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Electrical Effects And The Movement Of Water In Soils

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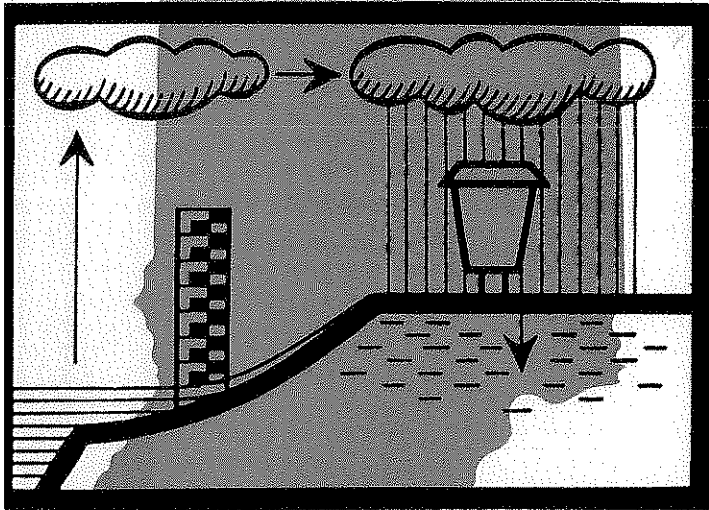
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ELECTRICAL EFFECTS and the MOVEMENT of WATER in SOILS



by
D. Swartzendruber
and
S. Gairon

July, 1970



**PURDUE UNIVERSITY
WATER RESOURCES RESEARCH CENTER
LAFAYETTE, INDIANA**

ELECTRICAL EFFECTS AND THE MOVEMENT
OF WATER IN SOILS

A completion report of OWRR Project No. B-005-IND, "Electrical Effects on Water Infiltration into Soils," Agreement No. 14-01-0001-1018. Period of Project: July, 1966 to June, 1969. Principal Investigator: D. Swartzendruber.

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FOREWORD

The project under which the reported study was performed was entitled "Electrical Effects on Water Infiltration into Soils." Financial support was provided by the United States Department of the Interior as authorized by the Water Resources Research Act of 1964, and by the Agricultural Experiment Station, Purdue University. The project was administered by Dr. Dan Wiersma, Director of the Purdue University Water Resources Research Center, and Dr. J. B. Peterson, Head of the Department of Agronomy.

Project personnel consisted of Dr. Schabtai Gairon, Postdoctoral Research Associate, who was on temporary leave from the Volcani Institute of Agricultural Research, Rehovot, Israel, and Dr. Dale Swartzendruber, Professor of Soils, who was Principal Investigator for the project.

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ABSTRACT

The electrical potential difference across a permeameter filled with a mixture of 12.5% kaolinite and 87.5% sand was measured for saturated flow of water containing 20 ppm of mercuric chloride. Measurements were taken continuously for alternate periods of rest and flow ranging from as small as 15 min to as large as 24 hr. Both silver--silver-chloride and bright platinum electrodes were placed in the end reservoirs of the permeameter to obtain electrical measurements, and the entire flow apparatus was enclosed in a grounded copper-screen Faraday cage. Even so, electrical potential differences, observed continuously with a high-resistance electrometer and strip-chart recorder over 24-hr periods, showed considerable variation with both types of electrodes. The only consistent response, qualitatively and quantitatively, was the step change in electrical potential at the time of initiation or cessation of hydraulic flow. The direction and magnitude of this "E step" were consistent with those of the streaming-potential phenomenon. The magnitude of the E step was essentially proportional to the hydraulic gradient causing the liquid flow, and was thus in conformity with classical double-layer theory. Water flux also was closely proportional to the hydraulic gradient.

Electrical potentials were also observed for upward entry of water (20 ppm mercuric chloride) into columns of initially air-dry sand-kaolinite. The electrical difference was measured between two bright platinum electrodes, one being in the water chamber at the inlet (lower) end of a column, and the other being one of five electrodes located in the sand-kaolinite at various positions along the column. Time records of electrical potential at the various electrodes, obtained with the high-resistance electrometer and strip-chart recorder, exhibited

characteristic negative peaks that could be very closely associated with the arrival of the visual wet front at the various electrodes. Thus, although the observed electrical potentials cannot be used to infer streaming potentials for the unsaturated water-flow process of infiltration, it does appear that such potentials can be used to trace quantitatively the progress of a wet front through the soil under circumstances wherein visual observations are not possible or feasible.

Electrical potential, water flux, and hydraulic gradient were also studied for saturated water flow through plugs of sodium bentonite at various concentrations ranging from 11.5 to 35.1% clay. A special permeameter with a movable piston allowed measurements to be taken with a given mass of clay, but with successively lower clay concentrations as the piston was moved out to increase the water content of the clay-water mixture. Water fluxes required at least 3 to 4 hr to stabilize at a steady-state value after a given hydraulic gradient had been imposed. At the lowest clay content, the relationships between electrical potential and hydraulic gradient and between water flux and hydraulic gradient were both distinctly less than proportional, in the sense of downward curvilinearity. This tendency decreased as clay concentration increased, and at 28.4% clay both relationships were strictly proportional. Furthermore, a less-than-proportional relationship between streaming potential and hydraulic gradient definitely did not induce a more-than-proportional relationship of water flux with gradient, in contrast with what has been reported for non-swelling quartz powder and would be inferred from classical double-layer theories of streaming potential and electroosmotic flow. Apparently, the relationship between electrical and hydraulic properties is substantially

different for swelling porous media than for nonswelling media. Finally, the only indication of a more-than-proportional flux-gradient relationship was found for a 35.1% clay concentration, but even this was in the form of a linear relationship displaced from the origin to yield a positive gradient intercept, along with a negative water flux at zero gradient; upward curvilinearity was not detectable.

INTRODUCTION AND OBJECTIVES

The entry of water into soils and the subsequent movement of this water within the soil are processes very complex in their microscopic detail. Of necessity, physical concepts and mathematical descriptions of soil-water flow processes have required a degree of simplification in order to be manageable. In this regard, it has been common to assume that soil-water movement occurs mainly as viscous liquid flow in response to hydraulic-type driving forces and gradients. Yet, it is also well known that there are electrical phenomena associated with the interaction of water, ions, and soil-particle surfaces. The project here reported has dealt with some of these electrical effects, especially with the role of the electrical streaming potential in affecting soil-water movement. The objectives originally set forth were:

1. To determine experimentally the magnitude of the electrical streaming potential developed under conditions of steady-state and transient-state (infiltration) water flow in unsaturated soils.
2. To predict streaming potential theoretically, by beginning with present saturated-flow theory for membranes and making suitable modifications for the effect of unsaturation.
3. To compare theoretical predictions of streaming potential with the experimental determinations.

Original intentions were to begin the study experimentally, with a quick validation of techniques to be performed on water-saturated porous media, and then to proceed with measurements on unsaturated porous media as described in Objective 1. With modern instrumentation it was soon found, however, that the

electrical responses encountered did not behave in the manner expected, particularly with regard to stability with time. Resolution of these experimental complications required a major commitment of effort to the development of a dependable method of measuring streaming potential just for water-saturated porous media. This was carried through successfully and is described in Section A of the present report. Unfortunately, however, this method of measuring streaming potential cannot be applied in principle to characterize unambiguously the streaming potential in unsaturated soil-water flow, neither in the steady state nor in the transient state. Nevertheless, some measurements of the type originally envisioned were still carried out, for the case of water infiltrating into an initially dry porous medium. While direct interpretations with regard to streaming potential were obviously not possible, characteristic patterns of electrical response were found to be an effective non-visual method of tracing the movement of a soil-water front. These findings are described in Section B of the present report. Hence, insofar as Objective 1 could be realized, its fulfillment is described in Sections A and B.

Because of the experimental complications encountered in dealing with Objective 1, the theoretical approaches in Objective 2 were directed primarily toward considerations of the classically predicted (from double-layer theory) proportional relationship between streaming potential and the flow-inducing hydraulic gradient, but only for water-saturated porous media. A straightforward analysis implies that if such proportionality exists, the relationship between water flux and hydraulic gradient should likewise be one of proportionality. The existence of both such proportionalities was indeed verified for water-saturated sand-kaolinite, as described in Section A.

As a logical continuation of concern with the relationship between streaming potential and hydraulic gradient in Objective 2, the comparative aspects of Objective 3 were approached by determining whether nonproportionality between streaming potential and hydraulic gradient would correctly predict the existence and direction of a corresponding nonproportional behavior between water flux and hydraulic gradient. For this purpose, measurements were obtained for flow through water-saturated, swelling-clay suspensions and pastes as described in Section C of this report. These experiments appear quite conclusive in showing that nonproportionality between streaming potential and hydraulic gradient does not possess even the same qualitative capability for predicting the flux-gradient relationship as was found for nonswelling porous media in connection with Objective 2.

In general, achievement of the original objectives with regard to unsaturated porous media could not be carried as far as originally anticipated, but this was the direct outgrowth of new information uncovered for the first time by the project experimentation. Nevertheless, the further experimentation suggested by this experience was brought to bear effectively on the objectives as viewed in the light of the new information. Hence, with regard to water-saturated and swelling porous media, achievement of the objectives has provided much more information and understanding than was originally anticipated.

DESCRIPTION OF RESEARCH

A description of research details and findings now follows, in the form of three distinct subdivisions designated as Sections A, B, and C. These sections relate to the original objectives in the manner already described in the immediately preceding portion of this report. Each section has a separate paging sequence, with the appropriate section letter (A, B, or C) prefixed ahead of each number.

SECTION A.
 STREAMING-POTENTIAL EFFECTS IN SATURATED WATER
 FLOW THROUGH A SAND-KAOLINITE MIXTURE ^{1/}

S. Gairon and D. Swartzendruber ^{2/}

That the viscous flow of water through a capillary tube or a water-saturated porous medium can give rise to an electrical streaming potential, directed oppositely to the direction of liquid flow, is a well-recognized phenomenon normally accounted for in terms of the electrical double layer (Abramson, 1934; Overbeek, 1952). Several recent reviews with special emphasis on soil water are available (Ravina and Zaslavsky, 1968a, b). To investigate the role of zeta potential in the mechanism of sand filtration, Edwards and Monke (1967a, b) have sought to use streaming potential, while Abaza and Clyde (1969) have suggested it as a measure of water flow rate.

On the basis of classical theories of both water flow and electrical streaming potential, the flux v of water in response to both the hydraulic gradient i and the streaming-potential gradient i_e is expressed as a correction to the Darcy equation in the form

$$v = Ki - c_e i_e \quad [1]$$

where K is the saturated hydraulic conductivity, and c_e is the coefficient of electroosmotic flow (Winterkorn, 1955). The gradients are further

^{1/} Contribution from the Department of Agronomy, Purdue University.

^{2/} Postdoctoral Research Associate, and Professor of Soils.

expressible as $i = -\Delta h/L$ and $i_e = E/L$, where Δh is the hydraulic head loss across the flow column of length L , and E is the electrical potential at the outlet end of the flow column minus that at the inlet end. Rearranging equation [1] into

$$v = (K - c_e i_e/i)i = K'i \quad [2]$$

where $K' = K - c_e i_e/i$, and

$$i_e/i = -E/\Delta h \quad [3]$$

shows that the flux v in equation [2] is still proportional to the hydraulic gradient i but with proportionality coefficient K' instead of K , so long as K , c_e , and i_e/i are the constants commonly presumed. Bull and Gortner (1932), however, found $E/|\Delta h|$ for powdered quartz to decrease quite perceptibly as $|\Delta h|$ increased, and a similar but smaller tendency for the kaolinite of Michaels and Lin (1955) has been pointed out by Swartzendruber (1966).

An evaluation of the constancy of $E/\Delta h$ for porous materials was the point of departure for the present research, but electrical measurements were found not to hold stable with time. It eventually became our feeling that most published literature on the subject fails to communicate the formidable difficulties attendant to the measurement of so-called streaming potentials, and in many instances fails to be cognizant of the variations inherent in such measurements on porous media. For this reason, the primary emphasis in our present work was expanded to include continuous monitoring of the electrical potential over alternating 24-hr periods of rest and flow, to evaluate stability and to develop a method for measuring the streaming potential under the highly variable conditions actually encountered.

EXPERIMENTAL METHODS AND MATERIALS

The experimental apparatus is diagrammed in Fig. 1. The sand-kaolinite column, 5.00 cm long (= L) and 3.87 cm in diameter, was held in the plexiglas tube (6 mm wall) between two perforated plexiglas plates (5 mm thick), with several thin layers of glass wool placed inside each perforated plate to confine the sand and kaolinite particles. Appropriate settings of the two three-way stopcocks enabled flow to be passed through the permeameter in either direction, and opening of one of the six two-way stopcocks enabled a quick selection and application of hydraulic head loss Δh (= outlet hydraulic head minus inlet hydraulic head) to the permeameter. Piezometers connected into the end chambers of the permeameter allowed measurement of Δh for each effective inlet water level for a fixed position of the drip outlet. Thereafter, the piezometer connections were closed off during actual flow experiments except for occasional checks, with gradient i calculated as $-\Delta h/L$. The flux v of equation [2] was obtained by timing the volumetric outflow from the drip outlet to obtain the rate, and dividing this rate by the cross sectional area of the permeameter (11.76 cm^2). At low rates, the drip outlet was protected against evaporation. The apparatus was completely enclosed in a copper-screen Faraday cage suitably grounded to lead off stray electrical potentials from the surroundings.

The platinum electrodes in the permeameter were made of 22-gauge platinum wire, each being soldered to its plug receptacle and passing through the electrode seal into the end chamber of the permeameter. About 3 cm of wire was exposed inside the chamber. The Ag-AgCl electrodes were very similar, except that the 3-cm interior portion of the platinum wire was first silvered and then chloridized, following the method of Janz and Tamiguchi (1953).

