

Final Report

Application of Electro-osmosis
to Marginal Soils

by

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SUMMARY

In 1968 the Joint Highway Research Advisory Council sponsored a research project to investigate the application of electro-osmosis to marginal soils in the Civil Engineering Department of the University of Connecticut. The experimental program involved laboratory as well as field measurements. Two types of marginal soil, varved clay and glacial till, were used in the experiments. Both of these soil types occur in Connecticut. However, in highway construction glacial till is not always considered marginal. In addition, the properties and electro-osmotic behavior of stratified deposits were studied using combinations of fritted glass disks having different pore sizes.

Careful analysis of the hydraulic and electrical results on the fritted glass disks has yielded a simple technique for measuring a pore size parameter. This pore size parameter correlates with the smallest cross-sectional area in an average flow path. This pore size appears promising as an indication of the susceptibility of a soil to frost heave.

RECOMMENDATIONS

Electro-osmosis could be used to dry a field deposit of extremely wet glacial till. The technique does not appear to be sufficiently effective in consolidating and strengthening varved clay. More fundamental work is required to completely understand the mechanisms of electro-osmotic treatment.

The exploitation of the pore size parameter should be undertaken immediately. Preliminary investigations indicate that there is a strong possibility this pore size parameter may correlate with frost effects; both frost heaving and frost pressure.

THE PHENOMENON OF ELECTRO-OSMOSIS

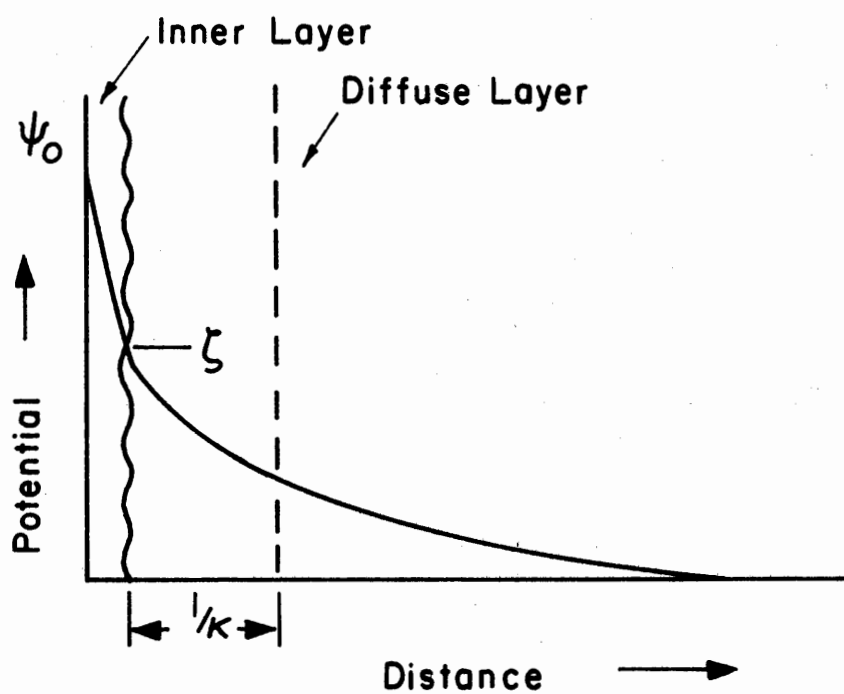
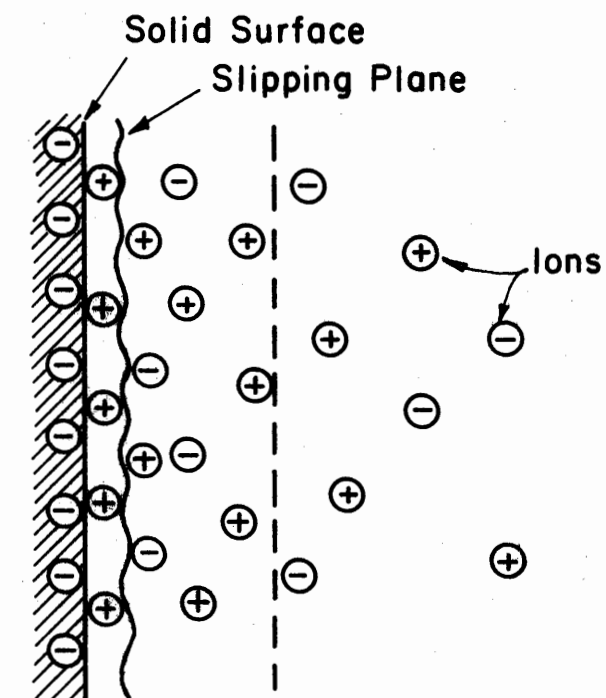
General

When direct current is applied to a porous medium saturated with water, the water moves toward the negative electrode (cathode). This phenomenon was first observed in a clay-water mixture by Reuss in 1808 (17) and has been named electro-osmosis. L. Casagrande made the first practical application of electro-osmosis in soil mechanics by stabilizing a railroad cut in Germany in 1939 (3). Over the years several field applications have been found useful in the United States and Norway (2)(8).

Direct current generation is the single biggest cost in applying this method in the field. The object of field treatments is to increase the strength of soil and reduce construction and post construction settlements. However, at the present time electro-osmosis is more expensive than conventional construction aids such as berms or surcharges. Electro-osmosis does appear to be a promising technique for very soft deposits which would require too slow an application of mechanical loads. In this case the application of electro-osmosis is faster and there is no danger of shear failure from the electrical treatment.

Mechanism of Electro-osmotic Treatment

Most surfaces in nature are charged negatively. To restore electrical neutrality the surfaces attract positively charged ions from solution. These positively charged ions distribute themselves in the water near the surface of the soil particle. The model used to envisage the arrangement of charges is shown in Figure 1. The top of Figure 1 shows the arrangement on the basis of discrete charges. The bottom diagram of Figure 1 shows the distribution of electro-static potentials generated by the surface charge. The symbol ψ_0



Simplified Representation of an Electric Double Layer

FIGURE 1

represents the potential at the soil surface, ζ represents the potential on the slipping plane during flow and l/K is a characteristic dimension of the ionic distribution.

When a potential gradient is placed across a porous medium, such as a soil plug, the positively charged ions which outnumber the negatives move towards the cathode. As the ions move they drag the water in the pores with them. When water cannot enter the system at the anode (positively charged electrode) the water content of the soil diminishes causing the soil to consolidate and become stronger. The soil strengthening results primarily from consolidation but passage of current generates some chemical bonds between the particles which also develop strength (6). This is especially true when aluminum is used as the anode (3). Other effects can be accomplished by introducing proper chemicals into the process. As an example, potassium chloride introduced in solution at the anode and transported through the soil can reduce the swell potential of clays (14).

The Treatment of Soils With Electro-osmosis

There have been many papers written on electro-osmotic treatment of soils. This section will deal only with the publications that reflect on the investigations contained herein. The most important papers and reviews on electro-osmosis have been cited by Mitchell (12).

1. Electro-osmotic Permeability

Models used to develop the theory of electro-osmosis have been advanced by Helmholtz (11) and Von Smoluchowski (24). Their work was directly applicable to capillary tubes only. L. Casagrande formulated an approach to electro-osmosis in soils and showed that the phenomenon could be described by an equation similar to Darcy's Law (3):

$$Q = k_e \frac{\Delta V}{L} \cdot A \quad [1]$$

where Q is the volume rate of water flow through the soil; ΔV is the electrical potential difference across the soil; L is the length and A the gross cross-sectional area; and k_e is the electro-osmotic permeability of the soil.

From extensive measurements Casagrande determined that k_e has an average value of 5×10^{-5} cm²/volt-sec. for most soils including clays (3). The hydraulic permeability of many soils is lower than this value, especially for soils containing more than 10 percent silt or clay. Casagrande attributed the decrease in water content during electro-osmotic treatment to the fact that direct current can remove water faster than it can flow back into these soils.

2. Electro-osmotic Efficiency

A phenomenon called streaming potential arises from the same surface charges that make electro-osmosis possible. When water is pushed through a porous medium such as soil, the ions near the surface of the soil particles are swept along with the flowing water causing a potential difference between the ends of the soil plug. This effect occurs each time a permeability test is run on a soil. Streaming potential in soils was studied by Gray and Mitchell to determine the efficiency of electro-osmotic treatment (9).

The efficiency of electro-osmotic treatment depends on the power required to induce consolidation. The power used is the product of the voltage across the soil and the current passed through the soil. Gray and Mitchell (9) studied the relative efficiency of electro-osmotic treatment of several types of clays. Their conclusions were that the amount of water able to be removed from a soil for each amp

of current can be found from the equation:

$$\left(\frac{Q}{I}\right)_{\Delta p=0} = - \left(\frac{\Delta E_s}{\Delta p}\right)_{I=0} \quad [2]$$

where Q is the volume rate of water removal by current I during electro-osmosis; ΔE_s is the electrical potential generated across the soil plug by the flow of water under a pressure difference Δp .

Equation 2 simplifies the measurement of electro-osmotic efficiency. The streaming potential can be measured in conjunction with a permeability test and the relative effectiveness of electro-osmotic treatment determined.

3. Electro-osmotic Consolidation

The process of consolidation during electro-osmotic treatment has been studied by Esrig (6)(7). He concluded that the application of direct current to a soil in which no free water is available at the anode causes consolidation according to Terzaghi's theory with the applied voltage developing negative pore pressures which in turn cause compression. The rate of consolidation according to Esrig's theoretical treatment depends on hydraulic soil properties similar to those that regulate consolidation by mechanical loads.

The solution of the basic equations for parallel electrodes in which the flow is one dimensional indicates that the negative pore pressures developed at long times after treatment begins are related to the applied potential at the point. During the electro-osmotic treatment the pore pressure at any point is given by the equation (6):

$$u = -\frac{k_e}{k_h} \gamma_w V(x) + \frac{2k_e \gamma_w V_m}{k_h \pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{\left(n + \frac{1}{2}\right)^2} \sin \left[\frac{\left(n + \frac{1}{2}\right) \pi x}{L} \right] \left[\exp - \left(n + \frac{1}{2}\right)^2 \pi^2 T_v \right] \quad [3]$$

where k_e = the electro-osmotic permeability

k_h = the hydraulic permeability

γ_w = the unit weight of water

$V(x)$ = the applied potential at a distance x

x = the distance along the sample measured from the cathode

u = the pore pressure; $T_v = \frac{C_v t}{L^2}$

t = time

T_v = the time factor

C_v = the coefficient of consolidation

L = the length of sample

The expression for average percent consolidation (U) is given by the equation:

$$U = 1 - \frac{4}{\pi^3} \sum_{n=0}^{\infty} \frac{(-1)^n}{\left(n + \frac{1}{2}\right)^3} \exp - \left(n + \frac{1}{2}\right)^2 \pi^2 T_v \quad [4]$$

A plot of Equation 4 is shown in Figure 2. As seen in Figure 2 the predicted progress of consolidation by direct current is similar to the progress of consolidation by mechanical loads. An important difference in consolidation by the two techniques is that when electricity is applied the compression is three dimensional even though the flow of water is in one direction. This is because the electrical treatment is accompanied by the development of negative pore pressures that compress the soil in all directions.

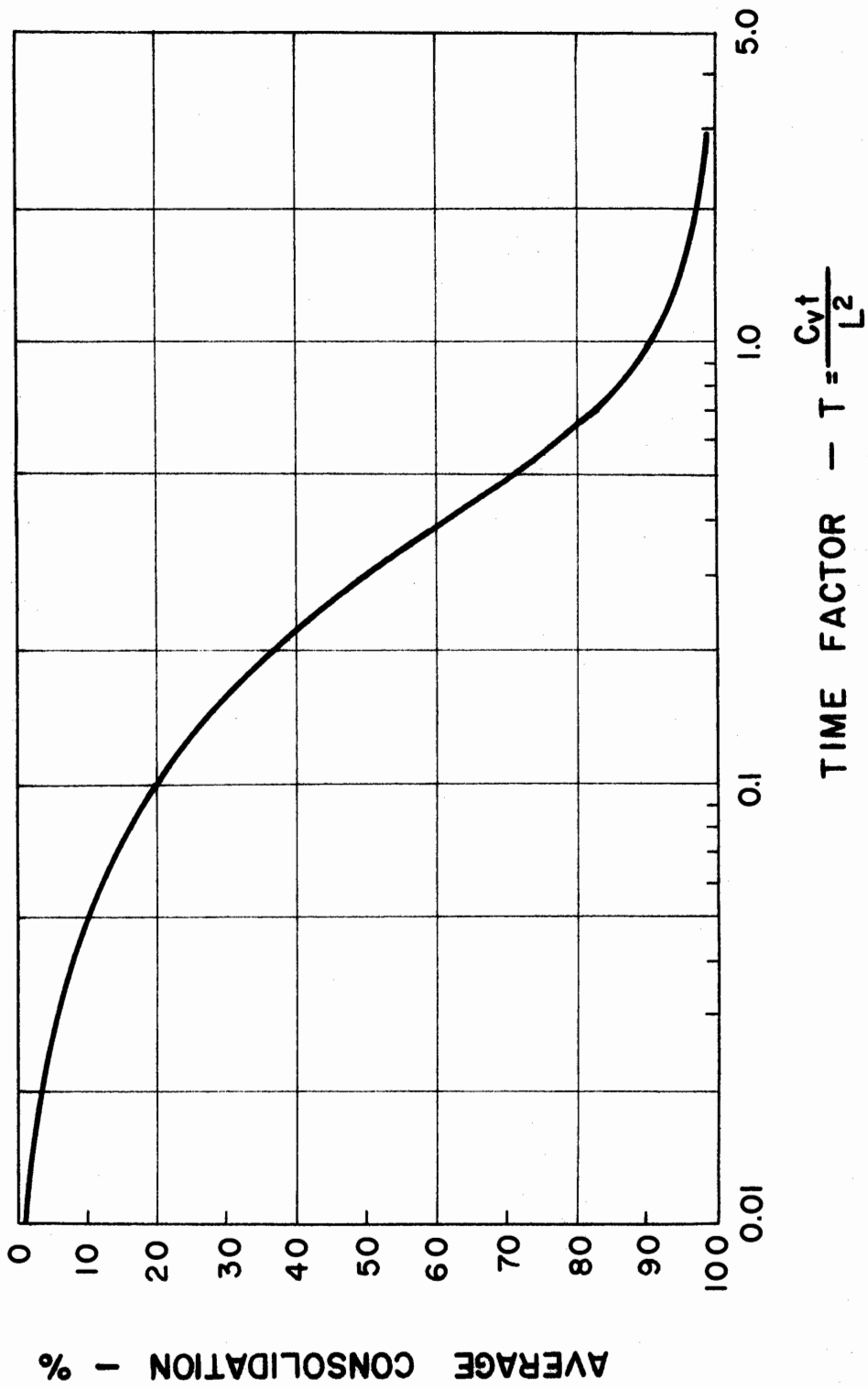


FIGURE 2

EXPERIMENTS ON GLACIAL TILL

In the Spring of 1969 an opportunity developed for a field trial of electro-osmosis on the University of Connecticut campus. The site was the west side of the drumlin beside the tennis courts. The installation of prefabricated underdrains into this slope was delayed by the high water content of the soil. A bulldozer attempted to work on the slope, became stuck and had to be pulled free by another dozer. An alternate installation procedure using a backhoe was devised. The backhoe, however, was not available for several days. During the interval a field trial of electro-osmosis was made in the wet glacial till.

