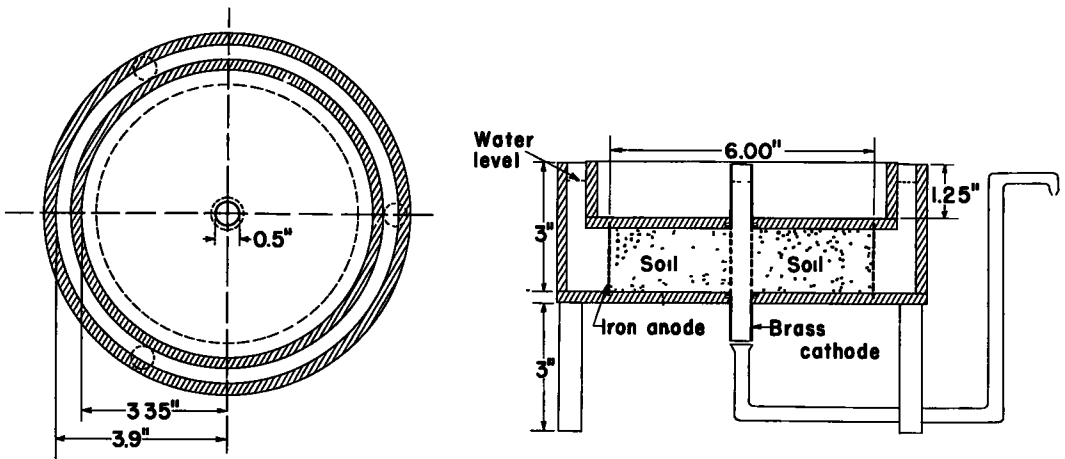


Figure 1. Electroosmotic-flow apparatus.

pounds of the normal exchangeable cations at various pH must be considered; since any electroosmotic operation on soils tends to replace the base ions with the hydrogen ions.

3. How much can the moisture content be reduced below the saturation point, and how is it affected by current density, porosity, clay mineral type, and adsorbed cation? The importance of this question is obvious. For a given dry density the supporting power of a subgrade is a function of the moisture content, and the reduction in moisture content below saturation is a measure of the improvement in the subgrade bearing capacity.

## METHODS AND PROCEDURE

All of the soils used in these experiments

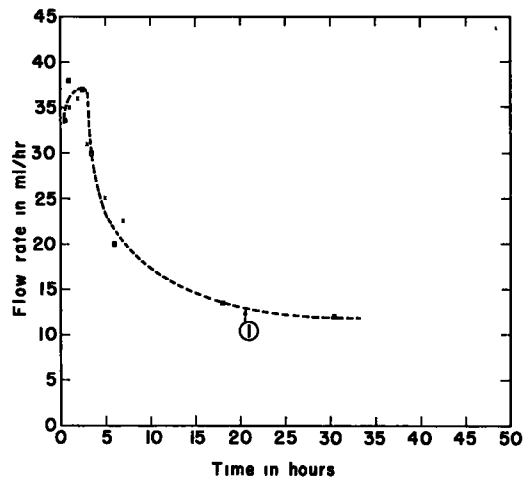


Figure 2.

magnesium to satisfy the exchange complex of the soil. This condition is found in many of the Iowa soils.

The radial flow apparatus used in these experiments is shown in Figure 1. Direct current was made available by using a transformer and rectifier. Holes were drilled in the top plate of the apparatus for observing changes in the electrical potential gradient. The soils were mixed thoroughly with water at approximately the liquid limit before being placed in the apparatus. The water level at the anode and cathode were maintained at the same elevation so there was no pressure flow. An applied voltage of 30 volts was used in all experiments, and periodic observations were made of the current and flow rate.

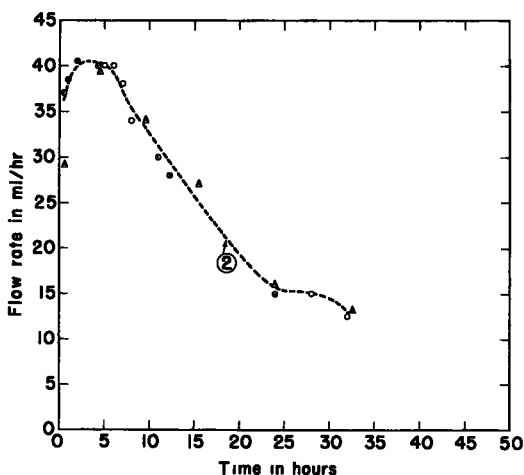


Figure 3.

