TEXAS WATER COMMISSION

Joe D. Carter, Chairman
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BULLETIN 6206

RESEARCH IN THE PROBLEM OF SCALING

OF ELECTRODIALYSIS DEMINERALIZERS

By

Donald A. Cowan

Final Report on Studies
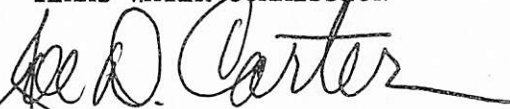by the University of Dallas
for the Texas Water Commission

April 1962

FOREWORD

Appropriation item 70 to the Board of Water Engineers under House Bill 4, Fifty-sixth Legislature of Texas, Third Called Session, 1959, provided a total of $20,000.00 "For the investigation of demineralization of the highly mineralized water of West Texas - initiation of research in an effort to improve quality." On July 13, 1960, the Board of Water Engineers, pursuant to the objective of this appropriation, entered into a contract with the University of Dallas for research and a report on the use of an electrodialysis process as a means of demineralization of brackish waters such as are encountered in West Texas.

This publication presents the final report of research accomplished under provisions of the above-mentioned contract. It is felt that the research undertaken as a result of this contract and this report thereon constitute an important step forward in providing means to obtain a usable quality water from the available highly mineralized waters of West Texas.

TEXAS WATER COMMISSION

Joe D. Carter, Chairman
April 30, 1962

TABLE OF CONTENTS

TABLE

TABLE OF CONTENTS (Cont'd.)

Page

ILLUSTRATIONS

Figures

RESEARCH IN THE PROBLEM

OF SCALING OF

ELECTRODIALYSIS DEMINERALIZERS

INTRODUCTION

The Texas Water Commission [formerly the Texas Board of Water Engineers] is charged with the responsibility for the development and conservation of water resources in the state of Texas. In the discharge of this responsibility, the Commission maintains a surveillance on research directed toward new resources. The State Legislature in 1959 made funds available to the Board [now referred to as the Commission] for investigations leading toward the practical use of electrodialysis in making potable the brackish water which occurs in many regions of the state.

Experiments in electrodialysis were underway at Fort Worth in the laboratory of Texas Electric Service Company, the object being to develop a large community-sized demineralizer. In the course of these experiments, a number of problems were uncovered which indicated more detailed investigations should be made. The principal problem concerned the scaling of membranes; in the operation of an electrodialysis demineralizer, from time to time, for seemingly unpredictable reasons, a hard deposit would occur in a membrane and would build up to such an extent that the entire stream would be blocked. When such an event occurred, it was necessary to dismantle the demineralizer, replace the membrane, and reassemble the apparatus. Economical operation could not be achieved under such conditions. The problem is a universal one, harassing development of electrodialysis in all parts of the world. The Board [Commission] was familiar with this situation, and, since the information which Texas Electric Service Company had generated was placed in the public domain, elected to further this process. Dr. Donald A. Cowan, professor of Physics at the University of Dallas, who was associated with the work at Texas Electric Service Company and who had published research in the field, agreed to undertake the investigation. Accordingly a contract was closed with the University of Dallas to perform a research contract directed toward the solution of the scaling troubles which beset the electrodialysis process, the project to be directed by Dr. Cowan. Texas Electric Service Company, which was not a party to the contract, furnished the electrodialysis test cell, pumps, piping, and associated equipment to prosecute the research program.

The following report describes the results of this project. The principal experimental work was performed by Mr. J. P. Lintz and Mr. P. R. Lintz. The Chemistry Staff at the University of Dallas served as consultants on the project. There is appended to this report an account of an experiment performed at Texas Electric Service Company which confirms some of the findings made under this contract. The experiments there was performed by Mr. Fred E. Jones; that project is under the direction of Mr. Howard Drew.

SUMMARY

A series of tests conducted under this research contract has established (a) that scaling occurs when a bicarbonate ion is changed--probably to a carbonate ion--in passage through a membrane, (b) that pH control has only a secondary significance, and (c) that a polarization 1.7 volts for each anion-permeable membrane must be exceeded in order for scaling to occur. A study has been made of the process by which polarization occurs; this study reveals that the specific resistance of the membrane plays an important role in polarization.

If it is economically feasible to operate an electrodialysis demineralizer at current densities sufficiently low for polarization to be avoided, scaling of membranes will not occur. If it is necessary for current densities to exceed this value, reversal must be practiced in order to keep polarization voltage below a critical value.

The problems that remain in electrodialysis include the disposal of brine and the determination of lifetime for membranes. A more complete understanding of the electrodialysis process is needed for further advances. The practical economics of electrodialysis demineralizers must be established by demonstration plants.

PURPOSE OF RESEARCH CONTRACT

The purpose of the research conducted under this contract is to determine the physical conditions which lead to scaling in electrodialysis demineralizers. This report describes the desalinization problem in general, the electrodialysis process in particular, and the equipment employed in the investigation, together with an account of results and presentation of pertinent data.

THE GENERAL PROBLEM OF DESALINIZATION

The development of surface-water reservoirs and conservation of water must remain the paramount problems confronting all those interested in the water supplies of Texas. Since no process of desalinization can compete with nature in the supply of good water, economy demands that every effort be bent toward the establishment of reservoirs and the protection of their waters against pollution. Even so, for all the efforts which might be expended on surface waters, it is apparent that the large supply of brackish waters abounding in West Texas must be desalinized and made available at reasonable expense if that region is to have the economic growth to which its potentialities otherwise entitle it.

Processes Available

Three general methods for desalinization are now being investigated rather widely: (1) that involving a change of state of water; (2) that involving a chemical change; and (3) that involving a direct expenditure of energy on the salt itself. Within each of these general methods many varied approaches are being used. To effect a change of state, for example, both freezing and distillation are offering promising results; and, adding to the profusion of possibilities, perhaps a score of distillation methods are being developed, methods which testify to the ingenuity of our engineers and scientists. All of these systems

are effective in removing salt from water; the problem arises in the cost of performing the operation.

Energy is the basis of any economic evaluation. In general, for any process an increase in expenditure for capital equipment can decrease the expenditure for energy. To take an extreme case: in solar stills the energy is free, but the production cost, including amortization, is extremely high. All the systems thus far developed have leaned toward large capital outlay and small energy expenditure but, in the eventual design, these two cost factors must be brought into parity.

The actual energy difference between pure water and sea water is only 2.9 kwhr (kilowatt hours) per thousand gallons, and for brackish waters the energy difference is about one-tenth of this amount. The smallness of this quantity is misleading, however, in that there is a large energy barrier between salty and pure water. For those systems involving a change of state the barrier is the familiar heat of fusion or heat of vaporization. For vaporization, this barrier (2,350 kwhr per thousand gallons) is almost a thousand times the difference between pure water and sea water; and, although in principle this energy is returnable to the system for re-use, in practice most of it is lost. A recent study [1] has placed the practicable lower limit of energy expenditure at greater than 38 kwhr per thousand gallons. In freezing, the barrier is in the opposite direction and is not so formidable in size, but the chances for recovery of energy are less good and the practicable limit, again, is 38 kwhr per thousand gallons. Since it is the water itself, and not the salt, which must be handled by these systems, the cost figures are no different for brackish water than for sea water. Accordingly, though we might somewhat optimistically hope that, eventually, careful engineering might lower the cost to 53 cents per gallon of water from the sea (2 x 38 x 0.7¢), we can expect nothing better for brackish water. And the progress from the presently projected one dollar cost to the 53 cents cost will be difficult and hard to earn.

DISTILLATION

2,350 kwhr/ kgl.

Brackish or Sea Water   Fresh Water

FREEZING

Brackish or Sea Water   Fresh Water

345 kwhr/kgl.

ELECTRODIALYSIS

35 kwhr/kgl.   Fresh Water

Sea Water

5 kwhr/kgl.   Fresh Water

Brackish Water

_____

[1] Dodge, B. F., and Eshaya, A. M., 1960, Thermodynamics of some desalting processes: Advances in Physics, no. 27, p. 7-20.

The other two categories of processes do not involve a change of state and thus do not face the large barrier between salty and potable water. Nonetheless a barrier does exist, arising from the establishment of a potential but irrecoverable electric energy in the separation of ions; on the basis of energy content as indicated by the velocity of sound, this barrier is about 35 kwhr per thousand gallons of sea water. However, since the barrier is directly proportional to salinity, the figure is only about one-tenth as high for brackish water. The energy expended in surmounting the barrier probably recurs as heat and is thus lost as a working energy of the system. Fortunately this lost energy is small; hence processes in categories (2) and (3) remain in a favorable position for handling brackish water, certainly, and possibly even sea water. The chemical processes for desalinization have not yet been engineered to a point susceptible to careful evaluation. These processes involve the intermixing of an organic compound with the water being treated, and consequently present serious problems in the conservation of chemicals and in the utility of working volume. A process in category (3) is the concern of the present study.

Electrodialysis

Electrodialysis effects desalinization by moving ions through plastic membranes under the influence of electricity. In water, salt dissociates into positive and negative ions which move in opposite directions in an electric field. These ions will pass through membranes; but membranes can be constructed which will allow only positive or only negative ions to pass. If these membranes are arranged alternately, then the water between one pair of membranes will lose ions while the water between the next pair will gain ions. (See Figure 1.) The principle is simple, and the process is effective. It can be engineered to produce potable water quite economically and is generally conceded to be the leading contender as the method to be used for brackish waters. Two major problems remain with this process: the disposal of brine and the scaling of membranes. Scaling is the more immediate problem. The scale that develops on membranes is quite similar to the scale that develops on teakettles. This scale can block the thin passage through which the water flows, can increase resistance to electricity, and can damage membranes to the point of replacement. The most serious consequence of scaling is the loss of production time resulting from the difficulties of dismantling and reassembling the equipment. If a desalinization process is to be economical, it must be very nearly trouble-free. It must avoid scaling. Scaling is not an inevitable consequence of operation, but the conditions that lead to scaling have never been defined. It is a definition of these characteristics which is the purpose of this project.