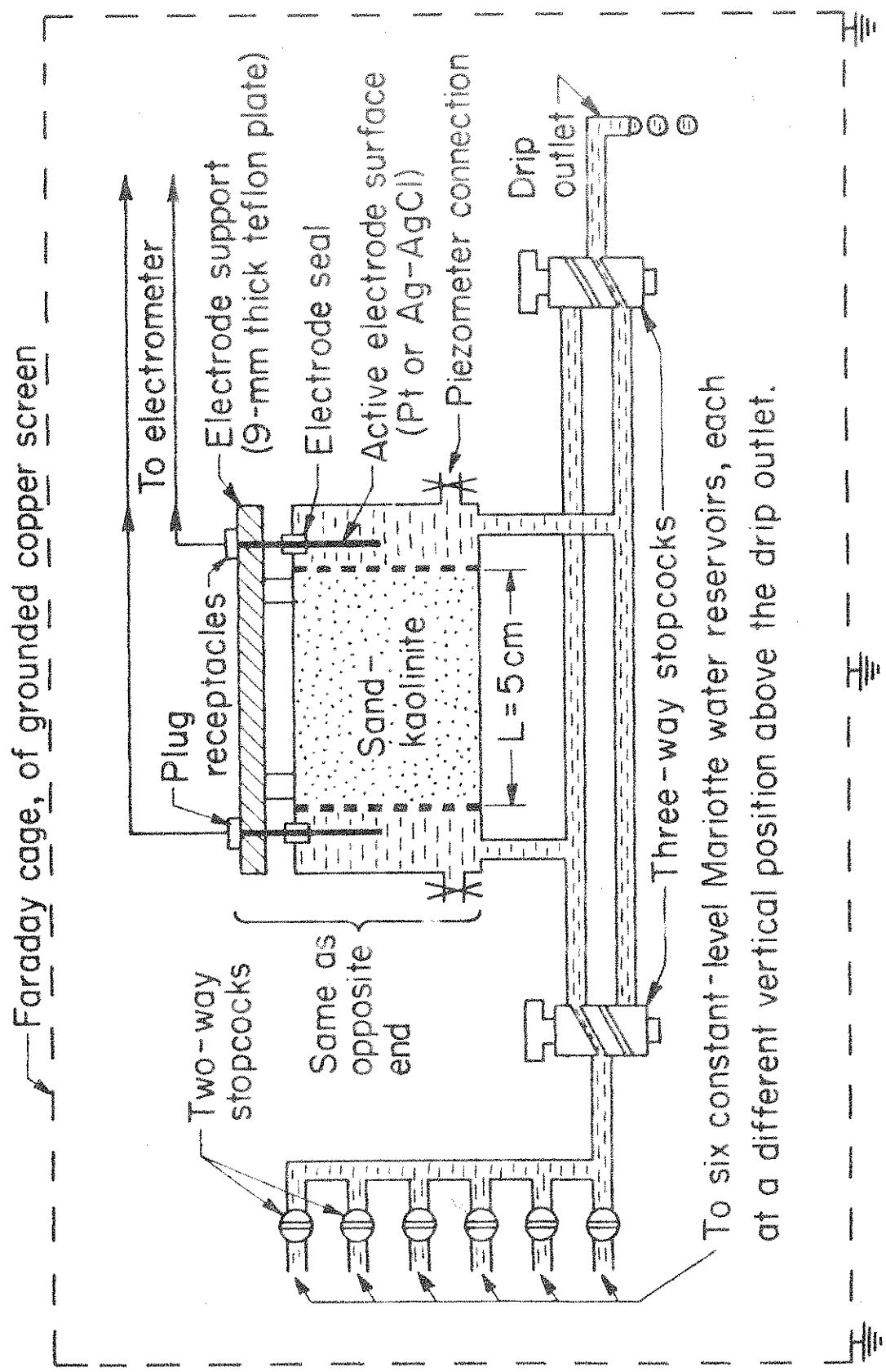


Figure 1. Diagrammatic sketch of the permeameter.

At first the electrode seals were merely short sections of 4-mm diameter cylindrical rubber through which the platinum wire passed. Later, the platinum-wire electrode (whether bright or silvered and chloridized) was fused into one end of a 2-cm length of 3-mm O.D. glass tubing, which in turn was glued with epoxy resin into a short threaded plexiglas sleeve (6 mm O.D.) that was screwed into the wall of the end chamber, thus serving as the electrode seal. External electrical connection was through a short length of platinum wire soldered to the plug receptacle and extending into the glass tubing of the seal, into which a small portion of mercury was poured to connect the two sections of platinum wire. The rigid teflon support for the plug receptacles and the electrodes was very essential, since it prevented bending or other stresses in the platinum wire which can cause extraneous electrical potentials.

The electrical leads from the plug receptacles were connected to a sensitive battery-powered electrometer ^{3/} of 10^{14} ohms internal resistance. The electrometer output was displayed on a strip-chart recorder ^{4/} to allow continuous observation as desired.

All flow experiments for which data will be reported are for a single filling of a sand-kaolinite mixture packed to a bulk density of 1.89 g/cc. On a weight basis, 87.5% of the mixture was quartz banding sand ^{5/}, with above 90% of its particles in the diameter size range 0.10 to 0.30 mm. The remaining 12.5% of the mixture was kaolinite ^{6/} of an individual platelet form in which

^{3/} Model 601, Keithley Instruments, Inc., Cleveland, Ohio.

^{4/} Model SR, Sargent-Welch Scientific Co., Skokie, Illinois.

^{5/} Ottawa Silica Company, Ottawa, Illinois.

^{6/} Hydrite 10, Georgia Kaolin Company, Elizabeth, New Jersey.

all particles were less than 2 microns in size, and the mean size was 0.22 microns. After packing the air-dry material into the permeameter, it was evacuated to less than 1 mm Hg of air pressure. It was then wetted at this pressure with boiled deionized water that contained 20 ppm of mercuric chloride (0.00015 molar in chloride) and had been passed through a Type HA millipore filter.^{1/} Mercuric chloride was used to provide antimicrobial action and to supply chloride ion for the reversible Ag-AgCl electrodes. This dilute mercuric chloride solution was used as the liquid in the flow experiments that followed, and which extended over a period of 43 days altogether. During this period, laboratory air temperatures were 24 ± 2 C, with even less variation occurring for measurements taken within a single day or a few hours.

To evaluate the time stability of the electrical potential difference between the two end chambers of the permeameter, the flow system was kept static for 24 hr during which the potential difference was monitored continuously on the electrometer and strip-chart recorder. Thereupon, a given hydraulic head difference Δh (gradient $i = -\Delta h/L$) was imposed for 24 hr, and the electrical potential was again monitored continuously. Such 24-hr periods of rest followed by flow were obtained for various gradients, for both directions of flow, and for both bright platinum and Ag-AgCl electrodes. In some instances the platinum and the Ag-AgCl electrodes were placed side by side into each end chamber, to facilitate shifting from one type of electrode to the other.

To obtain information on $E/\Delta h$ (equation [3]) for various Δh or gradients $-\Delta h/L$, the alternating periods of rest and flow were strictly maintained but

^{1/} Millipore Corporation, Bedford, Massachusetts.

were made much shorter than 1 day, on the order of 15 to 30 min. The alternating sequences were maintained so that the measured change in electrical potential associated with a given Δh would always be determined by going from rest to flow and vice versa, rather than by going to the given Δh from some other larger or smaller nonzero Δh . In all cases, strip-chart monitoring of the electrical potential difference was continuous over the transition from rest to flow and vice versa, as well as for the steady values of Δh between transitions.

RESULTS AND DISCUSSION

For the system of Fig. 1, the expected response of the electrometer for rest conditions would be a constant electrical potential difference with time, the difference being zero for Ag-AgCl electrodes but with some nonzero or asymmetry value (positive or negative) occurring for the bright platinum electrodes. When flow is imposed by a given nonzero Δh , the consequent development of the streaming potential should cause an abrupt response from the electrometer, with the new value of potential holding constant with time as long as Δh and the flux are not changed. For $h_{in} > h_{out}$, where $\Delta h = h_{out} - h_{in}$, the direction of the electrometer response should be positive if the electrical potential difference is formulated as $E_{out} - E_{in}$, where E_{out} is the electrical potential in the outflow chamber of the permeameter and E_{in} is that in the inflow chamber. Neither E_{out} nor E_{in} are measured individually, and the use of the symbolism $E_{out} - E_{in}$ means only that the electrometer is operated in such a fashion as to determine the polarity of the outlet-chamber electrode relative to the inlet-chamber electrode which is arbitrarily adopted as the reference.

Stability Evaluation

Results for $E_{out} - E_{in}$ versus time are shown in Fig. 2, where the origin of the time scale for each type of electrode is arbitrarily placed at the middle of the rest period for the first day of the 2-day observational span. These two sets of data were selected as typically representative of the 16 similar sets obtained altogether, 10 for Ag-AgCl electrodes and 6 for platinum electrodes. Although $E_{out} - E_{in}$ is more variable for the platinum electrodes than for the Ag-AgCl, the variations for the Ag-AgCl are still quite pronounced. Variations for either electrode appear to be somewhat greater for periods of flow than for the flanking periods of rest.

In spite of the pronounced variations present in Fig. 2, there is one feature of both qualitative and quantitative consistency that can be identified. When flow is initiated after a period of rest, there is an abrupt increase in $E_{out} - E_{in}$. When the flow is stopped, there is an abrupt decrease in $E_{out} - E_{in}$ of essentially the same magnitude as the previous abrupt increase that resulted from flow initiation, even though $E_{out} - E_{in}$ may have wandered to a pre-flow-cessation value rather different from the post-flow-initiation value. This is especially true for the platinum electrodes. The magnitude of the abrupt change, or E step, is essentially the same for both types of electrodes. The flow-inducing hydraulic gradient was 7.40 cm H₂O/cm throughout.

Because of the greatly compressed time scale in Fig. 2, the truly abrupt nature of the E steps, indicated by the heavy vertical lines, is not pictured as decisively as it really occurred. Hence, for the platinum electrodes Fig. 3 was prepared, using a 20-fold expansion of the time scale as compared with Fig. 2, and showing only data in the near vicinity of the two E steps. The trace of the strip-chart recorder pen was replotted as closely as possible, and on this

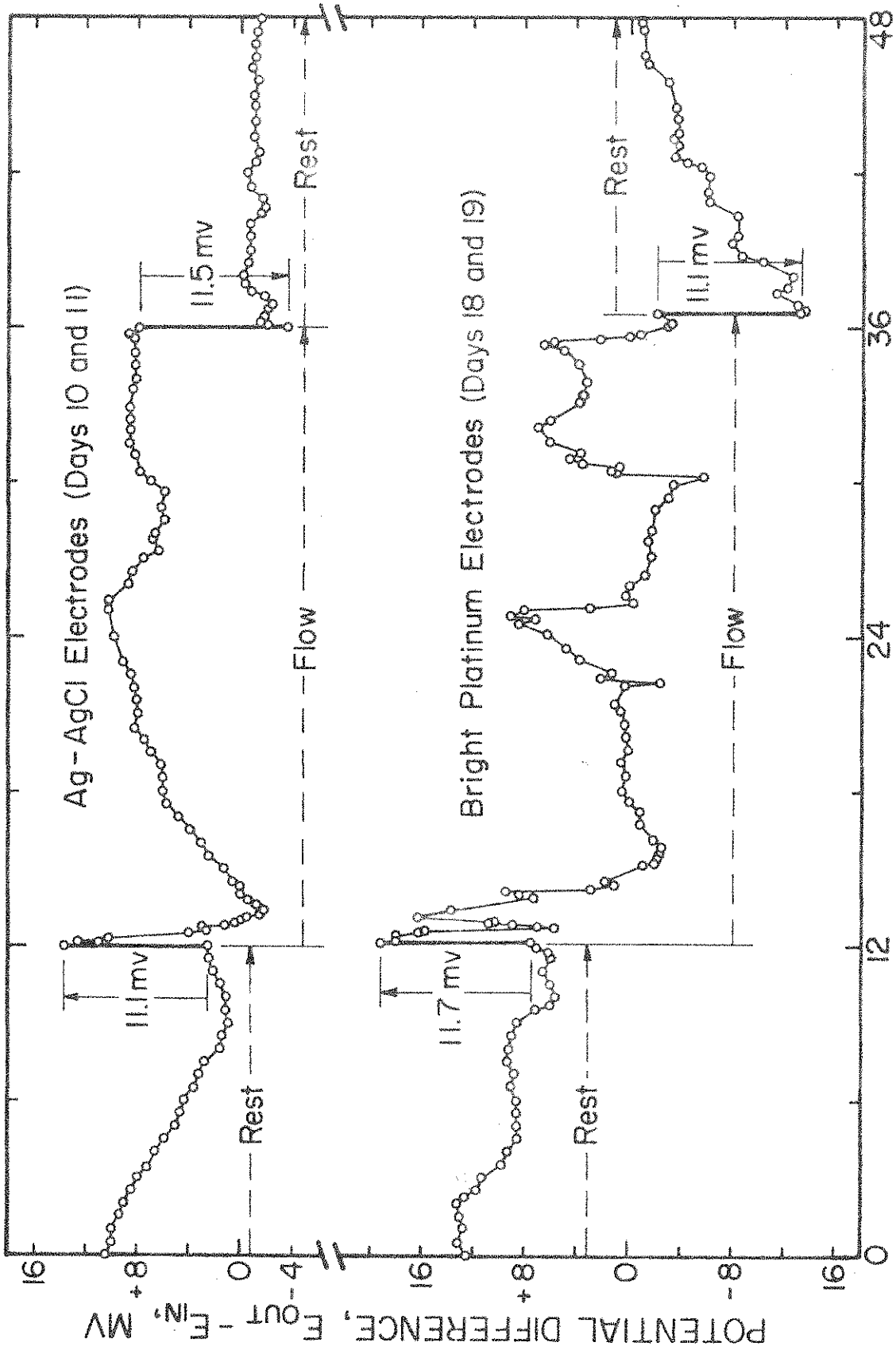


Figure 2. Time course of electrical potential difference across the permeameter of water-saturated sand-kaolinite, for a 1-day period of flow flanked on each side by a period of rest, for two types of electrode.

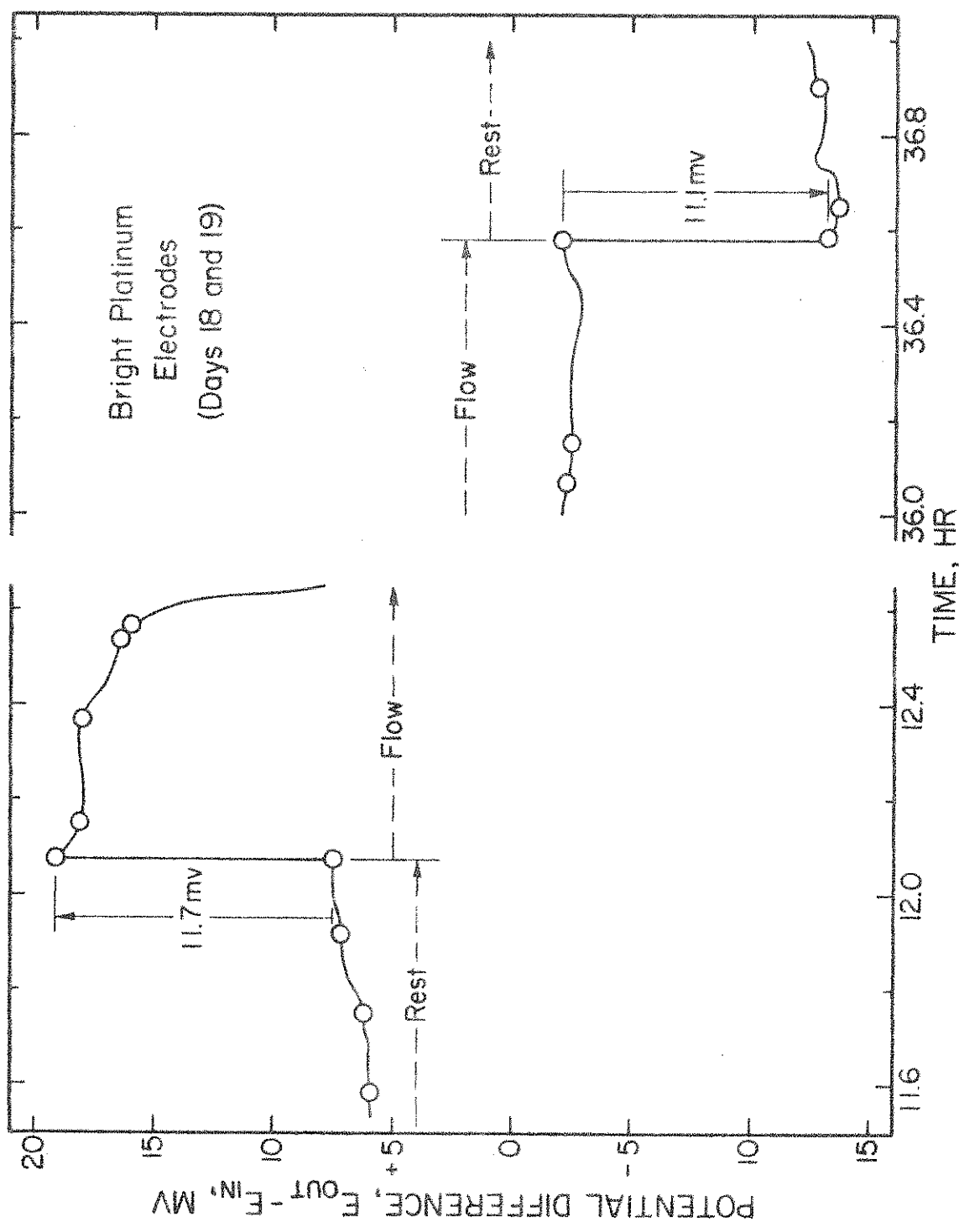


Figure 3. Expanded time scale for the platinum electrodes of Fig. 2, in the vicinity of the step changes in electrical potential.

replotted trace were placed the data points from Fig. 2 that were located near the E steps. It is clear that each strip-chart recorder trace contains an essentially vertical portion even on the expanded (20 fold) time scale, and hence provides a clear basis for specifying the E step. We therefore propose that the E step be taken as a measure of streaming potential E of equation [3], since it appears to be the only objective way of bringing order out of the otherwise chaotic behavior in Fig. 2.