### SOME EXPERIMENTAL RESULTS

Relationship between electroosmotic flow rate, electrical current, electrical potential gradient and time.

Figures 2 through 8 show the flow rate in milliliters per hour as a function of time. In all cases there is a considerable reduction in the flow rate with time. Soils 1, 2, 3, 4, and 7 have equivalent calcium carbonate percentages ranging from 1.6 to 3 percent.

The reduction in flow rate is much less for the silty soils than for the clays. A comparison of Soil 4 with Soil 3 (a clay and silt, respectively, having approximately equal equivalent calcium carbonate contents) shows very clearly this effect. Soil 5 is a silt, and Soil 8 is a clay; and both have equivalent calcium carbonate

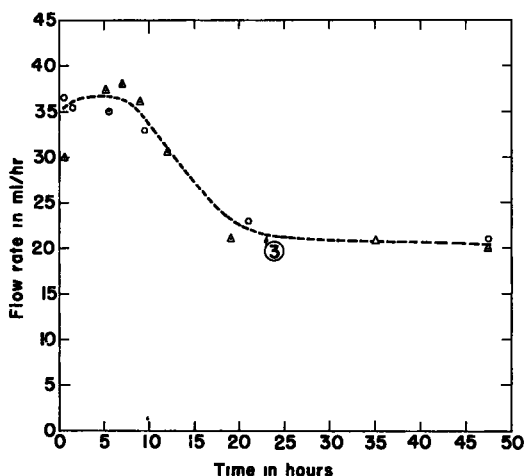


Figure 4.

percentages of about 10. In this example the reduction in flow rate also is greatest for the clay, although the reduction is lower for both than in soils with less initial calcium.

The reduction in electrical current closely paralleled the reduction in the flow of water; the current typically rose during the first hour or so and dropped off thereafter. Figure 9 is a plot of accumulative flow in milliliters per hour as a function of the accumulative charge in coulombs. The linear relationship between flow and charge on this plot is characteristic for all soils, which indicates that the reduction in flow is primarily caused by the reduction in current, since electroosmotic flow is known to be directly proportional to the current.

Electrical potential measurements were made periodically throughout an experi-

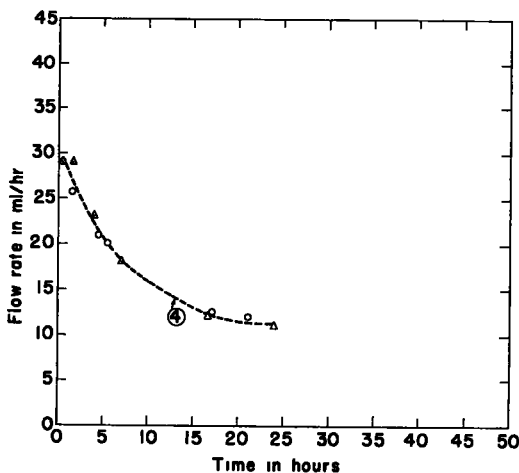


Figure 5.

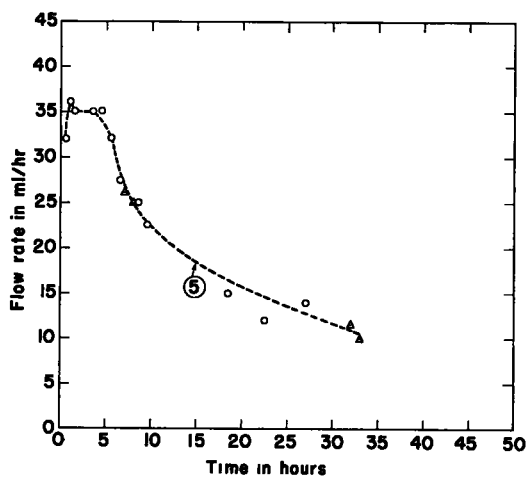


Figure 6.

ment. Figure 10 shows a typical plot of electrical potential versus the  $\text{Log } r/r_c$  at the beginning and end of an experiment, where  $r$  equals the radius from the center of the cathode to a point in consideration and  $r_c$  is the radius of the cathode. As might be expected such a plot is linear at the beginning of an experiment. As time elapses there is a continuous increase in the resistance toward the cathode in comparison with that toward the anode. This process continues until the majority of the resistance is concentrated in the vicinity of the cathode.