The Process Of Scaling

All matter tends to exist in its lowest energy state. If ions in solution have less energy than when they are collected in a solid, then they will stay in solution; but if conditions change so that the lowest energy state is the solid aggregate, then salt will be precipitated. Since theoretical treatment of these energy states is not complete and is quite complex, the available description of precipitation conditions are empirically based, the most widely used one being the Langler Index. This index compares the measured acidity of water against a calculated one, a discrepancy on one side indicating a tendency to scale and on the other indicating a tendency to corrode. This index appears to be reliable in the prediction of precipitation where local conditions are known with good accuracy; but, in electrodialysis, conditions at a membrane
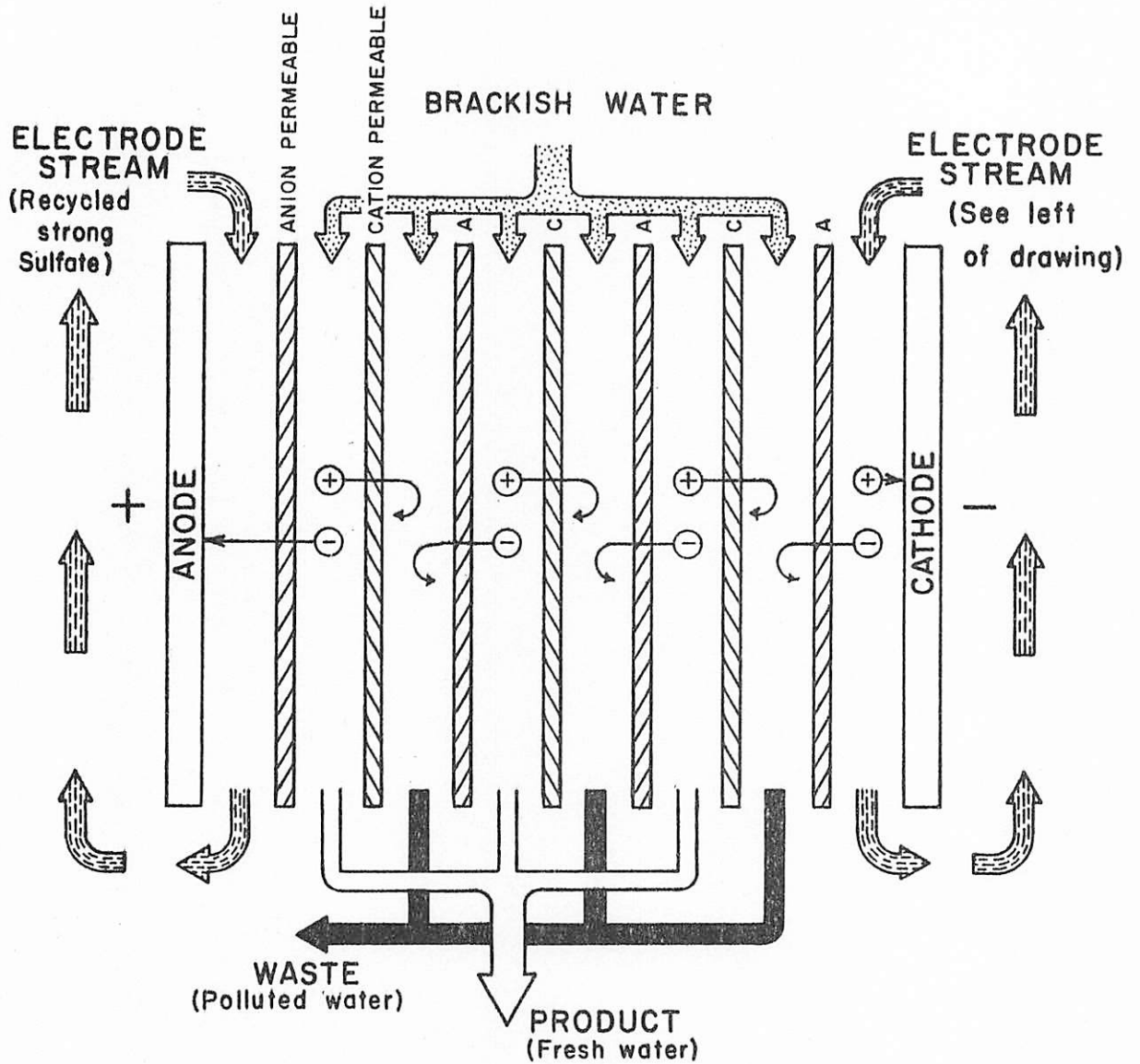
FIGURE I.— Diagrammatic sketch of the electrodialysis process

surface may be markedly different from those measurable in the bulk stream. Furthermore, electrodialysis can provide energy directly to ions, inducing reactions which yield insoluble compounds without the catalytic action of the hydroxyl ion. The artificial lowering of pH in the concentrate stream can depress the scaling tendency, but it appears to be neither necessary nor sufficient for scale control. A more direct cause for scaling must be identified. A search for this cause constitutes the major purpose of this research contract.

EQUIPMENT

The major electrodialysis system was supplied to the project as a gift from Texas Electric Service Company. Membranes have been supplied without charge by American Machine and Foundry and by Pfaudler Permutit Company. Conductivity meters, potentiometers, pH meters, and other instrumentation have been furnished by the University of Dallas. The major electrodialysis system was constructed at the laboratories of Texas Electric Service Company, and was installed at the University of Dallas on July 24, 1960.

A diagram of the flow pattern of the system is shown in Figure 2(a). The system consists of two major components, the water-supply unit and the demineralizing cell. The water-supply unit is mounted on a mobile carriage with dimensions 86 x 61 x 37 inches. The other component, the electrodialysis cell, measures 49 x 6 x 5 inches. Its construction is detailed in Figure 2(b).

The flow meters indicated in Figure 2(a) are manometers which measure the pressure difference across an orifice. Selection of orifice size was made experimentally, that size being used which gave a pressure difference equal to the range of the manometer--30 inches of mercury--at the maximum flow rate contemplated. The orifice is changed for different ranges of flow. Weir boxes were added to increase precision of flow measurement.

Conductivity meters were used to determine the salinity of water before and after passage through the cell. These meters were alternating current (1,000 cps) bridges, standard Leeds & Northrop conductivity cells constituting the sensing arms. Calibration of these meters was carried out over the range of salinities and temperatures experienced in the tests.

Small, static electrodialysis cells (cells with no streamflow) were constructed by project members. These cells are illustrated in Figure 3.

The direct current for the various cells was supplied by a bank of storage batteries. These batteries are maintained near full charge by a rectifier supply. Instrumentation for reading current and voltage across the various electrodialysis cells consists of potentiometers, specially constructed for the ranges of interest, which were calibrated against a Weston standard cell. A recording potentiometer was added to the system so that continuous readings of current could be taken. The chart position was made to agree with the reference voltage taken from a ten-turn helipot attached to the chart drive. The chart drive of the recorder turns the helipot potentiometer. The applied voltage was changed manually by an operator so that it would correspond to the changing reference voltage. The diagram of this arrangement is shown in Figure 4(a).

One further change has been introduced so recently that only one result is included in this report (See Figure 11, page 28.) The large cell has been altered in such a way that two separate streams flow in parallel with equal current

Reservoir for Study Stream

Reservoir for Buffer Stream

Reservoir for Electrode Streams

Flow Meters   Gate Valves   Pumps

Weir Boxes

ELECTRODE STREAM →
BUFFER STREAM →
STUDY STREAM →
ELECTRODE STREAM →

(a) Flow Pattern

LUCITE COVER PLATE

CARBON ELECTRODE

PVC SPACER FOR ELECTRODE STREAM

MEMBRANE

PVC SPACER FOR BUFFER STREAM

MEMBRANE

PVC SPACER FOR STUDY STREAM

MEMBRANE

PVC SPACER FOR ELECTRODE STREAM

CARBON ELECTRODE

Study Stream
Electrode Stream
Buffer Stream

LUCITE COVER PLATE

INLETS   OUTLETS

(b) Cell Construction

Note:
PVC = Polyvynil Chloride

91

FIGURE 2.– Schematic flow pattern and cell construction of the electrodialysis study system

Figure 3

Concentrated Electrolytic Solution

Dilute Electrolytic Solution

Glass Envelope

Membrane

0.9 cm.

Circular Platinum Disc Electrode

Plastic Sleeve

(a) Initial Static Cell

Concentrated Electrolytic Solution

Dilute Electrolytic Solution

Platinum Electrode

Membrane

Micrometer Drive for Adjusting Space Between Membranes

Lucite Tank

(b) Improved Static Cell

FIGURE 3.— Static cells used in studies of conductivity levels

(a) Single-Stream System

(b) Dual-Stream System

FIGURE 4.— Electrical diagrams of systems for continuous recording of cell current and voltage

densities: differences in voltage across the two cells can be read directly.
With this arrangement, two different membranes or two different species of salt
can be compared with greater precision than before. The electrical set-up for
this arrangement is shown in Figure 4(b). A common electrode is at the bottom
of the cell stack but separate electrodes are on top. A polyethylene strip sep-
arates the streams, which have independent inlets and outlets.

STUDIES

One hundred and thirty-three experiments were performed under this contract,
together with a number of theoretical studies. The results are grouped into the
seven studies reported below.
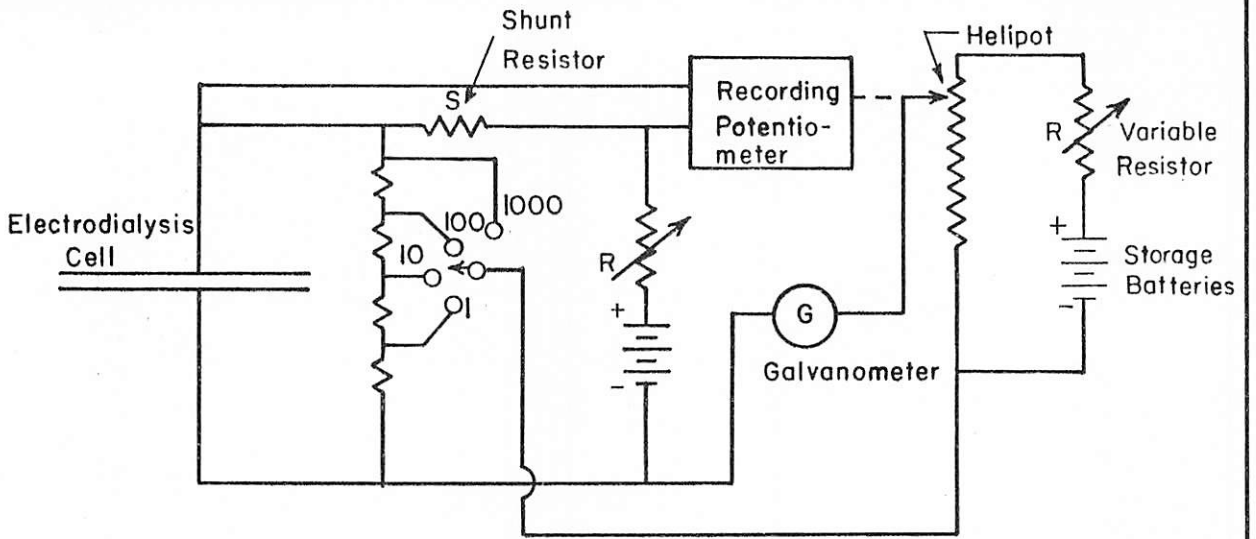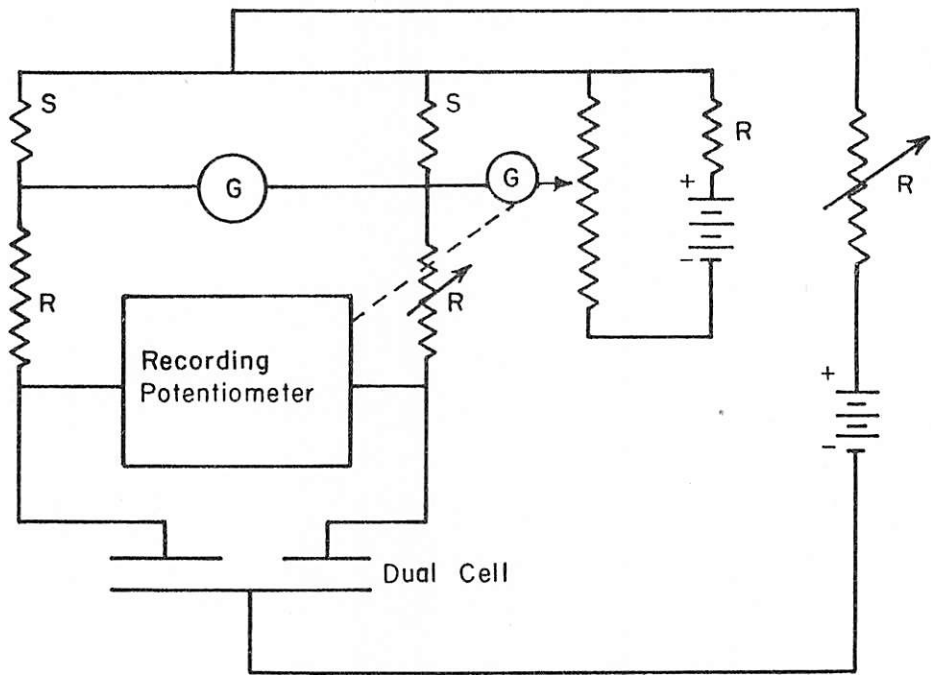

Charged Membranes

Studies of relaxation time had revealed that membranes can retain charges
for appreciable lengths of time. These charges do not merely adhere to the sur-
face but are part of the membrane matrix, a fact that is revealed by (1) shorting
the system out so that the surface charge is neutralized; subsequent voltage
drops to zero but quickly recovers and resumes its former decay curve; (2) re-
moval of a membrane from the cell in which it was charged and placing it in a
new cell; decaying voltage is present.