The dewatering of glacial till was first checked in the laboratory. The particle size distribution curve for the till is shown in Figure 3. A sample recovered from the tennis court slope was placed in an evaporating dish. Two zinc electrodes 2 in. by 2 in. square were placed between soil and dish on opposite sides of the sample. The sample and dish were then covered with a rubber membrane to prevent evaporation of water and the direct current switched on. The electrical potential gradient applied to the soil sample was approximately one volt per cm. This potential remained across the soil for 19 hours.

After the current was shut off, the final water contents at several positions in the soil sample were measured and compared with the original water content. The water content of a treated soil will vary with distance from the electrodes. The greatest reduction in water content occurs at the anode; the least at the cathode with intermediate reductions between the electrodes. Water contents on the glacial till were measured on samples in direct line between the electrodes. These results are shown

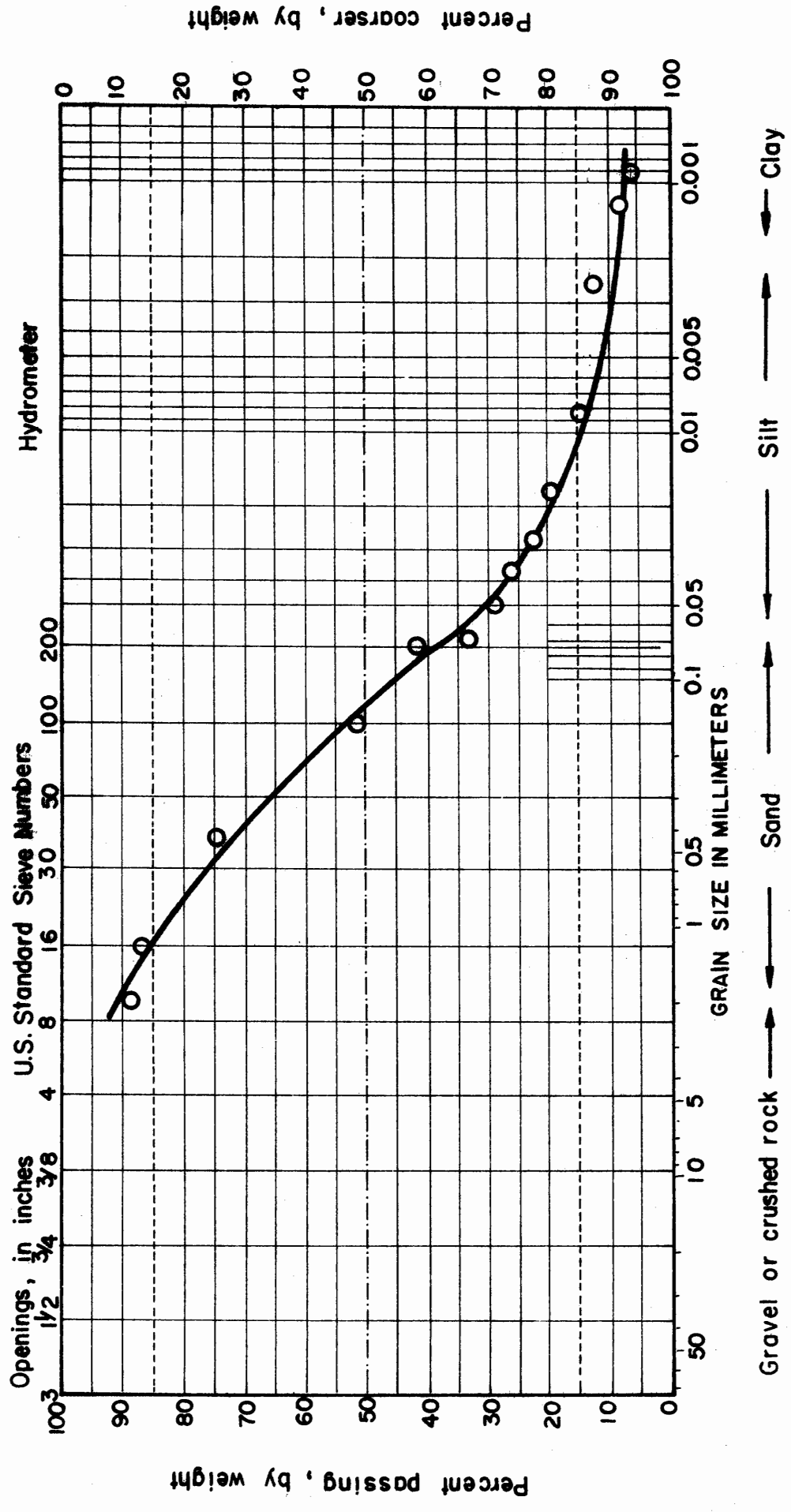


FIGURE 3

ELECTRO-OSMOTIC TEST
SILT FROM SLOPE BESIDE
TENNIS COURT

WATER CONTENT ALONG
C BETWEEN ANODE AND
CATHODE

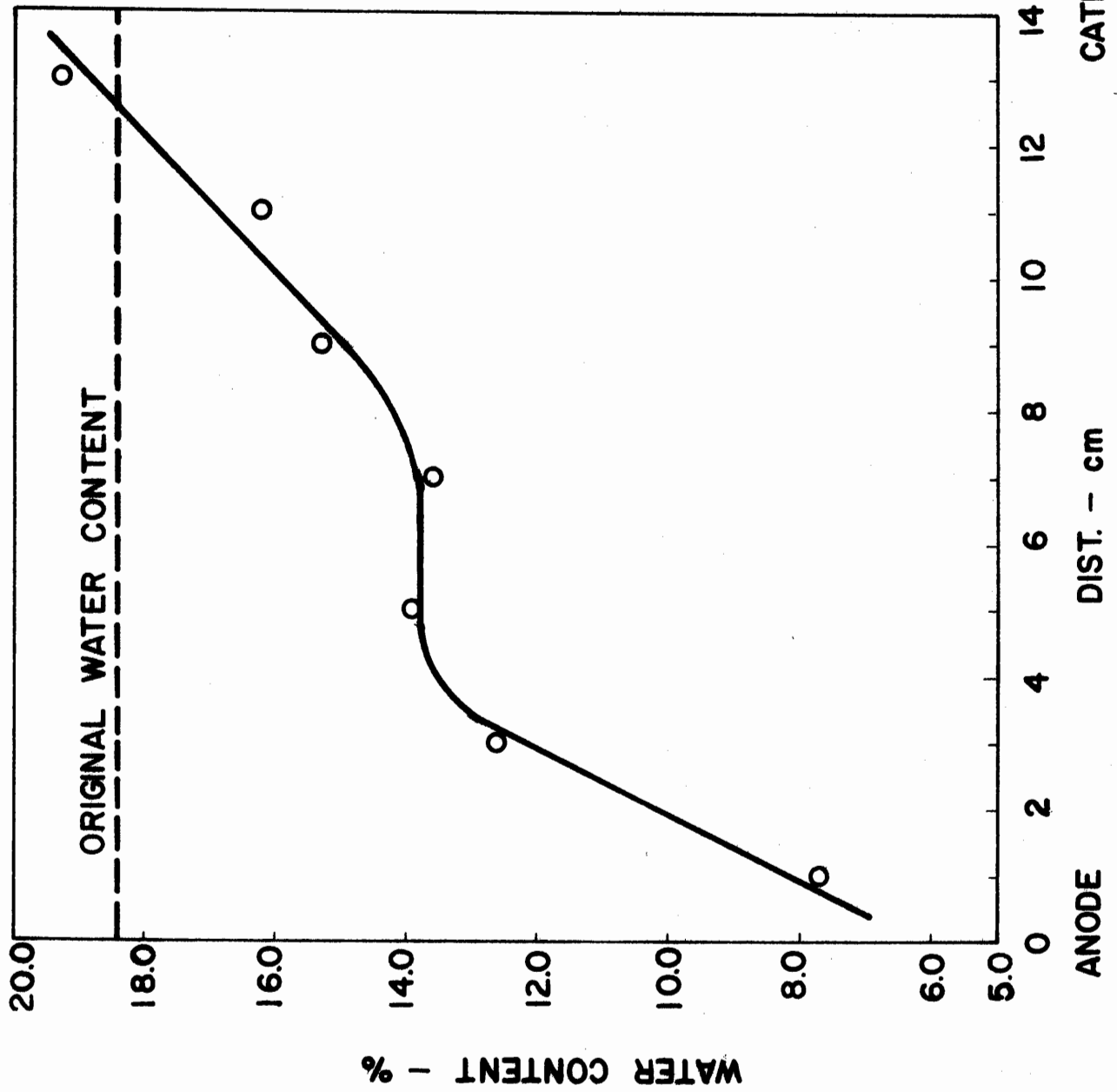


FIGURE 4

in Figure 4. The greatest reduction in water content as can be seen in Figure 4 is at the anode. The variation of water contents between the electrodes is not linear because the applied electric field was two dimensional causing the potential gradient to be greater near the electrodes and less in the center of the sample. A similar effect is realized in most field installations where the electric field is also two dimensional. Additional samples were removed across the sample midway between the electrodes; these water contents are shown in Figure 5. The water contents on this line are approximately constant and about a value that is the average of the final water contents at the electrodes.

A field layout was installed as shown in Figure 6. The soft soil on the slope was located on the berm halfway up the slope. The berm had been cut about eight months earlier for installation of the prefabricated under-drain. The anodes were steel reinforcing rods about 3 feet long and driven into the soil with a sledge hammer until about one-half foot remained above the surface. The cathodes were steel electrical conduit pipe thin wall bus duct. Holes, one-eighth inch in diameter spaced about three inches on center were drilled into the steel pipe to allow the water flowing toward the cathode to escape. The electrodes were placed in the slope as shown in Figure 6. The cathodes were positioned in the lower slope to allow easy escape of water. The anodes were placed close to the toe of the upper slope. The electrodes were connected in parallel to a welding generator which developed 60 volts in the field circuit. Flow of water was measured at the cathodes.

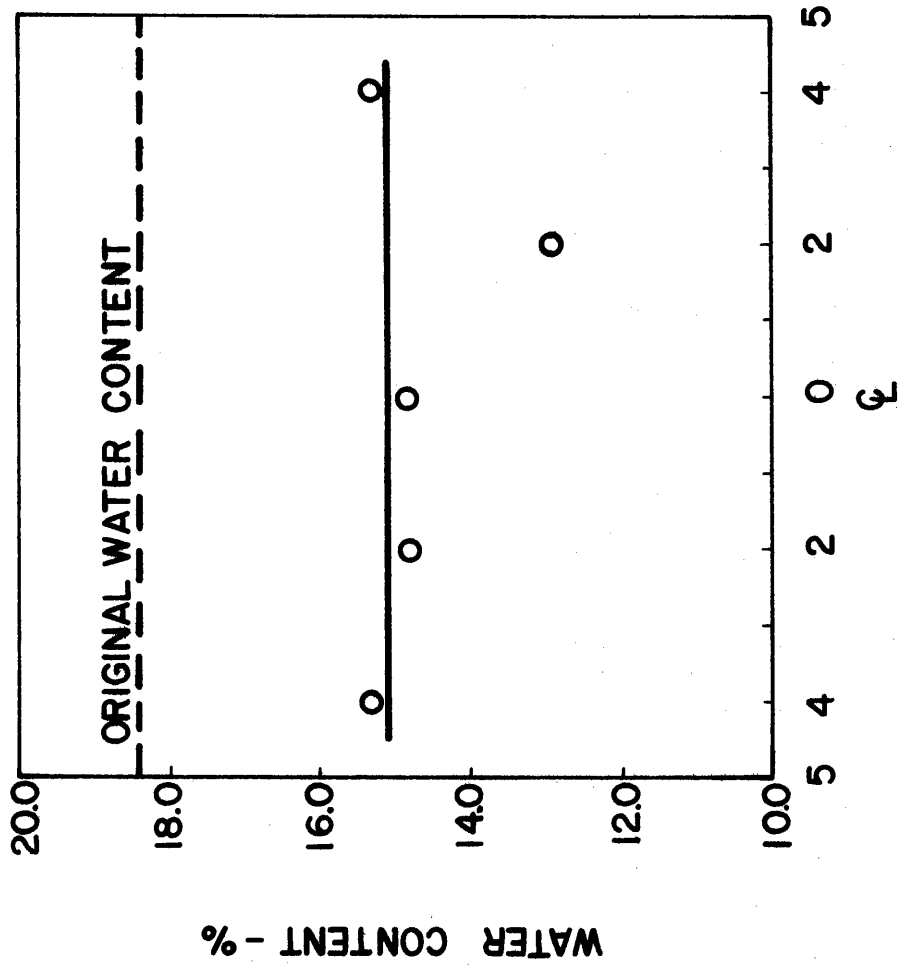
Direct current was applied continuously to the field installation for about 27 hours. At the end of this period the electro-osmotic treatment was discontinued because the backhoe became available for the installation