E Step and Hydraulic Gradient

All data taken were carefully perused to determine whether the E step was affected by electrode type, initiation or cessation of flow, or direction of flow through the permeameter. No consistent response of E step to any of these factors could be found. As an illustration of this, data taken on day 26 for short intervals of rest and flow, for both types of electrodes, and for both directions of flow are shown in Fig. 4 as plots of E step against hydraulic gradient. Designation of direction of flow is AB for left to right as obtained from the depicted settings of the two three-way stopcocks in Fig. 1, with BA being used for right-to-left flow when these two stopcock settings were reversed. Initiation of flow is indicated by "open", and cessation of flow by "close", while the results for the two types of electrode are shown in the two parts of the figure. Inspection of Fig. 4 shows that the E step is essentially independent of initiation or cessation of flow, direction of flow, and electrode type, this last being particularly well illustrated by the close agreement of the two least-squares lines shown in part B (Fig. 4).

That there is a distinct and direct relationship between E step and hydraulic gradient, however, is also clear from Fig. 4. The least-squares lines

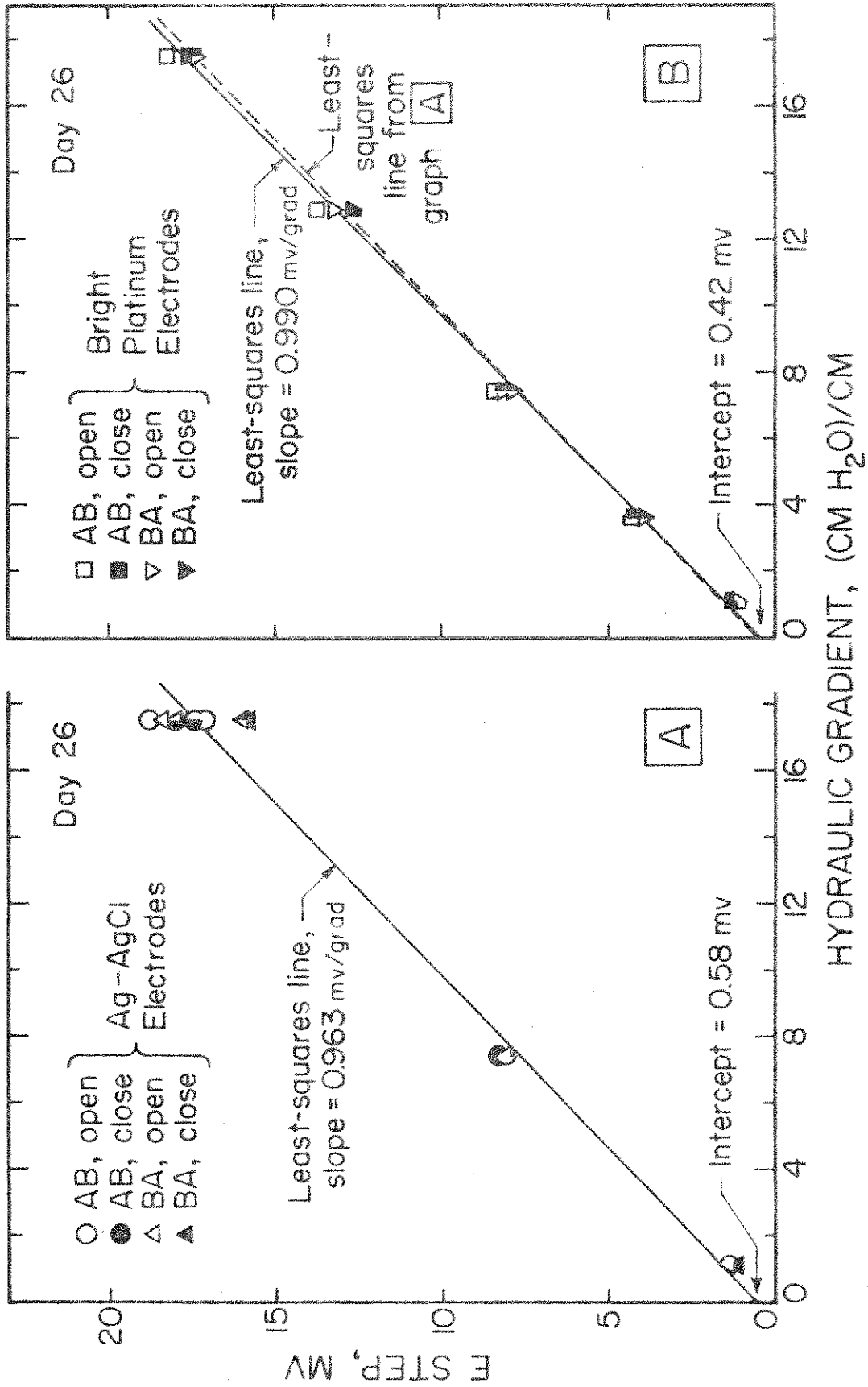


Figure 4. Electrical-potential step versus hydraulic gradient for (A) silver-silver-chloride electrodes and (B) platinum electrodes, for water-saturated flow through sand-kaolinite. See text for explanation of symbols.

were not forced through the origin, but the resulting intercepts nevertheless were quite small. Using the statistical t test, the intercept of 0.58 mv for the Ag-AgCl electrodes (Fig. 4A) failed to reach significance at a probability level of 10%, but the smaller intercept of 0.42 mv for the platinum electrodes (Fig. 4B) did reach significance at the 1% level. This latter case provides a conceivable possibility of claiming a tendency for $(E \text{ step})/i$, calculated at each gradient i , to decrease with increasing gradient, and hence that $(E \text{ step})/|\Delta h|$ decreases with increasing $|\Delta h|$ in the manner of Bull and Gortner (1932), since $(E \text{ step})/i$ is equal to $L(E \text{ step})/|\Delta h|$ and L is constant. We consider such a claim to be relatively weak, but must also grant that the failure of the 0.58-mv intercept for the Ag-AgCl electrodes to achieve higher statistical significance is likely due mainly to the scatter of points at the largest gradient of Fig. 4A. Even so, however, the intercepts are still relatively small and we consider them negligible, so that the data of Fig. 4 are taken as conforming essentially to proportionality of E step with gradient. This infers that $(E \text{ step})/i$ and hence $(E \text{ step})/|\Delta h|$ are constant, and, if the E step is taken as the measure of streaming potential E , then i_e/i and hence K' of equation [2] are constant, so that the flux-gradient relationship for this mixture of sand and kaolinite should be one of Darcian proportionality. Further evidence in support of this will be given subsequently.

The behavior of $(E \text{ step})/i$ over the whole period of experimentation is shown in Fig. 5, as plotted against the hydraulic conductivity K' (equation [2]) computed as v/i . The circular, square, and triangular point symbols are for the 24-hr periods of alternating rest and flow. To avoid crowding, the short-interval rest-flow data taken within a single day are portrayed by the variously shaped polygons drawn with solid, broken, and dotted lines, each polygon being

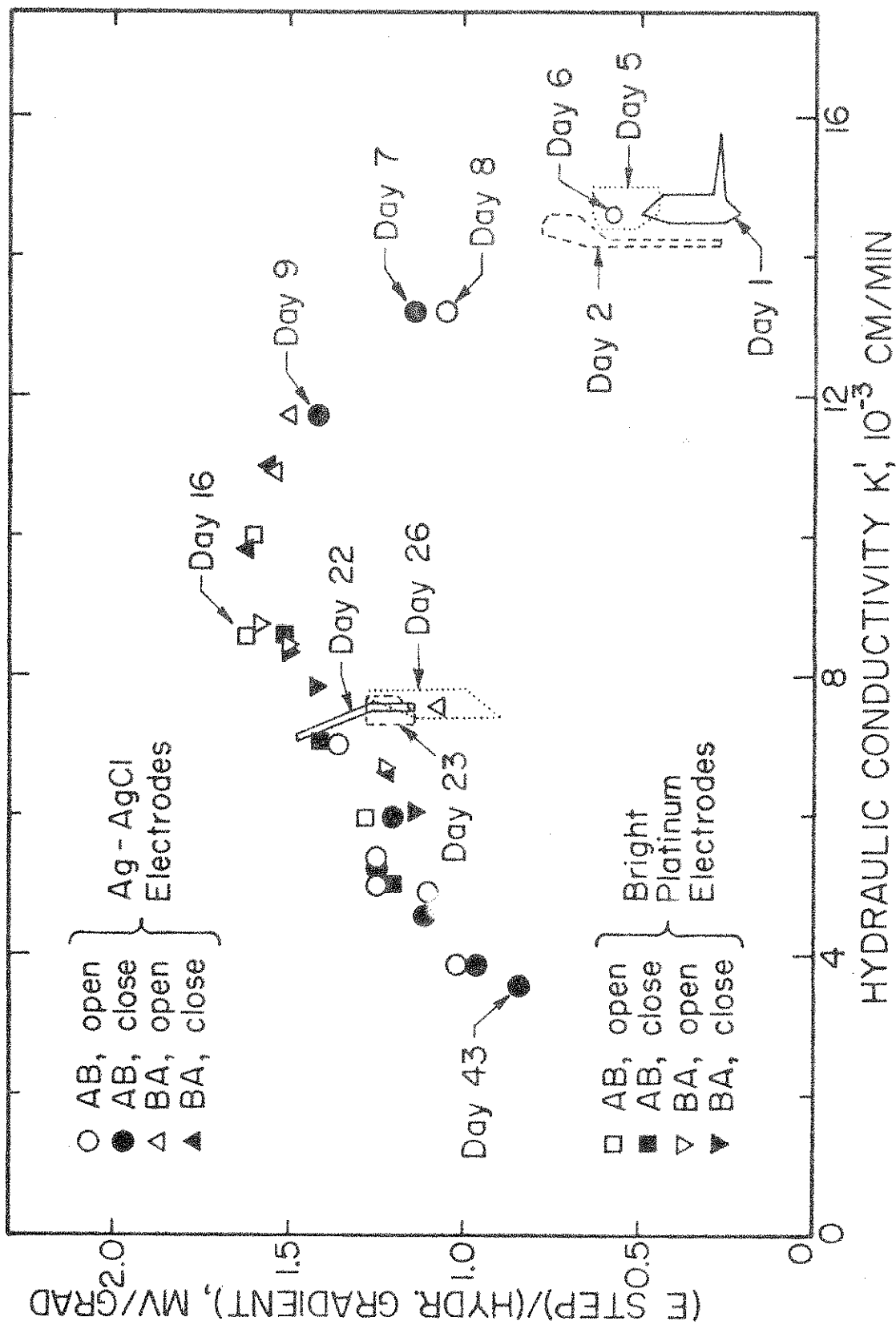


Figure 5. Ratio of electrical-potential step to hydraulic gradient, plotted against hydraulic conductivity K', for two types of electrode. See text for explanation of symbols.

of just sufficient size and shape to enclose all of the points of a given day. During the overall period a reduction in K' was encountered, changing from a maximum of 0.0158 cm/min on day 1 to 0.0036 cm/min on day 43. This may mean that the mercuric chloride in the water was not completely effective in preventing hydraulic conductivity reduction due to microbes, but at least the decrease is not the orders-of-magnitude reduction sometimes observed (Gupta and Swartzen-druber, 1962).

The data for the 24-hr rest-flow periods in Fig. 5 appear to specify a fairly definite single curve that begins near 0.60 mv/grad (mv/grad means millivolts per unit hydraulic gradient in water column) at $K' = 0.0146$ cm/min, increases to a maximum of 1.60 mv/grad as K' falls to about 0.0090 cm/min, and then decreases as K' is further reduced. From this single-curve nature of the relationship, it appears that $(E \text{ step})/i$ is not sensibly affected by direction of flow, initiation or cessation of flow, or type of electrode, all of which conforms with the similar conclusions already drawn from Fig. 4 for the E step alone. But if the single-curve data were to be taken as evidence of causality between K' and $(E \text{ step})/i$, it is not readily apparent why a steadily increasing K' should first cause $(E \text{ step})/i$ to increase and then to decrease. Such seeming inconsistency can, of course, be taken as an argument against causality.

Theoretically, considerations for a single capillary tube (Abramson, 1934; Overbeek, 1952) yield $E/|\Delta h|$ as independent of tube radius and hence of K or K' of the tube, provided that the electrical conductance along the interior solid surface of the tube is negligible compared with the electrical conductance of the flowing liquid. If the surface conductance cannot be so neglected, an alternative formulation by Overbeek (1952) does imply $E/|\Delta h|$ to depend on tube radius. Direct application of either of the foregoing theoretical results in

an analysis of Fig. 5 is questionable, however, simply because the pore geometry in the sand-kaolinite mixture is far more complex than just an assemblage of uniform-bore capillary tubes. Furthermore, if the reduction in K' is due to microbial activity, it is questionable whether a true change in pore geometry can realistically be invoked, particularly if the K' decrease involves by-products of microbial metabolism (Gupta and Swartzendruber, 1962).

If $(E \text{ step})/i$ is not causally dependent on K' , then Fig. 5 implies that the measurement of $(E \text{ step})/i$ is subject to substantial error, or that some other simultaneous process is operative. A further inspection of the data reveals features compatible with both of these suggestions. Firstly, the behavior of the short-interval rest-flow data (polygons in Fig. 5) suggests that much of the $(E \text{ step})/i$ variation cannot be attributed directly to a change in K' . For example, on days 1 and 2, K' changed very little, but the range of variation in $(E \text{ step})/i$ was nearly 0.6 mv/grad. The same is true for days 22, 23, and 26, at a smaller value of K' . Thus, 0.6 mv/grad may well represent a realistic "error" interval for $(E \text{ step})/i$ when K' is not changing.