The possibility that the charged membrane itself generated scale seemed wor-
thy of investigation. Accordingly, anion-permeable membranes were charged in a
0.02 normal solution of calcium sulfate at various current densities for various
lengths of time. A three-layer membrane charged to about one volt collected a
thin soft film when placed in a 0.03 normal solution of sodium bicarbonate. A
homogeneous membrane similarly charged did not scale.

It appears that a charged membrane of itself does not induce scaling, but
that ions can become trapped on a membrane in such a way as to be centers for
scale formation.

Cause of Scaling

The possibility that scaling occurs only with a change in acidity--specifi-
cally, an increase in pH--was investigated. The operation of an electrodialysis
cell was found to cause a change in pH if the current density exceeds some value
critical for the concentration of solute. The concentrating stream increases in
pH; scale formation is in this stream, usually on the anion-permeable membrane.
The local change of pH against the membrane may be quite large compared to the
bulk change, and as a result some ambiguity exists in interpreting results of
scaling tests. However, it appears from the series of experiments described be-
low that the change of pH is not sufficient to cause scaling against charged mem-
branes and, in all likelihood, is not necessary.

An anion-permeable membrane separated two compartments, one of which held a
solution of sodium bicarbonate, the other calcium sulfate. Current through the
cell was in the direction to carry the bicarbonate ions through the membrane.
Hard scaling resulted on the calcium sulfate side. The experiment was repeated

with current direction reversed so that sulfate ions were carried through the membrane. No scaling resulted. The experiment was repeated with a cation-permeable membrane; when the current direction was such that the calcium ions were carried through the membrane into the solution of sodium bicarbonate, a slight discoloration appeared on the membrane on that side. When the current was reversed, a white scale formed on the calcium sulfate side; the scale was soft, soluble, and easily rubbed off.

It seems apparent from this series of experiments that changes occur because energy is added to the ions that are transported through the membrane. In the first instance, it seems likely that the bicarbonate ions were broken into hydrogen and carbonate ions during their passage through the membrane, while being elevated in internal energy. The carbonate ions then attached to the membrane matrix at the interface between liquid and membrane and were joined by free calcium ions to form a scale. In the second instance, the sulfate ions may have been unchanged in passing through the membrane, or they may have been changed in such a way that the combination at the interface was soluble so that no scaling occurred. In the third instance, the calcium ions would not be altered on passage through the membrane and could combine with only the few carbonate ions in equilibrium with the fluid at the interface. In the fourth instance, the sodium ions were carried through and attached to the membrane, forming sodium sulfate in the concentrated region near the membrane. Only the first of these, the calcium carbonate scaling, was insoluble enough to create a problem in electrodialysis

It seems then, that an anion-permeable membrane which is polarized sufficiently can transfer energy to an ion passing through it, causing the ion to change its species. If the new species is of a kind that will form an insoluble compound with a constituent of the fluid on the receiving side, the membrane will scale. This conclusion is most important to the practical operation of electrodialysis cells. Varying the pH of the fluids seemed to have little effect on the results. The critical situation seemed to be the charge on the membrane.

An important observation was made in the course of these experiments. The foregoing tests were made with homogeneous membranes; membranes with backing material made by another manufacturer were tested and found to scale easily. The scaling was in the center of the membranes, next to the backing material. These membranes could be split apart with thin outer layers of about 0.009 cm. thickness. The specific resistance of these films was measured and found to be 160 ohm cm.^{2}, whereas that of the center section was 1,200 ohm cm.^{2}. It is obvious that charge will collect on the interface between backing and surface materials and that this interface can be the site of precipitation. Therefore, manufacturers of membranes must see to it that any backing material included in the membranes very nearly maintains electric homogeneity with the active material of the membranes.

The energy which will change the bicarbonate ion to a carbonate can be supplied by the electric field in the fluid or by the electric field in the membrane. The energy density in the membrane, however, is greater than that in the fluid by the ratio of the dielectric constant of water to that of the membrane. It is therefore likely that the energy is acquired in the membrane.

The polarization of the membrane plays an essential part in the process. The polarization occurs slowly because of the reluctance of the membrane, as evidenced by the relaxation times. The electric field is reduced by the polarization, resulting in a decrease of current through the membrane and therefore through the entire system. The voltage applied to the system must be increased if a given current density is to be maintained; this increase is the polarization

voltage and represents energy which must be stored in the ions moving through the membrane, once equilibrium is reached. That the added energy does not go into joule heating can be deduced from the fact that the same current is carried by the same number of carriers as before polarization. This energy can, therefore, be internal energy, available for the separation of the bicarbonate ion.

Measurement of the voltage required for separation is feasible because of the decreased resistance of the system once separation has occurred. A study was made in a small cell with an anion-permeable membrane separating a sodium bicarbonate solution from a calcium sulfate solution, and with current in a direction to carry the bicarbonate ions through the membrane. Figure 5 shows the voltage-to-current relationship in this cell. In the low-current region may be seen the structure of voltages and conductivities which accompanies the initiation of direct current through electrolytes. In the center of the graph, a "limiting current density" characteristic is evident in the rapid increase in slope of the curve. It is this phenomenon which elevates the electric field at the membrane and induces polarization. At a polarization of 1.7 volts above the ohmic value, a second conduction mode is evident in the sudden change of slope. Cause of this second conduction mode is taken to be the current generated by the breakdown of the bicarbonate ion. The membrane scaled in the test illustrated.

As a test of the interpretation made here, the large unit at the Texas Electric Service Company laboratory in Fort Worth was operated at current densities which would induce polarization; applied voltage was increased to compensate for the polarization and thus to maintain a fixed current density, but the polarization voltage was not allowed to rise above 1.7 volts per anion-permeable membrane. As this voltage was approached, the current direction was reversed and maintained until the polarization voltage approached the critical value in the opposite direction. Operation in this manner was continued for many days of operation with no scaling resulting. The voltage was then allowed to rise above this critical value, but not high enough to generate a marked change in pH. The membranes scaled markedly in one day's operation under this condition.

The tests reported here seem to be fairly conclusive in establishing that (a) scale formation is caused by the altering of an ion (bicarbonate) which is soluble when joined with ions of the opposite sign present in the fluid into an ion (carbonate) which can form insoluble products (such as calcium carbonate); (b) this alteration occurs in the process of an ion's passage through the membrane; and (c) the energy required to induce this alteration is 1.7 volts. If electrodialysis units are operated in such a manner that the polarization voltage induced in each anion-permeable membrane is less than 1.7 volts, the membranes will not scale.

Condition for the Onset of Polarization

The condition for the onset of polarization has been previously identified for streams in turbulent flow [2]. The value of j/C_o (j is current density; C_o is midstream conductivity of the dilute stream) is about 6 volts per cm. at the onset of turbulence and increases with the seven-eighths power of velocity. The comparable value for streamflow which is not in true turbulence but is mixed by a

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[2] Cowan, D. A., and Brown, J. H., 1959, Effect of turbulence on limiting currents in electrodialysis cells: Indus. and Eng. Chemistry, v. 51, p. 1445-1448.
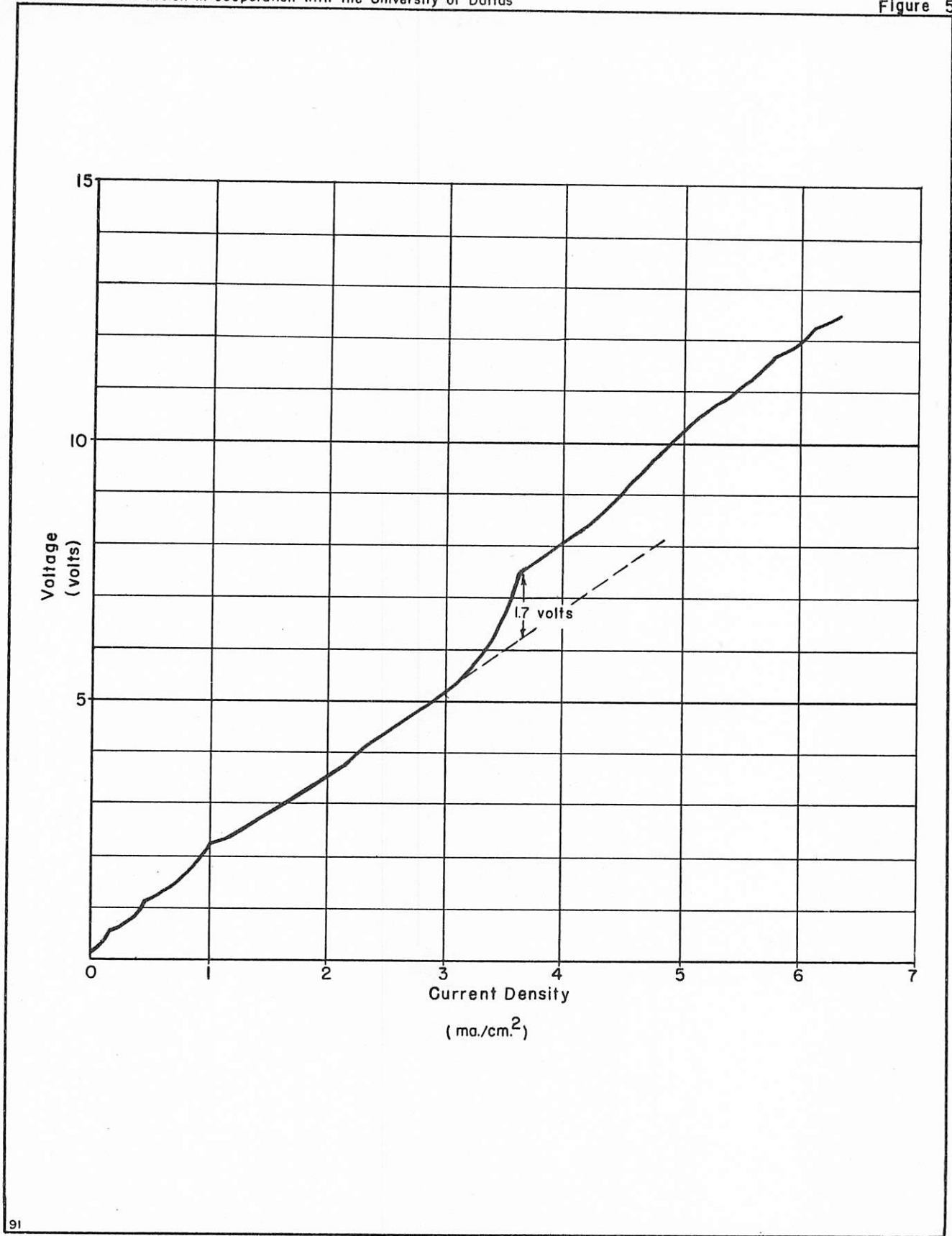
FIGURE 5.— Relation of voltage, across a single anion membrane through which bicarbonate ions are passing, to current density

grill cloth inserted between the membranes has not been fully determined. A study of this property is shown in Figure 6. The value is 6.6 volts per cm. at a flow velocity of 10.9 cm. per second; the value increases with the one-half power of velocity.

On the supposition that polarization results from the exhaustion of ions in the laminar layer at the interface of membrane and fluid, a theory predicting this critical value of current density for the onset of polarization can be made; the values so predicted can be identified with the experimental ones. This identification is consistent for turbulent flow where the onset is quite sudden, but for flow resulting from separation-mixing, the laminar layer is not so well defined. A slow-developing polarization has been found above a threshold value of about 1.6 volts per cm. The study which follows considers the contribution of the membrane to polarization. More investigation is needed on this point.