ELECTRO-OSMOSIS TEST

SILT FROM SLOPE BESIDE

TENNIS COURT

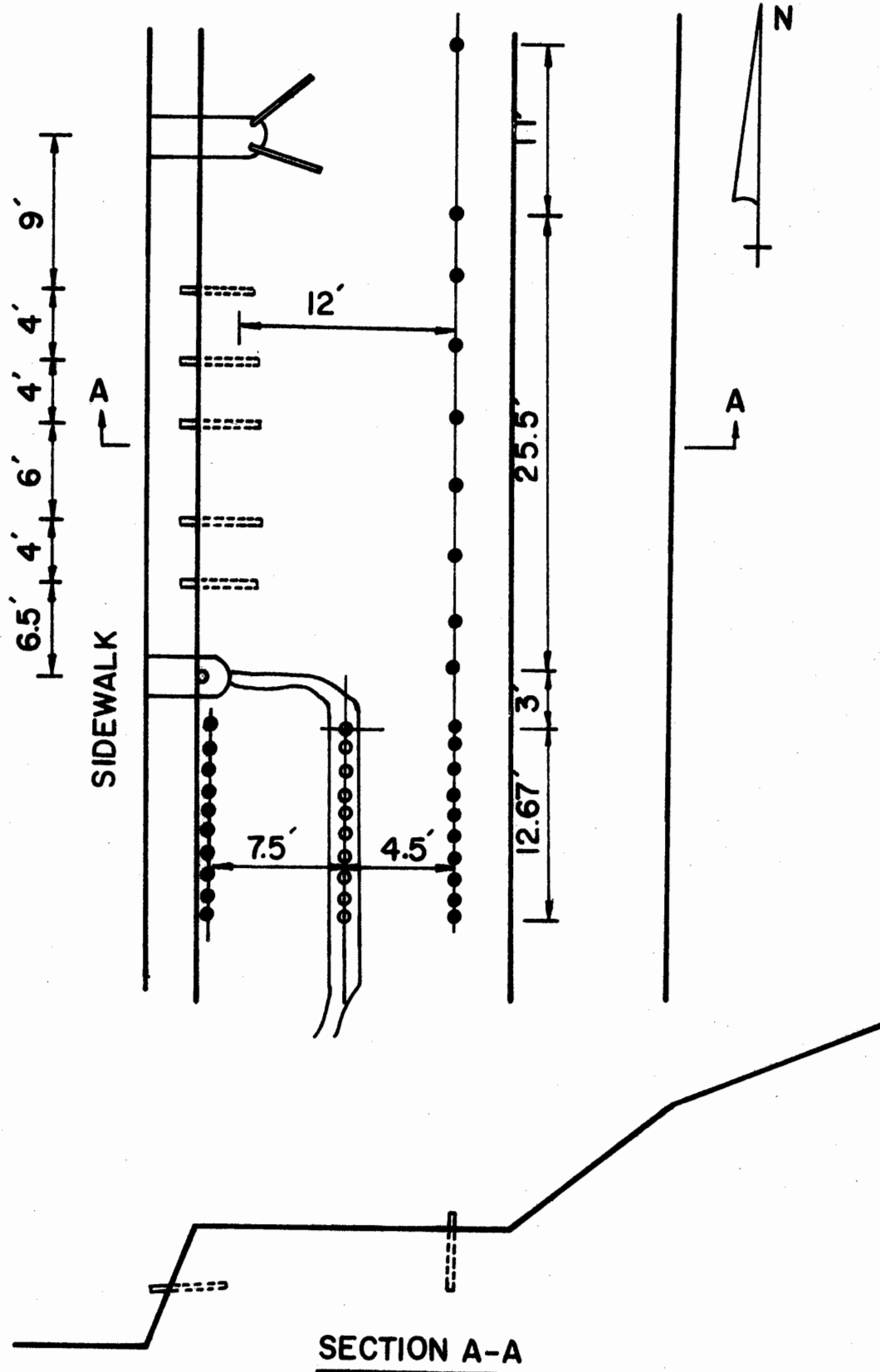
WATER CONTENTS ON A
TRANSVERSE LINE MIDWAY
BETWEEN ELECTRODES - AS
VIEWED FROM CATHODE



DIST. - cm

FIGURE 5

FIELD LAYOUT



LAYOUT OF ELECTRODES ON
SLOPE BESIDE TENNIS COURTS
SPRING 1969

LEGEND

- ANODES
- CATHODES

FIGURE 6

of the prefabricated underdrains.

Soil samples were taken from the berm before and after treatment for water content determinations. The laboratory and field treatments of the glacial till are compared in Table I. The water removed in the field per unit of power is approximately the same as that removed in the laboratory. Additional laboratory tests indicated that the water content of the glacial till could have been reduced to about an average of 14% which would have stabilized the berm enough to support the construction equipment.

EXPERIMENTS ON VARVED CLAY

General

The theoretical treatment on the mechanism of consolidation by electro-osmosis published by Esrig (6)(7) has some interesting aspects. The mathematical development indicates relations between applied potential and negative pore pressures as expressed in Equation 3. Experiments were conducted on undisturbed and remolded samples of varved clay to investigate the implications of Esrig's mathematical development.

Experimental Investigation

The object of these experimental investigations was to determine the accuracy of the theory with respect to the time rate of consolidation and the relation between compression and voltage and to measure the effect of electro-osmotic treatment on varved clay. When the relation among the soil and electrical properties are understood, better engineered field applications can be made.

The progress of average consolidation by electro-osmosis was investigated by measuring the compression of a soil sample in the vertical direction

TABLE I
 COMPARISON BETWEEN LAB AND FIELD
 TREATMENT FOR GLACIAL TILL

	LABORATORY TREATMENT	FIELD TREATMENT
Original Water Content	18.4%	18.2%
Duration of Treatment	19 hrs.	27 hrs.
Final Water Content	16.4% (Avg.)	16.6% (Avg.)
Rate of Water Removal	6.9 cc/Watt-hr.	7.0 cc/Watt-hr.
Voltage	25 v.	60 v.
Current	15 m. amps.	83.3 m. amps (per electrode pair)

with time and comparing the experimental curve to the theoretical curve in Figure 2. The relation between amount of applied voltage and pore pressure is more important because it indicates the amount of compression that can be realized in a soil. At very long times after treatment begins, Equation 3 reduces to:

$$u = \frac{k_e}{k_h} \gamma_w V(x) \quad [5]$$

An average value of k_e for all soils can be approximated as 5.0×10^{-5} $\text{cm}^2/\text{volt-sec}$. (3). An approximate value of k_h for varved clay is 1.0×10^{-7} cm/sec . (10). Using these values in Equation 5 indicates that applied potential of 20 volts will cause a negative pore pressure and therefore cause a compression equal to 10 tons/sq. ft. Furthermore greater voltages cause more compression. Electrical potentials greater than 20 V are easily obtained in the field so the theory indicates that electro-osmotic treatment can reduce and strengthen most soils substantially. The experiments reported herein indicate that the theory greatly overestimates the amount of compression that electro-osmosis can cause.

Experimental Procedure

A sample of undisturbed varved clay was trimmed into a plexiglass ring as shown in Figure 7. Two undisturbed samples were tested in all. One sample was trimmed so that the varves were horizontal. The other sample was trimmed so that the varves were vertical. A sample of remolded varved clay was also prepared by mixing dried pulverized clay with tap water so that the water content was above the liquid limit then, consolidating it mechanically inside a plexiglass tube to about $0.15 \text{ Tons}/\text{ft}^2$. Tap water was used in these experiments because its conductivity is close to that of ground water.

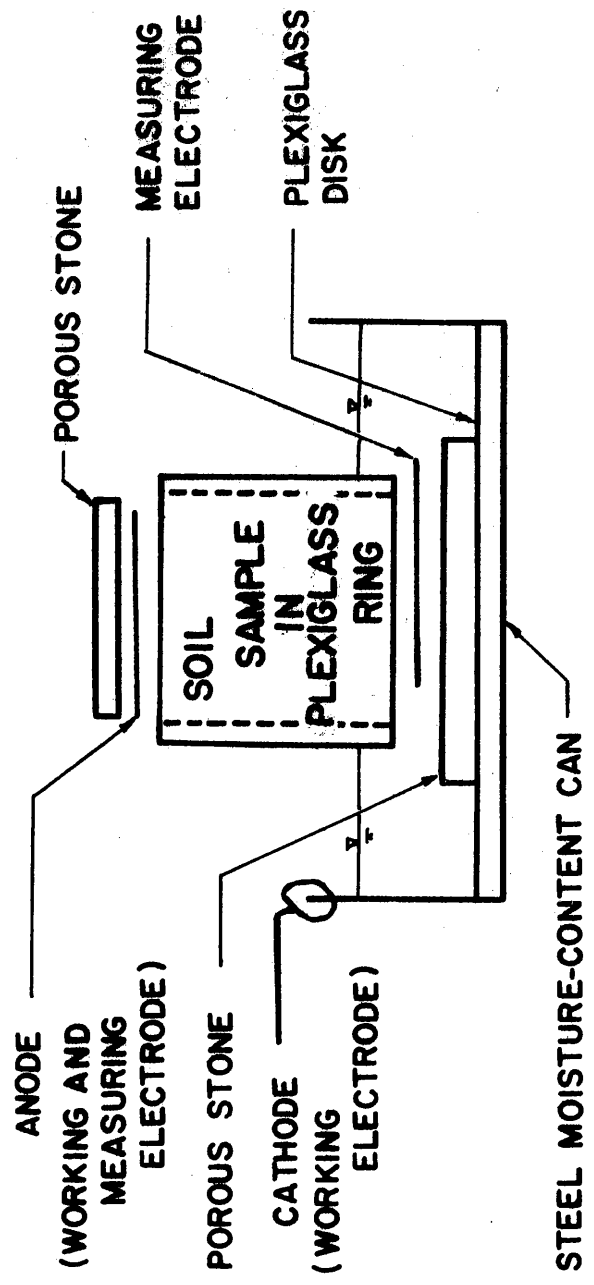


FIGURE 7

The experimental setup is shown in Figure 7. A steel moisture-content can, 8 cm in diameter, was used as the cathode. To insure that electrolysis would not interfere with the progress of consolidation a plexiglass disk was used to insulate the base of the can from the sample. The flow of electricity was then passed from the sample to the sides of the can so that any bubbles forming at the can could be passed to the surface of the water. A porous stone separated the soil sample from the plexiglass disk allowing the water expelled from the sample to escape freely. A loop of copper wire was placed between the soil sample and the porous stone to monitor the voltage dropped across the sample. A brass screen was used on top of the sample as the anode. A porous stone and a small weight were placed on top of the anode to keep it in place. A dial indicator reading in 10^{-4} inches was placed on top of the weight to measure vertical displacement. The soil was consolidated by applying a known voltage across the soil. The progress of consolidation was observed by measuring the vertical displacement with time. For the remolded sample all applied voltages caused consolidation. For the undisturbed varved clay samples no consolidation was apparent until the potential gradient across the sample was about 15 volts/cm.

Results

The progress of average consolidation with time is shown in Figure 8. The shape of the experimental curve in Figure 8 is similar to the shape of the theoretical curve in Figure 2 indicating that consolidation progresses as predicted by Esrig's theory. The strain against log-time plots for all the samples tested are similar to the experimental plot shown in Figure 8.

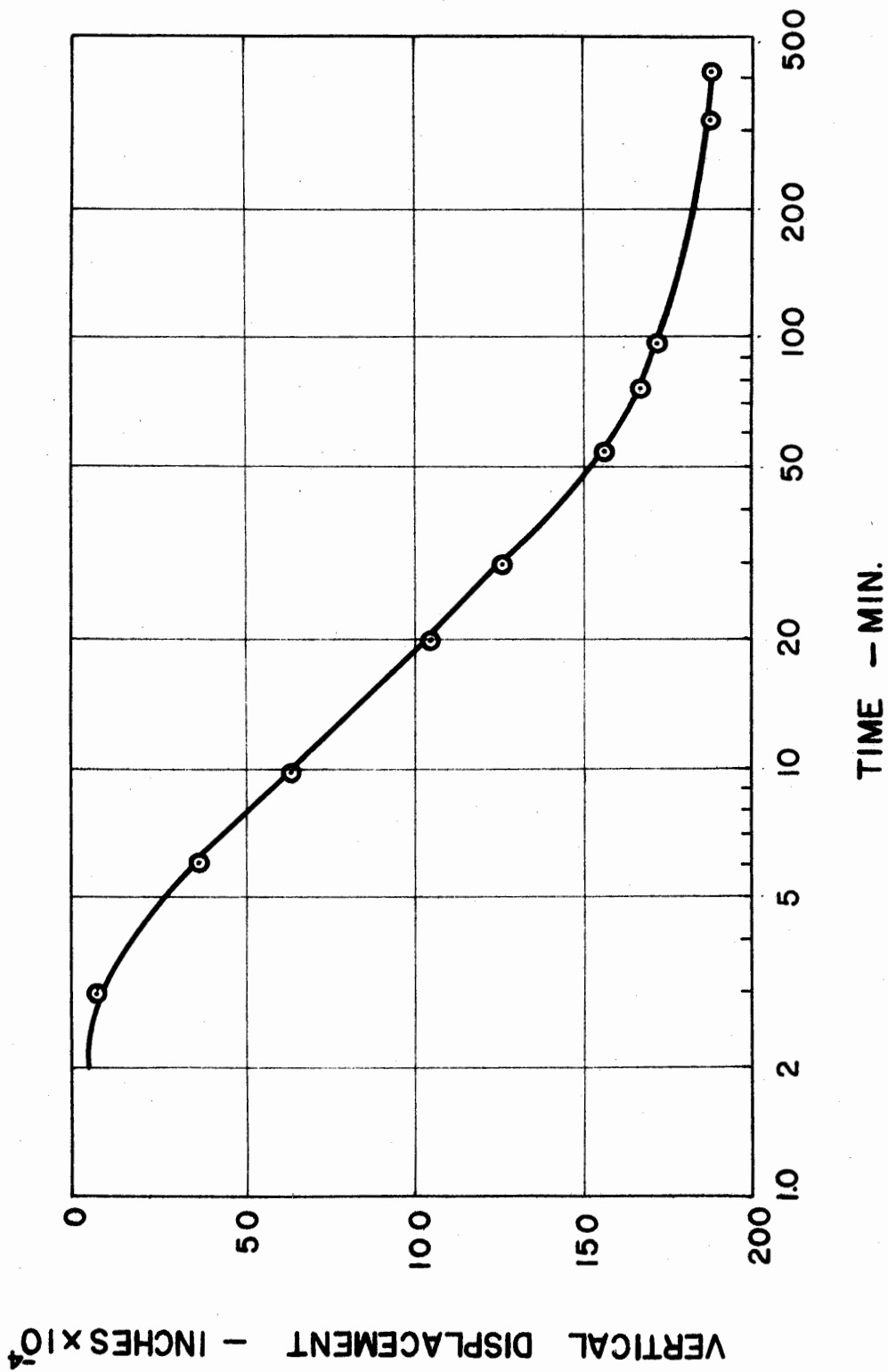


FIGURE 8

The experimental displacement versus log-time plots were compared with the theoretical plots to evaluate the coefficients of consolidation " C_v " for each voltage gradient applied to the remolded samples. The results are summarized in Table II. The data indicate that the rate of consolidation increases with increasing potential gradient. It also indicates that the amount of compression that direct current accomplishes may be limited in any given soil. The data presented in Table II are shown graphically in Figure 9. From Figure 9 the increase in the coefficient of electro-osmotic consolidation with increasing potential can be seen. The decrease in the amount of compression with increasing potential gradient is also shown in Figure 9.