Secondly, although in Fig. 5 the maximum range in all $(E \text{ step})/i$ data of 1.4 mv/grad (0.2 to 1.6 mv/grad) is more than twice the observed range of 0.6 mv/grad for a constant K' , the data can be separated into two groups on the basis of length of continuous-flow period. Since the point for day 6 is for the initiation ("opening") of flow, the data for day 1 through day 6 can all be consigned to a short-flow-interval regime, and all of these data do fall within the error interval of 0.6 mv/grad. The data for day 7 through day 43 can be consigned to a long-flow-interval regime, because of the great predominance of 24-hr flow periods. For these data, the total range of variation is 0.8 mv/grad, which is only slightly in excess of the error interval of 0.6 mv/grad. Since the point

for day 7 represents the first 24-hr period of continuous flow, it is conceivable that the electrical and hence streaming-potential characteristics of the flow system might have been shifted to a new level somehow induced by the first period of day-long flow. It is fairly reasonable to suppose that the imposition of a few short-flow intervals (days 22, 23, and 26) would not materially alter the long-flow-interval regime, so that even for these three days (22, 23, and 26) $(E \text{ step})/i$ would remain in the vicinity of the higher values characteristic of days 7 to 43, as indeed was actually found. The correctness of the explanation here proposed could only be assessed with further research, but at present we find it more tenable than accepting a maximum-type curve as an expression of causality between $(E \text{ step})/i$ and K' .

Flux-Gradient Behavior

The short-flow-interval experiments on days 1, 2, 5, 23, and 26 included flux measurements at different hydraulic gradients and both directions of flow. These results are summarized in Table 1, in the form of hydraulic conductivity $K' = v/i$ from equation [2], with K' being computed for each flow direction and gradient for which data were taken. If the Darcian proportionality of equation [2] is being obeyed, K' for a given day and flow direction should be a constant independent of gradient, and inspection of Table 1 shows that this is so to a rather high degree of accuracy. Also, K' is essentially unaffected by the direction of flow. There is, of course, a reduction in K' with time, particularly between days 1, 2, and 5 as compared with days 23 and 26, as already discussed in connection with Fig. 5.

A graphical presentation of the flux-gradient data for days 1 and 26 is given in Fig. 6. It is evident that the data points fall closely upon their respective proportional lines (drawn by eye), and that the results for the two

Table 1 -- Hydraulic conductivity at various gradients and flow directions for a water-saturated mixture of quartz sand and kaolinite.

Hydraulic gradient, (cm H ₂ O)/cm	Flow direction	Hydraulic conductivity K', in 10 ⁻³ cm/min, on specified days of the flow experiment				
		Day 1	Day 2	Day 5	Day 23	Day 26
1.09	AB	15.50	--	14.78	7.70	7.80
	BA	15.57	--	15.02	7.45	7.72
3.60	AB	14.60	14.58	14.57	7.46	7.65
	BA	14.70	--	14.44	7.58	7.76
6.57	AB	14.80	--	--	--	--
	BA	14.65	--	--	--	--
7.40	AB	--	--	--	7.40	7.50
	BA	--	--	--	7.50	7.54
9.66	AB	14.57	14.28	14.65	--	--
	BA	14.60	14.36	--	--	--
12.86	AB	--	14.28	--	7.35	7.49
	BA	--	14.27	--	7.34	--
17.49	AB	--	14.26	14.66	7.36	--
	BA	--	14.25	14.66	7.34	7.42

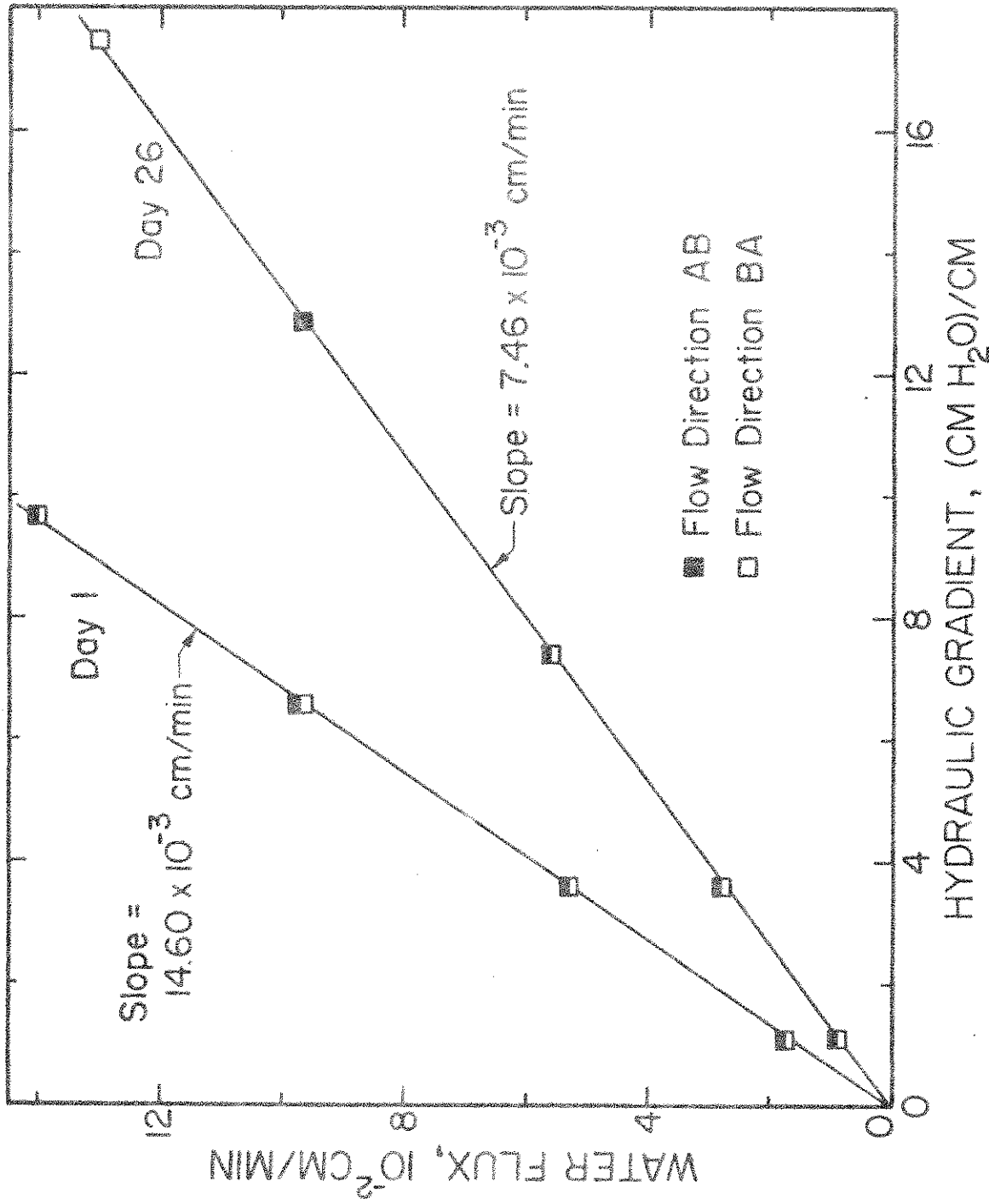


Figure 6. Water flux versus hydraulic gradient for water-saturated sand-kaolinite, for both directions of flow.

directions of flow are in close agreement. This overall close adherence to Darcian proportionality is in keeping with the earlier suggestion of flux-gradient proportionality as discussed in connection with Fig. 4.

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SECTION B.

ELECTRICAL POTENTIALS DURING WATER ENTRY INTO INITIALLY
AIR-DRY SAND-KAOLINITE ^{1/}D. Swartzendruber and S. Gairon ^{2/}

For water flow in an unsaturated porous medium, such as occurs when water enters an initially dry material, it is reasonable to expect that electrical streaming potentials would be produced in some fashion analogous to that taking place in the water-saturated case. For transient flow under unsaturated conditions, however, it is not easy to measure the streaming potential. It would be difficult, for example, to use such as Ag-AgCl electrodes since they would become desiccated if placed in the initially dry porous medium. This almost forces the use of bright platinum electrodes, with the accompanying need to determine the asymmetry potential for zero water flow. But, since water-saturation status generally changes with hydraulic suction and potential gradients in unsaturated media, it is not generally possible to impose a step change in gradient and hence in water flux and electrical potential, as has just been described for saturated flow (see Section A). Nevertheless, since there are practically no data at all available for electrical potentials under transient unsaturated flow conditions, it was deemed of interest to obtain some such measurements, to determine what types of response would be encountered and to assess the role they might fill in describing any particular facets of unsaturated soil-water flow.

^{1/} Contribution from the Department of Agronomy, Purdue University.

^{2/} Professor of Soils, and postdoctoral Research Associate.

MATERIALS AND METHODS

The porous material was a weight-basis mixture of 87.5% quartz banding sand,^{3/} with more than 90% of its particles in the size range 0.10 to 0.30 mm, while the remaining 12.5% of the mixture was kaolin Hydrite 10,^{4/} an individual platelet form with all particles smaller than 2 microns and of mean size 0.22 microns. By the addition and tamping of small increments, the sand-kaolinite was packed as uniformly as possible into a vertical plexiglas tube of 0.6-cm wall and inside diameter of 3.87 cm. This tube (Fig. 1) contained two confining perforated plexiglas end plates 15 cm apart, with several thin sheets of glass wool having been placed between the perforated plates and the ends of the sand-kaolinite column. Five electrodes, each consisting of 22-gauge platinum wire, were sealed at various positions into the wall of the tube and penetrated 0.5 cm into the sand-kaolinite, while the other end of each electrode terminated in a plug receptacle in the rigid teflon support. At time zero, the lower end chamber was filled quickly with water that would contact the bottom end of the air-dry sand kaolinite column, the water supply being a Mariotte burette delivering at a constant level 24.7 cm above the bottom end of the column. A platinum-wire electrode was also positioned in the water-filled lower-end inlet chamber, and was connected to one side of a sensitive battery-powered electrometer ^{5/} of 10^{14} ohms internal resistance. The other side of the electrometer was connected to an electrode in the sand-kaolinite. By connecting to these electrodes one at a

^{3/} Ottawa Silica Company, Ottawa, Illinois.

^{4/} Georgia Kaolin Company, Elizabeth, New Jersey.

^{5/} Model 601, Keithley Instruments, Inc., Cleveland, Ohio.

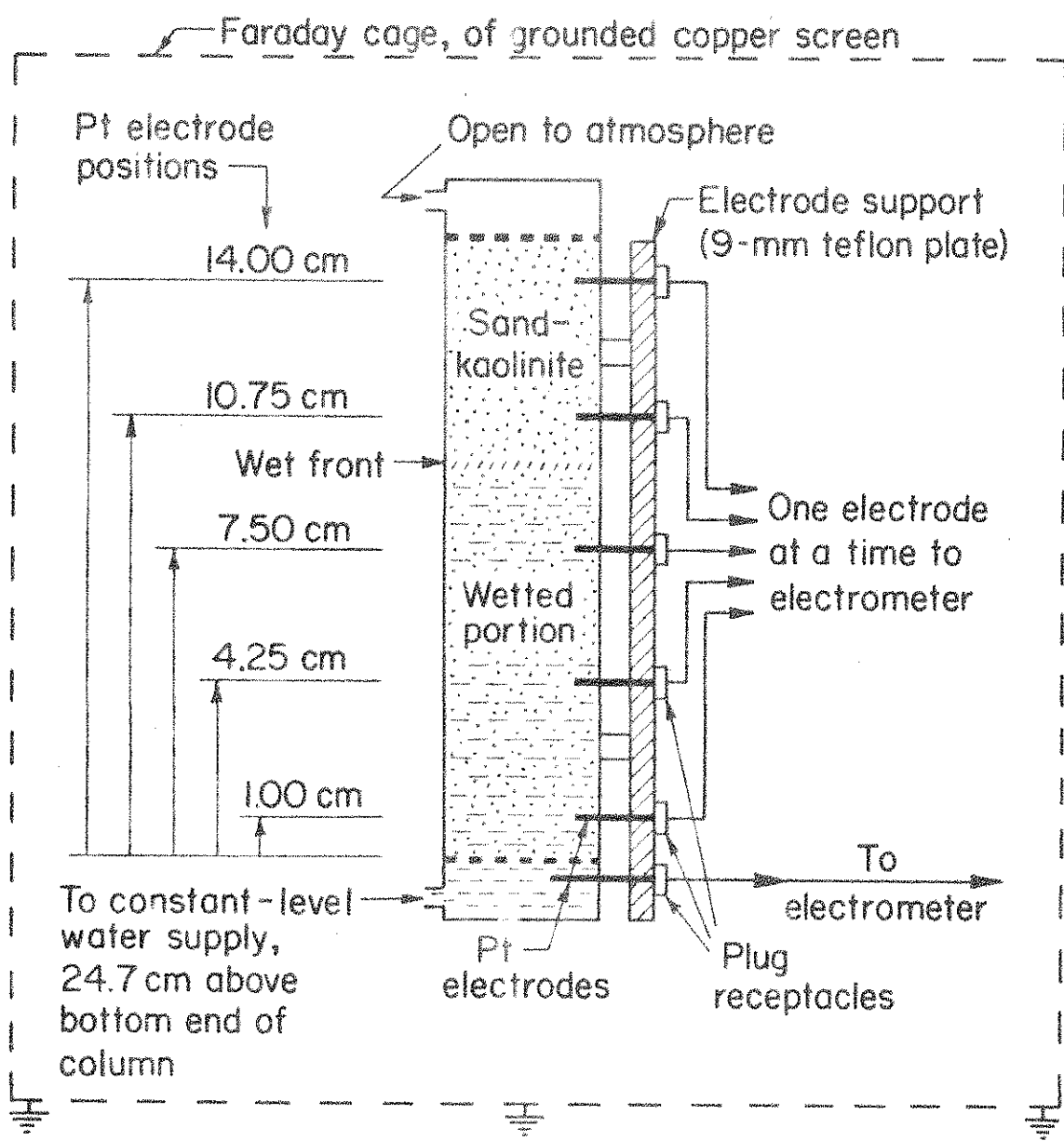


Figure 1. Diagrammatic sketch of flow column for vertically upward entry of water into initially air-dry sand-kaolinite.

time for appropriate observational periods, a fairly complete time record of electrical potential difference with reference to the inlet chamber was obtained as the wet front in the sand-kaolinite approached, reached, and passed each electrode. The electrometer output was displayed on a strip-chart recorder.^{6/} The wet front was also visually observed, and its position was noted periodically.

The cumulative amount of water entering the column from the Mariotte burette was also observed with time. This water had been drawn through a Type HA millipore filter,^{7/} and contained 20 ppm of mercuric chloride as an antimicrobial agent. Laboratory air temperatures were held within 21 ± 1 C.

RESULTS AND DISCUSSION

With the inlet chamber as reference, the time course of the electrical potential at each electrode along the column is shown in Fig. 2 for the first column of sand-kaolinite. Without exception, the potential was found to be positive at each electrode for the air-dry medium, but became negative and exhibited a pronounced negative peak as time progressed, eventually reaching a relatively stable post-peak level. Quantitatively, however, neither these post-peak levels nor the magnitudes of the negative peaks appeared to be consistently related to the positions of the electrodes.

Qualitatively similar results for a second column of sand-kaolinite can be noted from Fig. 3. At only two of the electrodes, however, was the potential positive for the air-dry medium. The eventual post-peak levels for the first four electrodes were consistently lower as the electrode distance increased

^{6/} Model SR, Sargent-Welch Scientific Co., Skokie, Illinois

^{7/} Millipore Corporation, Bedford, Massachusetts.