Polarization of Membranes in Electrodialysis

The electric current through an electrodialysis demineralizing cell decreases with time at a given applied voltage (Figure 7), this decrease diminishing the cell's efficiency. The time required for the decrease varies with the composition of the membranes and the operating conditions of the cell. Remedies in use for this disadvantageous characteristic are (a) periodic reversal of voltage with alternation of dilute and concentrate streams, (b) reverse-voltage pulsing, and (c) dismantling and reassembly of the cell. The analysis presented below may prove useful in an evaluation of these remedies.

Two characteristics of this decrease in current are worthy of note: first, it does not occur unless the operating current density exceeds critical value; second, if the cell has been operating in excess of this critical current density, the membranes retain a very slowly disappearing charge after the external voltage is removed. The resulting voltage, V, may be expressed as

$$V = V_o \sum_i a_i (1 - e^{-t/T_i}).$$

By the nature of its use, the material from which ion-selective membranes are made is polarizable; and its high-polymer structure ensures there being many different retention components, each with its own amplitude coefficient, a_i, and relaxation time, T_i. These same coefficients and relaxation times may be assumed to be applicable in the charging of membranes.

The voltage drop across an electrodialysis stack is

$$V = V_e + rj + V_p + V_m.$$

Here V_e is the electrode voltage plus any other constant voltages in the system, such as concentration voltage. The term r is the sum of all of the ohmic resistances: that of the diluting and concentrating streams and of the anion- and cation-permeable membranes. V_m is the voltage drop across the membranes.

The onset of polarization is more clearly shown by the choice of variables shown on the graph. The critical field value j/C_0, which is 6.6 volts/cm. on the graph, increases as the velocity of flow increases.

$C = 2,000$ μmho/cm. $A = 400$ cm.^{2} Flow is 19cc./sec. through passage 10 cm. x 0.25cm. filled with grill cloth (0.3 of volume). Average velocity is 10.9 cm./sec.

Y-axis: Voltage x Conductivity / Current Density (unit = cm.)

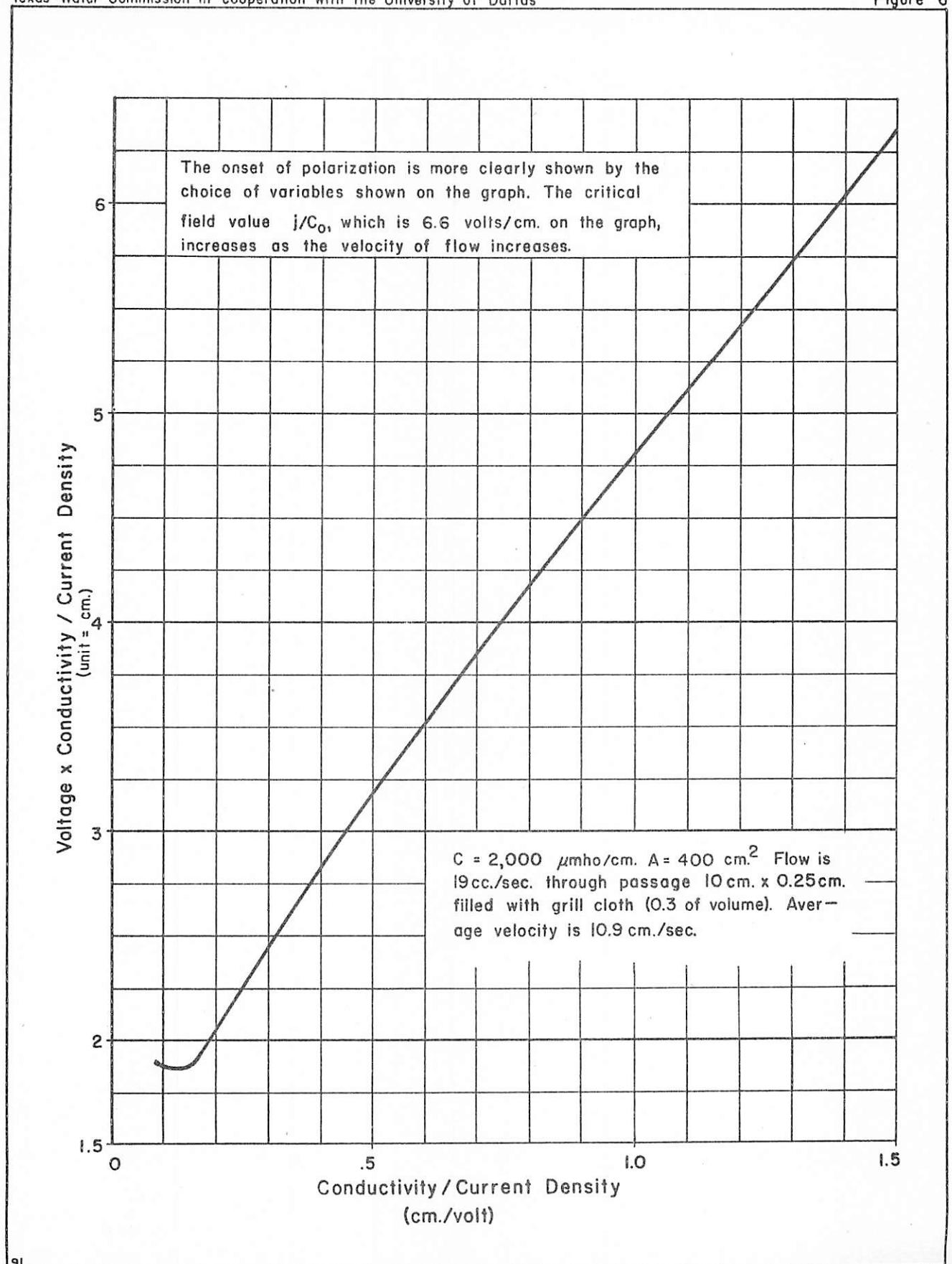**X-axis:** Conductivity / Current Density (cm./volt)

FIGURE 6.- Relation of critical field value, j/C_0, to velocity of flow for sodium sulfate solution
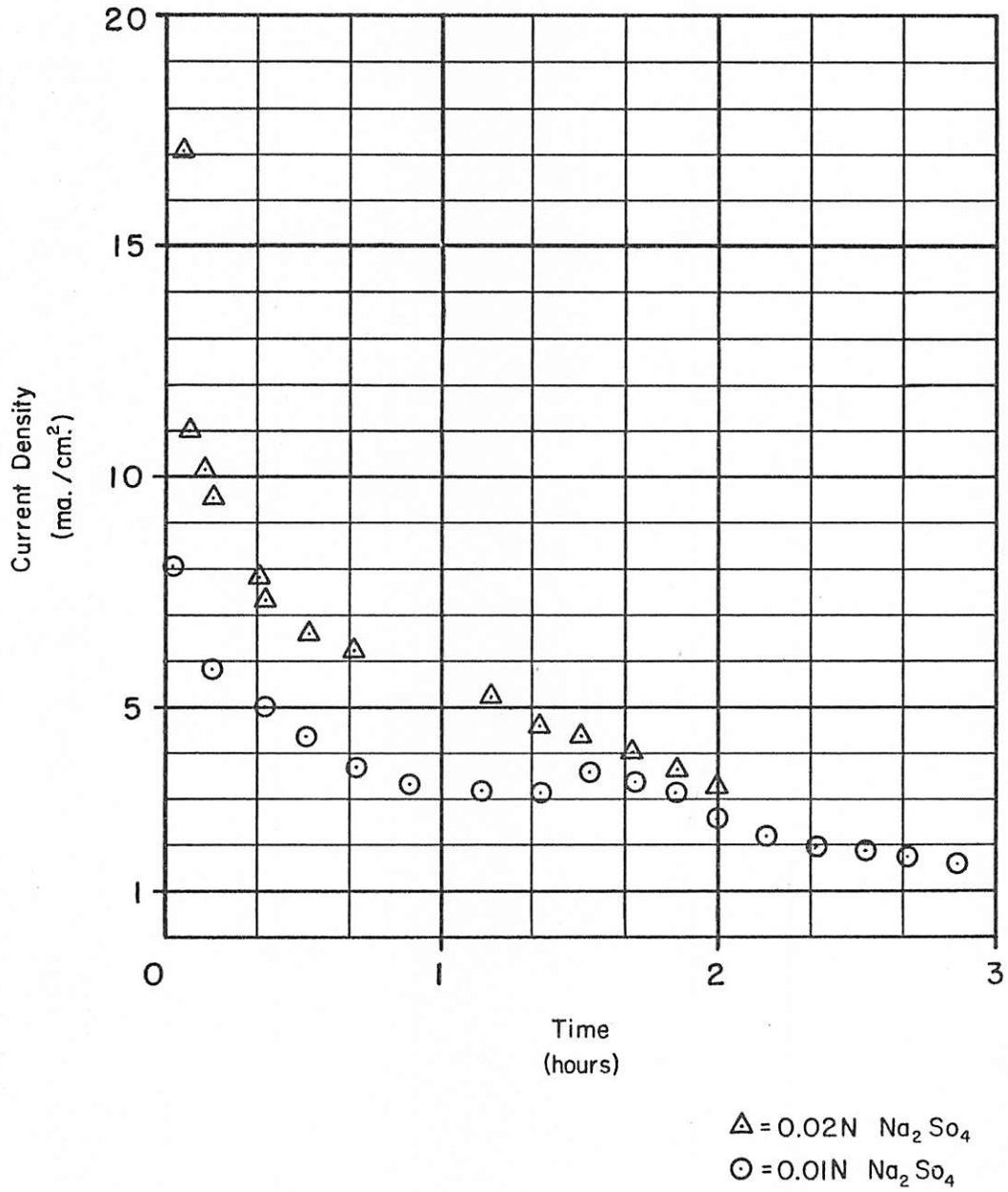
Figure 7.— Decrease of current density with time at a constant applied
voltage across a demineralizing cell

The voltage across a laminar layer in the dilute stream next to a membrane, V_p, is given by the expression

$$V_p = \theta \ln(1 - j\delta/C_o\theta)^{-1}.$$

The thickness of the laminar stream is δ, C_o is the dilute concentration in midstream, and θ is a voltage characteristic of the ion;

$$\theta = \frac{FDN}{tC_o},$$

where F is the Faraday, D is the diffusion coefficient of the salt, N is normality, and t is the transport number in the fluid of the ion not being carried through the membrane. A current density limit, j_o, may be defined:

$$j_o = C_o\theta/\delta.$$

In actuality this current density may be exceeded because of a second conduction mode which sets in at elevated voltages, but the extra conduction is at the expense of additional energy and is accompanied by pH changes in the streams.

The remaining voltage is the one which is of concern here. This voltage is induced by charge which occurs on the membrane surface. This charge is bound by the discontinuity of the electric field at the interface of fluid and membrane. Nevertheless the membrane polarizes, and as the charge is effectively transferred to its far side the entire membrane becomes penetrated by an additional field. (The surface charge density is, properly, the surface divergence in displacement, but the conductivity as measured on a low-frequency bridge (or by D.C.) includes the effect of the dielectric for water and also for membranes insofar as their prompt response is concerned.) Therefore the surface charge density on a membrane, σ, is given by

$$4\pi\sigma = j/C_o\left[(1 - j/j_o)^{-1} - C_o/C_m\right],$$

where C_m is the specific conductivity of the membrane. The voltage resulting from the consequent polarization, V_m, is given by

$$V_m = j/C_o\left[d_m(1 - j/j_o)^{-1} - C_o/C_m\sum_i a_i(1-e^{-t/T_i})\right],$$

where d_m is the thickness of the membrane.

