

ELECTROKINETIC POWER GENERATION

by

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## ELECTROKINETIC POWER GENERATION

### I. INTRODUCTION

Electrokinetic effects were first noticed by Quincke (11) in 1859. Since then many investigations have concentrated along the lines of determining the zeta potentials which are characteristic of these phenomena. Very little work has been done in the investigation of power output from such electrokinetic effects. Hurd and Lane (7) are among the few who have studied this line of application and their specific interest was the application of electrokinetic principles to control systems.

When a streaming potential device is used in a control system, it is necessary to have a knowledge of the power characteristics so that a design can be made which considers the proper coupling of electronic circuits so that these in turn can give a correct indication of the physical quantities being measured.

Examples of control systems would be the measurement of liquid flow rate, the measurement of total pressure, and the measurement of electrical conductivities. This present study investigates the characteristics of a streaming potential device as a source of such electrical power.

## II. THEORY

### A. Electrokinetic Phenomena

Electro-osmosis is the movement of a liquid with respect to a solid wall as the result of an applied electrical field. In Figure 1 a potential is applied across the two electrodes. This causes liquid to flow through the porous plug. The flow is measured in the capillary tube.

Streaming potential is the potential created by the movement of liquid through a porous plug by an external pressure and is the reciprocal effect of electro-osmosis. In Figure 2 an external pressure is applied by the piston, and the resulting potential is measured between the two electrodes.

### B. Basic Theory

Electro-osmosis and streaming potential are attributed to the presence of a potential difference between the solid wall and the liquid phase. This potential is known as the zeta potential and is written as  $\zeta$ .

The model which gives a very good picture of the electrokinetic effects is the double layer concept. This concept as conceived by Helmholtz (6), considers the double layer to be made of two distinct layers of molecules. One layer of charged molecules is adsorbed on the wall and gives rise to a layer of oppositely charged molecules directly next to the wall. Use of this model has led to many contradictions, and was later modified by Gouy (5), and Chapman (3). They stated that a layer of charged

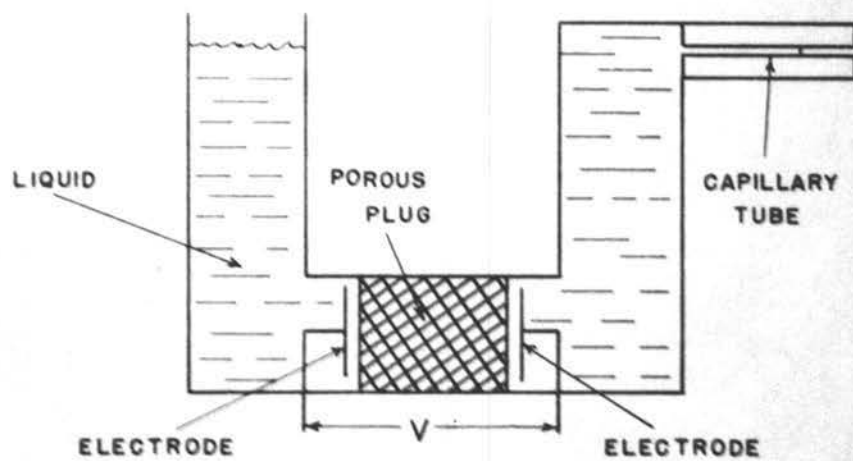


FIG. 1 ELECTRO-OSMOSIS CELL

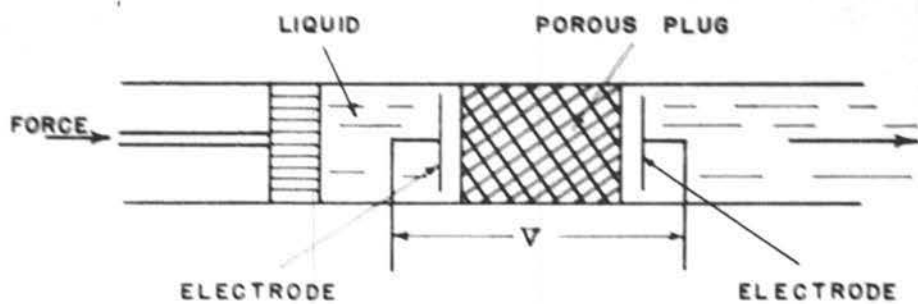


FIG. 2 STREAMING POTENTIAL CELL

molecules is adsorbed on the wall, and a diffuse layer of charged molecules in the solution is also attracted to the wall.

The theory accepted today is a combination of the two theories. The double layer consists of two parts. The first layer, located about a molecular diameter from the wall, is considered to be stationary while the second layer is considered to be a diffuse layer of charged molecules extending into the solution.

### C. Derivation of the Basic Equation

The basic equation relating streaming potential to the physical properties of the system is derived in order that a complete statement of the theory is present in this study. As derived, the basic equation will include both the electro-osmotic and streaming potential effects.

The assumptions involved in the theory are that an electric double layer is formed at the wall, the thickness of the double layer is extremely small, the layer of molecules in contact with the wall are not movable, the flow of fluid is laminar, the wall is an insulator, and the liquid has the property of an electrolytic conductor.

The equation is derived by making a force balance on a macroscopic portion of the fluid and the solid wall. The force balance is drawn in Figure 3.

The electrical potential applied across the fluid causes an electrical field to be generated. The force caused by this electric field on the molecules is written as  $F_x$  (consider only



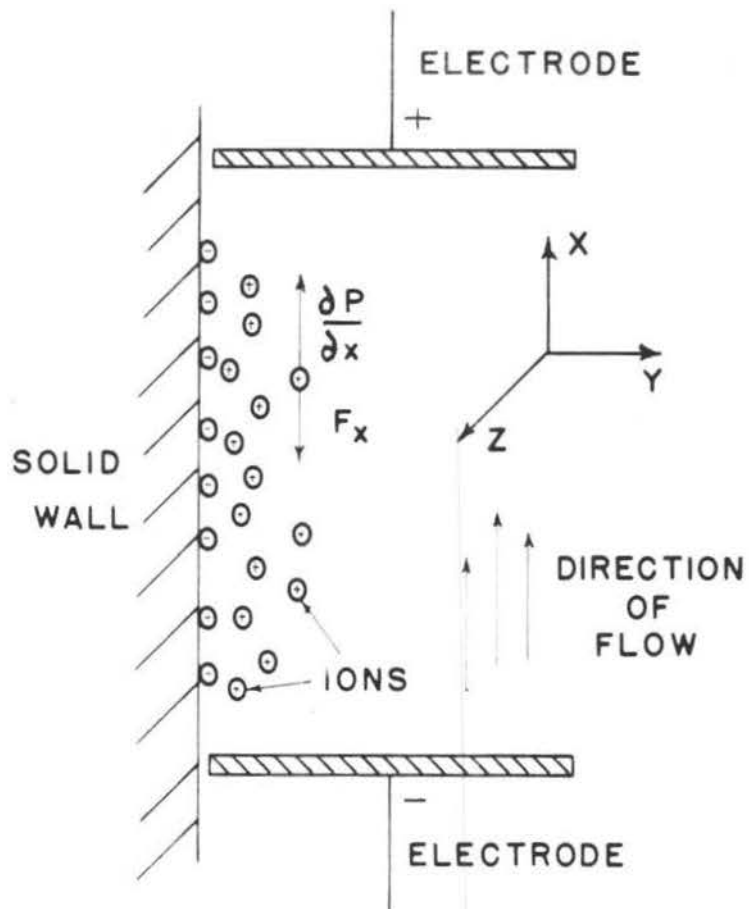


FIG. 3 FORCE BALANCE

the x-direction). The pressure gradient across the fluid also causes a force on the molecules. It is written as  $\frac{dP}{dx}$  (consider only the x-direction) where P is the pressure. The only force remaining is the frictional force which is present when the molecules are in motion. Since the molecules can move in three directions, the force is written in terms of the three coordinates as

$$- \eta \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right)$$

where  $\eta$  is the viscosity coefficient and u is the velocity. In order to simplify the equation, we will only consider the case in which the forces are only acting in the x-direction. This is a very good assumption because we are dealing with the region which is very close to the wall.

It is necessary to define the potential as a function of position in the fluid in order to continue the derivation. The potential is defined as

$$\Psi(x, y, z) = \phi(y, z) - i\sigma x \quad (1)$$

where i is the electric current,  $\sigma$  is the specific resistivity  $\phi(y, z)$  is the potential in the fluid before the external potential is applied to the electrodes, and  $\Psi(x, y, z)$  is the total potential at any point. We note from Equation 1 that the total potential is a linear function of x.

In order to equate  $F_x$  to the potential in the fluid we look at the basic laws of electrostatics. The force on a charged molecule is defined as the product of the electric field and the

charge on the molecule; therefore,

$$F_x = E_x q \quad (2)$$

where  $E_x$  is the electric field in the x-direction and  $q$  is the electric charge on the molecule. We also know that

$$E_x = - \frac{d\Psi}{dx} \quad , \quad (3)$$

$$= - \frac{d}{dx} (\phi - i \sigma x) \quad ,$$

and 
$$= i \sigma \quad . \quad (4)$$

From Equation 2 and Equation 4 we obtain

$$F_x = i \sigma q \quad .$$

Since we want  $F_x$  to be in units of force per unit volume, we will let the point charge become the charge density. The charge density is written as  $\rho$ , and therefore

$$F_x = \rho i \sigma \quad . \quad (5)$$

The electrical force on a molecule is now in terms of the charge density of the solution.