#### CHARACTERISTICS OF SOIL BETWEEN ANODE AND CATHODE AFTER ELECTROOSMOSIS

Visual inspection of the soil in the elec-

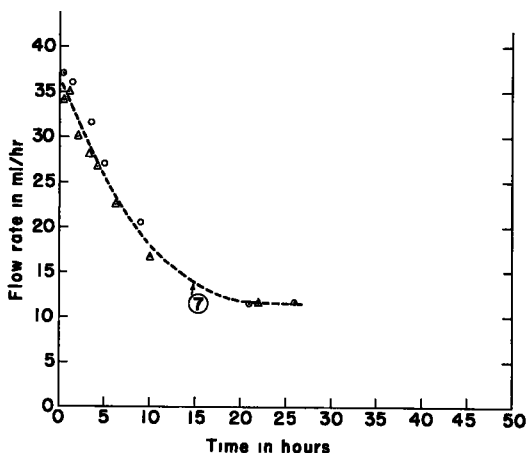


Figure 7.

troosmotic apparatus at the completion of a run showed that a dense core developed around the cathode.

A sharp line of demarcation was evident between the remainder of the soil and the core. The moisture content within the core was considerably less than in the surrounding soil and the cores for the clays appeared to be more compact than those for the silts. Table 3 shows the equivalent calcium carbonate and the pH for the raw soil, the soil at the anode, and the soil at the cathode at the completion of the experiment. As might be expected, the pH of the soil at the anode decreases and that of the soil at the cathode increases with the pH of the raw soil. The table also shows that considerable amounts of equiva-

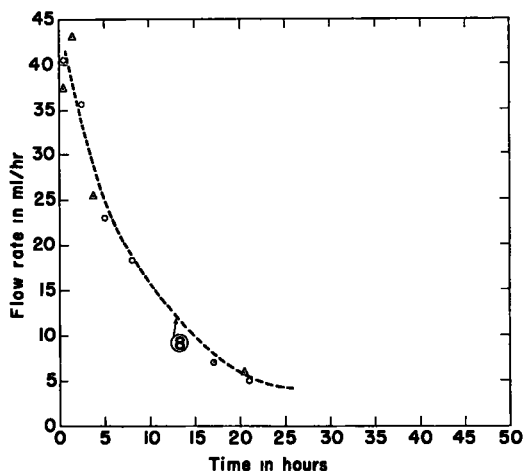


Figure 8.

lent calcium carbonate had collected at the cathode. Table 2 shows a comparison of the particle size distribution for the raw soil and for soil taken from around the cathode for Soil 1. It should be noted that the sample for this analysis had been allowed to air dry for several days. Comparative Atterberg limits are also listed in this figure.

#### DEMONSTRATION OF OHMIC OVER-POTENTIAL AT THE CATHODE

During normal experiments the cathode used was a  $\frac{1}{2}$ -inch perforated brass tube directly in contact with the soil. This type of cathode was modified by inserting a  $\frac{1}{8}$ -inch brass rod into the center of the old cathode. This rod when insulated from the half-inch tube then served as the cathode.

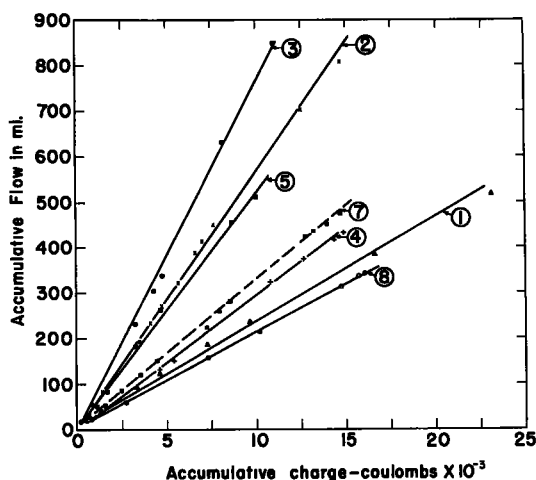


Figure 9. Relation between the accumulative electroosmotic-flow rate and accumulative charge.