The variations of water content in each sample after treatment are shown in Figure 10. The remolded clay sample showed increasing water content from anode to cathode. The undisturbed varved clay samples showed somewhat the same effect although the variations are not as regular as the remolded sample.

Discussion

The experiments presented in this section were designed to evaluate the possibility of treating varved clay electro-osmotically in the field for the strengthening of clay deposits and possible elimination of berms. The application of direct current to varved clay does not appear to be very effective. Increased strength results from higher density due to compression. The amount of compression developed in the varved clay at high potential gradients is small. Electro-osmosis does not therefore appear to be an effective means of strengthening varved clay. Mechanical loads appear to be much more effective.

TABLE II
RESULTS ON REMOLDED VARVED CLAY

Applied Potential Gradient Volts/cm	Computed Coef. of Consolidation C_v in cm^2/min	Total Vertical Displacement in $\mu\text{m}/\text{cm}$
1.2	0.032	37
2.5	0.068	23
3.0	0.154	19
5.0	0.320	13

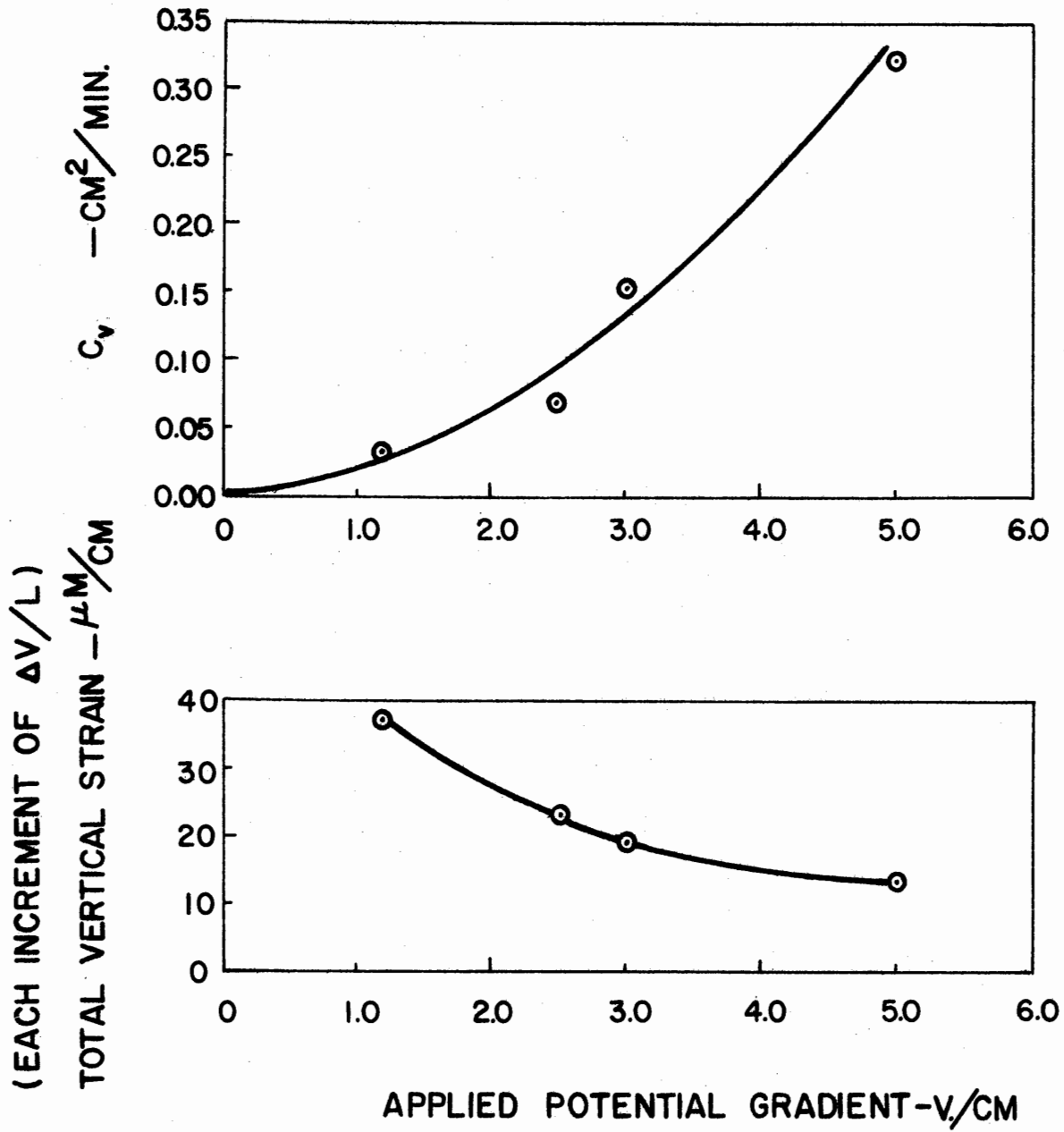


FIGURE 9

WATER CONTENT ω AS PERCENT

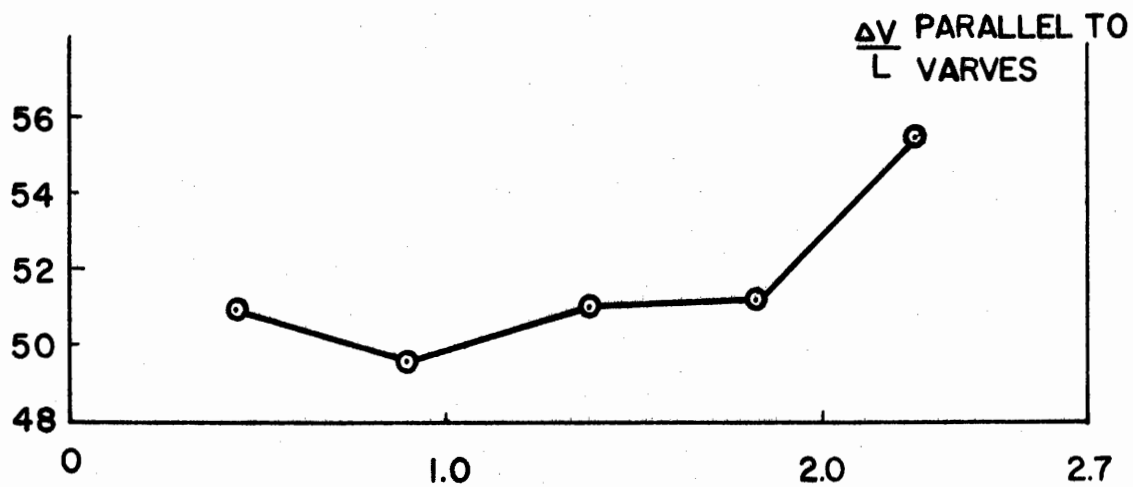
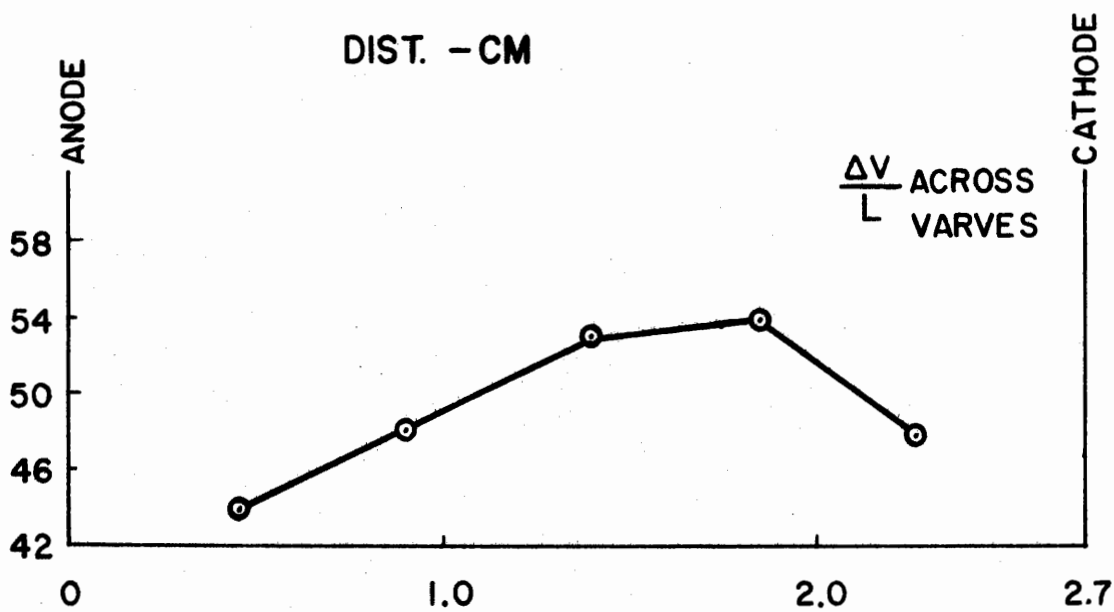
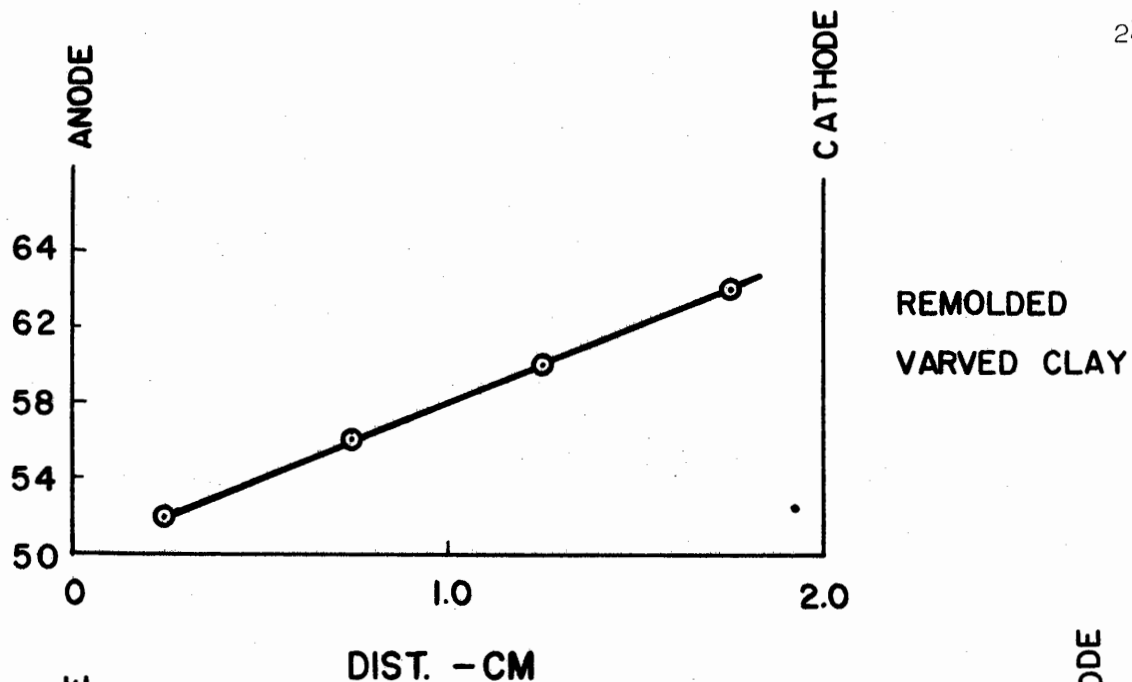


FIGURE 10

The experimental behavior observed in these tests indicates that the theory of electro-osmotic consolidation as formulated by Esrig has certain inaccuracies. The specific point that requires further investigation is the prediction of the pore pressure that can be developed in a soil by direct current. Based on the amounts of compression observed in these tests the developed pore pressures were much lower than predicted by theory. This is probably due to the fact that as the soil develops strength the matrix of the soil allows pore water to be circulated within the pores by a combination of electro-osmotic and hydraulic flows. A complete investigation of Esrig's theory requires an extensive experimental program beyond the scope of this project.

Conclusions

1. Electro-osmotic treatment is not very effective in consolidating varved clay.
2. Negative pore pressures developed during electro-osmotic consolidation appear to be lower than indicated by Esrig's theoretical treatment.

LABORATORY INVESTIGATIONS ON FRITTED GLASS DISKS

Few electro-osmotic investigations have been done on stratified or nonhomogeneous soil. There is some experimental evidence that indicates that electro-osmotic flow and treatment depends on pore size (9). Layered soils occur frequently in Connecticut and the pore size and permeability normally vary from stratum to stratum. To study the effects of pore size and electrolyte concentration on electro-osmotic flow, it was decided to use fritted glass disks to simulate soil. These disks are rigid and each is manufactured with a well controlled pore size distribution. Fritted glass disks are durable enough so that the same disk can be used over and over again in any number of tests. A pore size distribution can be determined independently for each disk by mercury porosimetry (18). The concept of mercury porosimetry is based on pushing a non-wetting liquid into a porous medium. Mercury is forced into the pores at various pressures. At each pressure the volume intruded is measured and the pore size relating to pressure computed.

The properties of the disks selected for the experiments are shown in Table III. The pore sizes range from a coarse silt to silty clay. Electro-osmotic experiments were made testing each disk separately and testing series of disks in various combinations of pore sizes. The electro-osmotic measurements were made using solutions having various concentrations of sodium chloride. The electro-osmotic flows were measured by timing the motion of a bubble in a capillary tube.