In order to relate the charge density to the total potential in the fluid, the following analysis is considered. A small element of fluid ( $dV$ ) with a volume charge density of  $\rho$  will emit an electric flux. The small element will also have input and output fluxes from (1) the electrodes, (2) the other charges, and (3) the solid wall. Gauss's theorem states that "the total electric flux associated with the volume of charge density is  $4\pi\rho dV$ ." Therefore, this must be equal to the net total flux passing through the surface of this element. Hence

$$\iiint_V 4\pi\rho dV = \iint_S \bar{E} \cdot \bar{n} dS \quad (6)$$

where  $\iint_S \bar{E} \cdot \bar{n} dS$

is the surface integral of the electric field normal to the surface of the element  $dV$  and  $\bar{n}$  is the unit vector of the surface. The divergence theorem states that

$$\iint_S \bar{E} \cdot \bar{n} dS = \iiint_V \text{div } \bar{E} dV \quad , \quad (7)$$

hence

$$\iiint_V 4\pi\rho dV = \iiint_V \text{div } \bar{E} dV$$

or  $4\pi\rho = \text{div } \bar{E} \quad .$

However, we know that

$$\bar{E} = - \overline{\text{grad } \Psi} \quad (8)$$

therefore

$$4\pi\rho = - \text{div } (\overline{\text{grad } \Psi})$$

or

$$4\pi\rho = -\nabla^2 \Psi \quad (9)$$

Equation 9 relates the total potential ( $\Psi$ ) to volume charge density and it is called Poisson's equation. Since the equation was derived assuming a perfect vacuum, it must be corrected so it can be applied to a system of some other media; therefore, a

constant is added to the equation. This constant is called the dielectric constant and is written as  $D$ . Rewriting Poisson's equation including the dielectric constant, we obtain

$$\rho = - \frac{D}{4\pi} \nabla^2 \Psi \quad . \quad (10)$$

Finally Equation 5 can be written as

$$F_x = - \frac{i\sigma D}{4\pi} \nabla^2 \Psi \quad . \quad (11)$$

The force due to the pressure gradient can be written as

$$\frac{dP}{dx} = \frac{\Delta P}{L} \quad (12)$$

since it is assumed that the pressure drop between the electrodes is linear.  $L$  is the distance between the two electrodes.

The final result of the force balance is a summation of the three forces on the molecules. This summation is written as

$$\frac{i\sigma D}{4\pi} \nabla^2 \Psi + \frac{\Delta P}{L} = \eta \nabla^2 u \quad . \quad (13)$$

This equation is a completely general equation in that both the electro-osmotic and streaming potential effects are included. The equation is, however, subject to the assumptions previously stated.

To make the solution of Equation 13 easier, the equation is divided into two parts, by stating that there are two separate

velocities. The first velocity is due to the electro-osmotic effect, and the second velocity is due to the streaming potential effect. The two equations are

$$\frac{i \sigma_D}{4 \pi} \nabla^2 \Psi = \eta \nabla^2 u_1 \quad (14)$$

and

$$\frac{\Delta P}{L} = \eta \nabla^2 u_2 \quad (15)$$

Since this study considers the streaming potential effect only, Equation 14 will be considered very small and negligible in comparison to Equation 15.

Since we are only considering the streaming potential effect, the calculation of the amount of electric charge carried down stream per unit time (electric current) can be obtained from the following equation.

$$Q = \int_0^y \int_0^z (\text{charge density})(\text{velocity in x-direction}) dy dz \quad (16)$$

where  $Q$  is the electric charge per unit time. We assume that the velocity of the fluid next to the wall is a linear function of  $y$ . This assumption is valid for our case since the electric charge is located almost entirely next to the wall. Therefore the velocity in the  $x$  direction can be written as

$$u_x = \left( \frac{du}{dy} \right) y \quad (17)$$

Equation (16) after substitution of Equation 17 can be written as

$$Q = \int_0^y \int_0^z \rho \left( \frac{du}{dy} \right) y \, dy \, dz \quad . \quad (18)$$

The volume charge density is a function of the total potential ( $\Psi$ ) and they are related to each other by Equation 10 (Poisson's equation). Substitution of Equation 10 into Equation 18 leads to

$$Q = \int_0^y - \frac{D}{4\pi} (\nabla^2 \Psi) y \, dy \int_0^z \left( \frac{du}{dy} \right) dz \quad (19)$$

because  $\left( \frac{du}{dy} \right)$  is a constant near the wall and therefore is not a function of  $y$ . In order to integrate Equation 19, the total potential ( $\Psi$ ) must be known as function of  $x$ ,  $y$  and  $z$ . Equation 1 is a relationship between  $\Psi$ ,  $\phi$ , and  $x$ . Since  $\Psi$  is a linear function of  $x$ , we may write

$$\frac{\partial^2 \Psi}{\partial x^2} = 0 \quad . \quad (20)$$

From the geometry of the system it is noticed that the change of potential in the  $z$  direction is zero; therefore

$$\frac{\partial \Psi}{\partial z} = 0$$

and also

$$\frac{\partial^2 \Psi}{\partial z^2} = 0 \quad . \quad (21)$$

From Equation 1 it can be seen that

$$\frac{\partial \Psi}{\partial y} = \frac{\partial \phi}{\partial y}$$

and also 
$$\frac{\partial^2 \Psi}{\partial y^2} = \frac{\partial^2 \phi}{\partial y^2} \quad . \quad (22)$$

Substitution of Equations 20, 21, and 22 into Equation 19 leads to

$$Q = - \frac{D}{4 \pi} \int_0^y \frac{d^2 \phi}{dy^2} y dy \int_0^z \left( \frac{du}{dy} \right) dz \quad . \quad (23)$$

Equation 23 is then integrated by parts and the result is

$$Q = - \frac{D}{4 \pi} \left( y \left( \frac{d \phi}{dy} \right) - \phi \right)_0^\infty \int_0^z \left( \frac{du}{dy} \right) dz \quad (24)$$

where the limits on  $y$  are 0 and  $\infty$  . The quantity  $\frac{d \phi}{dy}$

approaches zero as  $y$  becomes large, therefore Equation 24 can be written as

$$Q = - \frac{D}{4 \pi} \left( \phi_0 - \phi_\infty \right) \int_0^z \frac{du}{dy} dz \quad (25)$$

If we let  $(\phi_0 - \phi_\infty) = (\phi_s - \phi_l) = -\zeta$

where  $s$  and  $l$  refer to solid and liquid, then

$$Q = \frac{D \zeta}{4 \pi} \int_0^z \left( \frac{du}{dy} \right) dz \quad (26)$$



The integral in Equation 26 can be transformed into another integral by Stoke's theorem which states that

$$\int_c \bar{K} \cdot d\bar{c} = \iint_S (\text{curl } \bar{K} \cdot \bar{n}) dS \quad (27)$$

$$\text{where curl } \bar{K} = \left[ \left( \frac{\partial K_3}{\partial y} - \frac{\partial K_2}{\partial z} \right), \left( \frac{\partial K_1}{\partial z} - \frac{\partial K_3}{\partial x} \right), \left( \frac{\partial K_2}{\partial x} - \frac{\partial K_1}{\partial y} \right) \right].$$

In our case  $n=(1, 0, 0)$

so the curl  $\bar{K}$  will be somewhat simplified and the result is

$$(\text{curl } \bar{K} \cdot \bar{n}) = \frac{\partial K_3}{\partial y} - \frac{\partial K_2}{\partial z} \quad . \quad (28)$$

Substitution of Equation 28 into Equation 27 leads to

$$\int_c \bar{K} \cdot d\bar{c} = \iint_S \left( \frac{\partial K_3}{\partial y} - \frac{\partial K_2}{\partial z} \right) dS \quad . \quad (29)$$

Also in our case  $d\bar{c} = (0, dy, dz)$

$$\text{so } \bar{K} \cdot d\bar{c} = K_2 dy + K_3 dz \quad . \quad (30)$$

If we notice that  $dS = dy dz$ , then Equation 29 can be written as

$$\int_c K_2 dy + K_3 dz = \iint_S \left( \frac{\partial K_3}{\partial y} - \frac{\partial K_2}{\partial z} \right) dy dz \quad . \quad (31)$$

If we set  $K_2 = 0$ , then Equation 31 can be made similar to the integral of Equation 26. Equation 31 can be written as

$$\int_c K_3 dz = \iint_S \frac{\partial K_3}{\partial y} dy dz \quad . \quad (32)$$

Again in our case,  $K_3 = \frac{du}{dy}$  and then Equation 32 can be written as

$$\int_C \frac{du}{dy} dz = \iint_S \frac{d}{dy} \left( \frac{du}{dy} \right) dydz$$

$$\text{or } \int_C \frac{du}{dy} dz = \iint_S \frac{d^2u}{dy^2} dydz \quad . \quad (33)$$

We now notice that Equation 33 is an equivalent form of the integral in Equation 25; therefore, Equation 33 is substituted into Equation 25 and

$$Q = \frac{D \zeta}{4 \pi} \int_0^y \int_0^z \frac{d^2u}{dy^2} dydz \quad . \quad (34)$$

Since we assumed that we only have a velocity profile in the y-direction,

$$\frac{\partial^2 u}{\partial x^2} = \frac{\partial^2 u}{\partial z^2} = 0$$

$$\text{and } \nabla^2 u = \frac{d^2u}{dy^2} \quad . \quad (35)$$

Substitution of Equation 35 into Equation 34 leads to

$$Q = \frac{D \zeta}{4 \pi} \int_0^y \int_0^z \nabla^2 u dydz \quad . \quad (36)$$

Substitution of Equation 15 into Equation 36 leads to

$$Q = \frac{D \zeta}{4 \pi} \int_0^y \int_0^z \frac{\Delta_P}{L \eta} dydz \quad . \quad (37)$$

Integration of Equation 37 gives

$$Q = \frac{D \zeta}{4 \pi} \frac{\Delta P A}{L \eta} \quad (38)$$

where A is the cross sectional area perpendicular to the direction of fluid flow.