The annular space between the rod and tube was filled with distilled water, and the same water levels as before were maintained. A series of experiments were carried out using this type of system. A typical plot of the results for Soil 1 is shown in Figure 11.

The current and the flow rate are plotted as ordinates and the time as the abscissa. An experiment was started with distilled water around the cathode. Initially the current rose as salts moved into solution around the cathode. Then calcium hydroxide was deposited on the  $\frac{1}{8}$ -inch-diameter electrode with a consequent severe reduction in current and a simultaneous reduction in flow rate. At periodic intervals the cathode was removed and cleaned, after which the current and flow rate both increased and then decreased as the calcium hydroxide deposited. Such experiments were carried on for approximately 12 hours, and it was noted that there was a gradual reduction in flow as well as in current. Examination of the soil around the cathode showed that calcium had been deposited and that some cementation of the soil particles had taken place, which possibly accounts for the overall reduction in flow rate.

Figure 12 shows the relation between specific conductivity and time for Soils 1, 3, 4, and 5, which had been mixed at approximately the liquid limit with 4 percent of calcium hydroxide. Note that for all soils there was a decrease in conductivity with time which was greatest for the clays.

TABLE 2  
A COMPARISON OF THE PHYSICAL PROPERTIES OF THE NATURAL SOIL AND THE CATHODE SOIL

Soil 1	Atterberg Limits			Mechanical Analysis		
				% Sand	% Silt	% Clay
Natural Soil	71.5	24.5	47	2.11	27.89	70.00
Cathode Soil	53.3	39.5	13.8	37.60	27.65	34.75

TABLE 3  
A COMPARISON OF EQUIVALENT CALCIUM CARBONATE, AND pH FOR THE RAW SOIL, SOIL AT THE ANODE AND SOIL AT THE CATHODE

Soil	Equivalent Calcium Carbonate %			pH		
	Raw Soil	Anode	Cathode	Raw Soil	Anode	Cathode
1	3.0	2.0	10.7	7.95	3.93	10.10
2	1.6	1.5	8.0	6.70	4.10	10.20
3	1.9	1.3	5.8	7.00	4.50	8.43
4	1.6	1.1	7.3	6.25	3.90	9.10
5	10.3	8.0	13.4	8.40	7.60	9.60
7	3.0	1.4	6.5	7.00	4.20	9.20
8	9.8	7.8	10.2	7.75	7.40	9.50

## DISCUSSION OF RESULTS

Many of the results given above can be explained by elementary electrochemistry. In electrochemistry the standard electrode potential of an element is a measure of the tendency of that element to form positive ions in solution. The more positive (American convention) an electrode potential is, the greater is its tendency to form positive ions; and the more negative the standard potential, the greater is the tendency to gain electrons to form negative ions. Standard electrode potentials hold only for unit activity; however the electrode potentials may be computed at other concen-

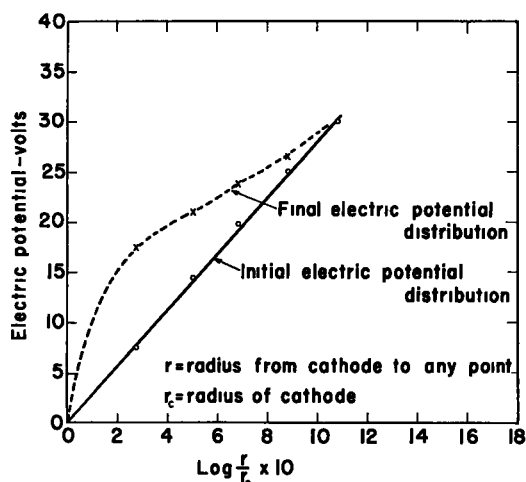


Figure 10. Relation between the electrical potential and the  $\log r/r_c$ .

trations if the activity is known. If two cations compete at an electrode for electrons, the one with the more negative electrode potential tends to be discharged first.