This voltage not only varies with time but also changes signs as current density is increased, passing through zero at a critical density, j_c, given by

$$j_c/j_o = 1 - C_o/C_m.$$

A high specific conductivity of the membrane places this critical current density near the limiting current density; but as the diluting stream becomes more dilute, not only does the limiting current decrease but the critical current density becomes a smaller fraction of the limiting current density. It is to be noted that the total resistance of the membrane is not concerned in this value; rather, it is the specific conductivity that is involved, regardless of thickness.

The longer term contribution of the relaxing voltage can be avoided by a reversal of roles for dilute and concentrate streams: the electric leads are switched and the outlets of the product water are exchanged. The more frequent this reversal the higher may be the value of current density for any predetermined voltage increase. Voltage is limited not only by economy but by the effects on ions with excess energy gained in passing through the charged membranes. Experience shows that it is the anion-permeable membrane which scales; it seems likely that the process consists of a bicarbonate ion becoming a carbonate ion under the influence of the field in the membrane and attaching itself to the concentrate surface of the anion-permeable membrane on which a positive charge resides. A polarization voltage of 1.7 volts per anion-permeable membrane seems to accomplish this transition. Therefore, it is expedient to keep membrane polarization below this level.

Short, high-value reverse pulses might be used to depolarize the membranes (as K. S. Spiegler suggested at the Saline Water Conference of the American Chemical Society in St. Louis, March 27, 1961); these pulses could be quite frequent and would therefore limit even the short relaxation voltages to low levels. A disadvantage of this method lies in its low current efficiency, the result of a relatively large charge that is released and sent backward through the system on each reverse pulse. (The possibility of membrane material as a memory element is obvious in this release of charge.)

Operation in the region of the critical current density obviates these troubles and thus allows a more simple design of equipment. This critical value, however, is likely to be less than economically feasible current densities at the dilute end of the stream unless the membranes are of high specific conductivity.

According to the analysis presented here, the conditions under which current reversal in electrodialysis demineralizers must be practiced can be determined from a knowledge of membrane conductivity and ionic characteristics of diffusion and conductivity.

$$j/(C_o - C_m) > j_o/C_o.$$

The minimum frequency of current reversal can be set from a knowledge of membrane relaxation characteristics and some criterion for maximum membrane polarization.

Energy with which Salt is Bound in Water

Ions of salt dissolved in water replace water molecules in the quasi-crystalline structure of liquids. It may be supposed that each ion has its charge neutralized by the polarization of the associated water molecules and that, in effect, one ion replaces one molecule of water in the continuum. Thus, each dissociated molecule of sodium chloride is bound in the fluid by an energy $E_{Na} + E_{Cl} - 2E_{H_2O}$.

A particle of mass m which participates in a sonic field is bound in that field by an energy mv^2, where v is the sonic velocity. Accordingly, the energy with which salt is bound in sea water of 36 parts per thousand (here considered as all sodium chloride) at 25°C is 35.1 kwhr per thousand gallons: $(m_{NaCl} - 2m_{H_2O}) v^2$. Alternatively, the density of sea water times the velocity of sound squared in sea water minus the like product in distilled water yields very nearly the same value. It is energy which does not become evident in vapor-pressure comparison of saline water to pure water. The energy expended in the separation of ions is not likely to be recovered in any desalinization process; therefore the entire energy of structure must be supplied in the separation of salt from water.

Binding Energy of Water

The proposition that a particle occupies a site in a sonic medium with an energy $-mv^2$, where m is the mass of the particle and v is the sonic velocity, appears to be a useful concept, applicable to evaluations of the physical properties of the medium. In the present paper, attention is confined to the specific heat of water and the heat of vaporization.

The molecules of water are bound in a quasi-crystalline lattice. Accordingly, it is to be expected that a least-volume of phase space is defined by the medium and its particles such that $mv\Delta x = nh$ where n is an integer, h is an action constant, and Δx is a least definable interval of space. If the relation $\Delta x = v/2\nu$ exists, where ν is frequency, then there follows the energy equation $mv^2 = 2nh\nu$, and a spectrum of frequencies is thus defined. A particle will not, in general, be in its ground state but is a state $mv^2/2n$ above this lowest level. Its total energy will then be $-mv^2(1-1/2n)$. The distribution among states may be supposed to be governed by the availability of oscillatory states proportional to

$$\int \nu^2 (\exp h\nu/kT -1)^{-1} d\nu,$$

integrated over an interval of interest. The constant k is Boltzman's constant. Substitution of the equality $mv^2/2n$ for $h\nu$, and a choice of frequency intervals associated with integers, results in an energy distribution

$$mv^2\left(\frac{2n-1}{2n}\right) \frac{n^{-4}(\exp mv^2/2nkT -1)^{-1}}{\sum\limits_{n=1}^{\infty} n^{-4}(\exp mv^2/2nkT -1)^{-1}} (\exp mv^2/kT -1)^{-1}.$$

The average kinetic energy in this scheme is 0.092 electron-volts at 100°C, or, that is, 2.85 kT. The ground state energy is -0.447 electron-volts and consequently the average total energy E is -0.355 electron-volts, or 451 calories per gram. The heat of vaporization must supply this energy as well as the kinetic energy of the molecules in the gaseous state, which is 3kT; as a credit, it gains the "energy of structure" of the gas, mv^2. The velocity of sound in steam is 404.8 meters per second, resulting in a ground state energy of the gas molecule E_g of -0.95 kT. The total heat of vaporization, H, is then

$$H = -E + 3kT + E_g = (451 + 124 - 39) \text{ cal./gm.}$$
$$= 536 \text{ cal./gm.}$$

The velocity of sound in water increases with temperature up to 74.5°C, where it passes through its maximum value. Accordingly, the ground state has its greatest negative value at this temperature. The excited (kinetic) energy increases steadily with temperature, however, because of the shifting of the molecules to higher energy states. The distribution exponent mv^2/kT maximizes at about 30°C. The two effects combine to place the minimum of the kT coefficient at about 35°C, where specific heat minimizes. In fact, the coefficient multiplied by k is very nearly three-tenths of the specific heat over the range from 0°C to 100°C. The trend is reflected accurately, but absolute comparison is limited by the accuracy with which the calculations for this paper were made-- about 1 percent.

A Beginning on a Theory of Conductivity

The spectrum of voltages which is encountered in polarography and in electrodialysis along with a spectrum of conductivities suggests that an understanding of electrolytic conduction might profit by a fresh approach to theory. The theory presented here is as yet incomplete. It accounts for the low-current structure of voltages and conductivities satisfactorily and is in fair agreement with the ratio of transference numbers. It has only an approximate agreement with equivalent conductances. Some features of the theory need redefinition; it is likely that in the process of redefinition new insight into the structure of fluids can be gained. Several features of the theory are appealing--among them, the possibility that weak electrolytes obey an exclusion principle while strong electrolytes do not.

Current density in an electrolyte can be assumed to be as it is in gasses,

$$j \, t = n \, q \, \bar{v},$$

where j is the current density, t is the fraction of the current being carried by the species under study, n is the number of current carries of charge q and average velocity $\bar{v}$. Because Ohm's law is observed to hold over a restricted region, the idea of mobility u is introduced to describe the drift of charge proportional to the applied electric field E.

$$j \, t = n \, q \, u \, E.$$

The concept of a drift velocity superimposed on a random motion of particles encounters anomalies having to do with mean-free-path in a liquid. The idea of an average velocity might better be replaced by a field velocity associated with discrete particles of mass m.

$$\bar{v} = \sqrt{Energy/m} \quad = \sqrt{KE^2/nm} \ ,$$

where K is the dielectric constant of the fluid.

The expression for current density becomes

$$jt = \hat{E}\sqrt{nK/mq} \ ,$$

where t is the transference number, or fraction of the total current carried by the ion species.

The coefficient of E is the conductivity, which can be expressed as equivalent conductance λ;

$$\lambda = f(c) \ \hat{F}\sqrt{K/nm} \ .$$

The Faraday F has been introduced, and a distinction must be made between the density of current carriers n and the concentration c of ions.

$$n = f(c)c.$$

The variation with the square root of n is in accord with the variation of weak electrolytes at dilute solution, but if the equivalent conductance of strong electrolytes is to be described as above, then the function f(c) must vary with concentration.

The function f(c) states the probability of an ion's being in a conducting state. The possible energy states of an ion may be presumed to be $E_0(1/s - 1)$, where E_0 is the binding energy of the ion in the fluid and s is an integer. For particles which do not obey an exclusion principle, the distribution is

$$n_s = g_s(\exp E_s/kT^{-1})^{-1},$$

where k is Boltzman's constant, T is absolute temperature, E_s is the energy in the s state, and g_s is the number of eigen states within the s cells.

The quantity g_s is proportional to the ratio of the volume V of the "container" to the "momentum volume" of the particle;

$$g_s \approx V(p/h)^3 = ca \ s^{-3/2}(s+1)^{-1},$$

where p is momentum, h is the action constant, $\underline{a}$ is a constant of the ion and the presumption is made that the "container" for all ions is available to any one ion.

The distribution function is then

$$f(c) = ca \sum_{1}^{s^1} s^{-3/2} (s+1)^{-1} (\exp E_O/skT -1)^{-1}.$$

The expression for equivalent conductance can now be stated:

$$\lambda = F\sqrt{K/m} \left[a \sum_{1}^{s^1} s^{-3/2} (s+1)^{-1} (\exp E_O/skT -1)^{-1} \right]^{1/2}.$$
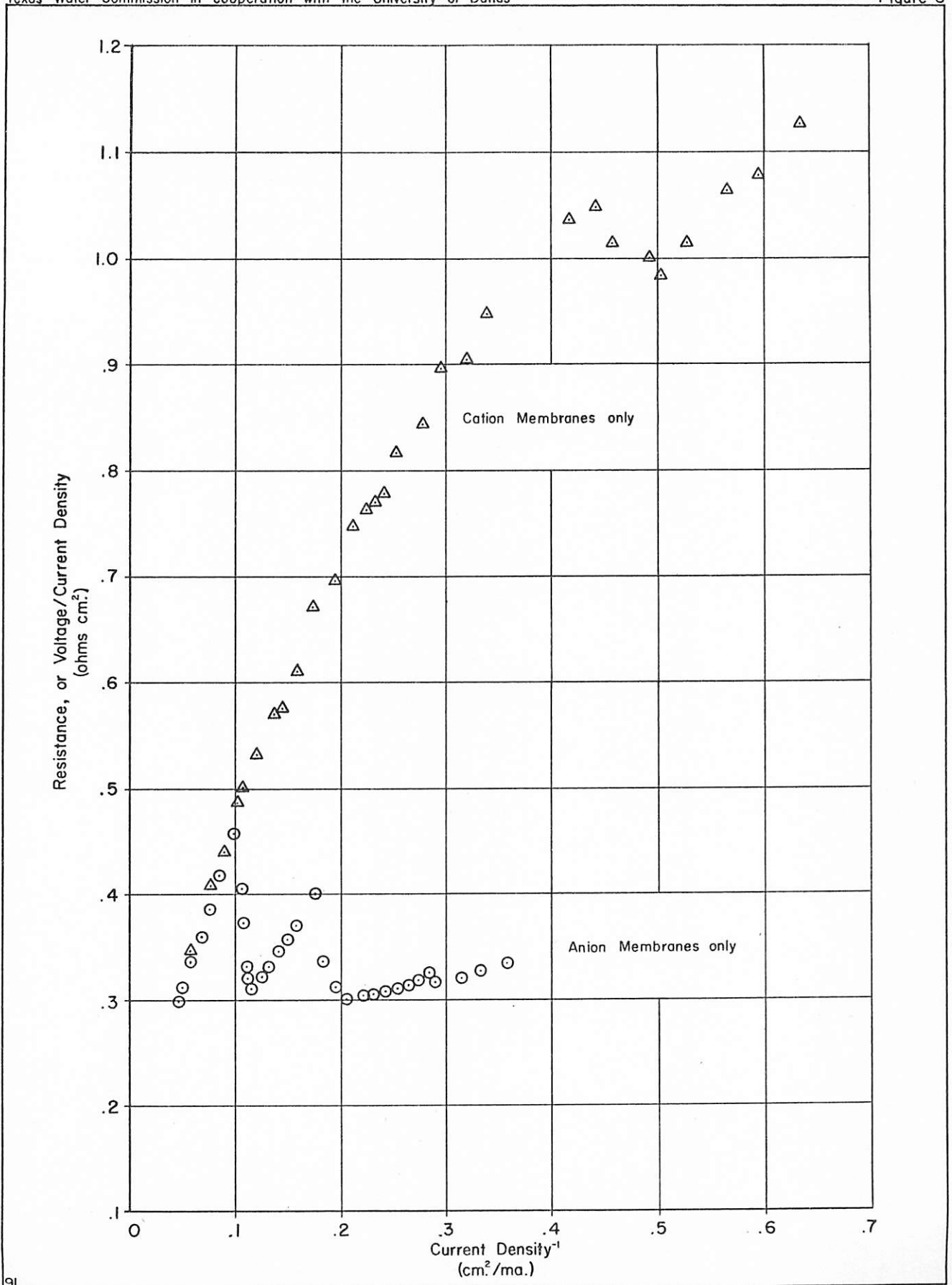
The binding energy E_O can be equated to mv^2 where m is the mass of the ion and v is the velocity of sound in the fluid. Such an identification yields a spectrum of voltages in agreement with some experimental values. The ion constant $\underline{a}$ should be derivable from geometric constants; if this derivation can be made, no adjustable parameters would remain in the expression. Limitation of the available volume to near neighbors would provide the desired decrease of equivalent conductance with concentration.