If there is no external conduction or surface conduction, the EMF between the two electrode surfaces can be defined as

$$\text{EMF} = \frac{Q \sigma L}{A} \quad (39)$$

where Q is the electrical charge of the fluid which is carried with the flowing fluid,  $\sigma$  is the specific resistivity of the fluid, L is the distance between the electrodes, and A is the area of the column. Substitution of Equation 38 into Equation 39 leads to

$$\text{EMF} = \frac{D \zeta \Delta P \sigma}{4 \pi \eta} \quad (40)$$

Let  $\sigma = \frac{1}{k}$  and substitute this into Equation 40. The result is

$$\text{EMF} = \frac{D \zeta \Delta P}{4 \pi \eta k} \quad (41)$$

This EMF is called the streaming potential and is denoted as  $V_S$ . Equation 41 is the result of Helmholtz (6) and is called the Helmholtz equation of streaming potential. The derivation of the streaming potential equation is also discussed by Schmoluchowski (12), Kortüm and Bockris (8), Glasstone (4), Abramson (1), Butler (2), and Kruyt (9).

#### D. Models

The streaming potential assumes that all of the conduction takes place in the solution as electrolytic conduction. In reality this is not the case. Conduction can also take place along the surface of the particles of the porous bed. This is called surface conduction and it can become very large in comparison to the electrolytic conduction in a very dilute ionic solution. Another method of conduction between the electrodes is called external conduction or conduction through a resistance outside the porous bed. The external resistance will be introduced in an effort to extract power from the streaming potential device.

There are many ways of visualizing such a system of conduction. In the next section, several methods or models of conduction will be discussed. Conduction through the solution and conduction along the surface of the solid particles will be grouped together and called internal conduction.

Before we consider various models let us note that a streaming potential device can be considered to be a constant current device. If we again look at Equation 38, we notice that  $Q$  or the current is proportional to the term  $\frac{(\Delta P)A}{L}$ . This term is a direct function of the volumetric flow rate. It is noticed that at a given pressure, an increase in cross sectional area will increase the flow rate and will also increase the total electric current. It is also noticed that at a given pressure an increase in the length will decrease the flow rate

and will also decrease the electric current. Therefore at a constant flow rate the streaming potential device will act as a constant current device regardless of the external load applied to it. In any given column, the total current will be a function of only the pressure difference.

Three models are postulated in an effort to describe a streaming potential device by an equivalent electrical circuit.

The first model is described as follows:

The packed bed with a liquid being forced through it at a constant flow rate can be considered to be a constant current source. That is, the current being generated from it is constant regardless of the load applied to it. The physical apparatus can be represented by Figure 4. The quantities represented in the diagram are defined as follows:

$I_t$  = total current from the packed bed

$I_{in}$  = internal current through the packed bed

$I_{ex}$  = external current through an external load

$R_{ex}$  = external load

$R_{in}$  = internal resistance,

The total resistance across the system is given by the equation

$$R_t = \frac{R_{in} R_{ex}}{R_{in} + R_{ex}} \quad (42)$$

where  $R_t$  is the total resistance across the packed bed.

Since we have assumed that the total current ( $I_t$ ) is a constant, we can write

$$I_t = \frac{V}{R_t} = \text{constant} \quad (43)$$

where  $V$  is the voltage across the packed bed. It should be realized that this voltage is not the streaming potential because the streaming potential is obtained when only pure electrolytic conduction is present.

We can measure the current in the external circuit ( $I_{ex}$ ) and we know the external resistance ( $R_{ex}$ ). From these two quantities we can calculate  $V$  from the equation

$$V = I_{ex} R_{ex} \quad (44)$$

Substitution of Equation (44) into (43) leads to

$$I_t = \frac{I_{ex} R_{ex}}{R_t} \quad (45)$$

and substitution of equation (42) into (45) leads to

$$I_t = \frac{I_{ex} (R_{in} + R_{ex})}{R_{in}} \quad (46)$$

or

$$I_t = I_{ex} + I_{ex} \left( \frac{R_{ex}}{R_{in}} \right) \quad (47)$$

Therefore, if the model is correct, Equation (47) will be obeyed.

The second model is a modification of the first model. Model II also assumes that the packed bed is a constant current device. The modification is in the addition of a resistance which would include any polarization at the electrode. A very dilute liquid passing through the column could result in a polarization effect due to the lack of ions which are needed in the electrochemical reaction at the electrodes. The physical apparatus is represented in Figure 5. The new quantity  $R_p$  represents the polarization resistance.

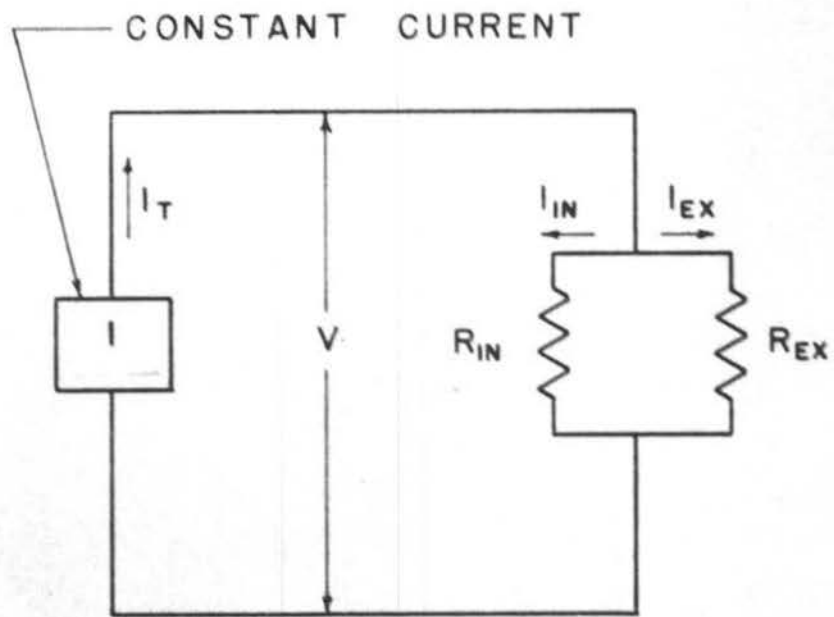


FIG. 4 MODEL I

The total resistance across the system is given by the equation

$$R_t = \frac{R_{in} (R_p + R_{ex})}{R_p + R_{ex} + R_{in}} \quad (48)$$

where  $R_t$  is the total resistance across the packed bed.

Since we have assumed that the total current ( $I_t$ ) is constant, we can write

$$I_t = \frac{V'}{R_t} = \text{constant} \quad (49)$$

where  $V'$  cannot be measured; and therefore, an expression using  $V$  is necessary where  $V$  is the voltage across the external resistance. We know that

$$I_{ex} = \frac{V}{R_{ex}} = \frac{V'}{R_{ex} + R_p}$$

and therefore

$$V' = I_{ex} (R_{ex} + R_p) \quad (50)$$

Substitution of Equation 50 into Equation 49 leads to

$$I_t = \frac{I_{ex} (R_{ex} + R_p)}{R_t} \quad (51)$$

Substitution of Equation 48 into Equation 51 leads to

$$I_t = \frac{I_{ex} (R_p + R_{ex} + R_{in})}{R_{in}} \quad (52)$$

or

$$I_t = I_{ex} \frac{(R_p + R_{ex} + R_{in})}{(R_{in})} \quad .$$



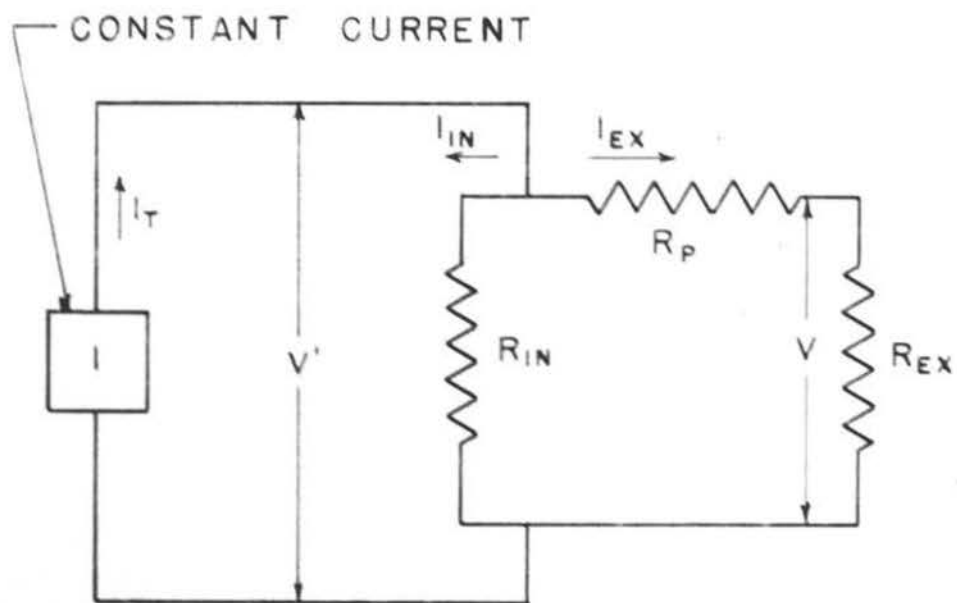


FIG. 5 MODEL II

The polarization resistance ( $R_p$ ) can be obtained from the fact that as the external load ( $R_{ex}$ ) increases to a very large value, Model II becomes Model I. This is illustrated as follows where

$$I_t = I_{ex} \frac{(R_p + R_{ex} + R_{in})}{R_{in}} \quad (53)$$

As  $R_{ex}$  increases, that is  $R_{ex} \gg R_p$ ,

$$I_t = I_{ex} \left( \frac{R_{ex} + R_{in}}{R_{in}} \right) \quad (54)$$

which is the equation for Model I. Thus the total current can be obtained from Model I when the external load ( $R_{ex}$ ) is very large.