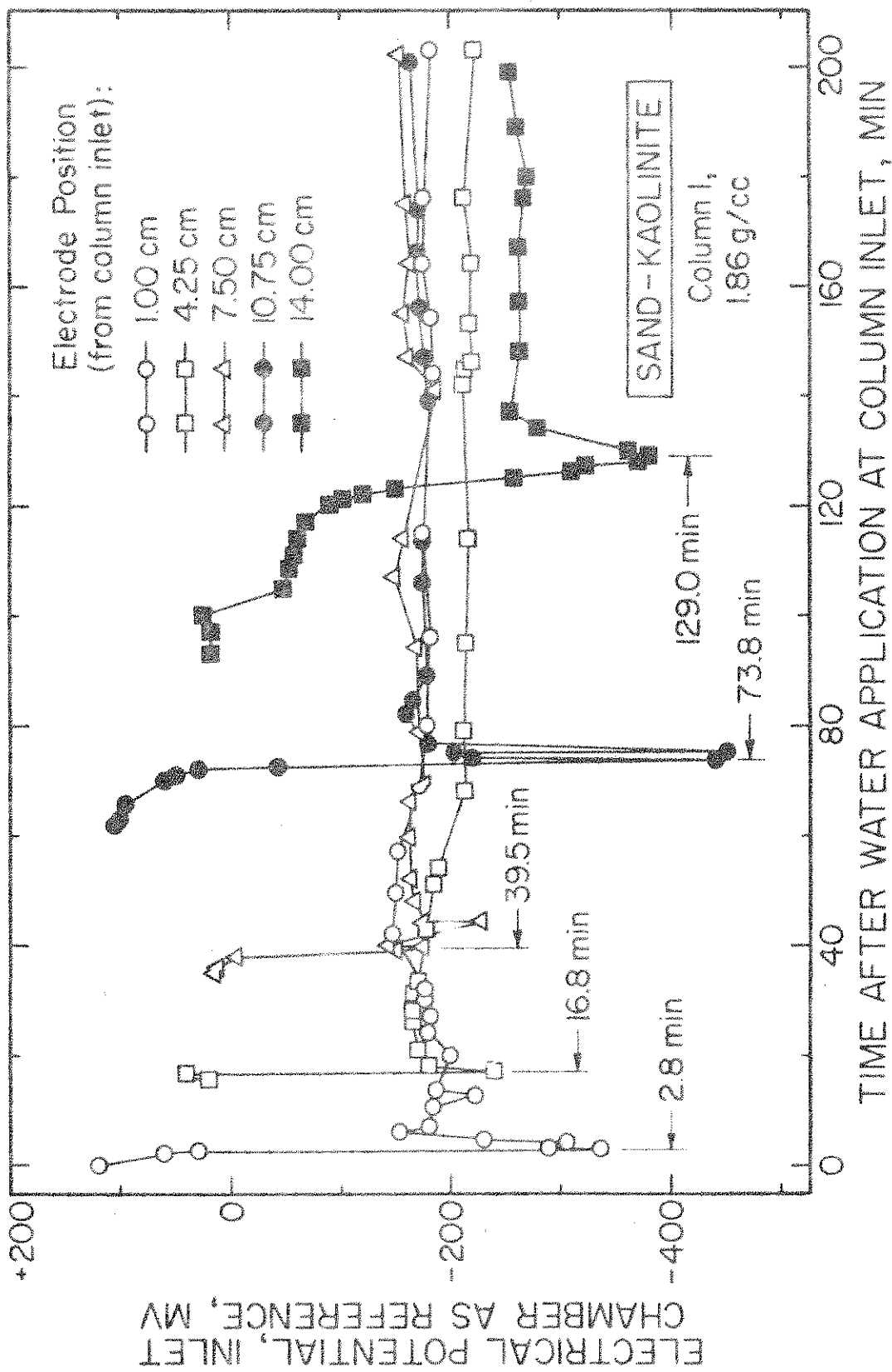


Figure 2. Time course of electrical potential at five platinum-electrode positions during upward water entry into initially air-dry sand-kaolinite (column 1).

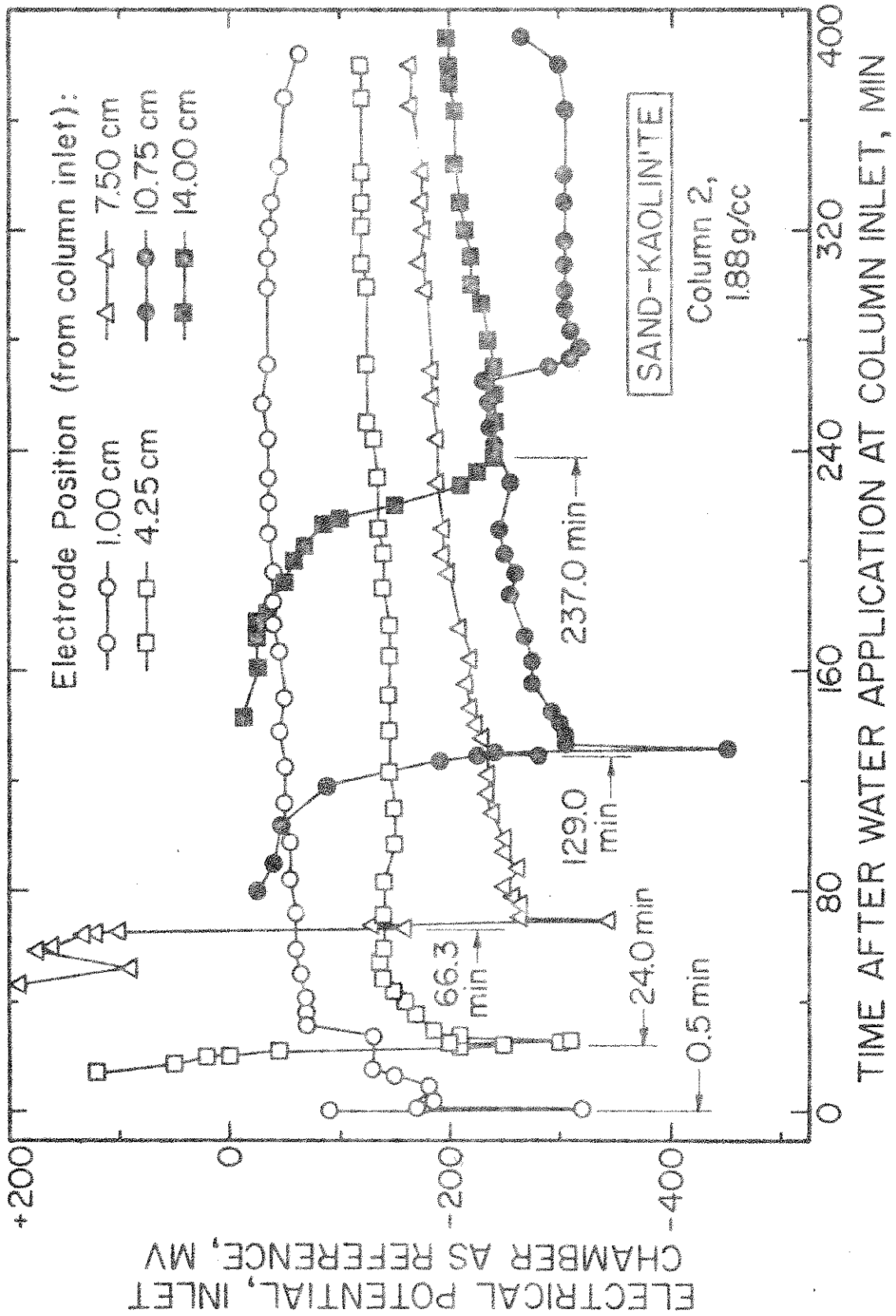


Figure 3. Time course of electrical potential at five platinum-electrode positions during upward water entry into initially air-dry sand-kaolinite (column 2).

from the column inlet, but the fifth electrode (14 cm) did not conform to this decreasing trend. Also, for this fifth electrode the negative peak was not nearly as sharp as in Fig. 2.

Inspection of both Figs. 2 and 3 from another standpoint, however, does reveal a consistent response pattern in the sense of progressively increasing times at which the pronounced negative peaks occur for the successively positioned electrodes. The most straightforward explanation for this behavior would be that a given negative peak marks the arrival of the visual wet front in the sand-kaolinite at that electrode. To test this hypothesis, the first clearly identifiable negative peak of substantial magnitude was marked and labelled with its time of occurrence, for each electrode-position response curve in Figs. 2 and 3. These position-time points were then compared with the more complete wetting-front curves established from visual observations and plotted in Fig. 4. Near the end of each wetting-front curve, there were gaps in actual wetting-front observations. However, separate plots of wet-front position versus the cumulative amount of water absorbed (from the burette) were found to be nicely linear for both columns, and were thus used to infer the wet-front position for these gaps in actual visual wet-front data.

It is clear from Fig. 4 that the position-time points obtained from the electrical response curves of Figs 2 and 3 fall closely upon the wet-front position curves determined visually, the poorest agreement again being for the point from the fifth electrode (14 cm) of the second column (Fig. 3). It is thus concluded that the negative-peak electrical responses as measured in this study can be used to detect and trace the progress of the wet front as it moves into an initially air-dry porous medium.

It is not known why the wet-front position curves (Fig. 4) for the two columns are so different, especially when they were prepared to be duplicates

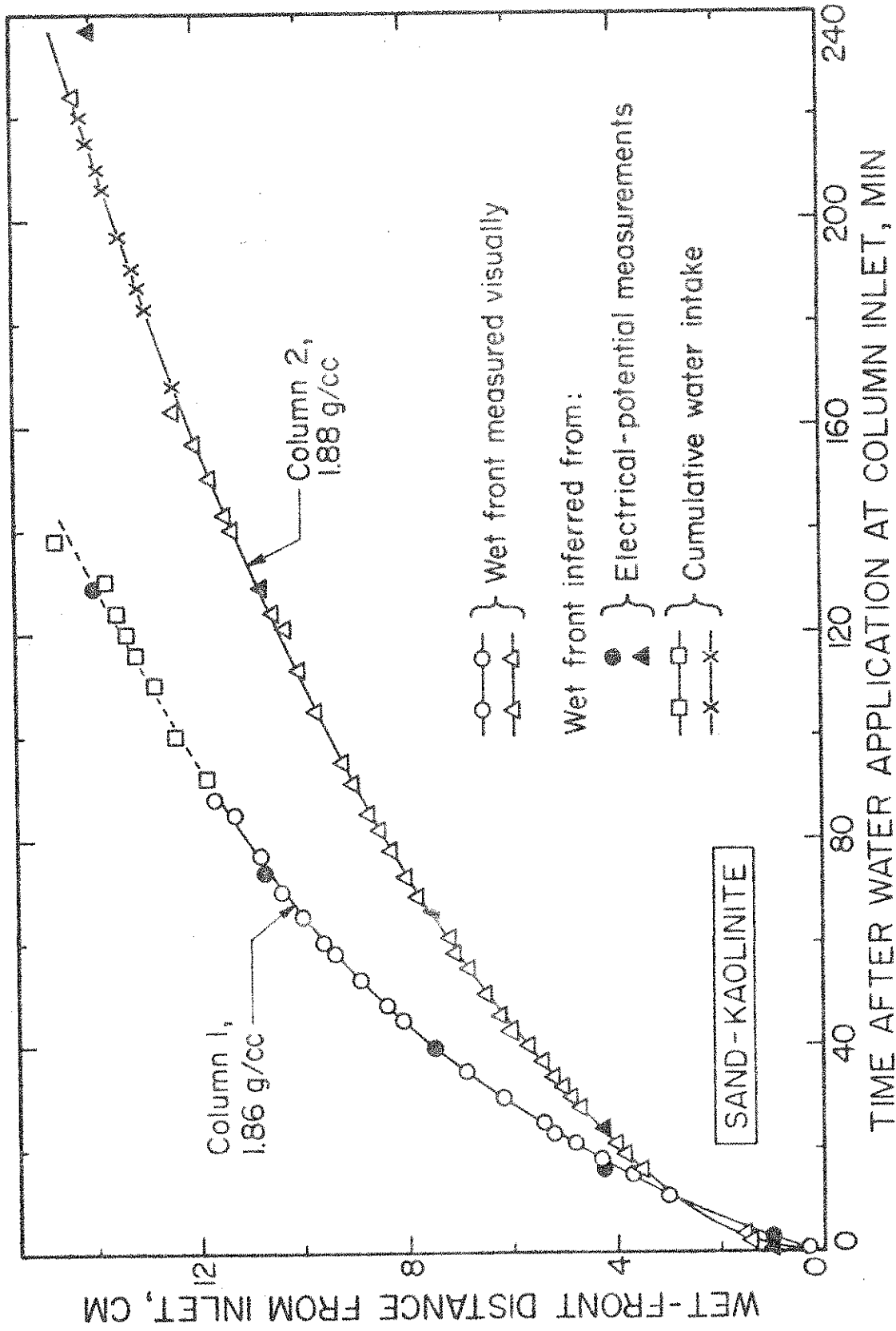


Figure 4. Time course of wet-front position in initially air-dry sand-kaolinite, as determined visually and by the negative peaks of the curves in Figs. 2 and 3.

and were very nearly the same in bulk density (1.86 and 1.88 g/cc). The slower curve for column 2 is in conformity with the slightly higher bulk density. More importantly, however, the electrical-potential characterizations of wet-front position are in close agreement with visual measurements in both cases, even though the wet-front position curves are definitely different for the two columns.

The use of electrical sensing of wet-front position has conceivable application under circumstances in which visual observation of a wet front is inconvenient or impossible. In the laboratory, this would occur when the confining soil tube needs to be opaque instead of transparent. In the field, visual observation of a downward-moving wet front can hardly ever be construed as practical or feasible. In this connection, it can be noted that the battery-powered electrometer is reasonably portable, although it is not known whether this particular model would be the most suitable for field use. Finally, it is not known whether the method would be successful if the initial water content were greater than air dry, but this possibility would seem to warrant at least a preliminary trial. If successful, it would provide a method of detecting and tracing a water front under circumstances wherein a color change due to soil wetting is not even observable visually.

SECTION C.

WATER FLUX AND ELECTRICAL POTENTIALS IN

WATER-SATURATED MONTMORILLONITE ^{1/}S. Gairon and D. Swartzendruber ^{2/}

In view of the absence of nonproportional flux-gradient behavior in water-saturated flow through a sand-kaolinite mixture (Section A), it was deemed advisable to consider swelling-clay media as studied by Lutz and Kemper (1959), and as repeated by Kutilek (1964, 1965). These investigators worked with clay-water slurries which were then concentrated by withdrawing water through a fritted-glass plate which retained the clay. For sodium montmorillonites thus handled, the measured flux-gradient relationships were found to be distinctly more than proportional.

When we used this approach on an essentially sodium-saturated montmorillonite, a bentonite from Clay Spur, Wyoming, a more-than-proportional response of water flux to hydraulic gradient was observed in only one series out of six series of measurements. An attempt to repeat that more-than-proportional result on a separate sample of clay was not successful, the attempted repetition actually yielding a distinctly less-than-proportional flux-gradient curve. Nor could a reason for this lack of repeatability be deduced by perusal of the longer description of Kemper's experimental methods (W. D. Kemper, 1952 . Clay-water interaction affecting the

^{1/} Contribution from the Department of Agronomy, Purdue University

^{2/} Postdoctoral Research Associate, and Professor of Soils.

permeability of soils. M.S. Thesis. North Carolina State University, Raleigh, N.C.) In general, we found the flux to increase less than proportionally with gradient, which suggested that possibly our technique of concentrating the clay slurry might somehow have been inadequate. Hence, our procedure was modified to provide clay plugs of higher clay concentration, and it is this work which will here be presented.