Evidence for the energy levels E_s has been obtained in experiments performed under this contract. Figures 8 and 9 show ratios of voltage to current density plotted against reciprocals of current density for potassium chloride and sodium bicarbonate solutions. Data for these graphs were gathered from small static cells.

The same type of information shows up in the larger, flowing cell. Experiments Nos. 45 and 46 were made with no membranes between the carbon electrodes. The thickness of the stream--that is, the distance between electrodes--was 1 cm.; the width was 5 cm.; the flow rate was 1.3 gpm or 16.4 cm. per second, a rather slow flow rate, but corrugated spacers were included in the stream so that turbulence was simulated. The two runs were identical except that Experiment 46 had three times the concentration of salt that Experiment 45 had. The salt used was sodium sulfate. The results are displayed in Figure 10.

Experiment 47 was similar in all dimensions except for the insertion of membranes. Three membranes--one anion-permeable and two cation-permeable--separated the flow into four stream of 0.25 cm. thickness each. The corrugated spacers were in each stream. The two electrode streams were of the same concentration as in Experiment 45 and flowed at about the same velocity. One of the center streams had cation-permeable membranes on both sides so as to be non-diluting; this stream had an intermediate concentration and ran at intermediate velocity. The other stream, the study stream, had the concentration of Experiment 46 and a flow velocity of 21.6 cm. per second. (See Table 1.)

The run consists of voltage measurements at increasing current densities. These data are then plotted as V/I against 1/I, V being the voltage and I the current across the 400 cm.^{2} area of the cell. This manner of plotting identifies the resistance of the circuit as the intercept on the V/I axis and identifies the voltage of activation or other non-ohmic response as the slope of the graph, and is, therefore, much more revealing of variations than the more commonly used voltage against current graphs. The beginning, low-current densities are in the upper right hand corner of the graph, and the intercept with the resistance axis represents an infinite current.

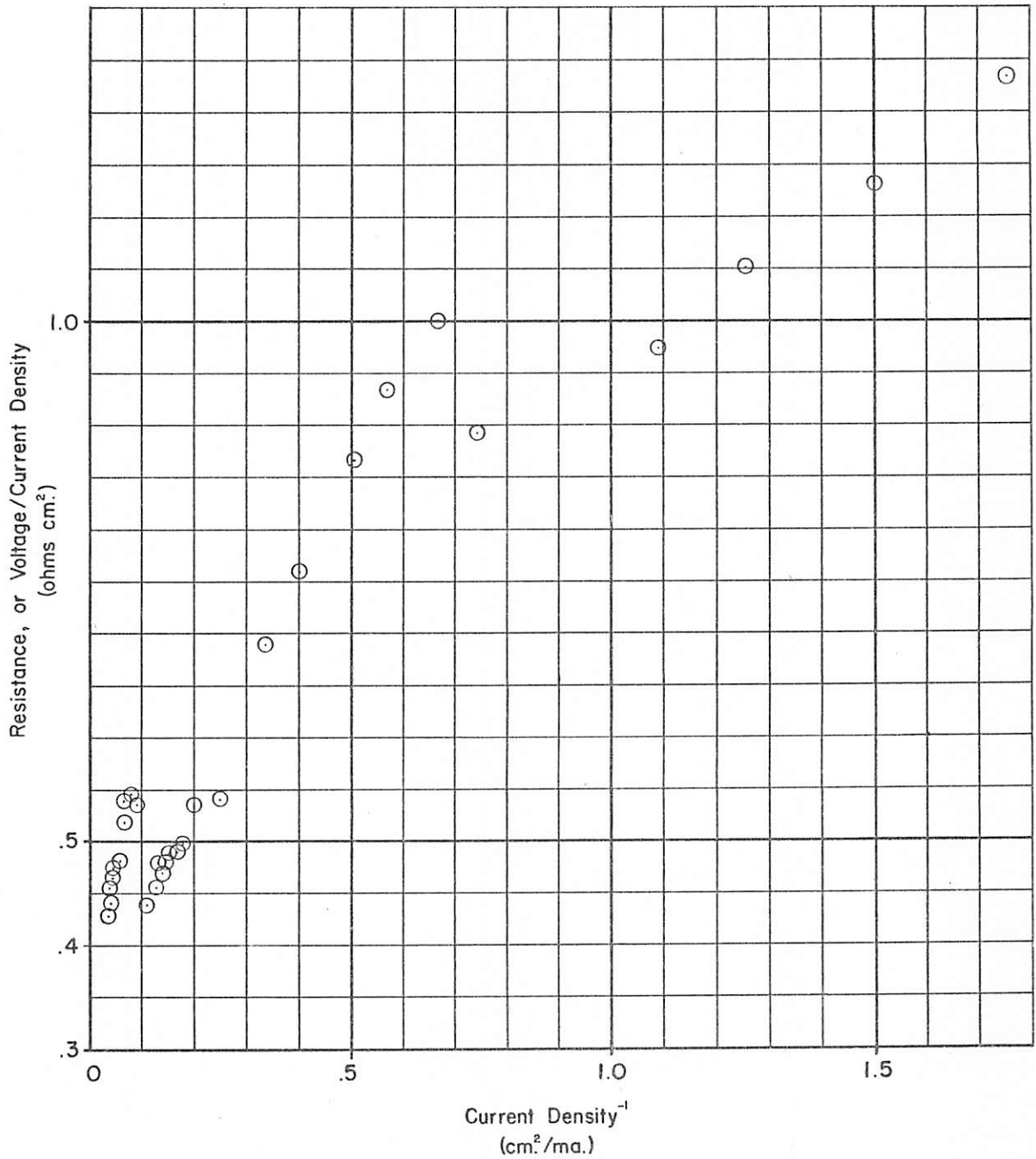Figure 8.—Resistances of 0.1 normal potassium chloride solution, determined with static cells

Figure 9.—Resistances of 0.1 normal sodium bicarbonate solution,
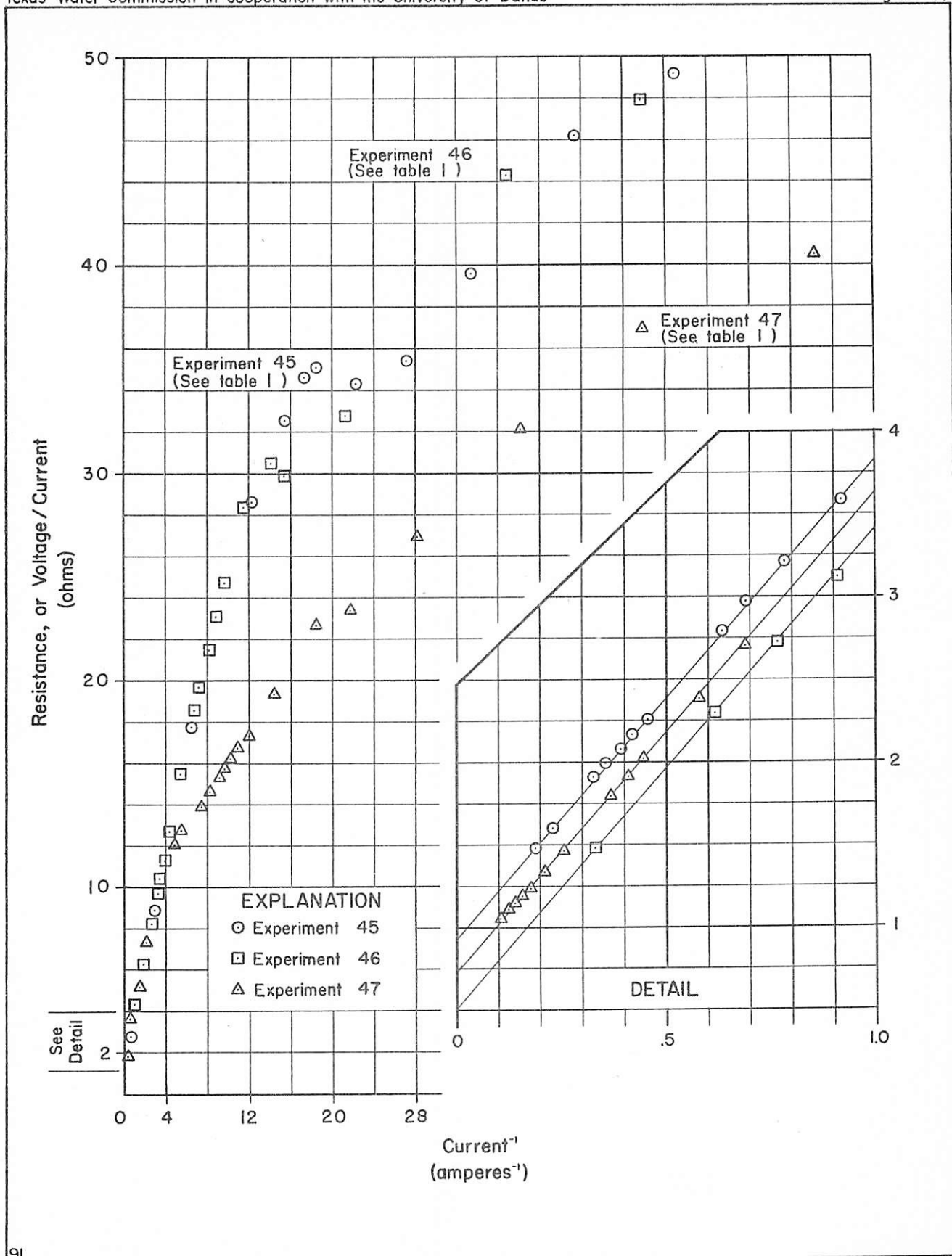determined with static cells

FIGURE IO. — Resistances of sodium sulfate solutions, determined with flowing cell

Table 1. - Experimental conditions under which data plotted
in Figure 10 were obtained.

Experiment 45
(No Membranes)

Fluid normality 0.004. Calculated cell resistance 0.95 ohm. Flow velocity 16.4
cm./sec.

Voltage	0.5	0.67	2.55	2.87
Resistance (ohms)	17.3	12.7	2.40	.95
Limiting current (ma./cm^2.)	.09	.11	.2	--

Experiment 46
(No Membranes)

Fluid normality 0.012. Calculated cell resistance 0.52 ohm. Flow velocity 16.4
cm./sec.