The value for the total current ( $I_t$ ) is then substituted into Model II, and the polarization resistance is obtained. The equation is

$$R_p = \frac{R_{in} I_t}{I_{ex}} - R_{ex} - R_{in} \quad (55)$$

The polarization resistance is evaluated when  $R_{ex}$  is very small so as to decrease the amount of error in the  $(I_t/I_{ex})$  term.

With the evaluation of  $R_p$ , Model II will give the total current at any external load. Also, the total current of Model II will equal the total current of Model I as  $R_p$  approaches zero.

Model III is the same as Model II except  $R_p$  is considered to be a function of the external current ( $I_{ex}$ ). Therefore we can write the equation for the total current as

$$I_t = I_{ex} \frac{R_p(I) + R_{ex} + R_{in}}{R_{in}} \quad . \quad (56)$$

Since the currents dealt with in this study are extremely small, it will be impossible to show a correlation between the external current and the polarization resistance.

In order to further verify the models postulated, it is necessary to determine if the total electric currents obtained from the models satisfy the Helmholtz equation and the assumption of constant zeta potential.

Streaming potential is defined as the potential across a packed bed that has a liquid pressure gradient across it. Surface conduction and external conduction must not be present. Streaming potential can be defined in mathematical terms as

$$V_s = I_t R_v$$

where  $V_s$  is the streaming potential,  $I_t$  is the total current generated by the flow of fluid through the packed bed, and  $R_v$  is the volumetric resistance.

Volumetric resistance is defined as the resistance of the continuous phase in a packed bed. In a bed of glass spheres and a liquid, the volumetric resistance would be the resistance of the liquid phase. This resistance cannot be measured directly but instead, must be calculated from the physical and geometrical

constants of the particular packed bed. The volumetric resistance can be obtained from the equation

$$R_v = \frac{L}{A k_s} \quad (57)$$

where  $L$  is the length of the packed bed,  $A$  is the cross sectional area of the packed bed, and  $k_s$  is the conductivity of the packed bed. In his thesis, Meredith (10), defines a ratio ( $K_m$ ) of the conductivity of the combined mixture of continuous and dispersed phases to the conductivity of the continuous phase. The ratio can be written as

$$K_m = \frac{k_s}{k} \quad (58)$$

where  $k$  is the conductivity of the continuous phase. Figure 6 is a graph of this relationship. Requirements for this relationship are that the dispersed phase must be a nonconductor and surface conduction is not present. With this graph, the volumetric resistance of the column will be equal to

$$R_v = \frac{L}{A k K_m} \quad (59)$$

Since the volumetric resistance ( $R_v$ ) is calculated and the total current ( $I_t$ ) is measured, the streaming potential can be calculated.

If the models obey the Helmholtz equation, a plot of streaming potential versus pressure drop will result in a straight line.

The zeta potential can be calculated directly from the Helmholtz equation. If the models are correct, the zeta potential will be a constant regardless of pressure drop.

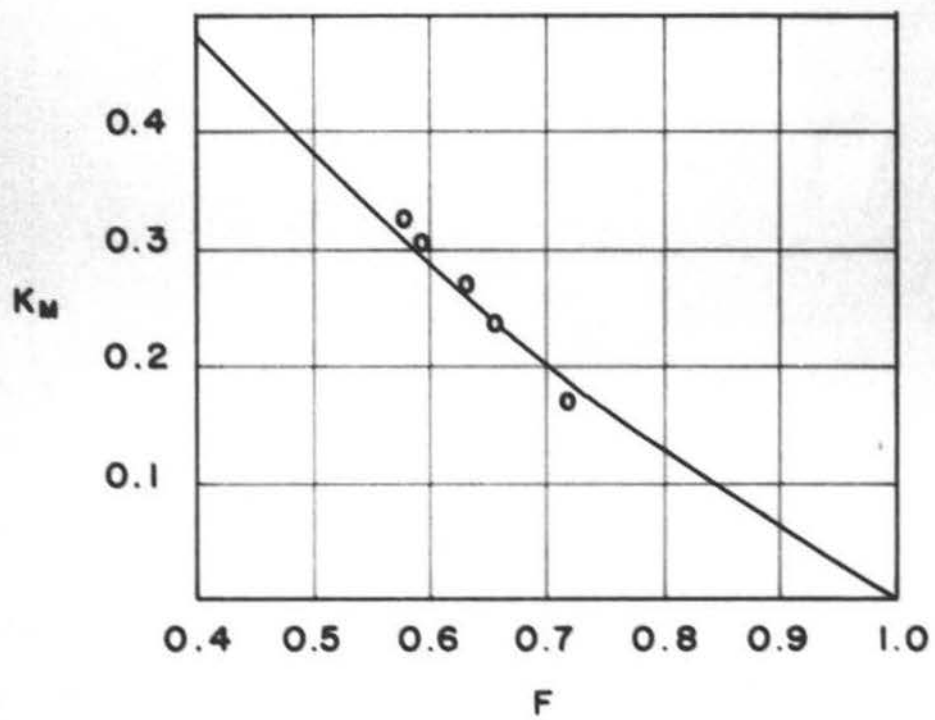


FIG . 6 CONDUCTIVITY RATIO ( $K_M$ )  
VS SOLID FRACTION (F)

Finally, it is postulated that, if the models are correct the maximum power output will occur when the external resistance is equal to the internal resistance.

### III. EXPERIMENTAL PROCEDURE AND APPARATUS

The apparatus used for the determination of the data needed is illustrated in Figure 7. The packed bed was made of glass beads which were sifted through a 100 mesh screen. The packed bed was enclosed by a cylindrical column which was made of a hard nonconductive fiberglass material. The column measurements were 5 feet in length and 1.75 inches in diameter. The fiberglass column was tested at a pressure of 750 pounds per square inch to determine if it would withstand the pressures of the experimental runs. The pressure test was successful in that no leaks of any kind were noticed. Electrodes of platinum black were located at each end of the packed bed and the electrical wires from the electrodes were passed through the packed bed and out the top of the column. The fluid was forced through the column by pressurizing an auxiliary tank which contained the fluid. The maximum pressure drop obtained in the column was 400 pounds per square inch. The wires from the electrodes were connected through a micro-microammeter to a calibrated external resistance box. Measurements of external resistance and external current were taken with these two instruments. The pressure difference was obtained by reading the inlet pressure and outlet pressure on the pressure gauges located at each end of the packed bed.