Calcium has one of the highest standard electrode potentials of any of the elements, and it does not form metallic calcium at ordinary temperatures in aqueous solutions. The other most common cation likely to be available to accept electrons in the system described above is hydrogen. Hydrogen gas then is liberated at the

the drop in current. Figure 11 shows that the reduction in current is associated with the deposition of calcium hydroxide on the metal surface of the cathode, and Figure 12 shows that the current will also be reduced when calcium hydroxide is deposited in the soil. The cementing affect, indicated by the changes in particle size distribution and consistency limits, undoubtedly blocks some of the exchange positions and restricts the movement of ions in these areas.

Considerable densification developed around the cathode, and some of the re-

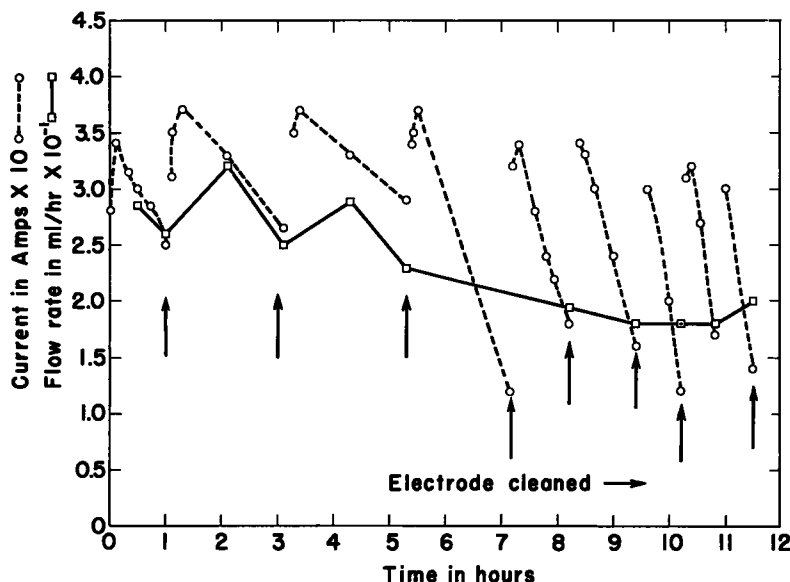


Figure 11. Relation between current, flow rate, and time for special cathode.

cathode, and hydroxyl ions tend to accumulate. Table 4 shows the pH at which the hydroxides and basic salts of various cations precipitate. Thus all calcium ions accumulating near the cathode will usually precipitate as calcium hydroxide. Other cations, such as the ferrous ion, will precipitate as hydroxides when they reach the appropriate pH value in the electro-osmotic system.

Figure 9 shows in addition that the reduction in flow is directly proportional to

TABLE 4  
THE pH AT WHICH SOME METAL HYDROXIDES OR  
BASIC SALTS ARE PRECIPITATED

Metal	pH	Metal	pH
Ferric	2.3	Nickel	6.7
Aluminum	4.1	Magnesium	10.5
Zinc	5.2	Calcium	Sparingly Soluble
Cupric	5.4	Potassium	Soluble
Ferrous	5.5	Sodium	Soluble

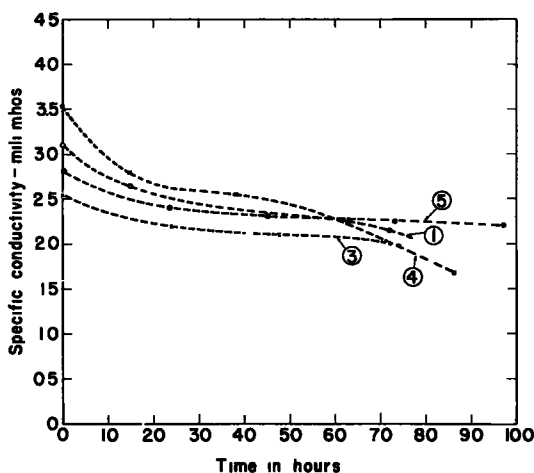


Figure 12. Relation between specific conductivity and time for soils treated with 4 percent of  $\text{CaOH}_2$ .

duction in flow might have been due to the reduction in the porosity at this position. Soils taken from around the cathode developed a fair amount of strength, even though the porosity at the liquid limit was quite high. The soils were also considerably waterproofed, as was evidenced by the fact that no slaking took place after extended periods of soaking. This stabilizing effect in soils high in calcium probably should be investigated further.