Voltage	0.5	0.73	2.55	2.87
Resistance	17.1	--	2.05	.53
Limiting current	--	.16	.21	--

Experiment 47
(Two anion-permeable, one cation-permeable membrane)

Study stream normality 0.004, 21.6 cm./sec.; buffer stream, 183 ohm cm., 21.5°C,
18 cm./sec.; electrode streams 83.9 ohm cm., 18 cm./sec.

Voltage	--	1.08	1.9	2.87
Resistance	11.8	8.1	1.96	.74
Limiting current	.11	.35	.83	--

The high-current response for this study, constituting the lower end of the graph in Figure 10, is substantially the same for all three runs. An expanded detail of this section is included in the lower right portion of the graph. The intercepts can be easily identified; the resistance they indicate is quite in accord with expectations. If we assign a value 0.30 ohm to the resistance of the external circuit and the electrodes, then Experiments 45 and 46 have the resistance values calculated for them, and Experiment 47 has a value indicating that the resistance of the three membranes is 16 ohm cm.^{2}, very nearly the value specified by the manufacturer.

The voltage slope in the high-current region is 2.87 volts for all three runs. At current densities less than about 8 milliamperes per cm.^{2} the voltage slope varies, running through a spectrum of slopes and intercepts--that is, activation voltages and fluid resistance--for each run. These spectra are displayed in Figure 10. This information provides new and important clues to the nature of electrolytic conduction.

One of the surprising features of these results is the lower resistance of the fluid with membranes, compared to no membranes in the cell, at all levels of operation other than full conductivity. Evidently current carriers are generated at each surface.
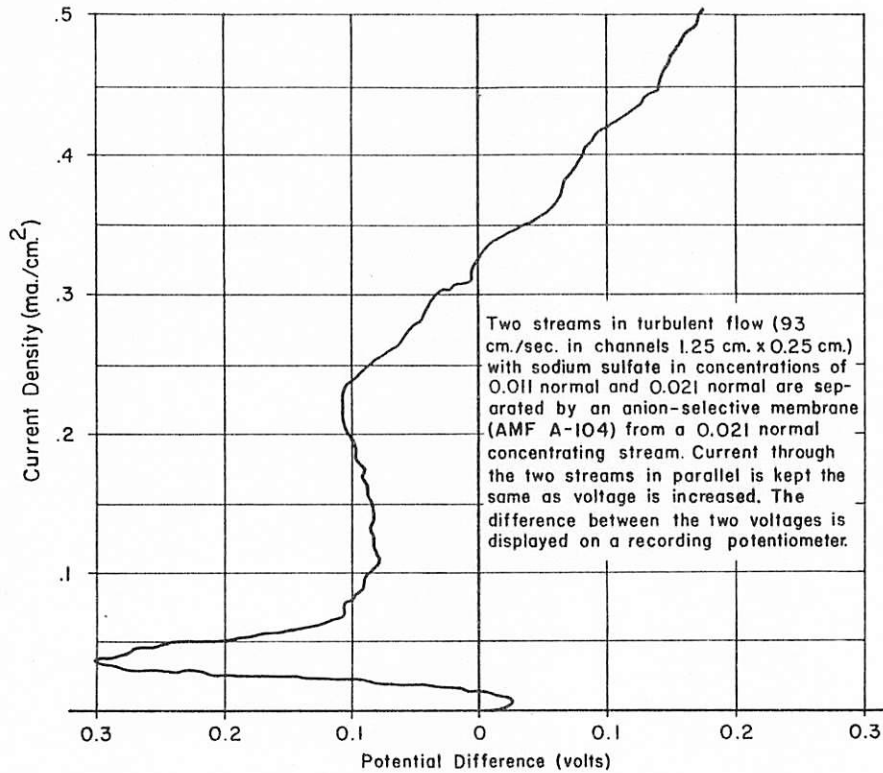
A study in the flowing cell arranged for parallel flow compared the voltages across streams of two different concentrations of sodium sulfate (Figure 11); the structure of voltages was evident but an unanticipated result was the indication that these voltages, which are the energy per charge needed to bring ions from their equilibrium state into a conducting state, increases with concentration. The theory presented above did not provide for this variation; it may be, however, that the variation of the distribution function with concentration, introduced ad hoc into the theory, can be related to the energy variation. Considerably more investigation is needed on this point; it seems likely to be an important one in the development of an adequate theory of electrolytic conduction.
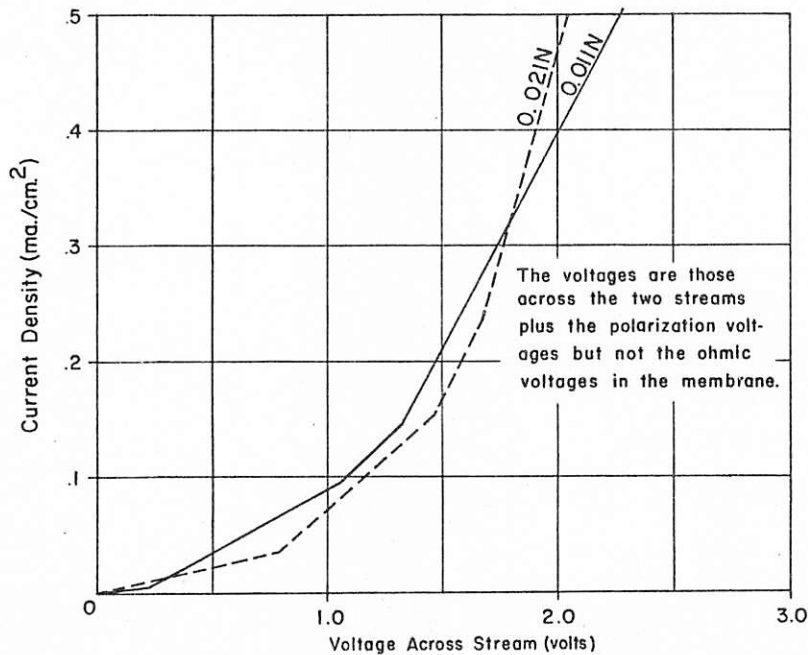
CONCLUSION AND RECOMMENDATION

This research project has established the fact that scale forms when ions pass through membranes which are polarized above some critical value, this polarization voltage being in addition to the ohmic voltage. The critical polarization voltage for the bicarbonate ion, which is the usual offender, is 1.7 volts. Polarization occurs if the current density is great enough to demineralize the water against the membrane sufficiently to cause the electric field in the water to exceed the field in the membrane; the polarization voltage can rise slowly, with the critical value not reached for several hours or days, the time depending on the current density and membrane reluctance. The resistance of the membranes is an important parameter for the determination of an acceptable current density.

A large demineralizer could be built at the present time with some assurance of successful operation if precautions against the critical polarization voltage were insured. It would be wise, however, to settle the following points before a field installation is initiated:

1. A method of measurement for membrane conductivity must be developed. Present methods do not give correct or useful values. The dielectric constant must also be established in these measurements. These two parameters are essential to the design of a non-polarizing system.

- 27 -

Current Density (ma./cm.²)

Two streams in turbulent flow (93 cm./sec. in channels 1.25 cm. x 0.25 cm.) with sodium sulfate in concentrations of 0.011 normal and 0.021 normal are separated by an anion-selective membrane (AMF A-104) from a 0.021 normal concentrating stream. Current through the two streams in parallel is kept the same as voltage is increased. The difference between the two voltages is displayed on a recording potentiometer.

Potential Difference (volts)

(a) Variation with current density of the difference of potential between two cells of different concentrations

Current Density (ma./cm.²)

The voltages are those across the two streams plus the polarization voltages but not the ohmic voltages in the membrane.

Voltage Across Stream (volts)

(b) Possible polarization voltages which would account for the curve in (a), above

FIGURE II.–Polorization voltages for two streams of different concentrations

2. Membrane reluctance and lifetime under current reversals must be determined.

3. The extent to which concentration and precipitation can be used in the disposal of brine must be determined.

When these three unknown conditions are ascertained, a field installation should be designed and constructed. This plant should be placed in operation and tested for an extended period. The plan of gradually increasing desalinization up to rated design in two years should prove practical.

A practical plant can be built in the absence of a total theory for electrolytic conduction and permselective transmission. But optimum designs and innovations are largely dependent on an adequate theory. A full study of the levels of conductivity which have been uncovered in this research needs to be made in order to provide the data which can guide the development of a complete theory.

It is recommended, therefore, that the studies initiated under this contract be continued along the lines enumerated above, with the subsequent intention of initiating a field unit implicit in this continuation.

APPENDIX

A STUDY OF MEMBRANE POLARIZATION

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A STUDY OF MEMBRANE POLARIZATION

An electrodialysis demineralizer exhibits membrane polarization if it is operated above some critical current density. An experimental study of this polarization has been made on the 40-foot experimental demineralizer at the Texas Electric Service Company laboratories. This unit has passages 0.1 inch thick and 7 inches wide; the flow is straight for 40 feet. Grill cloth fills each stream so that membrane separation is maintained and mixing is effected to simulate turbulence. The arrangement employed here has seven cation-permeable membranes (AMF ion C-103) and six anion-permeable membranes (AMF ion A-60), resulting in six diluting, six concentrating, and two electrode streams. The electrode streams employ highly concentrated solutions of sodium sulfate and are mixed and recirculated. A mixture of salts is used in the other streams (625 ppm $CaSO_4$, 450 ppm $MgSO_4$, 110 ppm Na_2SO_4, and 225 ppm N_aHCO_3 in municipally treated water), and this water, too, is remixed and recirculated until the composition changes markedly. (Calcium is preferentially removed to the electrode stream.) Some results of the study are here reported.

Polarization Voltage

The membrane polarization voltage measured agrees with calculated values, if calculations are based on the assumption that the voltage is a result of the charge at the interface between fluid and membrane. The expression for this voltage is

$$V_{pm} = j\frac{nd}{C_o}\left[(1 - j/j_o)^{-1} - \frac{C_o}{C_m}\right].$$

In this expression j is current density, j_o is limiting current density, n is the number of polarized membranes and d is the thickness of each, C_o is the midstream conductivity of the diluting stream, and C_m is the membrane _specific_ conductivity. The agreement of experimental data with curves obtained from this expression is shown in Figure A1. In plotting the upper curve, values of limiting current, membrane conductivity, and membrane thickness were chosen for best fit to the data; however, the value of conductivity determined, 1,160 micromhos per cm., may be compared to the measured value of 1,280 micromhos per cm.; and the thickness nd of 0.46 cm., with n being 12 in the arrangement used, may be compared to measured values of 0.36 cm. The limiting current density is given by the expression

$$j_o = FND/\delta t,$$

where F is the Faraday, N is normality of the solution (in equivalents per cc.), D is the diffusion coefficient, δ is the thickness of the laminar layer next to the membranes in the diluting streams, and t is the larger of the transport numbers for the conducting ions in the fluid. Since thickness of the laminar layer is not known, the limiting current must be evaluated from data; however, in low-velocity flow in which turbulence is effected by a grill cloth placed in the stream, the laminar layer thickness decreases very nearly with the square root

of flow velocity increase. In fact, the limiting current density, j_o, in the flow region of interest is very nearly

$$j_o/C_o = 4.4\ U^{\frac{1}{2}},$$

in volts per centimeter, where U is the flow rate in gallons per minute per square inch of cross section. (A flow rate of 1 gpm in channels 7 inches wide and 0.1 inch thick yields 5.24 volts/cm.) The lower curve of Figure A1 is based on the assumption that this thickness-velocity relationship holds; it employs the same constants as the curve above and is not fitted to data, and still the agreement is good. Other studies have revealed that a second mode of conduction sets in at voltages slightly in excess of those shown here so that the current "limit" can be exceeded.