As a conceptual framework, we shall treat streaming-potential effects on water flow as a correction to the Darcy equation, in the manner already developed (see Section A), namely

$$v = Ki - c_e i_e \quad [1]$$

where v is the water flux, i is the hydraulic gradient, K is the hydraulic conductivity, c_e is the coefficient of electroosmotic flow, and i_e is the streaming-potential gradient. The gradients are expressible as $i = -\Delta h/L$ and $i_e = (E_{out} - E_{in})/L$, where Δh is the hydraulic head loss across the flow column of length L , and streaming-potential $E_{out} - E_{in}$ is the electrical potential at the outlet end of the flow column minus that at the inlet end. Equation [1] can be rearranged to

$$v = (K - c_e i_e / i) i = K' i \quad [2]$$

where

$$K' = K - c_e i_e / i \quad [3]$$

Using the further expressions of i_e and i in terms of $E_{out} - E_{in}$, Δh , and L , yields

$$i_e / i = (E_{out} - E_{in}) / (-\Delta h) \quad [4]$$

Under experimental test will be whether v is proportional to i as in equation [2] (Darcian flow) when K , c_e , and i_e/i are constant, and whether i_e/i as defined by equation [4] is constant as i increases.

EXPERIMENTAL METHODS AND MATERIALS

Flow System

A diagram of the experimental apparatus is shown in Fig. 1, with water-saturated clay contained within the central interior chamber of the double-wall glass permeameter. Fiberglass micropore prefilters^{3/} were located at each end of the clay plug, between the clay and the supporting fritted-glass plate, and between the top end of the clay plug and the perforated confining piston. The piston was constructed entirely of plexiglas, the tubular shaft being of 0.952 cm outside diameter and 0.635 cm inside diameter, while the piston disc was cut from solid stock 0.635 cm thick prior to being perforated with 1-mm holes. The diameter of the clay plug was 3.24 cm, except for the slight constriction near the fritted-glass plate. Water movement through the clay was induced by the partial vacuum created in the carboy and flask by the vacuum pump, adjustment and control of the vacuum being achieved by an appropriate setting of the bleed valve.

Since the water-outlet tube in the flask was placed at the same level as the horizontal small-bore glass inflow tube, the sole hydraulic driving force was that measured by the mercury manometer connected to the partial-vacuum system. The difference in mercury column was converted to the hy-

^{3/} Millipore Corporation, Bedford, Mass.

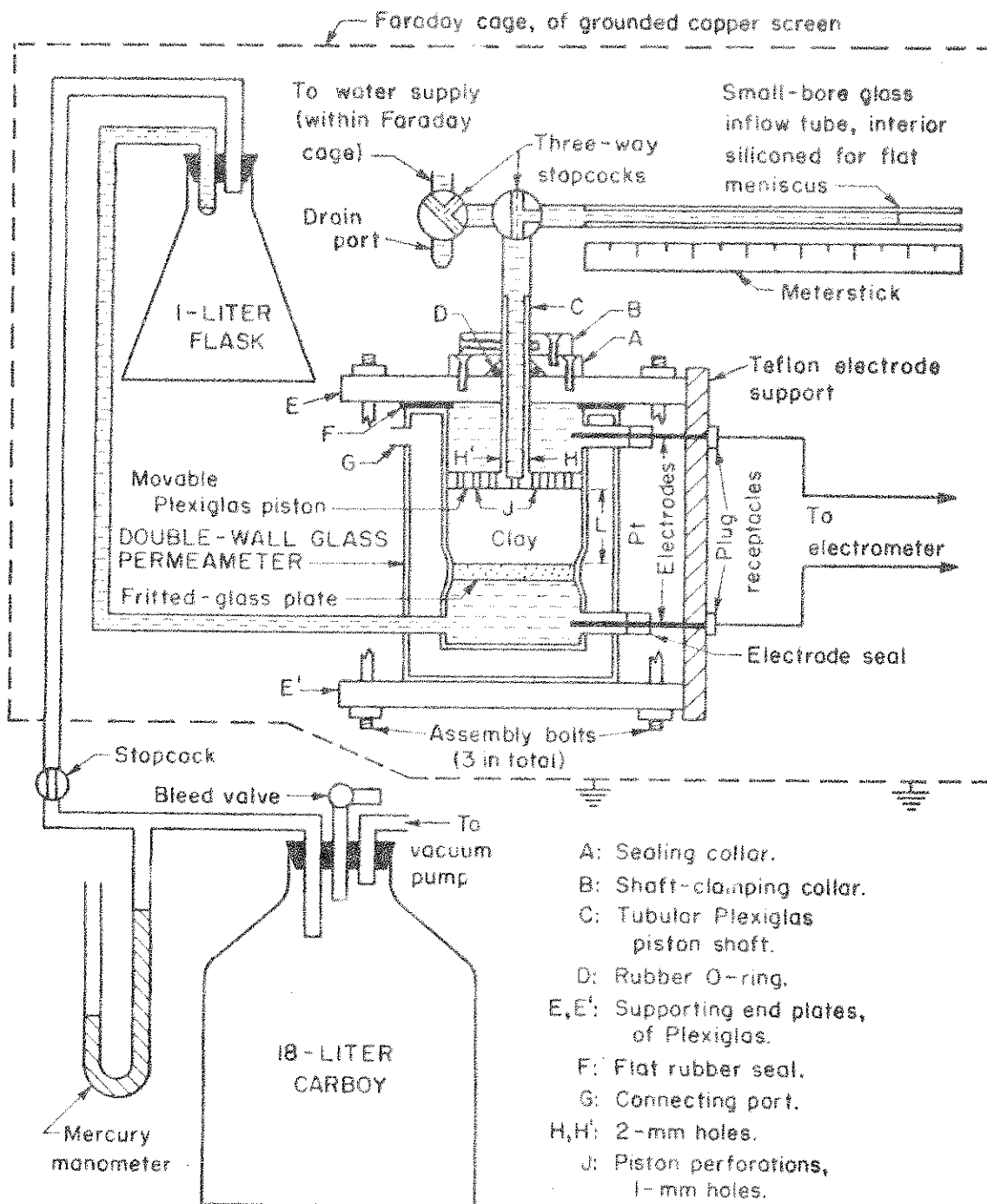


Figure 1. Diagrammatic sketch of permeameter and associated flow apparatus.

draulic head loss Δh in centimeters of water. From this, the hydraulic gradient $i = -\Delta h/L$ was calculated, where L was the length of clay plug as established by cathetometer measurements on the fritted-glass plate and the piston, and which remained constant for any given clay concentration of the plug. Curved water-interface effects in the inflow tube were eliminated by treating the inside of the tube with silicone, and the water-outlet tube in the flask was not small enough to make droplet curvature capable of sensibly affecting the values of Δh as employed in this study. Water fluxes were determined by measuring the time rate of movement of the meniscus in the small-bore horizontal glass tube, multiplying this rate by the calibrated cross-sectional area of the tube ($9.06 \times 10^{-3} \text{ cm}^2$), and dividing the product by the cross-sectional area of the clay plug. The horizontal tube was 100 cm long. As the meniscus approached the left end of the tube, refilling was accomplished by appropriate settings of the two three-way stopcocks.

Electrical Measurements

The electrical potential difference ($E_{\text{out}} - E_{\text{in}}$) between the two bright platinum electrodes was measured with a sensitive battery-powered electrometer^{4/} of 10^{14} ohms maximum internal resistance, the electrometer output being displayed on a strip-chart recorder.^{5/} The symbolism $E_{\text{out}} - E_{\text{in}}$ simply means that the polarity of the electrometer was set to measure the electrical

^{4/} Model 601, Keithley Instruments, Inc., Cleveland, Ohio.

^{5/} Model SR, Sargent-Welch Scientific Co., Skokie, Ill.

potential of the electrode in the outflow chamber (below the fritted-glass plate in Fig. 1) with reference to that of the electrode in the inflow chamber. The particular value of $E_{\text{out}} - E_{\text{in}}$ utilized was the step response (E step) induced in it when the value of Δh was changed abruptly from one steady value to another. Such change in Δh was brought about as follows: After the flux for a given Δh had become steady and was measured, the stopcock between the flask and the carboy was closed and a new value of partial vacuum, and hence of Δh as read from the mercury manometer, was imposed in the carboy by adjusting the bleed valve. During the brief time that this was being done, the partial vacuum in the flask remained essentially constant at its previous value, since the rate of liquid flow into the flask was always relatively low. The stopcock between carboy and flask was then reopened quickly to impose the change in Δh practically instantaneously, and the resulting abrupt response in $E_{\text{out}} - E_{\text{in}}$ was termed the E step. While Δh was being increased in magnitude, the resulting E steps were always positive; while Δh was being decreased in magnitude the resulting E steps were always negative. This is entirely consistent with the earlier suggestions and findings (see Section A) that the E steps are valid measurements of change in electrical streaming potential. The magnitude of $E_{\text{out}} - E_{\text{in}}$ associated with a given Δh was taken as the sum of all E-step magnitudes between $\Delta h = 0$ and the particular Δh concerned, and was taken as the measure of electrical streaming potential of equation [4].

The rigid teflon support for the 22-gauge platinum-wire electrodes was an essential part of the apparatus, since it kept the electrodes from bending and hence from introducing bending-stress electrical potentials in the platinum electrodes. The grounded Faraday cage, surrounding the

permeameter and the nearest components of the flow system, was employed to carry off stray electrical potentials from the atmosphere.

Clay Material and Preparation

To load it with a plug of clay, the permeameter was disconnected from the flask and the small-bore water-inlet tube, was dismantled to remove the piston, and was carefully dried of all water. A disc of fiberglass micropore prefilter as already described was placed on the fritted-glass plate, and a specified mass of dry sodium bentonite^{6/} was placed in turn on the fiberglass. With a tiny droplet of plexiglas solvent, a second disc of fiberglass prefilter was secured lightly to the face of the perforated movable piston which was then re-inserted into the central chamber of the permeameter as indicated in Fig. 1. The plexiglas end-plates were once again secured with the assembly bolts. With collars A and B loosened, the piston could be moved to any desired position above the dry clay sample. The piston was then fixed in position by tightening collars A and B. The value of L was chosen to provide the desired clay concentration, calculated as mass of dry clay divided by the total mass of dry clay and water contained between the piston and the fritted-glass plate, and expressed as percentage.

The permeameter assembly was then placed in an evacuation chamber and evacuated in the dry condition at 0.3 mm Hg pressure. Thereupon, previously

^{6/} Montmorillonite No. 26 (Bentonite), from Clay Spur, Wyoming, distributed by Wards Natural Science Establishment, Rochester, New York.

boiled, millipore^{1/} filtered, evacuated, deionized water was admitted into the permeameter from the top through the tubular piston shaft while the vacuum was being maintained. This continued until the clay chamber, the inlet and outlet chambers, and the tubular piston shaft were completely saturated with water. The water-filled permeameter assembly was then removed from the evacuation chamber and once more connected into the flow system of Fig. 1. With no partial vacuum imposed in the carboy, the position of the meniscus in the inflow tube was observed until it either remained stationary or moved at a constant small rate, to establish whether or not the water flux through the clay was zero at zero hydraulic gradient.

Other Aspects of Procedure

Immediately following the zero-gradient flux observation, the first increment of partial vacuum was applied by way of the carboy-stopcock-flask system, the resulting E step was recorded, and the consequent movement of the inflow-tube meniscus was observed until the time rate became steady. All steps of this procedure were then repeated at progressively higher partial vacuums until a value of $|\Delta h|$ on the order of 550 to 650 cm H₂O was reached, whereupon all steps were once again repeated at successively smaller $|\Delta h|$ until zero gradient was again reached. For any given series of increasing gradients followed by decreasing, the ambient temperatures were held within a range of 2 C, while for all experiments they were between 22 and 26 C.

^{1/} Type HA, Millipore Corporation, Bedford, Mass.

It is important to note that the rate of movement of the inflow-tube meniscus was by no means constant over the period of flow during which a given Δh was being maintained. Immediately upon raising $|\Delta h|$ from a previously smaller steady value, the rate of meniscus movement toward the clay during the first minute was much greater than the terminal steady rate. On the average for the increasing $|\Delta h|$'s here involved, the first-minute rate was 8 times that of the terminal steady rate. Immediately upon lowering $|\Delta h|$ from a previously larger steady value, the first-minute rate on the average was 10 times larger than the terminal steady rate, but, in addition, was negative. This means that right after changing $|\Delta h|$ from a larger to a smaller value (but not reversing the sign of Δh), the inflow meniscus would move away from the clay for a time, before halting and commencing normal movement back toward the clay once again. Therefore, it was necessary to allow enough time for the attainment of steady-rate movement of the inflow meniscus before calculating the flux. At least 1 hr of constant-rate movement of the meniscus toward the clay was allowed, which generally required a total flow period of at least 3 to 4 hr at a given Δh .

The cause for the particular observed changes in inflow rate is not known, and was not studied at length. It can be argued that the flow-rate measuring system is extremely sensitive, and that some kind of slight deformation of the internal permeameter cylinder due to changing of the outlet partial vacuum might induce an initial effect on the inlet-tube meniscus movement. Indeed, this explanation seems consistent with the fact that the raising of $|\Delta h|$ caused high initial rates of inflow-meniscus movement toward

the clay, whereas the lowering of $|\Delta h|$ caused such a profound reverse effect that meniscus movement was temporarily in the direction away from the clay. We had also encountered similar flow-rate behavior in our initial attempts to repeat Lutz and Kemper's (1959) results. It was for this reason that the double-wall glass permeameter (Fig. 1) was designed with port G to allow for connection to the partial vacuum of the 1-liter flask, in the hope of possibly subjecting the inner glass cylinder to less differential pressure. When this was done, however, the high-magnitude initial-rate behavior did not disappear. Hence, we are inclined to allow the possibility that the observed flow-rate behavior might have been a characteristic of the clay-water mixture itself. Also, for all experiments to be reported here, the port G was left open to the atmosphere.

For a given clay mass, the maximum intended clay concentration was obtained by making the first setting of the movable piston (Fig. 1) be the smallest L intended for that sample of clay. After the fluxes and electrical potentials were obtained for a complete series of increasing and decreasing gradients, collars A and B were loosened. The piston was moved gently upward to a larger value of L, as required by the next desired lower concentration of clay, and collars A and B were re-tightened. When the clay plug had swelled up against the new position of the piston, zero-gradient fluxes were again observed, followed once more by fluxes and electrical potentials for a complete series of increasing and decreasing gradients. Results for five different clay concentrations will here be reported: 35.1% on one sample of clay, and 28.4, 18.4, 15.5, and 11.5% on a separate sample, the respective values of L being 0.64, 0.45, 0.73, 0.88, and 1.21 cm.