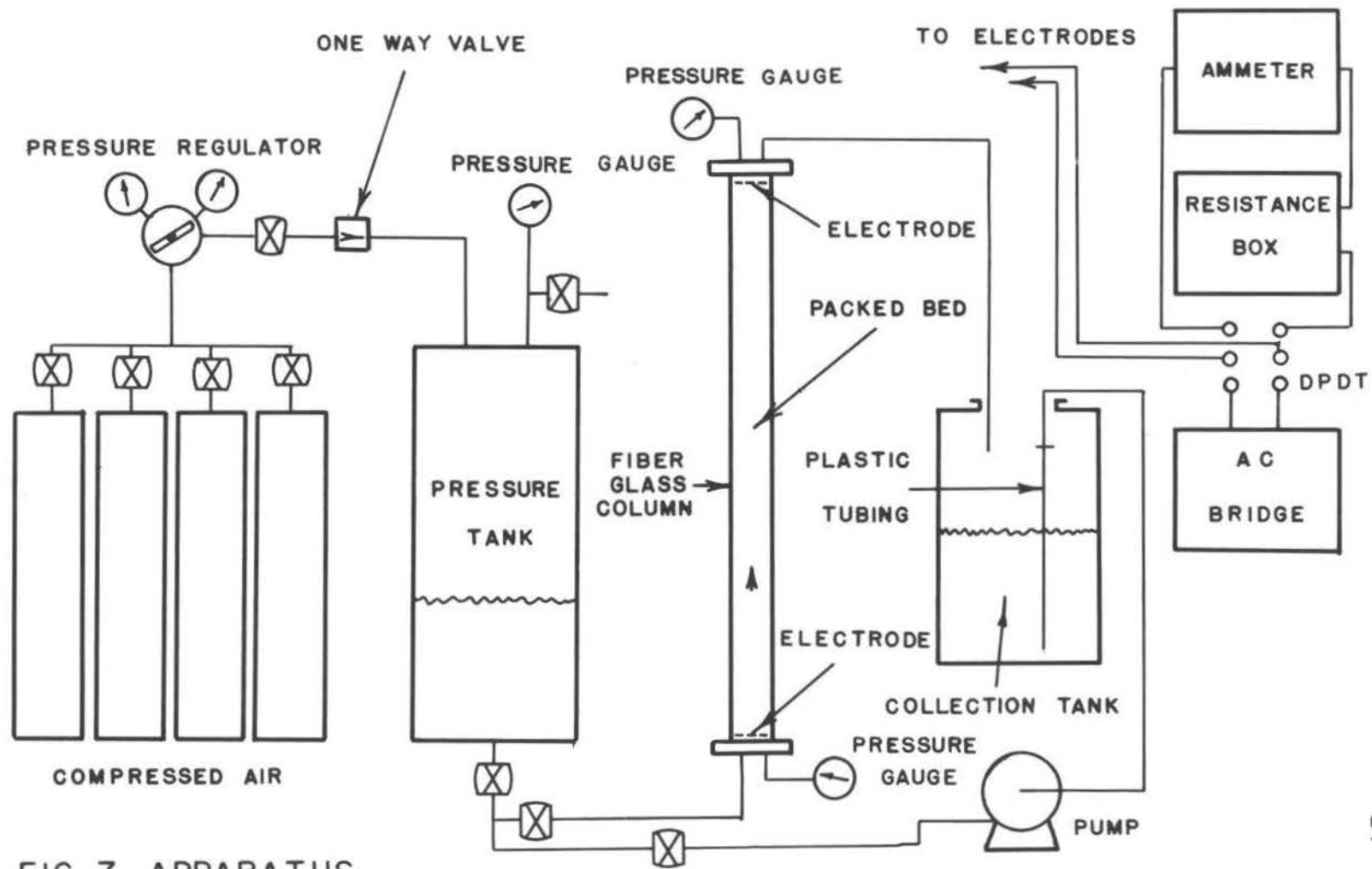


FIG. 7 APPARATUS

The internal resistance of the packed bed was measured by means of an AC bridge. The appendix contains a list of the data obtained with the above-mentioned instruments.

#### IV. EXPERIMENTAL RESULTS

##### Experimental Results of Model I.

The validity of Model I can be observed by a plot of the total current ( $I_t$ ) versus the external resistance ( $R_{ex}$ ). If the model is correct, the resulting graphical plot should be a straight line of zero slope.

The quantities necessary for the calculation of the total current by Equation 47 were the external current ( $I_{ex}$ ), the internal resistance ( $R_{in}$ ), and the external resistance ( $R_{ex}$ ). All of these quantities were measured with the instruments listed in the apparatus section.

Figure 8 shows that the total current lines deviate from a straight line when the external current ( $I_{ex}$ ) is increased. This deviation was attributed to the increase in the polarization on the electrode surfaces. It is also to be noticed that at high pressure gradients, the total current line has an increased slope. This is also attributed to the increased polarization resistance. The data for Figure 8 is given in Table 1.

These results indicate that some modifications were needed in order that a true model could be formulated. These modifications are included in Model II.



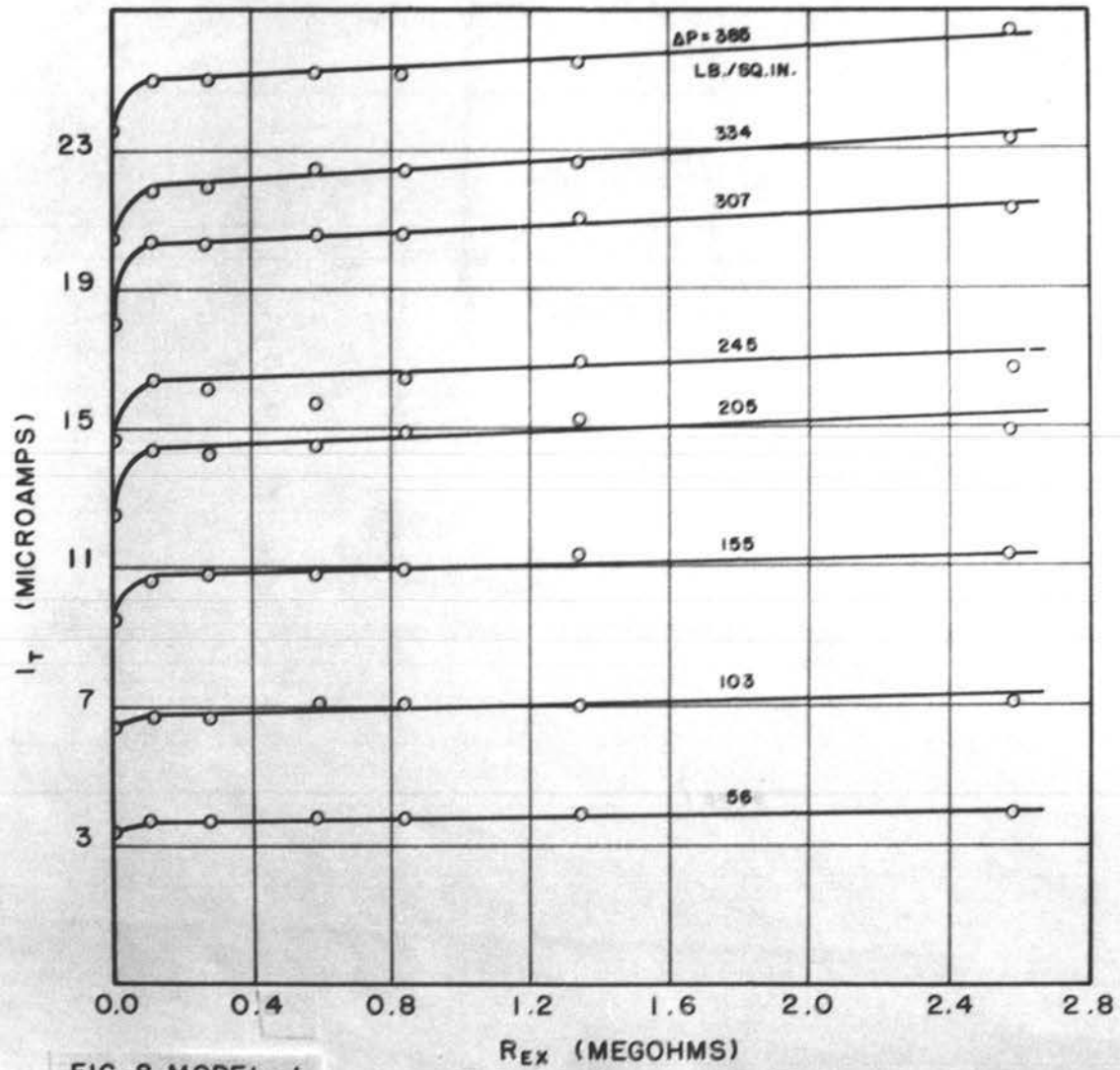


FIG. 8 MODEL 1

Table 1. Model I - Total Current ( $T_i$ ) (Microamps)

$\frac{\Delta P}{R_{ex}}$ (lb/in <sup>2</sup> ) (ohms)	56.	103.	155.	205.	245.	307.	334.	385.
Shunt	3.50	6.40	9.50	12.5	14.7	18.0	20.4	23.5
1.272	3.50	6.40	9.50	12.5	14.5	18.0	20.4	23.5
11.66	3.50	6.40	9.50	12.5	14.5	18.0	20.4	23.5
96.48	3.50	6.30	9.50	12.5	14.5	18.0	20.4	23.5
1064.	3.41	6.22	9.53	12.5	14.5	18.0	20.4	23.6
11,390.	3.41	6.20	9.62	12.6	14.6	18.1	20.6	23.6
111,000.	3.61	6.65	10.2	13.4	15.6	19.3	21.6	24.6
282,600.	3.55	6.28	10.1	13.6	15.6	19.3	21.4	24.1
599,100.	3.62	6.71	10.6	13.9	15.9	19.8	21.7	25.0
821,000.	3.65	6.71	10.7	14.1	16.2	20.0	21.7	24.8
998,600.	3.73	6.75	10.6	14.3	16.3	20.3	21.8	25.0
2,829,000.	3.76	6.87	10.8	14.2	16.1	20.3	21.9	25.0
5,927,000.	3.80	7.08	10.8	14.5	15.7	20.5	22.4	25.2
8,407,000.	3.82	7.00	10.9	14.8	16.4	20.6	22.4	25.2
13,490,000.	3.95	7.00	11.3	15.2	16.9	21.0	22.6	25.5
25,800,000.	3.96	7.08	11.3	14.9	16.7	21.2	23.3	26.4

Experimental Results of Model II.

The total current obtained in model II takes into account the polarization resistance at the electrode surfaces. If the model is correct, a plot of the total current ( $I_t$ ) versus the external resistance ( $R_{ex}$ ) will result in a straight line of zero slope.

The quantities necessary for the calculations of the total current by Equation (52) are the external current ( $I_{ex}$ ), the internal resistance ( $R_{in}$ ), the external resistance ( $R_{ex}$ ), and the polarization resistance ( $R_p$ ). The polarization resistance was calculated from Equation (55) for each individual pressure difference and the individual resistances were averaged together to obtain a common polarization resistance. These polarization resistances are listed in Table 2.

Figure 9 indicates that a straight line did result and that it had slope of zero. The only significant deviations are at high external currents. The high external current caused an increase in the polarization resistance at the electrodes which caused the deviations.

The third postulated model would have taken the changing polarization into account. However, the equipment used did not have the accuracy for such a determination.

Table 2. Polarization resistance

$\Delta P$ (lbs/in <sup>2</sup> )	$R_p$ (ohms)
56.	41,000.
103.	35,300.
155.	63,900.
205.	64,100.
245.	45,600.
307.	60,200.
334.	47,400.
385.	41,300.
<u>Average</u>	49,800.