The polarization voltage in the _fluid_,

$$V_{pf} = FND/C_o{}^t\ \ln(1 - j/j_o)^{-1},$$

would have observable values only at current densities very near the limiting current density and would rise very sharply in this region. The shape of the voltage curve is good evidence that the polarization observed arises from charge on the membrane.

Creeping Voltage

A further indication that the observed polarization is within the membrane lies in the phenomenon of "creeping voltage": if a constant current through the stack of electrodialysis cells is to be maintained, the voltage must be increased steadily when the cells are in operation. The creeping occurs if the current density exceeds a critical value:
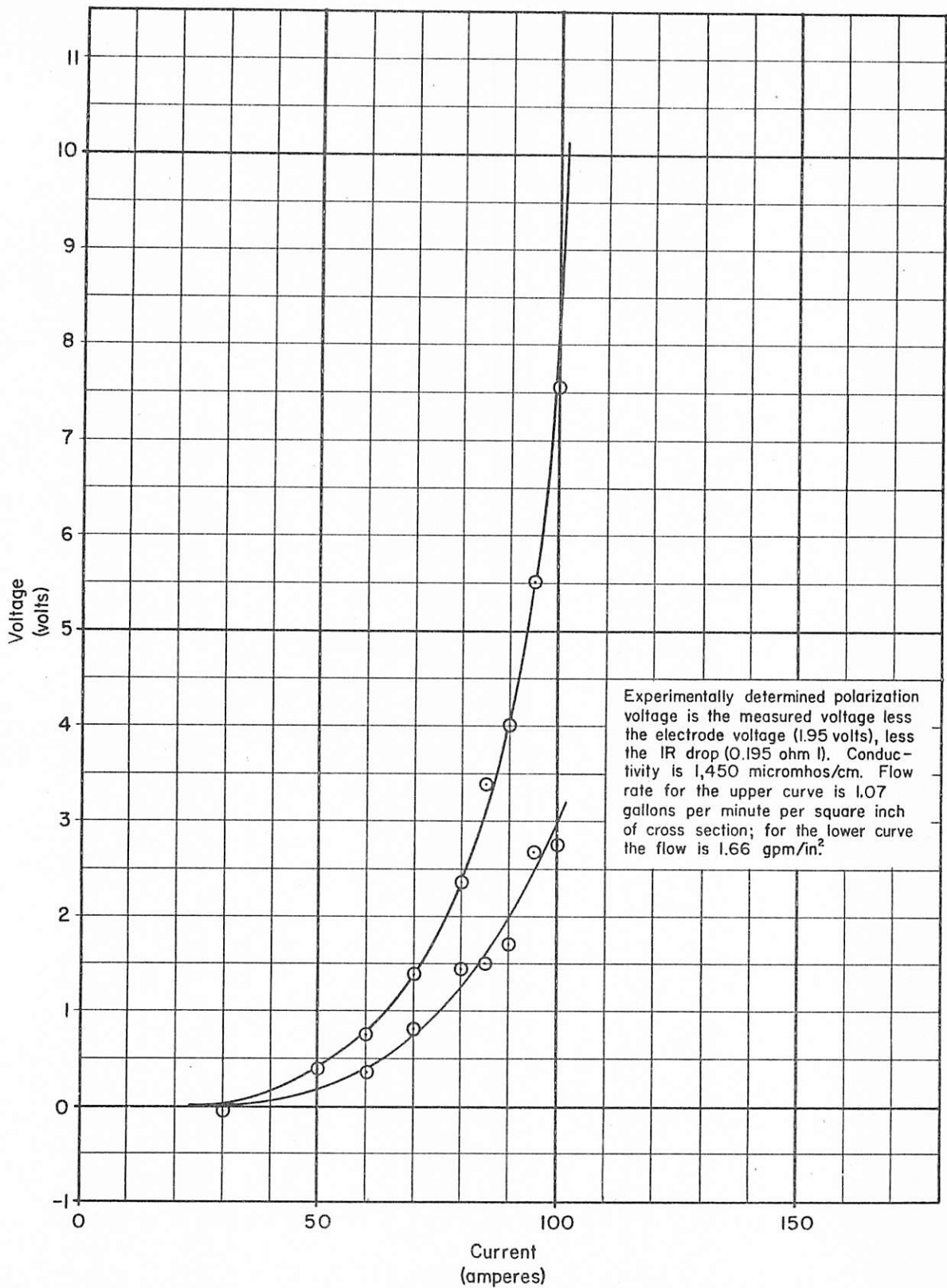
$$j/(C_o - C_m) > j_o/C_o.$$

A high specific resistivity is, somewhat paradoxically, advantageous in putting this critical current density near the limiting current density. The creeping occurs because of some relaxation characteristics of the membranes. The measured voltages for various ratios of these two numbers is plotted against time in Figure A2. It is apparent that the rate of creeping is related to this ratio and that a ratio not greatly exceeding unity is desirable. However, economical use of equipment may demand a heavier current density. The possibility suggests itself of limiting the voltage rise by reversing the direction of current flow, thus exchanging dilute and concentrate roles for alternate streams. A study of this possibility is reported in Figure A3.

For water of salinity above a given concentration, depending on membrane conductivity and current density, voltage reversal need not be practiced. If the critical value is not greatly exceeded, reversal is an expedient for the limiting of polarization voltage rise with its possible deleterious effects, but the period

of reversal must become quite short if the water conductivity becomes near or less than membrane conductivity. Membrane material of lower specific conductivity-- less than that of the product water--would be desirable and probably would not add to electric cost, in that ohmic voltage would be exchanged for polarization voltage.

The desired reduction of membrane conductivity cannot be effected by the inclusion of a backing material in the membrane. Indeed, a sandwich of different conductivities would lead to undesirable charge concentrations in the membrane interior. Thin, homogeneous membranes of rather poor conductivity are desirable at the dilute end of a demineralizer, although at the concentrate end, particularly for sea water, a low resistance is required.

Experimentally determined polarization voltage is the measured voltage less the electrode voltage (1.95 volts), less the IR drop (0.195 ohm I). Conductivity is 1,450 micromhos/cm. Flow rate for the upper curve is 1.07 gallons per minute per square inch of cross section; for the lower curve the flow is 1.66 gpm/in.^{2}

Figure AI.- Agreement of experimental data with theory for membrane polarization voltage

A-4

Figure A2.— Voltage creep at various ratios of current density to critical current density
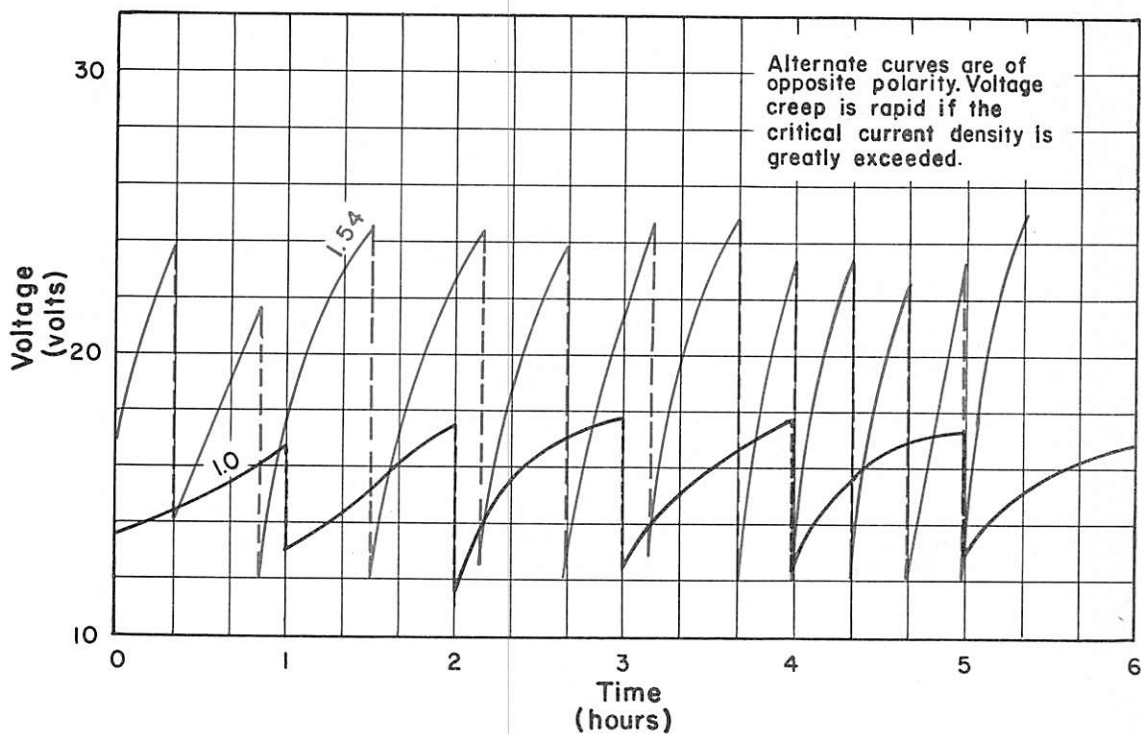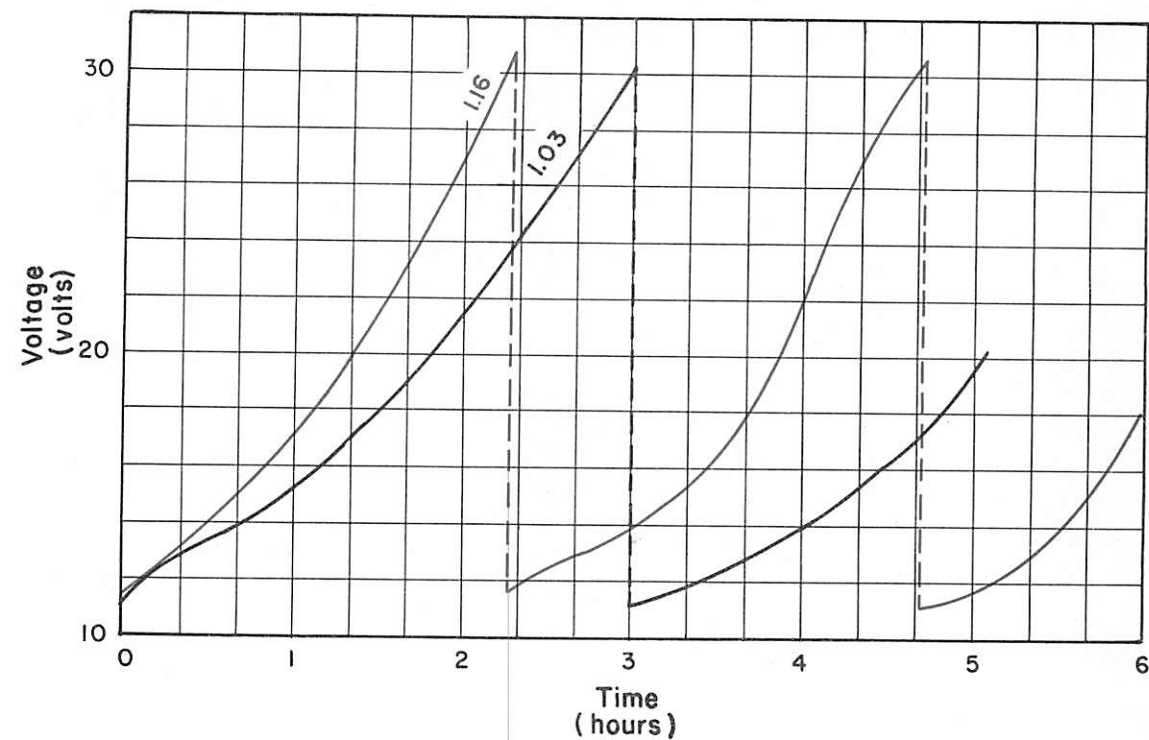
A-5

FIGURE A3.- Voltage creep, limited by current reversals, at various ratios of
current density to critical current density