Experimental Procedure

1. Porous Media (Fritted Glass Disks):

Commercially available Pyrex Brand Fritted Glass Disks 31001 were

TABLE III

FRITTED GLASS DISK DATA

Disk Type	Total Porosity By Direct Method S.G. = 2.23	Porosity By Hg Porosimeter S.G. = 2.23	Porosity By Com-bined Data	Specific Gravity by Com-bined Data	Nominal Max. Pore Radius (Microns)	Mean Pore Radius From Porosimetry 50% Volume (Microns)	Avg. Pore Radius From Surface Area (Microns)	Surface Area By Graphical Analysis (m ² /gm.)
Medium	.246	.237	.227	2.17	5 - 7.5	6.1	5.5	.049
Fine	.268	.250	.244	2.17	2 - 2.75	2.3	1.7	.172
Very Fine	.223	.233	.233	2.24	1 - 1.25	0.8	0.7	.384
Ultra Fine	.157	.142	.140	2.19	.45 - .7	0.4	0.3	.467

Length L (cm.)	Water Content W (%)	Gross Area (cm ²)	Void Ratio
Medium	15.	12.6	0.326
Fine	16.	12.6	0.366
Very Fine	13.	12.6	0.287
Ultra Fine	8.	12.6	0.186

used in the tests. The disks were about 40 mm in diameter and about 4-5 mm thick. The disks were fabricated from Corning chemical glass no. 7740, a borosilicate glass with a specific gravity of 2.23 grams per cc (4). The disks are usually used for filtration, and are obtainable with different nominal pore size designations. The Medium, Fine, Very Fine, and Ultra Fine disks were used in these tests. Detailed characteristics of the disks are given in Table III.

Prior to use, the disks were cleaned with hot nitric acid, then rinsed thoroughly with demineralized water until no change of conductivity was observed in demineralized water, for at least a period of 12 hours. The disks were then stored in demineralized water. Prior to testing, the disks were deaired under vacuum, to insure saturation. In order to observe the effect of air bubbles, an electro-osmotic test was performed on a nonsaturated disk. The voltage and current meters exhibited very erratic and inconsistent behavior, and it was evident that something was wrong. Mysels and McBain (13) also found that air bubbles in fritted glass disks led to erratic behavior and were easily detected.

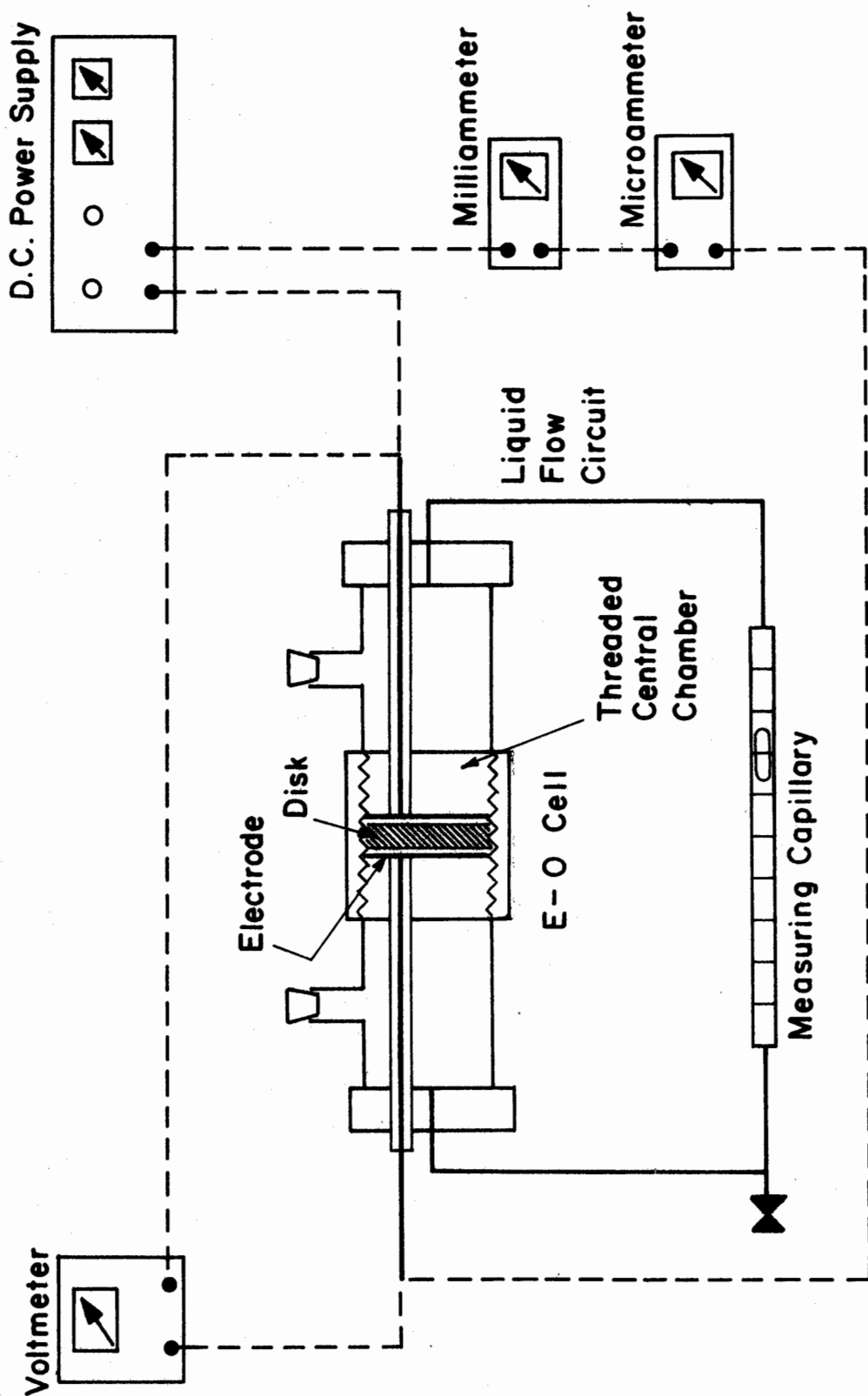
After testing, the disks were rinsed with demineralized water to remove the NaCl, until no change of conductivity was observed for at least 12 hours. When sodium lauryl sulfate (a soap) was used in several tests, the nitric acid cleaning procedure was used to insure that all soap was removed from the disks.

Mysels and McBain (13) found in their experiments on fritted glass disks that thermal effects occur upon change of concentration of electrolytes, which change the resistance of the disks. The effects are more pronounced for dilute solutions, and require a lengthy time for

equilibrium; "overnight" soaking being sufficient. A typical time for equilibrium with a concentrated solution was about 20 minutes, but in any case the change in resistance was only .05% - 0.01%, a negligible amount. The disks in this investigation were always stored in demineralized water prior to testing, at least "overnight". Since tests proceed from dilute to concentrated solutions, thermal effects were negligible.

2. Electro-osmotic Cell:

Figure 11 shows details of the electro-osmotic apparatus. The main body of the cell consists entirely of clear acrylic plastic, the electrode chambers were made from cylindrical tubing, 2 inches (51 mm) O.D., with 0.5 inch (12 mm) flat plates for the end caps. Each outer half is about 78 mm long and is threaded on both ends; one end receives the end cap and the other end screws into the central sample holder. Rubber O-rings seal the end cap threaded-connection. Two holes were drilled into each end cap: one hole for liquid flow into a capillary tube and the other for electrode insertion. Each outer half of the cell contains a threaded hole which receives a 10 mm I.D. piece of acrylic plastic tubing about 2 inches (51 mm) long. Rubber O-rings seal the threaded connection and small corks seal the outer portion of the acrylic tubing. The central portion of the cell holds the disks and is also made of acrylic plastic tubing, 2 inches (51 mm) O.D. This portion of the cell was threaded internally throughout its full length (51 mm), and the resulting I.D. was 42 mm. If leaks occurred at the threaded connection between the outer portion of the cell and the central sample holder, Teflon thread tape was used as a sealer.



SCHEMATIC OF EXPERIMENTAL APPARATUS

FIGURE II

Rubber gaskets (I.D. 42 mm, O.D. 28 mm, compressed thickness 1.3 mm) were used on each face of the glass disks to prevent abrasion and for sealing, i.e. 2 gaskets for a single disk test, 3 for a 2 disk test, and 4 for a 3 disk test. The outer sections of the cell were screwed into the central portion of the cell until a tight fit was obtained.

A piece of glass tubing was inserted into one end cap, and connected to a calibrated glass capillary tube by a length of Tygon tubing. An identical piece of glass tubing was inserted into the other end cap, and connected to a glass "T"-connection which was joined to the other end of the capillary tube by a short piece of Tygon tubing, thus completing the flow measurement circuit. The remaining opening in the "T"-connection was stoppered with a soft rubber self-sealing ampoule stopper through which a hypodermic needle was inserted and an air bubble injected into the capillary tube.

The capillary tube was a precision bore pipette having etched volumetric calibrations. The total length of the tube was 25.0 cm and the internal diameter was 0.267 cm. The calibrated length for a volume of 1.00 ml was 17.85 cm, which could be read directly to 0.01 ml.

Each wire connecting the electrode was sealed with silicone rubber sealer in glass tubing which passed through the second hole in each end cap. Only the disk electrode was in contact with the electrolyte.

The volume of each end section was about 75 ml, with a total electrolyte volume of about 150 ml. This volume was the same for all tests, since each end section was always treaded to an outer disk face.

All materials utilized in the cell were checked for chemical inertness by first cleaning them and then placing them in demineralized water for at least 12 hours. If there was no change in conductivity

and pH values over this period, it was assumed there would be no change during the few hours of a typical test. Rubber O-rings, gaskets, tubing, cured sealants, Teflon tape, etc. were found to be inert on the basis of the above test. All materials used for cell construction were inert.

3. Electrodes:

One set of reversible silver-silver chloride disk electrodes was used as both the working and measuring electrodes. A thin loop of platinum wire formed the perimeter of each electrode and was connected by copper wire to the power source. Platinum gauze was attached to the platinum wire by heat to form the main body of the disk electrode, whose outside dimension roughly approximated the interior shape of the cell. The wire connecting the electrode to the power supply was passed through a piece of glass tubing, which entered the cell through a hole in the end cap. The interior portion of the wire was sealed at the entrance to the glass tubing, so that only the disk electrode was exposed to electrolyte.

The silver-silver chloride electrodes were prepared by following the procedures of Shoemaker and Garland (20), which basically consist of plating the bare platinum electrodes with high purity silver, and then after a period of aging, coating the electrodes with silver chloride.

4. Additional Equipment:

Other equipment that can be considered standard laboratory apparatus was used for measuring conductivity and pH. The power supply was a Heathkit Model IP-17 Regulated High Voltage Power Supply. The voltmeter was Hickok Model 470A. Simpson ammeters

were used to measure currents. The water used in the cell was distilled and demineralized.

5. Assembling and Measuring with the Apparatus:

Each fritted glass disk was deaired and stored in demineralized deaired water. To prepare a disk for measurement, half of the E-O cell was filled with water, and the disk and appropriate gaskets were assembled under water. The remaining half of the cell was connected and filled with water, care being taken to eliminate air bubbles. The cell was then connected to the hydraulic permeability apparatus, and a constant head permeability test was performed by causing the water to flow in each direction through the disk. The reported coefficient of hydraulic permeability, k_h , is the average of the two tests. The permeability tests were performed under a differential head of water equal to 44.3 cm. During the permeability tests the apparatus was checked for hydraulic leaks. If the cell was free of leaks at this point, leaks never occurred later on during the no head conditions of electro-osmotic measurements. Following the cell disconnection from the hydraulic permeability apparatus, the capillary flow measuring system was connected to the cell. A hypodermic needle was inserted through the rubber self-sealing ampoule stopper, an air bubble was injected into the capillary tube, and the needle extracted. The cell was placed on top of the two magnetic stirrers which were used to minimize concentration gradients. The stirrers were turned on, rotating small plastic coated magnets which had previously been placed in each half of the cell. Electrical connections were made, the D.C. current applied, and the bubble was made to move up and down the capillary tube. This was a check point; tube

cleanliness was visually checked, meter functions were checked, and hydraulic leak checks were made.

The E-0 measurements consisted of volume, voltage, time and current readings. Electro-osmotic measurements at a given voltage were taken in both directions. The voltages and volumes were equal for both directions, and time was taken as the average time of the two runs. Since a constant voltage power supply was utilized as the source of D.C. current, any electrode polarization effects would be reflected as a change of current. Therefore, a current reading was taken at the beginning and end of a run, and the current value for a data point is the average of the four current readings. For each concentration of electrolyte, E-0 was measured at four voltages, 20, 40, 70 and 100 volts, except in the case of 10^{-2} N and 10^{-1} N NaCl. At those concentrations the current density was too great, and at 10^{-2} NaCl, 40 volts was the maximum voltage utilized. At 10^{-1} NaCl, 10 or 15 volts was the maximum voltage difference obtainable.

Prior to, and after completion of a test run at a given concentration, pH and conductivity measurements were made on the electrolyte. After a test run, the cell was emptied and a new, higher concentration added for the next complete run. Testing proceeded from dilute to concentrated electrolytes, beginning with demineralized water.

In the case of multiple disk tests, it was found that the electrolyte remaining in the gap between the disks had the concentration of the previous test run, and it was not sufficient to simply run the bubble up and down the capillary tube to assure equal concentration throughout, as in the case of single disk tests. Therefore, 10-20 ml of electrolyte was hydraulically forced through the cell at a pressure

of about 2 psi, first in one direction and then in the other. This assured equal concentrations of electrolyte in the cell, disks and gaps between disks.

To make accurate electrokinetic measurements on porous media, electrochemical effects must be eliminated as much as possible, reducing the number of major side effects in the experiments. Reversible silver-silver chloride electrodes were used in these experiments to eliminate gassing at the electrodes. Electro-osmotic runs were made by reversing the current, and an E-0 value consists of the average values obtained from two runs in opposite directions. This procedure minimizes polarization of the electrodes, minor equipment biases which appear to occur randomly, and concentration and pH gradients in the electrolyte. Stirring bars were placed on both sides of the cell and the solution stirred to minimize concentration gradients. The total electrolyte volume in the cell was about 150 ml., compared to an average void volume of about 1.2 ml. for a disk. This also tended to minimize concentration and pH changes. The duration of a typical test run was about 15 sec., long enough for adequate measurements, and short enough so that undesirable electro-chemical effects were minimized.

The current densities ranged from 0.1 ma./cm² to 10 ma./cm², but most of the experiments were conducted using current densities of less than 2 ma./cm². The current densities exceeded 2 ma./cm² only in the cases of 10⁻² and 10⁻¹ N NaCl concentrations.