Note that the data so far presented pertain to radial flow. Experiments have been conducted with rectilinear flow in an apparatus approximately 6 inches square and  $1\frac{1}{2}$  inches deep. These experiments were carried on for approximately 30 hours for Soil 1. The densely calcified section around the cathode was approximately  $\frac{3}{4}$  inch thick, and the flow rate and current dropped off to a considerable extent although not quite as rapidly as in radial flow. Iron electrodes were used, and the formation of a band of ferrous hydroxide was observed immediately behind the calcium hydroxide after a period of about 48 hours. This formation further reduced both the current and the flow.

These results indicate that before electroösmosis can be used to dewater soils of this type some method must be developed to prevent deposition of the calcium, or provisions must be made for cleaning the cathode. An alternative to this system might be to deposit the calcium in the surface of the subgrade followed by a relocation of the electrodes for dewatering.

From the above discussion, it is also evident that anodes such as iron should not be used for electroösmosis in soils similar to those used in these investiga-

tions. Experiments are now under way to determine the possibility of using as anodes plastic materials coated with various colloidal graphite material. Research directed toward the development of practical means of depolarizing the cathode is also continuing.

## SUMMARY

The results of this investigation show that the electroösmotic flow rate for soils relatively high in calcium is characterized by a relatively high initial flow rate which drops off rapidly with time. The reduction in flow is greater for clays than for sand. Analysis of the soil between the anode and cathode at the completion of a run shows that the pH has decreased at the anode and increased at the cathode and that considerable amounts of calcium hydroxide has deposited at the cathode. This calcium hydroxide coats the metallic cathode, cements the soil particles, and densifies the soil adjacent to the cathode. It is shown that the first two effects considerably increase the electrical resistance and decrease the current flowing in the system. It is further shown that the reduction in flow of water is directly proportional to the reduction in electrical current.

## ACKNOWLEDGMENT

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## Elastic Behavior of Soil-Cement Mixtures

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Introductory Remarks by the Chairman: Modern soil-cement is a remarkable construction material. Aside from its excellent structural properties, it is noteworthy that from its early infancy in South Carolina to its present worldwide use, it was guided and supervised scientifically and that more precise records have been kept on its development than on any other large-scale construction material.

But do we know as much as we should even with respect to the mechanical properties of this material? Have we been completely fair to it and studied and developed all its potentialities? Or have we treated it as a dependable slave that can carry the loads we place on it without bothering how it does it?

Reinhold looks at soil-cement as a unique construction material that is not just a poor concrete or a stabilized soil but a material that may prove to be superior in certain highway and other applications than traditional materials presently employed for them. From this point of view, Reinhold has studied the elastic behavior of soil-cement as a function of cement and clay content and has given in his paper a precise account of the results so far obtained in his important work.

● THE modulus of elasticity and Poisson's number play an important role in the dimensional design of homogeneous pavements. Questions regarding the strength of a pavement, its reaction to temperature and moisture changes, and the distance and type of joints to be used are directly related to the elasticity constants. These constants must be determined for soil-cement if we want to understand its actual behavior under stresses caused by externally applied forces. From a knowledge of their magnitudes, a better utilization of the properties of this new construction material may result as well as an expansion of its field of application.

### GENERAL REMARKS CONCERNING ELASTIC BEHAVIOR

For the purpose of defining fundamental concepts and of determining the type of experiments necessary to measure the elastic behavior of soil-cement mixtures, the following general considerations are presented.

The elastic behavior of homogeneous isotropic materials is essentially char-

acterized by two coefficients, the modulus of elasticity  $E$  (or its inverse  $a$ ) and the Poisson number  $m$  (or its inverse  $\mu$  = Poisson's Ratio). In the general case these coefficients are not constants. They are determined by measurements of changes in longitudinal and lateral dimensions in uniaxial tension or compression, which are evaluated by means of the stress-strain diagram.

Stresses  $s = \frac{P}{A}$  are forces per unit area that are caused by externally applied loads.

Strains are defined by  $\epsilon = \frac{\Delta l}{l}$  i. e., by the ratio of change in a dimension to the original dimension and, hence are dimensionless. Strains may be caused by compression, tension or shear forces.

Fundamentally, there exists no proportionality between stress and strain. The law established by Hooke in 1678 "Ut tensio, sic vis":

$$\epsilon = \frac{s}{E} = a \times s$$

which for a long time had been considered as a natural law covering the behavior of all materials, is strictly true only for the