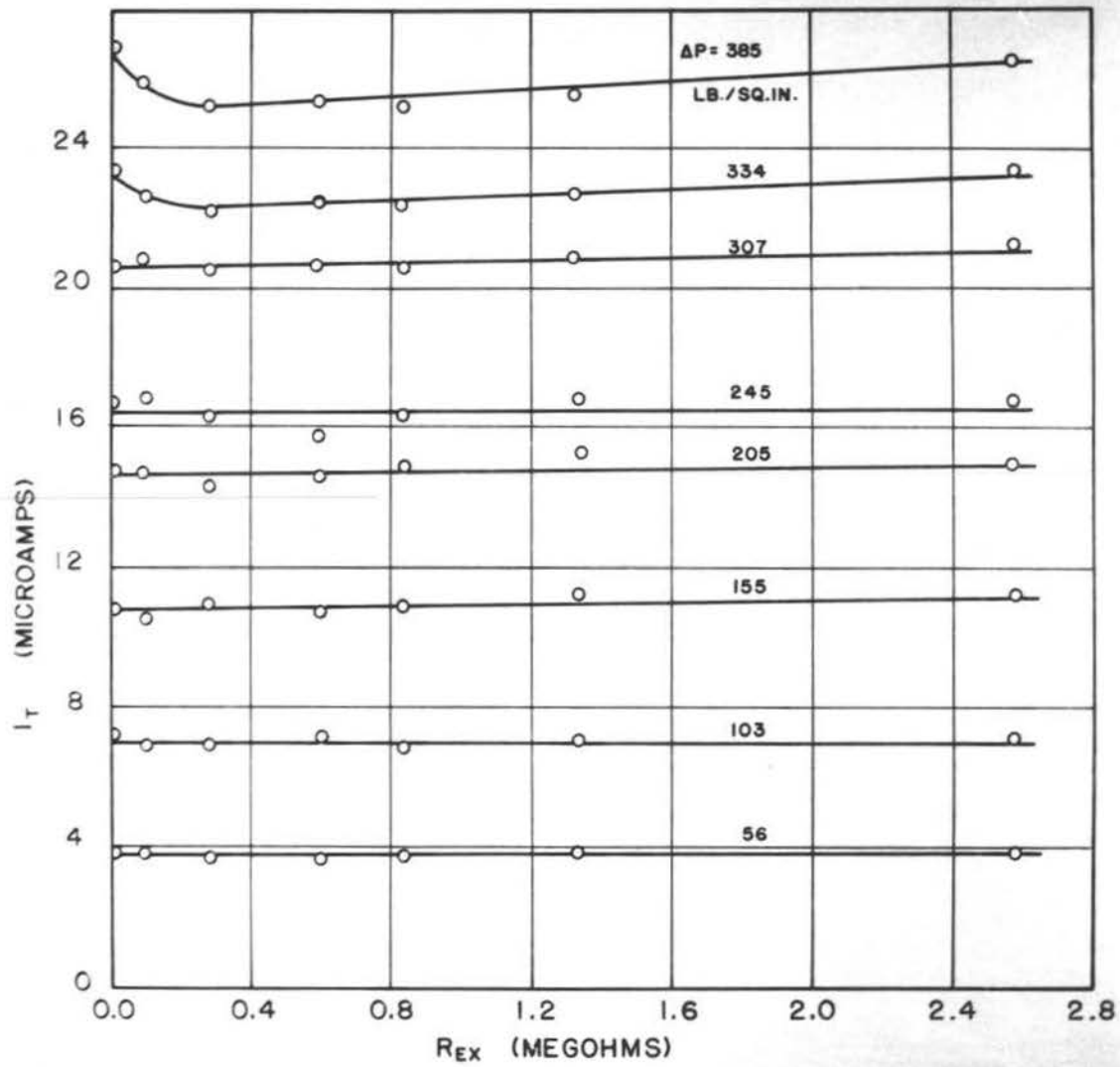


FIG.9 MODEL II

Table 3. Model II - Total Current ( $I_t$ ) - (Microamps)

$\Delta P$ (lbs/in <sup>2</sup> )	56.	103.	155.	205.	245.	307.	334.	385.
$R_{ex}$ ohms								
Shunt	4.03	7.36	10.9	14.4	16.9	20.7	23.5	27.0
1.272	4.03	7.36	10.9	14.4	16.9	20.7	23.5	27.0
11.66	4.03	7.36	10.9	14.4	16.7	20.7	23.5	27.0
96.48	4.03	7.25	10.9	14.4	16.7	20.7	23.5	27.0
1064.	3.92	7.14	10.9	14.4	16.7	20.6	23.4	27.1
11,390.	3.90	7.09	11.1	14.4	16.6	20.7	23.5	26.9
111,000.	4.01	7.40	11.4	14.9	17.3	21.5	24.0	27.4
282,600.	3.84	7.16	10.9	14.7	16.9	20.9	23.1	26.0
599,100.	3.81	7.06	11.1	14.6	16.7	20.8	22.9	26.4
821,000.	3.81	7.00	11.1	14.7	16.9	20.8	22.6	25.8
998,600.	3.87	7.00	10.6	14.8	16.9	21.0	22.7	25.9
2,829,000.	3.82	6.98	11.0	14.4	16.3	20.6	22.3	25.3
5,927,000.	3.83	7.14	10.9	14.7	15.8	20.7	22.5	25.4
8,407,000.	3.84	7.02	10.9	14.9	16.4	20.6	22.4	25.3
13,490,000.	3.96	7.01	11.3	15.3	16.9	21.0	22.7	25.6
25,800,000.	3.98	7.10	11.3	14.9	16.8	21.3	23.4	26.5

### Experimental Results of the Zeta Potential

The results of the zeta potential are listed in Table 4. It was noticed that the zeta potential was a constant with respect to the pressure difference across the packed bed. This result was as it should be and it gives evidence that the two models were the true equivalent circuits of the streaming potential device. Model II was shown to be more applicable at high pressure gradients and high current densities.

### Linearity of the Helmholtz Equation at High Pressure Gradients

It was noticed that the Helmholtz equation remained linear with pressure differences up to 385 pounds per square inch. Figure 10 shows a plot of the corrected streaming potential versus pressure difference. The corrected streaming potential takes into account the surface conduction due to the large surface area present in the packed bed. If the surface conduction had not been taken into account, the plot of uncorrected streaming potential versus pressure drop would still remain a straight line but the slope of the line would decrease.

The fact that the streaming potential versus pressure difference was a straight line gives further verification of the equivalent circuits defined by the models.

### Experimental Results of Maximum Power Output

Previous to this study there was some doubt as to whether the internal resistance remained constant with changing pressure gradient or with changing electrical field across the packed bed.

Table 4. Zeta Potential

$\Delta P$ (lb/in <sup>2</sup> )	$\zeta$ (volts)
56.	0.0571
103.	0.0554
155.	0.0586
205.	0.0577
245.	0.0552
307.	0.0559
334.	0.0564
385.	0.0554



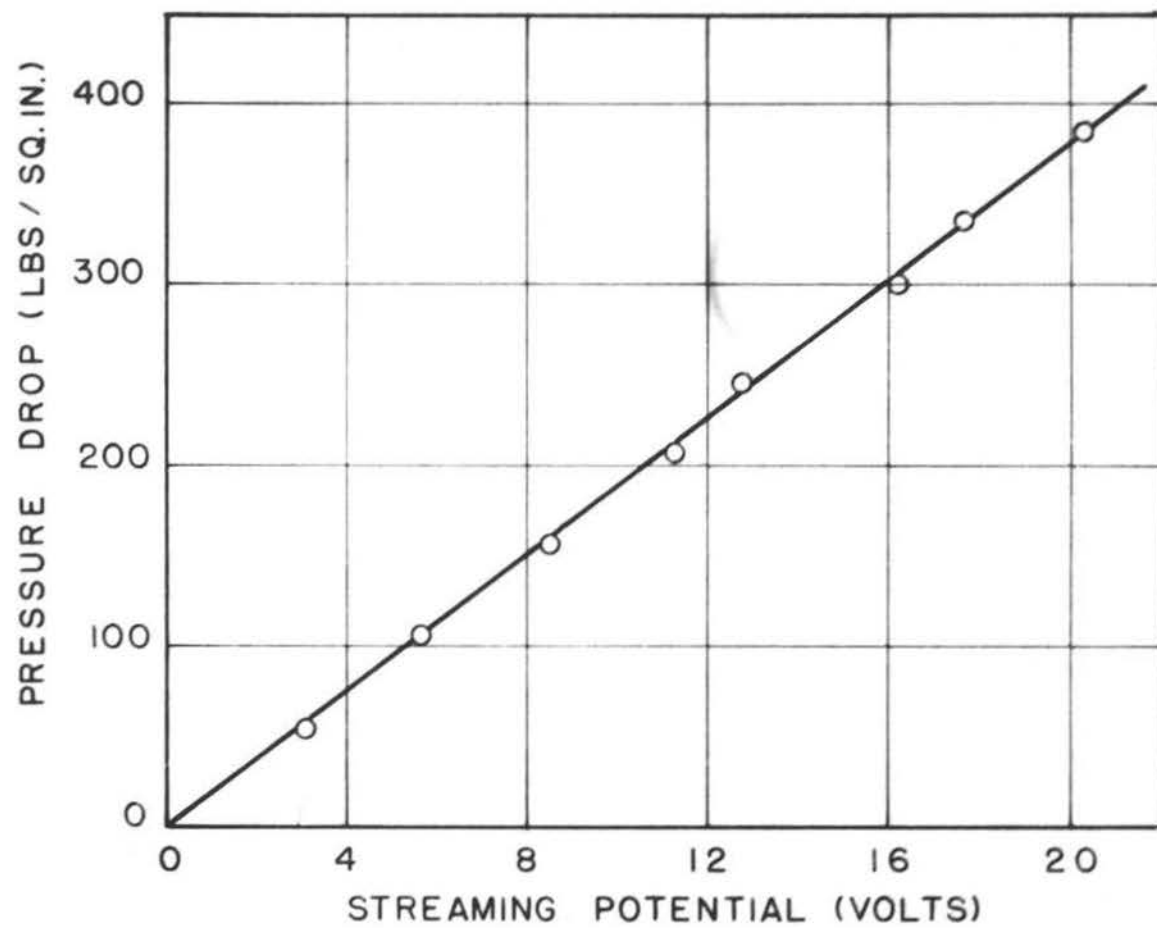


FIG. 10 STREAMING POTENTIAL VS PRESSURE DROP

Table 5. Pressure Drop and Streaming Potential

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$\Delta P$ (lbs/in <sup>2</sup> )	$V_s$ volts
56.	3.02
103.	5.39
155.	8.58
205.	11.17
245.	12.76
307.	16.18
334.	17.78
385.	20.13

---

If the streaming potential device acted as an electrostatic device, there would be no reason to think that the internal resistance would remain a constant. It is known that when the internal resistance is equal to the external resistance, the power output will be a maximum. Therefore, if the streaming potential device is a true power source, it will have a maximization of power at a constant external resistance and this external resistance will be equal to the internal resistance.