6. Capillary Tube Considerations:

In order to measure the volume of E-0 flow, an air bubble was injected inside a capillary tube using a hypodermic needle. When using

an air bubble-capillary tube system to measure the rate of E-0 flow, consideration must be given to the following major problems: cleanliness of the tube, liquid bypassing the bubble, capillary E-0, and liquid backflow through the porous media.

The selection of a capillary tube for a given set of experiments represents an optimization problem for the system as a whole. For this set of experiments, it was found by trial and error that the optimum diameter of capillary tube was 2-3 mm.

Bubble movement in a clean tube is smooth and steady, while the movement in a dirty tube is jerky and erratic from the drag exerted on the menisci. In this set of experiments, the above visual indicators of cleanliness were used, and both the appearance and behavior of the air bubble were routinely checked. During the few hours of a complete test, there were no indications of contamination. There was no measurable difference in performance between a clean tube used throughout a complete test versus a tube re-cleaned during the test. The capillary tube was cleaned by soaking it in chromic acid, and then rinsing it thoroughly with demineralized water prior to testing. The chromic acid treatment caused no measurable changes in tube volume.

A contaminated tube containing an air bubble can give rise to inaccurate flow rate measurements due to movement of liquid around the bubble (16). Two different organic tracing dyes and potassium permanganate dye were injected separately on one side of the air bubble, and the bubble was moved in the tube in both directions. None of the dyes were observed to bypass the bubble when clean tubes were used. Only with vigorous back and forth motion, (conditions far exceeding those of the actual E-0 tests) could liquid be made to bypass the bubble.

A clean tube is apparently the best solution to all of the above problems.

A potential gradient impressed across a capillary tube causes E-0 flow in the capillary, which might be a source of error when using a capillary tube-air bubble system to measure E-0 flow. In order to measure the rate of capillary E-0 flow the cell was assembled and a test run as for a normal single disk test, except that no disk was inserted in the cell. The electrodes were spaced 5 mm. apart, approximately the thickness of a disk. The error, relative to the flow characteristics of the ultra-fine disk (which gives the largest error), was 0.8% for the rate of flow versus voltage gradient, and 0.4% for the rate of flow versus current. The error relative to the flow rates of the other disks is proportionately less.

7. Mercury Porosimetry Measurements:

The pore size distributions in the fritted glass disks were checked by mercury porosimetry. The porosimetry measurements were contracted out to American Instrument Company, Silver Spring, Maryland because no porosimeter was available on campus. The results of each measurement were supplied from American Instrument in graph form. An example of the results are shown in Figure 12. As indicated in Figure 12, the diameter of the pores in a "medium" fritted glass disk vary from about 18 to 5 μ with the median being about 12 μ .

RESULTS

The electro-osmotic flow Q_E is plotted against current in Figure 13. The data in Figure 13 are for single disks in distilled water. The rate of flow through each disk is proportional to the current passed. The straight line formed by the data points for each disk extrapolate

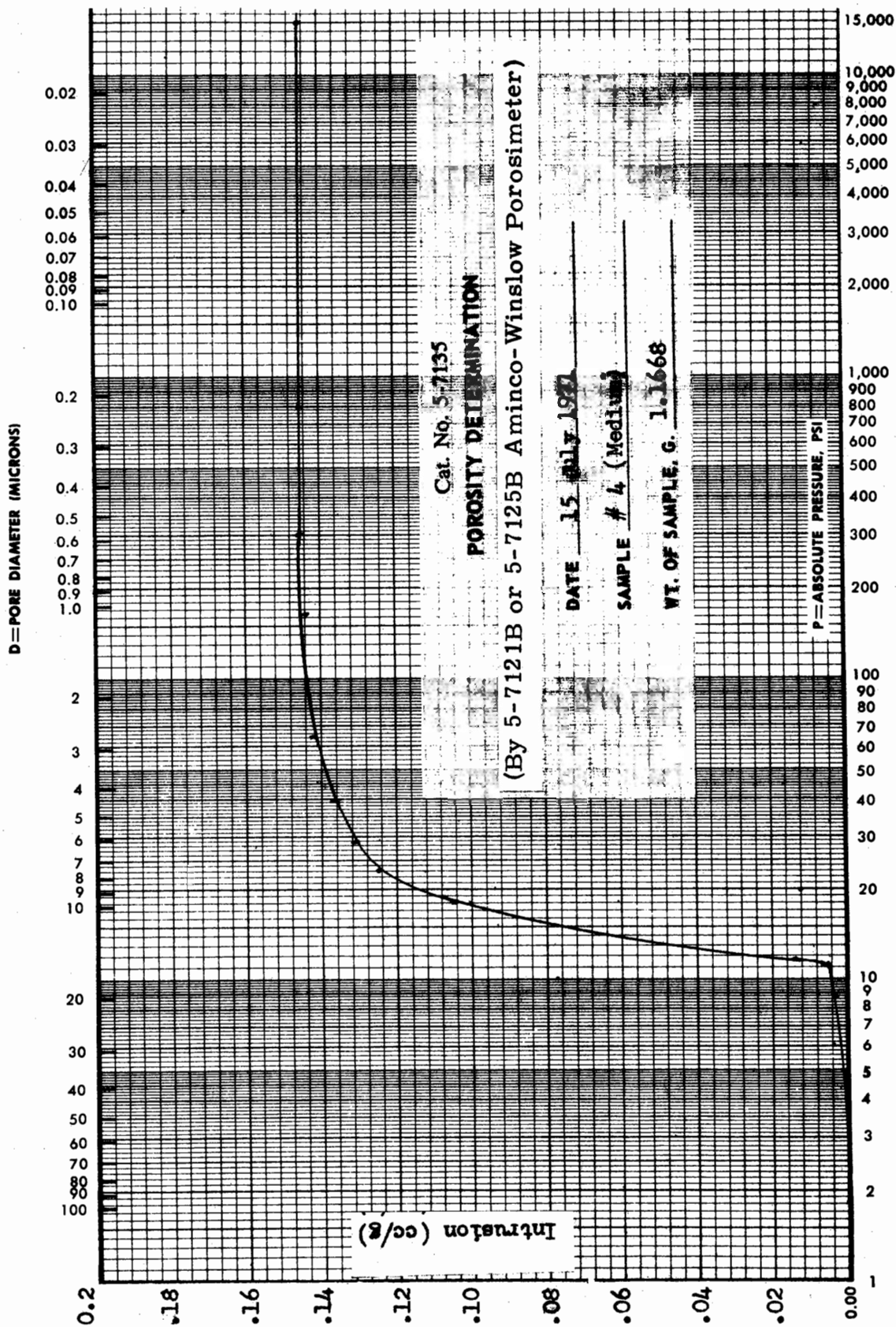


FIGURE 12

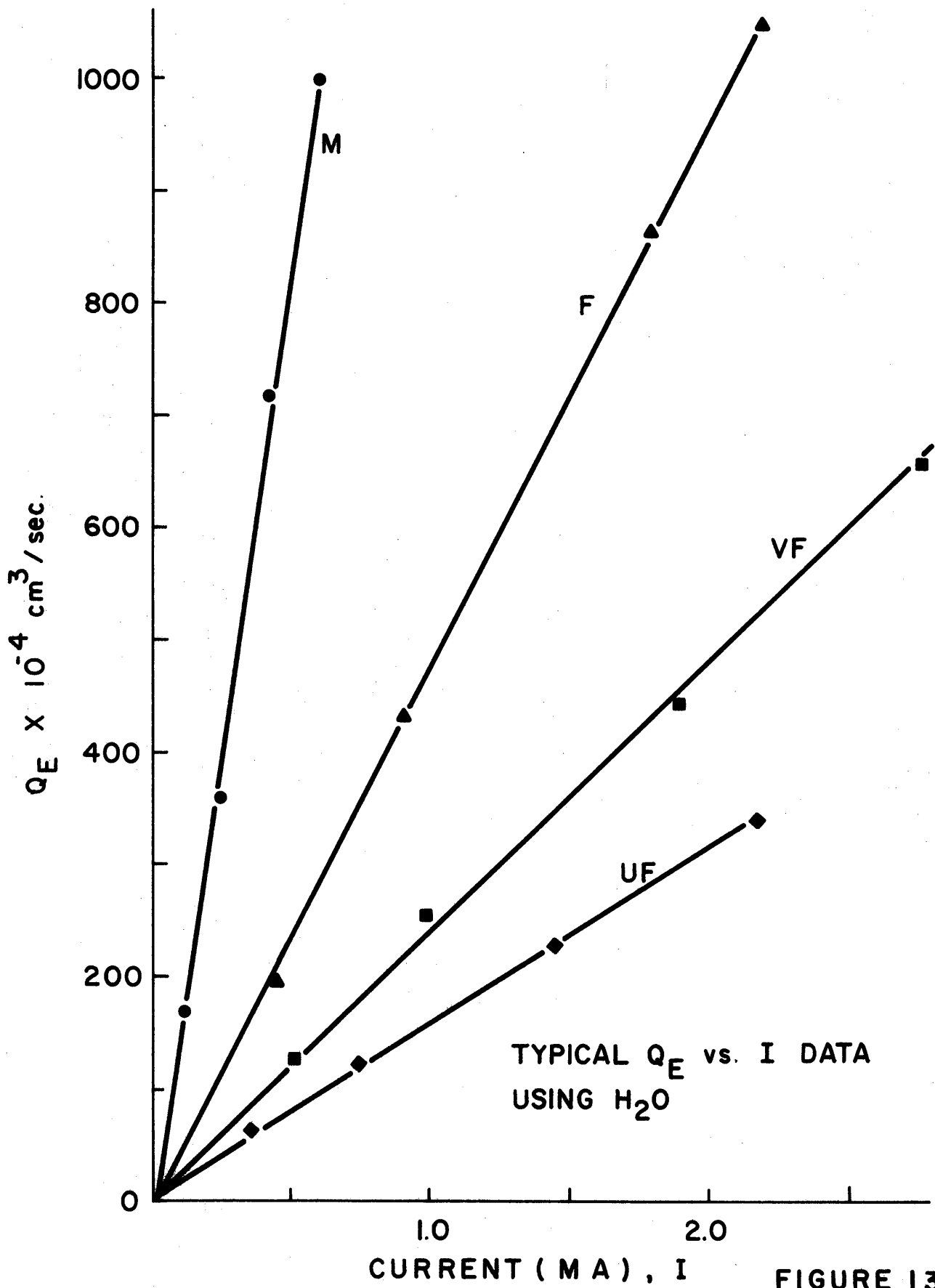


FIGURE 13

through the origin indicating that proper experimental procedures were followed.

The same flow rates are plotted against the voltage drop across the disk and are shown in Figure 14. The data for each disk again generate a straight line. The extrapolated straight line does not pass through the origin for the medium and fine disks. The discrepancy was traced to the resistance of the bubble to flow. The results for the medium and fine disks were corrected by the technique of Biefer and Mason (1). The correction equation is:

$$Q_E(\text{true}) = Q_E(\text{observed}) [1 + \phi_D / \phi_C] \quad [6]$$

where ϕ_D and ϕ_C are the hydraulic conductivities of the disk and capillary tube respectively. The slope of the straight lines in Figure 14 are related to k_E the electro-osmotic permeability. On the basis of current, the efficiency of electro-osmotic flow with distilled water is greater for larger pore sizes decreasing as the pore size becomes smaller.

The disks were also tested in solutions of sodium chloride of various concentrations. In this series of experiments the disks were placed in the electro-osmotic apparatus separately and in various size combinations. The electro-osmotic permeabilities k_E are shown in Figure 15. The data plotted in Figure 15 indicate that the smallest pore sizes tend to control the flow. This effect is readily seen in Figure 16. The rate of flow per unit of current is plotted against the concentration of sodium chloride (NaCl) in Figure 16. At low concentrations of electrolyte the medium disk carries relatively large flows, per amp passed, the ultra fine disk has the least flow per amp for a single disk with a variation between the extremes according to pore size. The electro-osmotic flow