RESULTS AND DISCUSSION

The results for a clay concentration of 11.5% are shown in Fig. 2, in a manner which will be followed as well for all of the remaining clay concentrations. The lower graph shows the hydraulic data in terms of water flux versus hydraulic gradient, while the upper graph shows the electrical data as $E_{out} - E_{in}$ versus hydraulic gradient. As mentioned before (see subsection Electrical Measurements), each value of $E_{out} - E_{in}$ at a given gradient is the sum of all E steps between zero gradient and the given gradient (or, correspondingly, between $\Delta h = 0$ and the value of Δh used to calculate the given gradient). The separation between the two values of $E_{out} - E_{in}$ for increasing and decreasing gradients at the highest gradient (483 cm H_2O/cm) does not imply some kind of discontinuous behavior at this gradient. Instead, it means that the five E steps taken for decreasing gradients did not accumulate to as large a value as the five E steps for increasing gradients, and, since zero gradient is the common reference point from which the curves begin, the two values do not agree at the highest gradient.

The tendency toward smaller E steps for decreasing gradients is present consistently, in that the curve for decreasing gradients is generally lower than that for increasing gradients. Furthermore, neither curve is proportional, even though both are forced to pass through the origin by the nature of their evaluation. If $(E_{out} - E_{in})/gradient = (E_{out} - E_{in})/i$ were to be calculated for each curve in the upper part of Fig. 2, this quantity would decrease as the gradient increased, and, since $(E_{out} - E_{in})/i = L(E_{out} - E_{in})/(-\Delta h)$, it means that i_e/i from equation [4] would also decrease with increasing gradient, since L is constant. This means in turn,

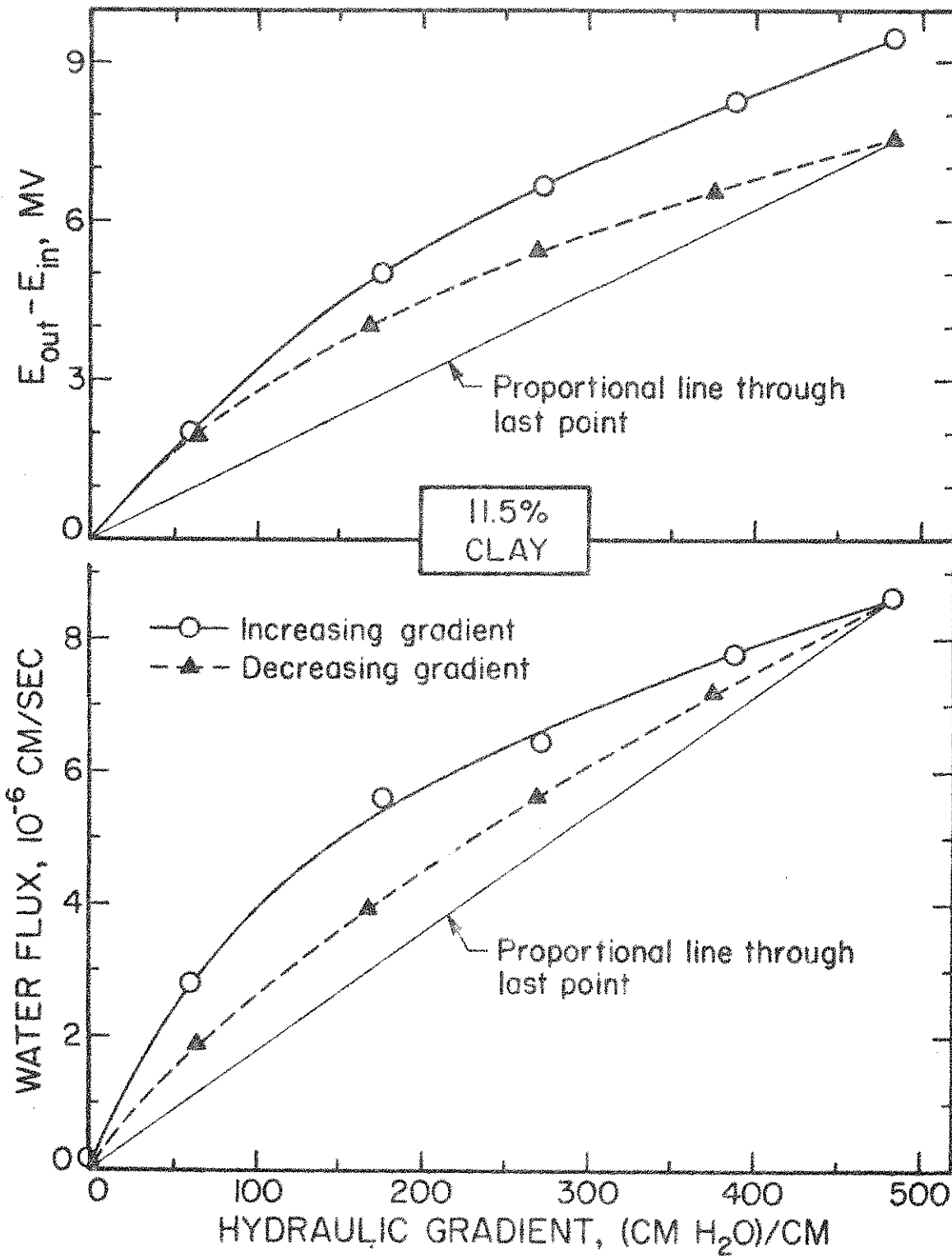


Figure 2. Electrical potential difference (upper graph) and water flux (lower graph) versus hydraulic gradient, increasing-gradient series followed immediately by decreasing-gradient series, for 11.5% sodium bentonite.

if K and c_e can be taken as constant, that K' of equation [3] should increase with gradient i , so that from equation [2] the water flux v should increase more than proportionally with gradient.

Inspection of the lower graph of Fig. 2 reveals, however, that the flux increases less than proportionally with gradient. That is, if $K' = v/i$ (basis of equation [2]) were calculated for both the increasing- and decreasing-gradient curves, it would decrease with increasing gradient, which is just the opposite of the inference from the upper graph as based on equation [3]. This disparate behavior is in contrast to that found by Bull and Gortner (1932) for powdered quartz, in which a less-than-proportional response of streaming-potential to gradient was associated with a more-than-proportional flux-gradient relationship, in accord with equations [1] to [4] (Swartzendruber, 1969). It may thus be that a swelling clay behaves differently from a nonswelling quartz medium as regards the relationship between hydraulic and electrical properties, so that the approach embodied by equations [1] through [4] does not hold for swelling media.

It is not known why the curves of Fig. 2 fail to reproduce each other for increasing and decreasing gradients. In the case of the flux-gradient data, it may be worth noting for the increasing-gradient curve that attainment of steady-state flux was approached from initially high inlet-meniscus rates, whereas steady-state flux for the decreasing-gradient curve was approached from initially low (even negative) inlet-meniscus rates. It could thus be argued that a minimum flow period of 3 to 4 hr was not long enough to reach true steady-state flux, and, if sufficient time had been allowed, the two curves would have merged at some intermediate place

between them. Even as performed, however, these experiments were very time consuming, and if drastically longer flow periods were to be attempted, possible long-term flow effects of other adverse nature could also be encountered.

Results for the higher clay concentration of 15.5% are shown in Fig. 3, and are still qualitatively similar to Fig. 2, but the magnitudes of the less-than-proportional deviations in both the upper and lower graphs are much less than in Fig. 2. In the lower graph, the flux-gradient relationship is very near to proportional for decreasing gradients, although there is still a slight tendency toward less than proportional.

For the still higher clay concentration of 18.4%, Fig. 4 shows that the trends of the previous paragraph have continued. The flux-gradient data for decreasing gradient (lower graph) are now proportional, and all other data in the figure are only slightly less than proportional. In the upper graph, however, the data for increasing and decreasing gradients appear somewhat more separated than for the 15.5% clay in Fig. 3.

For the next higher clay concentration of 28.4%, as shown in Fig. 5, the flux-gradient data in the lower graph are not only proportional but have merged into the same straight line through the origin. In the upper graph, the electrical data are all proportional, but the smaller slope of the proportional line for decreasing gradients preserves the trend of separation noted for the three previous clay concentrations.

As has been already noted (see subsection Other Aspects of Procedure), all of the foregoing concentrations were obtained on the same sample mass of clay but with different settings of the movable piston of Fig. 1. For a concentration of 35.1% clay, a different sample was prepared, for which

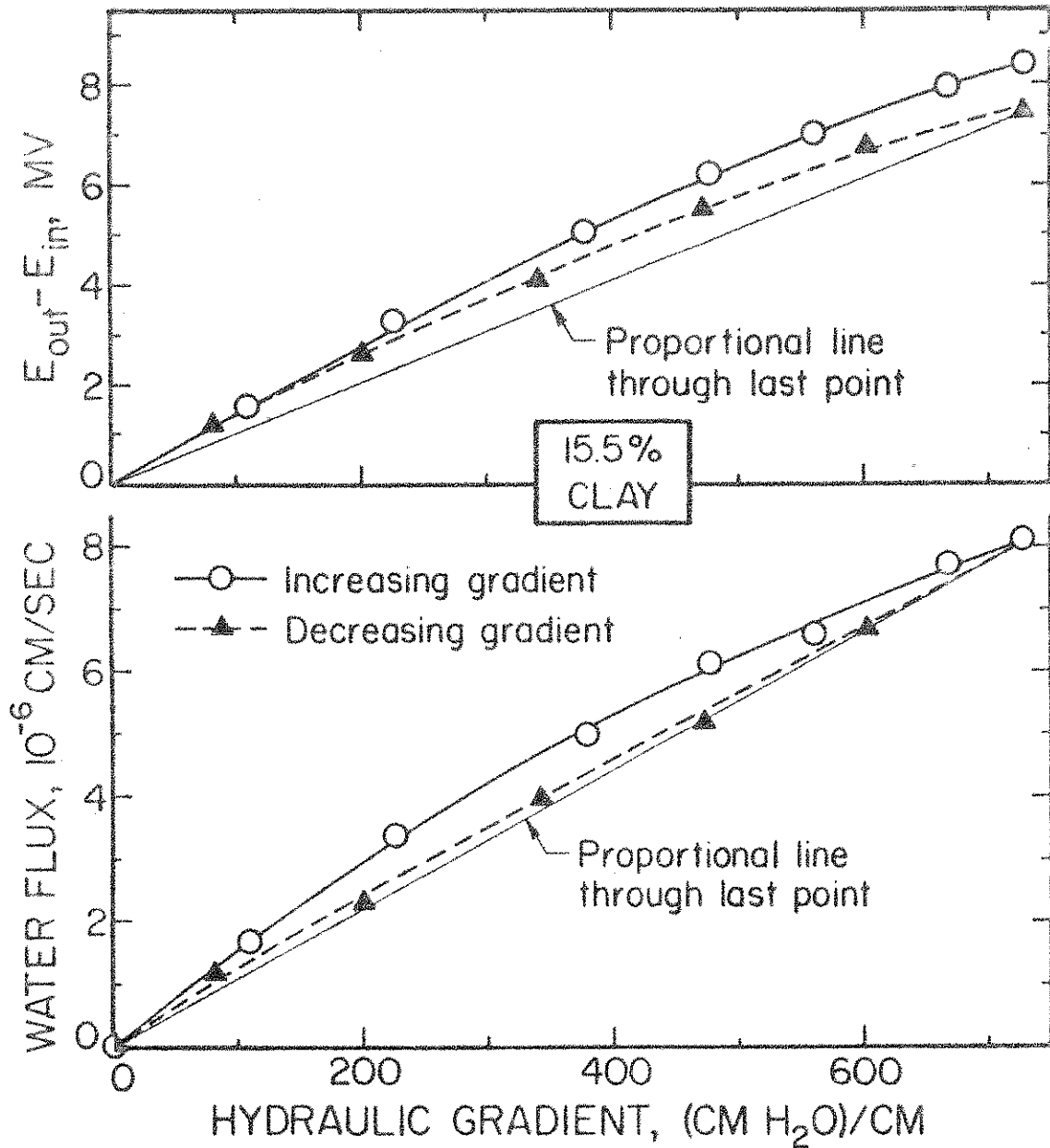


Figure 3. Electrical potential difference (upper graph) and water flux (lower graph) versus hydraulic gradient, increasing-gradient series followed immediately by decreasing-gradient series, for 15.5% sodium bentonite.

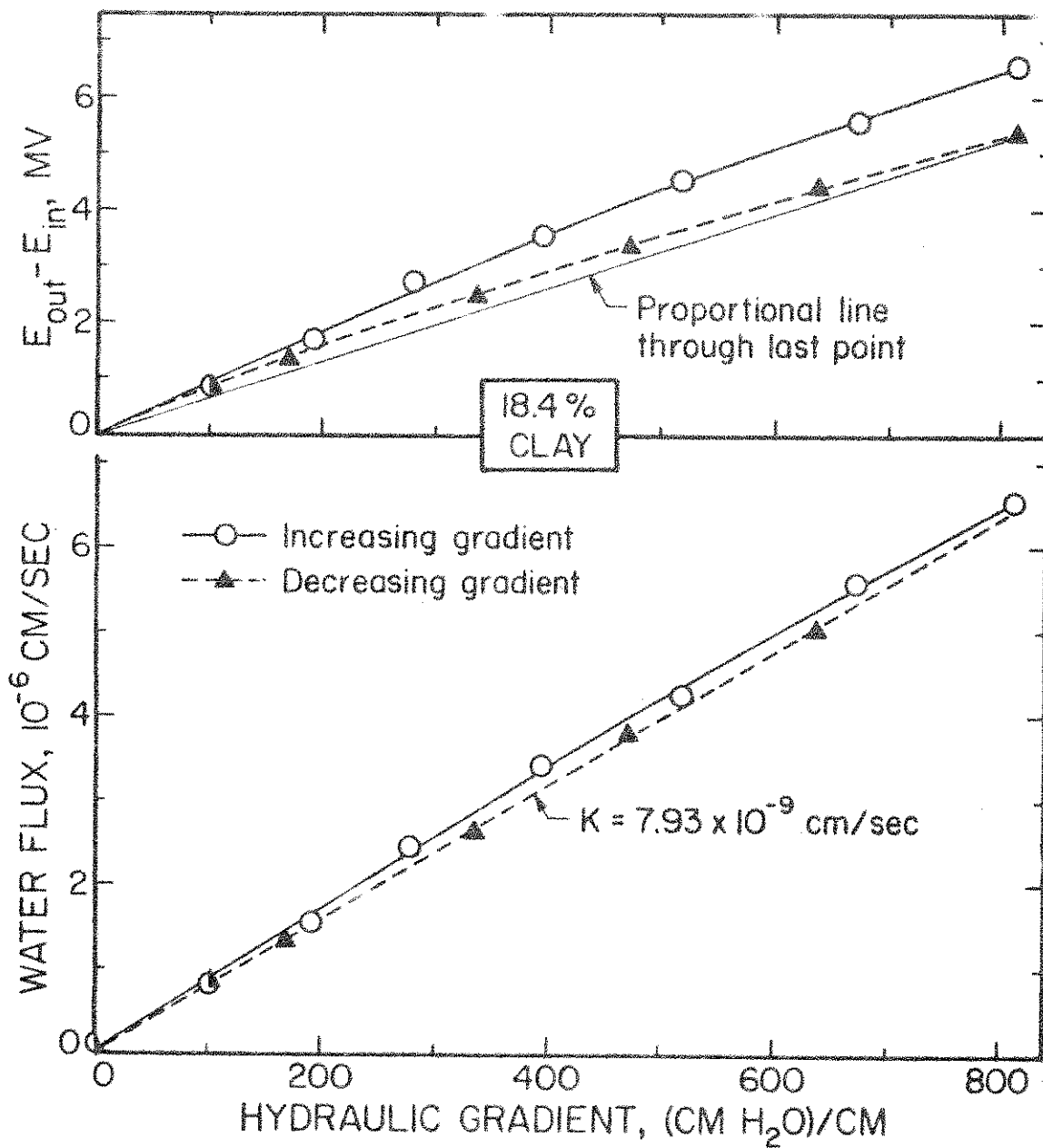


Figure 4. Electrical potential difference (upper graph) and water flux (lower graph) versus hydraulic gradient, increasing-gradient series followed immediately by decreasing-gradient series, for 18.4% bentonite.