The maximization of power is illustrated in Figure 11 where the external power is plotted against the external resistance. It was verified that a maximum occurs between an external resistance of 300,000 ohms and 400,000 ohms. This experimental fact agreed with theory in that the previously determined internal resistance was equal to 336,000 ohms.

This maximization of power at a constant external resistance also gives merit to the fact that such a device is a true power source.

Table 6 is a list of the data plotted in Figure 11.

## V. APPLICATION

One possible application for a control system based on the principles of electrokinetic streaming potential would be a device which would measure the total pressure of a closed system.

Such a device would consist of a small packed bed of glass particles which would be maintained at a constant pressure at one end. The other end would be placed inside the vessel with which

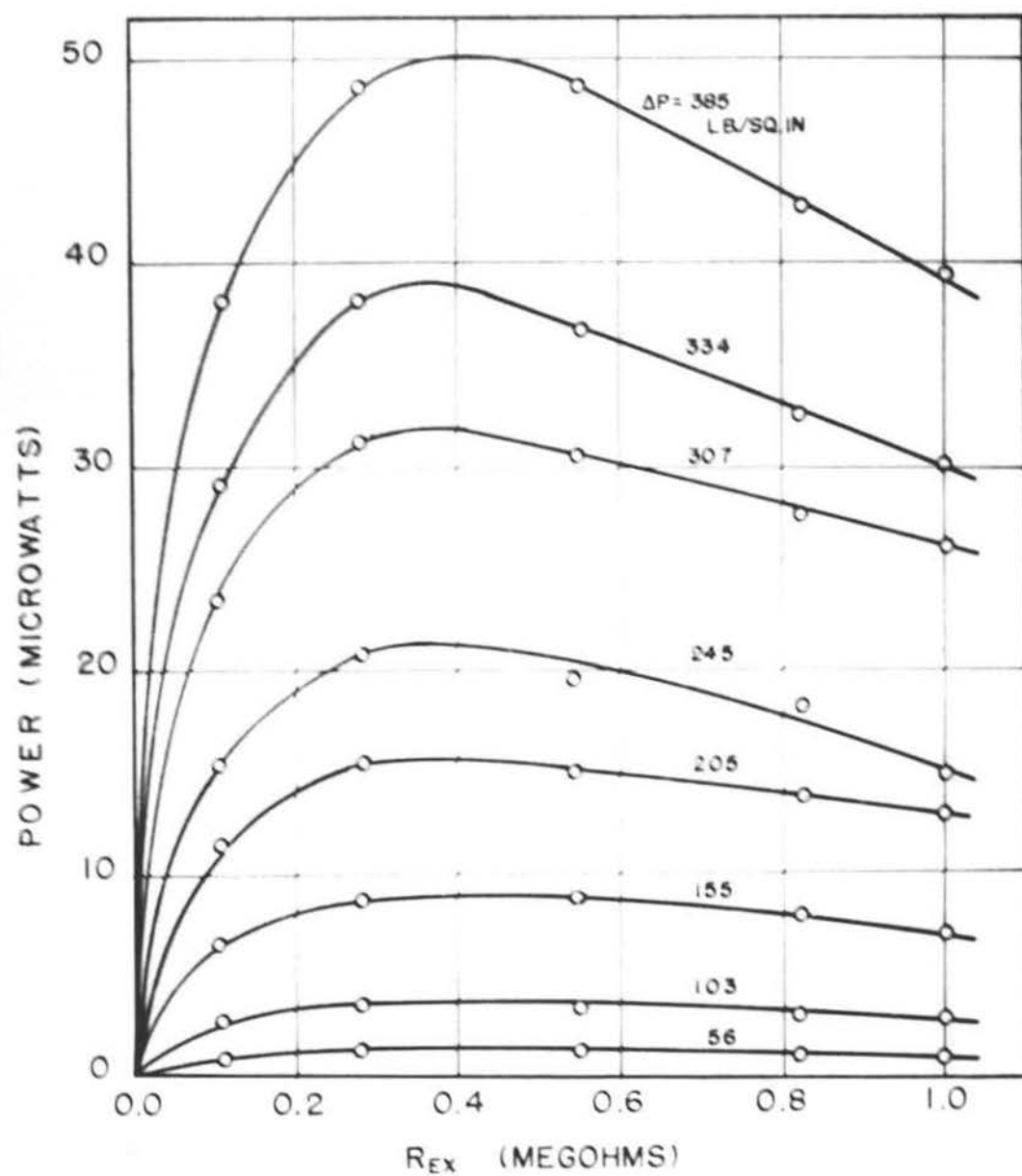


FIG. II MAXIMUM POWER

Table 6. Power (Microwatts)

$R_{ex}$ (ohms) \ $\Delta P$ (lbs/in <sup>2</sup> )	56.	103.	155.	205.	245.	307.	334.	385.
Shunt	--	--	--	--	--	--	--	--
1.272	--	--	--	--	--	--	--	--
11.66	--	--	--	--	--	--	--	--
96.48	--	0.004	0.009	0.0151	0.020	0.031	0.041	0.053
1064.	0.012	0.042	0.096	0.1663	0.224	0.341	0.439	0.588
11,390.	0.124	0.410	0.985	1.695	2.264	3.488	4.511	5.921
111,000.	0.815	2.775	6.581	11.323	15.195	23.338	29.131	37.990
282,600.	1.053	3.663	8.549	15.475	20.418	31.157	38.027	48.497
599,100.	1.012	3.480	8.651	14.978	19.465	30.201	36.450	48.527
821,000.	0.923	3.122	7.890	13.801	18.136	27.618	32.585	42.561
998,600.	0.882	2.886	7.066	12.942	16.786	25.974	30.208	39.634
2,829,000.	0.452	1.508	3.741	6.450	8.272	13.077	15.358	19.867
5,927,000.	0.247	0.856	1.994	3.606	4.182	7.172	8.535	10.802
8,407,000.	0.182	0.608	1.483	2.731	3.337	5.247	6.218	7.910
13,490,000.	0.124	0.390	1.020	1.847	2.268	3.509	4.081	5.186
25,800,000.	0.067	0.214	0.542	0.941	1.193	1.923	2.322	2.982

one intends to measure the total pressure. The total current generated from the electrodes of the packed bed would be a direct function of the pressure difference across the packed bed. Since the streaming potential device is a direct means of obtaining an electric current, it would be unnecessary to use any mechanical devices. The electric current from the electrodes would be used to activate some type of electronic relay. Figure 12 is a diagram of such a control system.

One requirement is that the constant pressure be greater than the internal pressure in order to avoid any contamination of the packed bed. Also, the flow rate should be as small as possible so as to avoid a large excess of liquid to flow into the vessel being measured.

It can be seen from the models postulated, that the internal resistance of the packed bed should equal the external resistance of the electronic relay. Also, the polarization resistance of the electrodes should be taken into account.