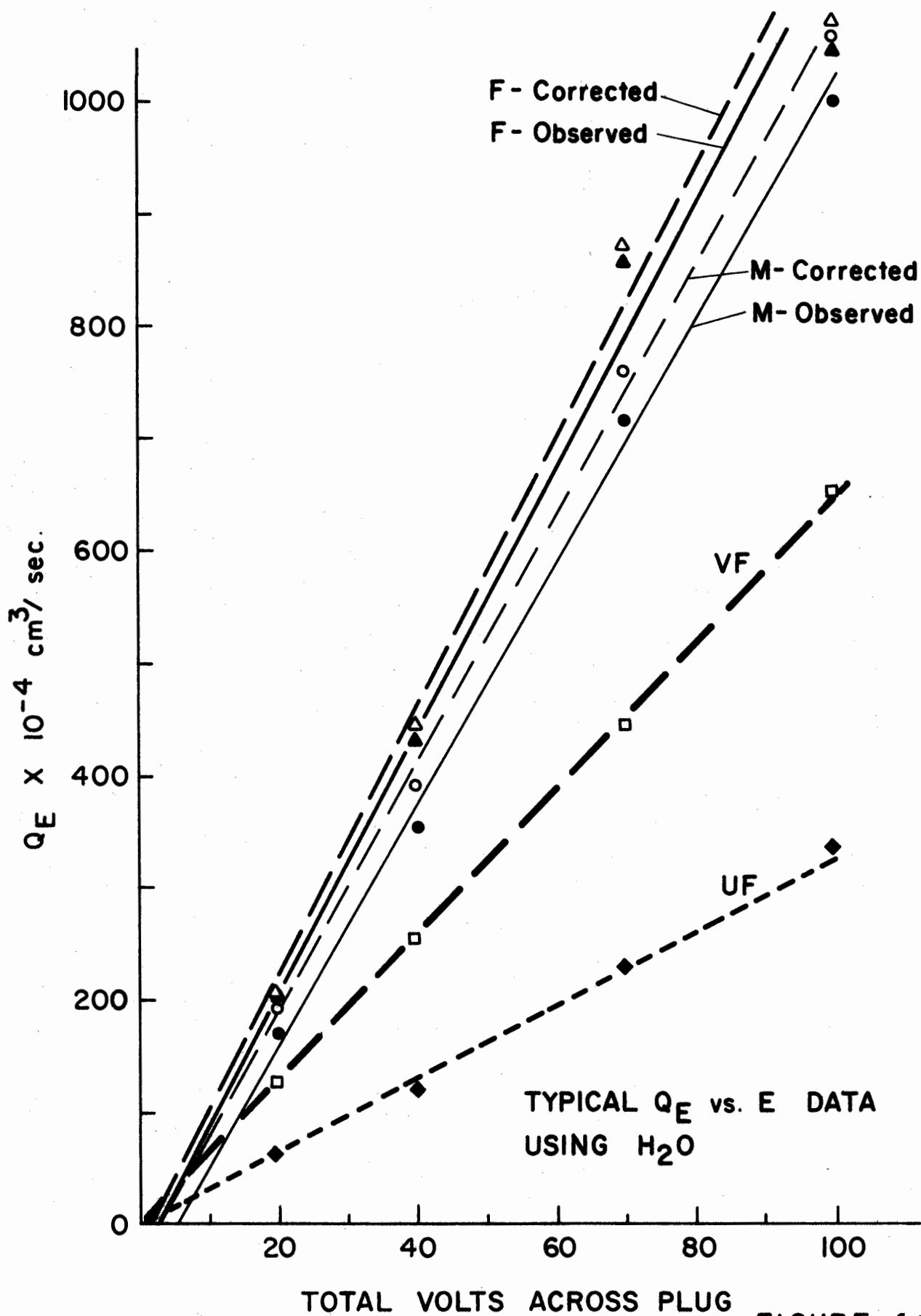


FIGURE 14

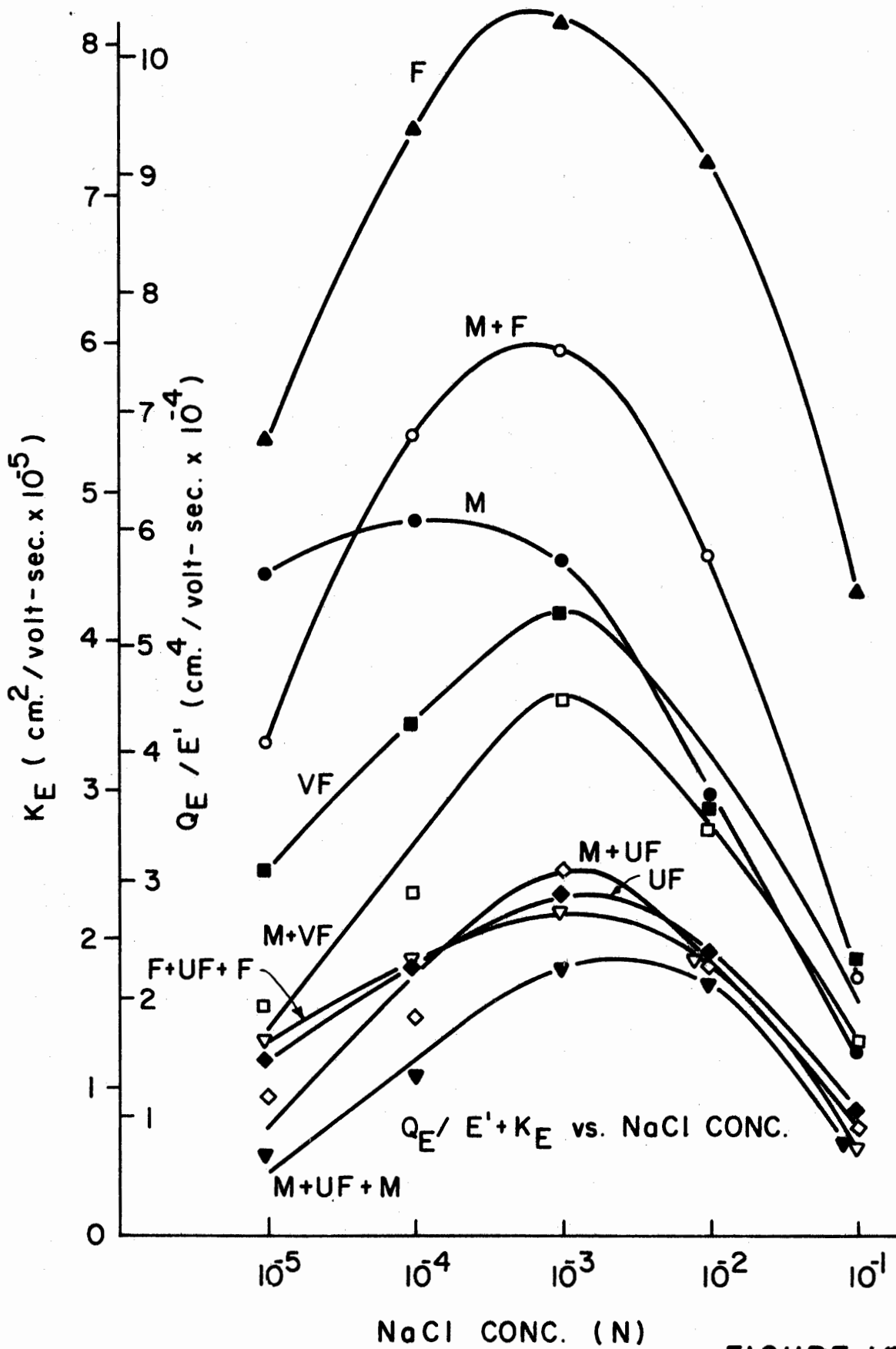


FIGURE 15

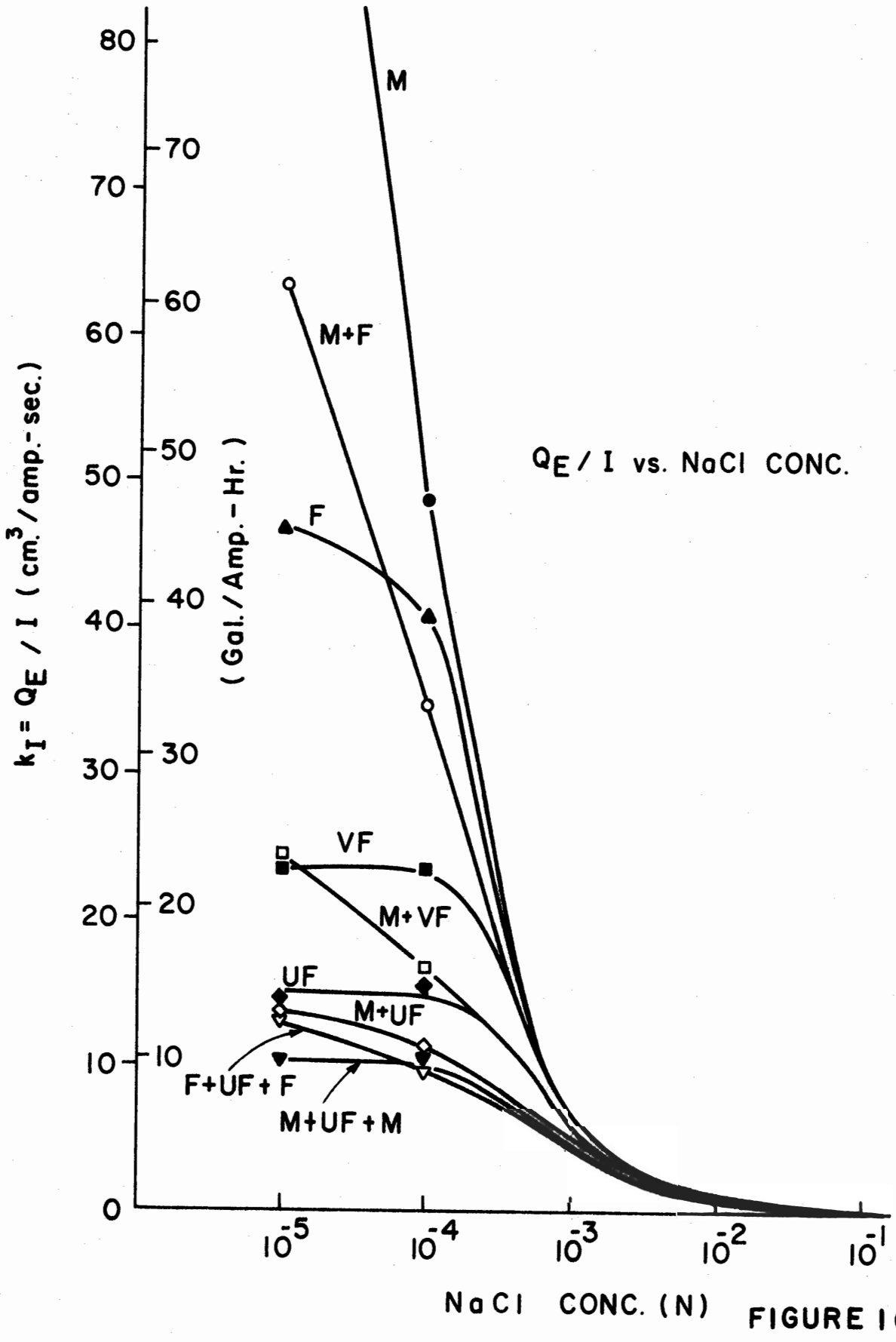


FIGURE 16

results based on current for combinations of disks again indicate that at the dilute concentrations of electrolyte, the smallest pore size in the series controls the electro-osmotic flow. Above a concentration of sodium chloride equal to 10^{-3} N NaCl the rates of flow for all disks converge.

A series of measurements were made to determine if electro-osmotic flows in the porous glass disks could be increased by adding a surface active agent in this case sodium lauryl sulfate. This agent contains a negative charge on the end of a chemical chain that is adsorbed by glass surfaces in water. If the agent could be absorbed at low enough concentration, the potential at the surface would increase faster than the concentration of free electrolyte in the pores thereby enhancing the electro-osmotic flow properties. Figure 17 shows that the measurements with sodium lauryl sulfate are essentially the same as the measurements with sodium chloride alone indicating that the addition of a surface active agent does not increase electro-osmotic efficiency.

CONCLUSIONS

1. Electro-osmotic flow and treatment are most efficiently achieved under conditions of relatively large pore size and low electrolyte concentrations.
2. Flow of water per amp of current decreases rapidly as the concentration of free electrolyte is increased becoming very small above 10^{-2} N Sodium chloride.
3. When disks of differing pore size are placed in series, the electro-osmotic properties of the series are governed by the smallest pore sizes.

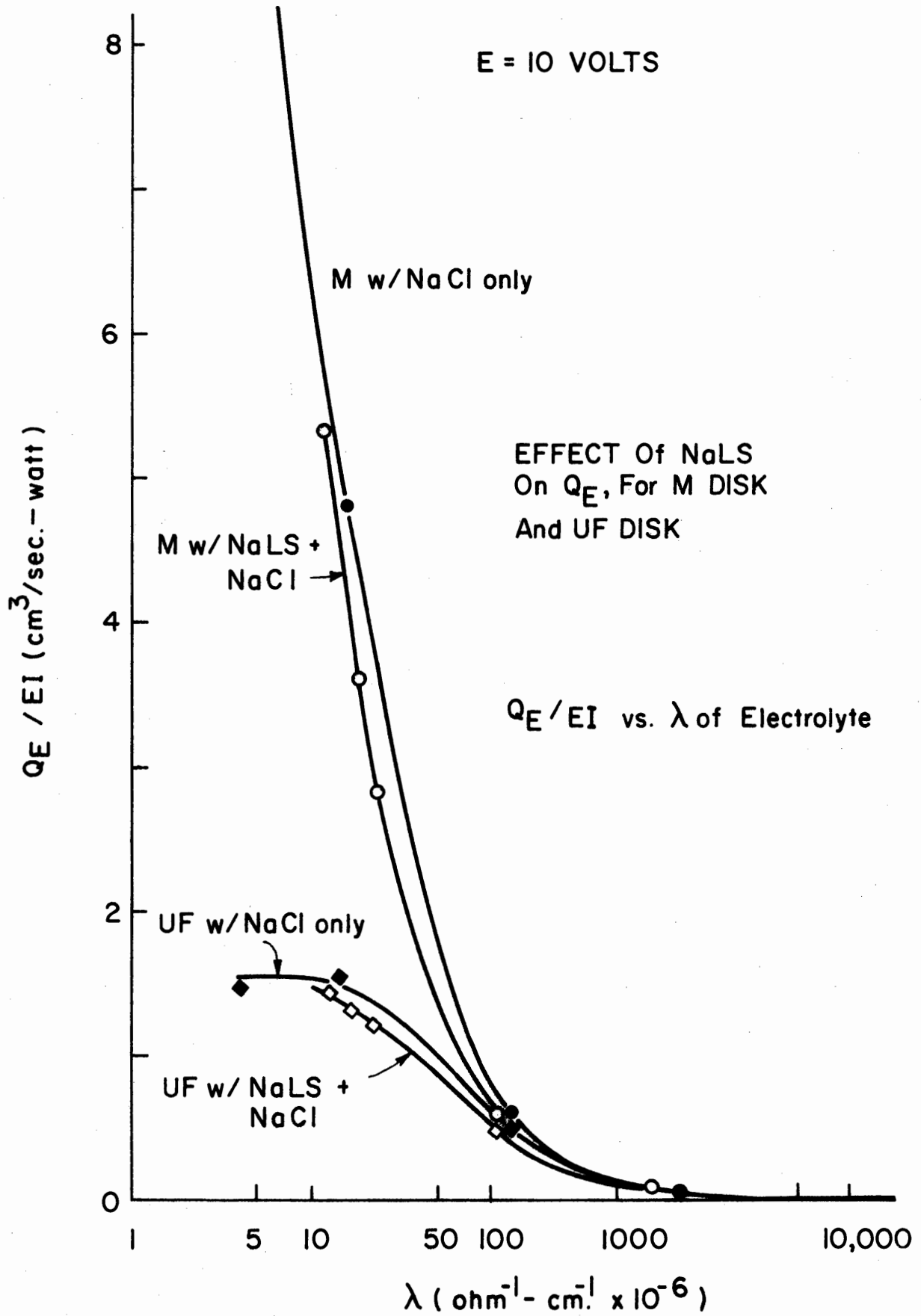


FIGURE 17

MEAN PORE SIZES FROM FLOW MEASUREMENTS

General

In the process of analyzing the electrical surface properties of the fritted glass disks a technique was developed which allows the mean pore size of the fritted glass disks to be determined from the electrical properties of the disk and electrolyte. The technique is nearly as simple as the basic permeability test. Further tests on sands indicate that the pore parameter which is determined both by this technique and mercury porosimetry should correlate with other soil behavior such as frost heave.