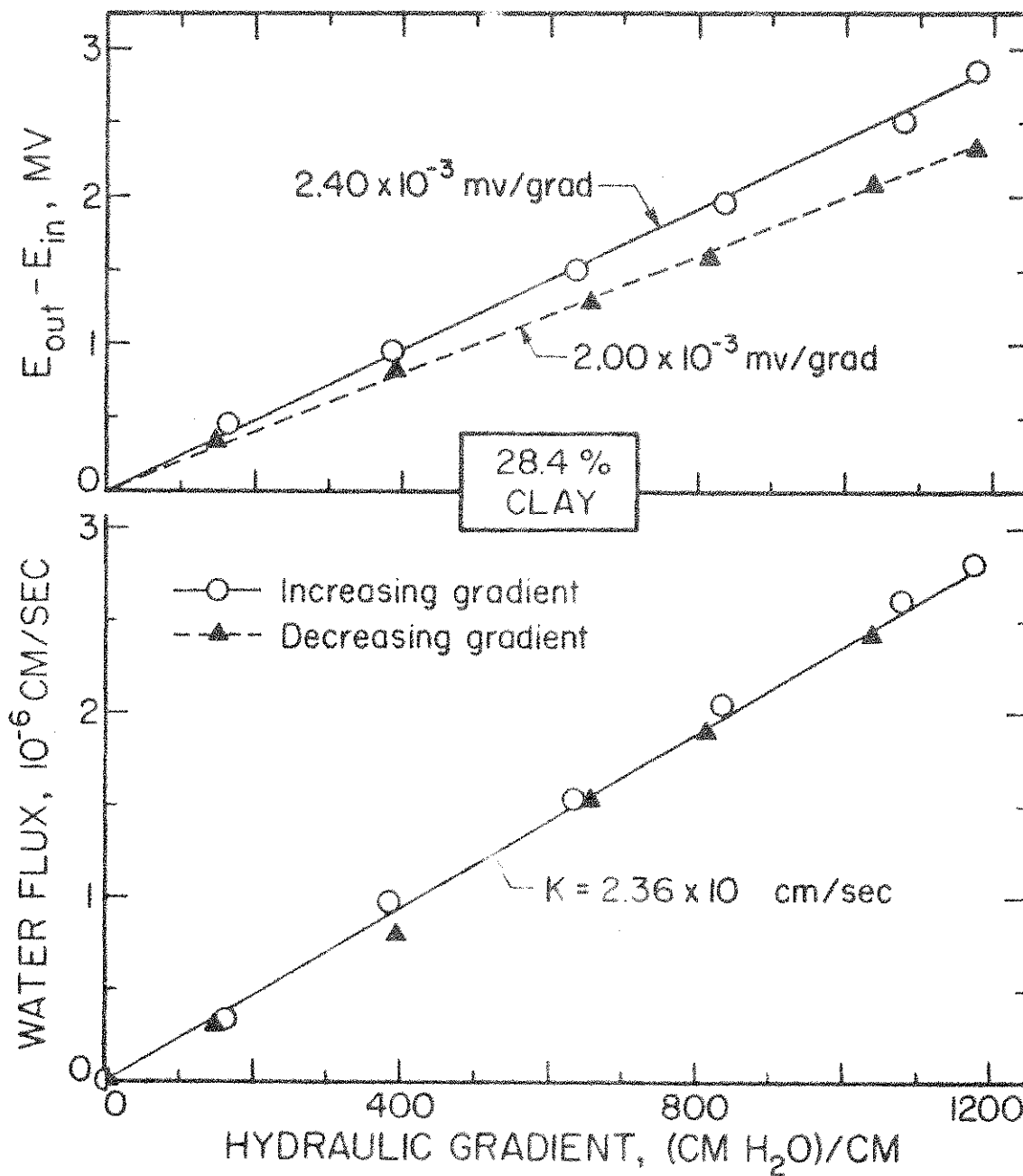


Figure 5. Electrical potential difference (upper graph) and water flux (lower graph) versus hydraulic gradient, increasing-gradient series followed immediately by decreasing-gradient series, for 28.4% sodium bentonite.

the results are shown in Fig. 6. Unfortunately, the flux at zero gradient was not recorded for the first increasing-gradient series (lower graph), and this is why the solid-line curve is not drawn all the way to the origin. To compensate for this omission, a second set of increasing and decreasing gradients was imposed and measurements taken, as indicated by the open- and solid-square symbols in Fig. 6. If one ignores the low-gradient range (lower graph), where the solid-line curve is directed rather arbitrarily toward the origin, the experimental points are seen to conform rather well to a straight line, but not a straight line through the origin as required for proportionality. The cause of the negative fluxes at zero gradient is not known, but appears real since the two experimental points at zero gradient agree well with each other and line up well with the other points, even though they were obtained at substantially different times and with considerable flow history in between. The agreement between data for increasing and decreasing gradients is very good, and in this sense corroborates the findings for 28.4% clay.

For the first series of increasing and decreasing gradients for the streaming-potential data in the upper graph of Fig. 6, a similar corroboration occurs; that is, the data are proportional but with the points for decreasing gradients below those for increasing gradients. When repeated in trial 2, however, the agreement between increasing and decreasing gradients is very close, and the straight line is proportional and in close agreement with the first increasing-gradient series. This implies that perhaps the first series of decreasing gradients somehow yields values that are too low, but that this does not necessarily persist for subsequent repeated applications of increasing and decreasing gradients.

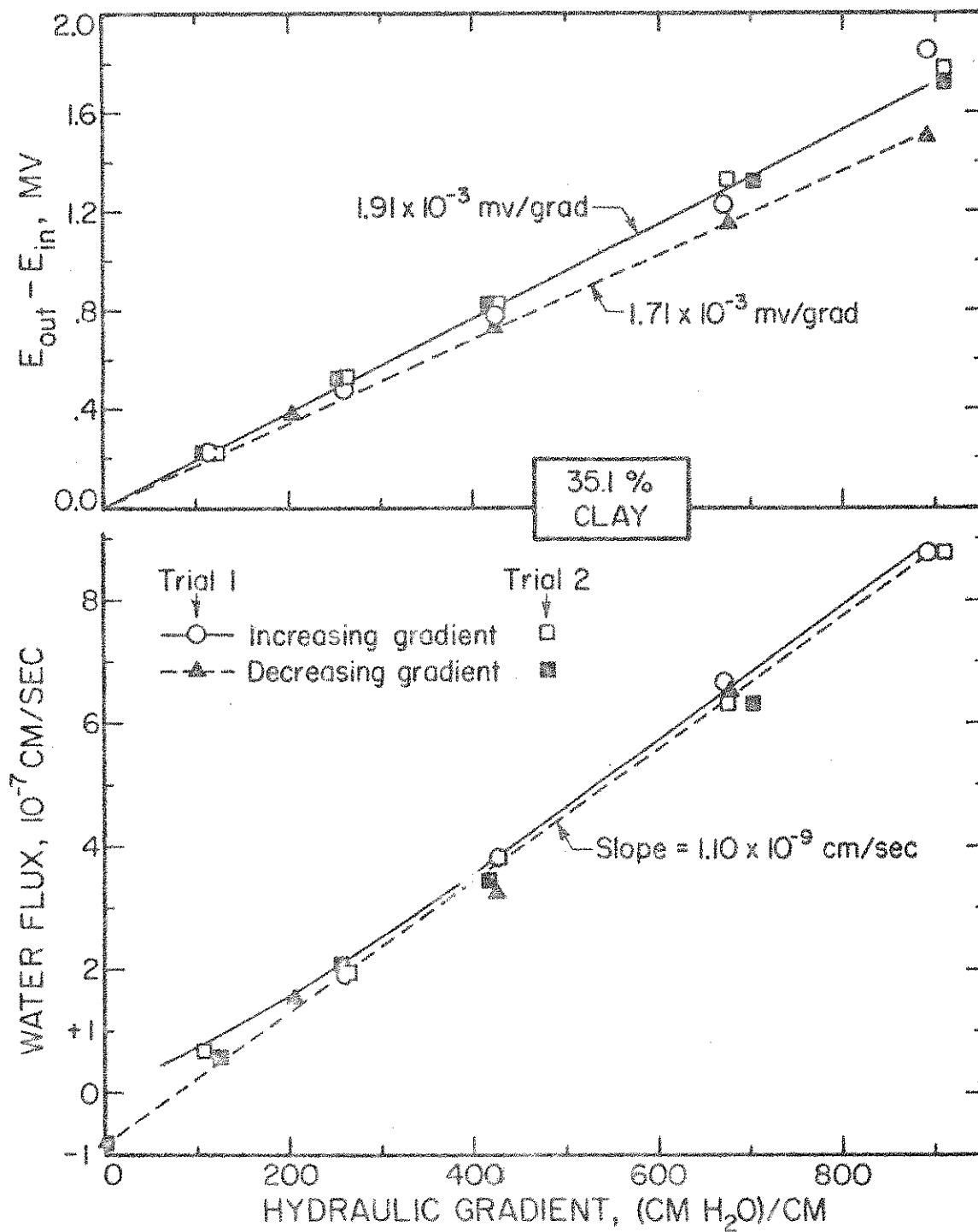


Figure 6. Electrical potential difference (upper graph) and water flux (lower graph) versus hydraulic gradient, for 35.1% sodium bentonite. In each trial, the increasing-gradient series was followed immediately by the decreasing-gradient series, with trial 1 followed immediately by trial 2.

Following the measurements on the 35.1% clay concentration, the movable piston of Fig. 1 was shifted upward to reduce the clay concentration, and a complete set of data was obtained at 28.0% clay. The results agreed well with those in Fig. 5 for 28.4% clay, so that they are not presented here explicitly, but they do thus constitute the basis for considering the data of Fig. 6 as a justifiable continuation of the results of the previous figures, even though obtained on a separate sample of clay.

Overall, from Figs. 2 through 6, there is no evidence that less-than-proportional responses of $E_{out} - E_{in}$ to hydraulic gradient will induce more-than-proportional flux-gradient behavior for the swelling clay-water systems studied here. This differs from the contrary findings of Bull and Gortner (1932) for nonswelling quartz mixtures. Also, there is relatively little evidence for more-than-proportional responses of water flux to hydraulic gradient, and in the one definite case (Fig. 6) this appears to be of a type wherein a linear flux-gradient curve is simply shifted to the right to produce a positive gradient intercept. How this is caused, however, cannot be deduced without further study. More prevalent in actuality is the appearance of a number of less-than-proportional flux-gradient relationships, especially at the lower clay concentrations. This is somewhat suggestive of compressional effects which progressively decrease the overall permeability, the compression increasing as gradients are increased. It must be emphasized, however, that a simple overall length-shortening of the clay plug does not sensibly occur as gradients are increased. That is, the upper end of the clay plug was essentially in contact with the piston for all fluxes imposed at a given clay concentration. This does not rule out the possibility of some reversible clay-

particle redistribution within the clay plug, to yield an overall decrease in permeability in response to increasing gradients. Perhaps this might occur somewhat along the lines suggested by Blackmore and Marshall (1965).

For a further assessment of hydraulic and electrical characteristics as related to clay concentration, values were read from the curves of Figs. 2 through 6 at a common gradient of 450 cm H₂O/cm, since not all of the data relationships were straight lines through the origin. These common-gradient calculations consisted of $E_{out} - E_{in}$ per unit hydraulic gradient, of hydraulic conductivity $K' = v/i$ (equation [2]), and of intrinsic permeability $k = K'\eta/\rho g$, where η is the viscosity of water at the temperature of measurement for a given clay concentration, ρ is the density of water, and g is the acceleration due to gravity. These numerical values are presented in Table 1. As clay percentage increased from 11.5 to 35.1, both K' and k decreased progressively, the ultimate reduction being on the order of 20 fold. This compares with only a 3-fold increase in clay concentration, and is a remainder of how sensitive a hydraulic-conductivity or permeability parameter can be to the compaction status of a porous medium. The intrinsic permeability k was calculated especially to allow comparison with Lutz and Kemper's (1959) values, which, at an inferred gradient of 450 cm H₂O/cm were 3.1 and $4.9 \times 10^{-6} \mu^2$ for calcium and hydrogen Wyoming bentonite, respectively. These values would fall in Table 1 between 18.4 and 28.4% clay, insofar as it is justified to compare Lutz and Kemper's calcium and hydrogen clays with the sodium clay used here. This indicates that the technique of the present study did achieve clay-plug compactions that yielded intrinsic permeabilities not only as low as but substantially lower than those of Lutz and Kemper, at the two highest clay concentrations used (28.4 and 35.1%).

Table 1--Hydraulic and electrical properties at different concentrations of clay (bentonite).

Clay conc., wt. basis	Gradient status	At gradient of 450 cm H ₂ O/cm		
		$K' = \frac{v}{1}$	$k = \frac{K'n}{\rho g}$	$E_{out} - E_{in}$ per unit gradient
%		10^{-9} cm/sec	$10^{-6} \mu^2$	10^{-2} mv/grad
11.5	Increasing	18.52	16.93	2.008
	Decreasing	18.18	16.62	1.611
	Mean	18.35	16.78	1.810
15.5	Increasing	12.87	12.03	1.301
	Decreasing	11.40	10.67	1.179
	Mean	12.14	11.35	1.240
18.4	Increasing	8.55	7.99	0.896
	Decreasing	7.93	7.40	0.698
	Mean	8.24	7.70	0.797
28.4	Increasing	2.36	2.20	0.240
	Decreasing	2.36	2.20	0.200
	Mean	2.36	2.20	0.220
35.1	Increasing	0.91	0.88	0.191
	Decreasing	0.88	0.85	0.171
	Mean	0.90	0.86	0.181

The streaming-potential parameter, $E_{out} - E_{in}$ per unit gradient in Table 1, also undergoes progressive reduction as the clay concentration increases, with an ultimate reduction of about 10 fold. Furthermore, these values, which range from about 2 to 20×10^{-3} mv/grad, are substantially smaller than those ranging from about 2 to 16×10^{-1} mv/grad for the sand-kaolinite studied earlier (see Section A). This might seem surprising, since one commonly construes bentonite as the more electrically and surface active, but two matters should be borne in mind. First, the flux per unit gradient (hydraulic conductivity K') is four to five orders of magnitude smaller (10^{-4} to 10^{-5}) for the bentonite suspensions here studied, as compared with the sand-kaolinite. Second, the ionic environment in the bentonite likely is conducive to much higher electrical conductance through the liquid and along clay-particle surfaces than is true in the sand-kaolinite. Hence, it is more difficult to build up an electrical potential difference in the bentonite than in the sand-kaolinite, even though salt in the amount of 20 ppm mercuric chloride was not added to the deionized water used for flow through the bentonite.

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