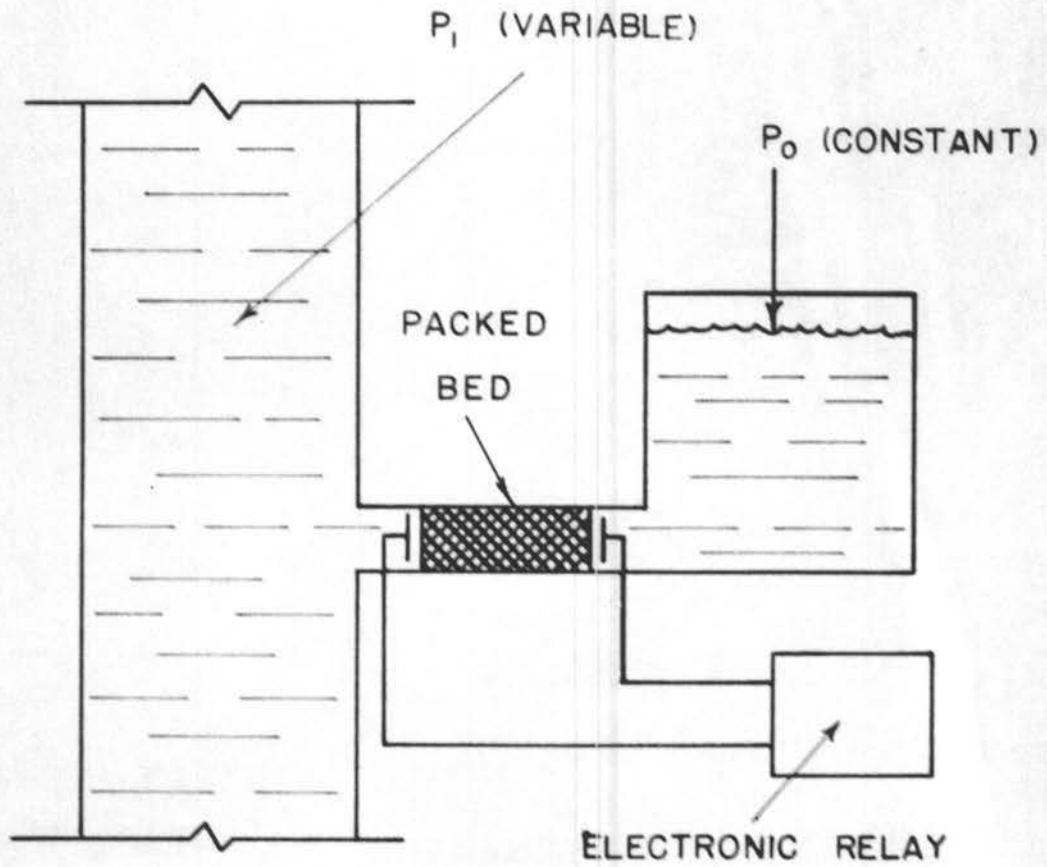


FIG. 12 TOTAL PRESSURE CONTROL DEVICE

## VI. CONCLUSION

A streaming potential device was investigated as a source of electrical power. In the investigation, the basic theory of the development of the streaming potential equation or Helmholtz equation was derived showing that the total current in the device was a constant in a particular column and at a particular pressure. The total current was also independent of the external load applied to the platinum electrodes. In order to look at a streaming potential device as a method of obtaining power, several equivalent circuits or models were developed. The first model was shown to be correct if there was little or no polarization at the electrodes. However as the current increased, a deviation from linearity was noticed and a correction was made to the equivalent circuit. The corrected version was called model II and it included the polarization resistance at the electrodes. The polarization resistance was assumed to be a constant with respect to the external current. This model fit the data much better than model I; however, there was also some deviation at high currents. This deviation was not as great as the previous deviation in model I. The deviation was attributed to the fact that the polarization resistance was not a constant but was actually a function of the external current. Model III was the equivalent circuit of the case where the polarization was a function of the external current. The third model was only postulated and was not verified by experimental data.



To further verify the models, the zeta potential was calculated from the models and was shown to be constant. This result indicates the validity of the models.

The corrected streaming potential was also calculated from the models compared to the basic Helmholtz equation. These results further verify the models in that a straight line was obtained which followed the Helmholtz equation.

Finally, the power was calculated and the results indicated that the maximum power was obtained at a constant external load which was equal to the internal resistance. This fact also verifies the equivalent circuit of the models.

It was shown that the streaming potential was a linear function of the pressure gradient up to 6.64 psi/inch.

The maximum power obtained from the device was 48.5 microwatts. This corresponds to 0.328 microwatts per cubic inch of packed bed.

All of these facts verify the idea that a streaming potential device acts as a true source of power and a source of power which can do useful work such as the activation of devices in control systems.

## NOMENCLATURE

A	Area
D	Dielectric Constant
E	Electrical Force
F	Electrical Field
$I_{ex}$	External Current
$I_{in}$	Internal Current
$I_t$	Total Current
i	Current
k	Conductivity of the Fluid
$k_s$	Conductivity of the Packed Bed
$K_m$	Ratio of Conductivities
L	Length of the Column
$\bar{n}$	Unit Vector
$\Delta P$	Pressure
q	Electronic Charge
Q	Charge per unit time
$R_{ex}$	External Resistance
$R_{in}$	Internal Resistance
$R_p$	Polarization Resistance
$R_v$	Volumetric Resistance
S	Surface Area
u	Velocity
V	Volume, Volts

$V_s$	Streaming Potential
$x,y,z$	Coordinates
$\eta$	Viscosity
$\rho$	Volume Charge Density
$\sigma$	Specific Resistivity
$\Psi$	Total Potential with Applied EMF
$\phi$	Total Potential without Applied EMF
$\zeta$	Zeta Potential

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APPENDIX

## APPENDIX

Run #8

Temperature 22 C

100 mesh beads

Length of column 58 inches

Diameter of column 1.75 inches

Data:

$\Delta P$	$R_{ex}$	$I_{ex}$ (Amps)
0 psia	#1	$1.1 \times 10^{-8}$
	#2	1.0
	#3	1.0
	#4	$9.5 \times 10^{-9}$
	#5	9.5
	#6	$1.0 \times 10^{-8}$
	#7	$8.4 \times 10^{-9}$
	#8	5.0
	#9	4.6
	#10	3.1
	#11	3.3
	#12	1.2
	#13	$5.5 \times 10^{-10}$
	#14	4.9
	#15	2.2
	#16	1.5
56 psia	#1	$3.5 \times 10^{-6}$
	#2	3.5
	#3	3.5
	#4	3.5
	#5	3.4
	#6	3.3
	#7	2.71
	#8	1.93
	#9	1.30
	#10	1.06

$\Delta P$	$R_{ex}$	$I_{ex}$ (Amps)
	#11	$9.4 \times 10^{-7}$
	#12	4.0
	#13	2.04
	#14	1.47
	#15	$9.6 \times 10^{-8}$
	#16	5.1
103 psia	#1	$6.4 \times 10^{-6}$
	#2	6.4
	#3	6.4
	#4	6.3
	#5	6.2
	#6	6.0
	#7	5.0
	#8	3.6
	#9	2.41
	#10	1.95
	#11	1.70
	#12	$7.3 \times 10^{-7}$
	#13	3.8
	#14	2.69
	#15	1.70
	#16	$9.1 \times 10^{-8}$
155 psia	#1	$9.5 \times 10^{-6}$
	#2	9.5
	#3	9.5
	#4	9.5
	#5	9.5
	#6	9.3
	#7	7.7
	#8	5.5
	#9	3.8
	#10	3.1
	#11	2.66
	#12	1.15
	#13	$5.8 \times 10^{-7}$
	#14	4.2
	#15	2.75
	#16	1.45

$\Delta P$	$R_{ex}$	$I_{ex}$ (Amps)
205 psia	#1	$1.25 \times 10^{-5}$
	#2	1.25
	#3	1.25
	#4	1.25
	#5	1.25
	#6	1.22
	#7	1.01
	#8	$7.4 \times 10^{-6}$
	#9	5.0
	#10	4.1
	#11	3.6
	#12	1.51
	#13	$7.8 \times 10^{-7}$
	#14	5.7
	#15	3.7
	#16	1.91
245 psia	#1	$1.47 \times 10^{-5}$
	#2	1.45
	#3	1.45
	#4	1.45
	#5	1.45
	#6	1.41
	#7	1.17
	#8	8.5
	#9	5.7
	#10	4.7
	#11	4.1
	#12	1.71
	#13	$8.40 \times 10^{-7}$
	#14	6.3
	#15	4.1
	#16	2.15



$\Delta P$	$R_{ex}$	$I_{ex}$ (Amps)
307 psia	#1	$1.80 \times 10^{-5}$
	#2	1.80
	#3	1.80
	#4	1.80
	#5	1.79
	#6	1.75
	#7	1.45
	#8	1.05
	#9	$7.1 \times 10^{-6}$
	#10	5.8
	#11	5.1
	#12	2.15
	#13	1.10
	#14	7.9
	#15	5.1
	#16	2.73
334 psia	#1	$2.04 \times 10^{-5}$
	#2	2.04
	#3	2.04
	#4	2.04
	#5	2.03
	#6	1.99
	#7	1.62
	#8	1.16
	#9	$7.8 \times 10^{-6}$
	#10	6.3
	#11	5.5
	#12	2.33
	#13	1.20
	#14	$8.6 \times 10^{-7}$
	#15	5.5
	#16	3.0

$\Delta P$	$R_{ex}$	$I_{ex}$ (Amps)
385 psia		
	#1	$2.35 \times 10^{-5}$
	#2	2.35
	#3	2.35
	#4	2.35
	#5	2.35
	#6	2.28
	#7	1.85
	#8	1.31
	#9	$9.0 \times 10^{-6}$
	#10	7.2
	#11	6.3
	#12	2.65
	#13	1.35
	#14	$9.7 \times 10^{-7}$
	#15	6.2
	#16	3.4

#### EXTERNAL RESISTANCES

Number	Resistance (ohms)
#1	shunt
#2	1.272
#3	11.66
#4	96.48
#5	1064
#6	11,390
#7	111,000
#8	282,600
#9	599,100
#10	821,000
#11	998,600
#12	2,829,000
#13	5,927,000
#14	8,407,000
#15	13,490,000
#16	25,800,000

Conductivity of the distilled water

---

#1 sample	(19,900. ohms cm) <sup>-1</sup>
#2 sample	(19,720. ohms cm) <sup>-1</sup>
#3 sample	(19,040. ohms cm) <sup>-1</sup>
#4 sample	(19,030. ohms cm) <sup>-1</sup>
#5 sample	(18,970. ohms cm) <sup>-1</sup>
#6 sample	(18,820. ohms cm) <sup>-1</sup>

---

Internal resistance of the column (running)

---

#1 sample	352,000. ohms
#2 sample	345,000. ohms
#3 sample	344,000. ohms
#4 sample	329,000. ohms
#5 sample	340,000. ohms
#6 sample	320,000. ohms
#7 sample	323,000. ohms

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Electrodes

Platinum (Platinized)