Theoretical Development

A capillary model for the hydraulic permeability of a porous plug was derived by Taylor (23):

$$k_H = \left(C_s \frac{\gamma_w}{\eta} n R_H^2 \right) \quad [7]$$

where: k_H is the permeability; R_H is an equivalent hydraulic radius equal to $R/2$; R is the equivalent capillary tube radius; γ_w is the unit weight of water; η is the viscosity of water; n is the porosity; and C_s is a shape factor.

A mean pore size can be computed from Equation 7 when the shape factor is evaluated. The shape factor is a term which compensates for various characteristics of a porous plug which deviate from those in the capillary model. Among the characteristics for which C_s compensates are: variations in pore openings, tortuosity, differences between total and effective porosity and unequal pore sizes along the flow path. The most important effect of these properties is that they modify the superficial potential drop imposed across the ends of the porous plug to a lesser potential

gradient inside the pores. The potential gradient inside the pores is more directly related to the flow of liquid.

The basic equation of flow with this model could be rearranged to read:

$$Q = \left(\frac{\gamma_w}{\eta} R_H^2 \right) \frac{\Delta H}{L} (C_s \cdot n) A \quad [8]$$

where: Q is the flow rate through the porous plug; A is the gross cross-sectional area; L is the length of the plug; and ΔH is the drop in head across the plug.

The correction term ($C_s \cdot n$) includes the porosity because the porosity which supports flow may be less than the total. The evaluation of the correction term is not possible from hydraulic measurements alone. There is, however, a well known analogy between laminar hydraulic flow under a difference in head and the flow of direct current under a voltage difference (5). The flow of water is analogous to the current. The hydraulic gradient is analogous to the electrical gradient. Both flows are influenced by the size of the area through which they move. When direct current is passed by an electrolyte solution in a capillary tube, the potential gradient can be determined from either the voltage or the current and the specific conductivity. In a straight capillary tube the relation is:

$$\frac{\Delta V}{L} = \frac{i}{\lambda a} \quad [9]$$

where: ΔV is the voltage drop over a length L; "i" is the current passed through a capillary of cross-sectional area "a" and λ is the specific conductivity in mho/cm.

Direct current passing through a porous plug indicates that the average potential gradient inside the pores is smaller than the superficial gradient. The relation can be written thus;

$$\frac{\Delta V}{L} C_s = \frac{i}{\lambda n A} \text{ or } C_s n = \frac{L}{\Delta V \lambda A} \quad [10]$$

The correction factor ($C_s n$) can be determined from Equation 10 when the surface conductivity inside the plug is negligible and used in Equation 7 to compute a mean pore size. Most materials, including soils, carry a surface charge which influences the conductivity of the pore fluid near the particles. To make the effect of surface conductivity in soils negligible the electrolyte concentration must be 10^{-1} N or greater (19)(22). An electrolyte concentration of 10^{-1} should be adequate for soils having a cation exchange capacity equal to or less than a kaolin. Clays having higher cation exchange capacities require a more detailed analysis because of the persistence of surface conductivity even when the electrode chambers contain a concentrated electrolyte solution.

The validity of combining Equation 10 with Equation 7 was checked with measurements on fritted glass disks, whose pore sizes were also measured by mercury porosimetry.

Experimental Procedure

The direct current measurements were made on fritted glass disks in an acrylic-plastic cell described before. The cell was designed for electro-osmotic experiments and contains the basic components of that type apparatus.

Rate of flow, voltage and current were measured in both directions for each test. The results reported herein were obtained at an electrolyte concentration of 10^{-1} N sodium chloride in the cell. At this concentration the surface conductivity within the disk is negligible. In addition the conductivity and pH of the solution were monitored and only minor changes

were noted during the tests.

Results and Discussion

The mean pore sizes for each fritted glass disk computed from Equations 7 and 10 are shown in Table IV. Also included in Table IV are the mean pore sizes based on volume as measured by mercury porosimetry and the nominal pore sizes listed in the manufacturer's catalogue. As can be seen from the results listed in Table IV the mean pore sizes measured for each disk by various methods agree. The mercury porosimetry results for Fine Disk No. 1 show a much higher pore size than the hydraulic flow or direct current characteristics indicate. The manufacturer's nominal size agrees with the flow results. The porosimetry result for this disk was checked with two additional tests. All yielded similar results. The discrepancy for this one disk may be due to an unusual combination of unequal pore sizes that biased the mercury porosimetry results.

No published results are available for direct current measurements and mercury porosimetry sizes on the same clay sample. However, mean pore sizes by mercury porosimetry have been reported for a kaolin by Sridharan et al (21) and the necessary direct current information can be extracted from electrokinetic data for a different kaolin reported by Olsen (15). In an effort to determine if analysis by Equations 10 and 7 yield reasonable results for a kaolin clay, Olsen's electrokinetic results were analyzed and plotted along with the mercury porosimetry results of Sridharan et al. The mean pore sizes are shown in Figure 18. The computed mean pore sizes appear reasonable. Both techniques indicate that the mean pore size in each sample varies linearly with void ratio in the range reported.

TABLE IV
Summary of Mean Pore Sizes

Disk	Gross Porosity	Mean Pore Radius - μm			k_H in cm/sec X 10^{-6}
		Hg Porosimetry	Eq. 1 and 4	Manufacturer's Data	
MEDIUM	0.25	6.1	6.8	5-7.5	500
Fine No. 1	0.45	10.0	3.0	2-2.75	260
Fine No. 2	0.27	2.3	2.9	2-2.75	125
Very Fine	0.22	0.8	0.9	1-1.25	6.2
Ultra Fine	0.16	0.4	0.4	0.45-0.7	1.3

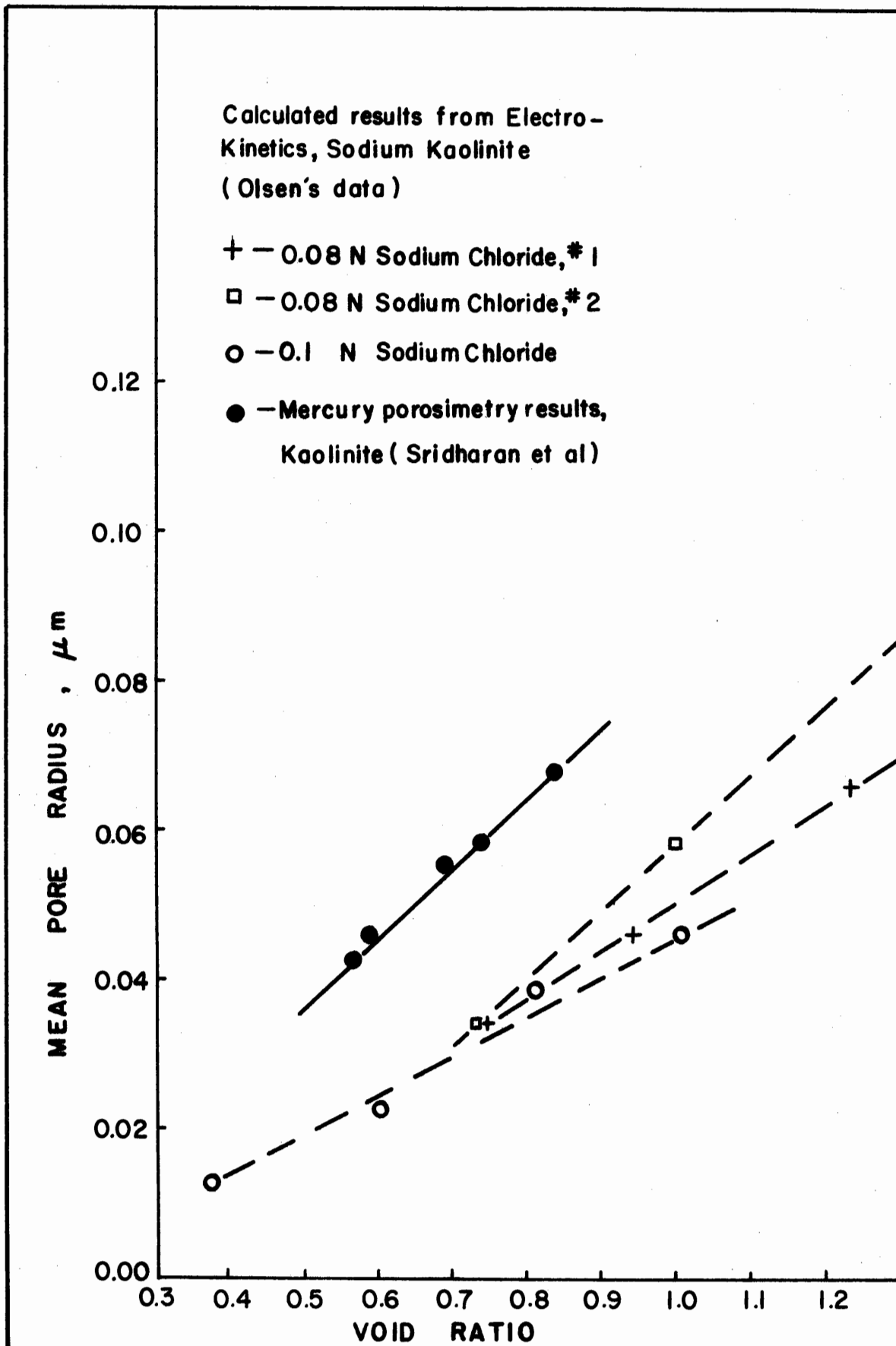


FIGURE 18

Conclusions

The mean pore size of fritted glass disks having characteristics similar to soil ranging from sand to silty clay can be determined by combining direct current characteristics with hydraulic permeability. The technique also appears promising for inactive clay. Mean pore sizes can be obtained without removing the sample from the apparatus or the water from the sample.

REFERENCES

1. Biefer, G.J. and Mason, S.F., "Electro-osmosis and Streaming in Natural and Synthetic Fibers", J. Colloid Sci., Vol. 9, 1954, pp. 20-35.
2. Bjerrum, L., Moum, J. and Eide, O., "Application of Electro-osmosis to a Foundation Problem in a Norwegian Quick Clay", Geotechnique, Vol. 17, 1967, pp. 214-235.
3. Casagrande, L., "Electro-osmotic Stabilization of Soils", Boston Society of Civil Engineers, Contribution to Soil Mechanics 1941-1953, B.S.C.E., 1953, pg. 285.
4. Corning Glass Works, Properties of Selected Commercial Glasses, Corning, N.Y., 1965.
5. Daugherty, R.L. and Franzini, J.B., Fluid Mechanics with Engineering Applications, 6th Ed., McGraw-Hill, New York, 1965, pp. 242.
6. Esrig, M.E., "Pore Pressures, Consolidation, and Electrokinetics", Proc. ASCE, J. Soil Mechanics and Foundations Div., Vol. 94, No. SM4, July 1968, pp. 899-921.
7. Esrig, M.I., "Electrokinetics in Soil Mechanics and Foundation Engineering", Trans. of New York Academy of Sciences Series II, Vol. 33, No. 2, pp. 234-245.
8. Fetzer, C.A., "Electro-Osmotic Stabilization of West Branch Dam", Proc. ASCE J. Soil Mechanics and Foundations Div., Vol. 93, No. SM4, July 1967.
9. Gray, D.H. and Mitchell, J.K., "Fundamental Aspects of Electro-osmosis in Soils", Proc. ASCE, J. Soil Mechanics and Foundations Div., Vol. 93, No. SM6, Nov. 1967, pp. 209-236.

10. Healy, K.A. and Ramanjaneya, G.S., "Final Report, Consolidation Characteristics of a Varved Clay", Dept. of Civil Engineering, Univ. of Connecticut, JHR 70-30, July 1970.
11. Helmholtz, H., Ann. Physik, 7,337 (1879).
12. Mitchell, J.K., "In Place Treatment of Foundation Soils", Proceedings ASCE, J. Soil Mechanics and Foundations Div., Vol. 96, No. SM1, Jan. 1970, pg. 73-110.
13. Mysels, K.J. and McBain, J.W., "Conductivity at the Interface Between Pyrex Glass and Solutions of Potassium Chloride", J. of Colloid Science, Vol. 3, 1948, pp. 45-51.
14. O'Bannon, Charles E., "Stabilization of Soils", United States Patent Office, U.S. Patent No. 3,497,439, Feb. 24, 1970.
15. Olsen, H.W., "Hydraulic Flow Through Saturated Clays", thesis presented to Massachusetts Institute of Technology of Cambridge, Mass. in 1961, in partial fulfillment of the requirement for the degree of Doctor of Science.
16. Olsen, H.W., "Deviations from Darcy's Law in Saturated Clays", Soil Science Society of America Proceedings, Vol. 29, No. 2, Mar.-Apr. 1965, pp. 135-140.
17. Reuss, F.F., Mem. Soc. Imperiale, Natural, Moscow 2, 327(1809).
18. Roatare, H.M., "A Short Literature Review of Mercury Porosimetry as a Method of Measuring Pore-Size Distributions in Porous Materials and a Discussion of Possible Sources of Errors in the Method." Aminco Lab News, Vol. 4, 1968, American Instrument Co., Silver Springs, Md.
19. Shaw, D.J., Electrophoresis, Academic Press, New York, 1969, Chap.5.
20. Shoemaker, D.P. and Garland, C.W., Experiments in Physical Chemistry, McGraw-Hill Book Co., New York, 1962, p. 445.
21. Sridharan, A., Altschoeffl, A.G. and Diamond, S., "Pore Size Distribution Studies", Proc. ASCE J. of Soil Mechanics and Foundations Div., Vol. 97, No. SM5, May 1971, pp. 771-787.
22. Street, N., "The Surface Conductance of Kaolinite", Australian Journal of Chemistry, Vol. 9, 1956, pp. 333-346.
23. Taylor, D.W., Fundamentals of Soil Mechanics, John Wiley and Sons, New York, 1948, pg. 108.

24. Von Smoluchowski, M., L. Graetz, Ed., Handbuch der Elektrizitat und des Magnetismus, Vol. 2, J.A. Barth, Leipzig, 1921, p. 366.
25. Zimmie, T.F., "The Effect of Pore Size and Electrolyte Concentration on Electro-osmotic Flow in Porous Plugs", thesis presented to the University of Connecticut in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1972.