A Study of some Electro-Kinetic properties of Rocks

by

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ABSTRACT

A STUDY OF SOME ELECTRO-KINETIC PROPERTIES OF ROCKS

In this paper the author investigates the effects and importance of streaming potentials in the measurement of induced polarization.

Several specimens of sedimentary rocks of various pore sizes were investigated.

Water was pushed through solid and ground rocks and the streaming potentials measured.

Surface conductance appeared to be an important factor which was computed to make the necessary corrections in the potentials of the various specimens.

In order to correlate the streaming potentials with the determination of the potentials and to explain any discrepancies in the results, all the possible physical characteristics of the rocks which might influence these results (porosity, permeability, tortuosity), were measured.

The potentials computed from solid rocks seem to be very close of the potential of the minerals
composing the rocks.

However the streaming potentials were found to be small and therefore their effects practically negligible when measuring induced polarization.

Thus, after measuring the streaming potential, the \( \xi \) potential and the surface conduction, the induced polarization can be determined.
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I- INTRODUCTION

In about 1860, Quincke discovered that when he forced water through a clay diaphragm a potential developed across it. He realized that this effect was a phenomenon inverse to electro-osmosis, which had been observed as early as 1807 by Reuss. The next significant contribution to a clarification of streaming potential—in fact, to the whole field of electro-kinetics; was made by Helmholtz in his classical theoretical analysis;

When a liquid flows through a conduit, the ions of the movable layer are carried along with the liquid flow. If there is a surplus of charge in the displaced layer (subsequently referred as a displaceable charge), a streaming current is generated.

This ionic convection current tends to cause a deficiency of charge at the entrance of the conduit and a surplus of charge at its exit. To prevent the formation of the deficiency and surplus of charge at the opposite ends, a conduction current develops through any electrical path that may be present. If no external path exists and the walls of the tube are a non conductor, the only path for the conduction current is through the bulk of the solution.
It was originally thought that this electro-kinetic electrical property of rocks might be of importance as a property of rocks that might cause induced polarization type effects.

Although the first experiments showed no important effect from this point of view, it was decided to tie down the effects enough so that one had a reasonable understanding of the phenomena.

The general theory of electro-kinetic effects is made in the case of laminar fluid flow. However it is possible to make corrections in the case of surface conduction.

If the fluid flow is turbulent, the problem of setting up an equation for the streaming potential becomes difficult to handle mathematically.

In order to explain the possible discrepancies of the results, it was decided to measure all the possible physical characteristics of the rocks which might play a role.

The surface conductance, (the detailed conception of this phenomenon will be given later), can be relatively important in the case of low resistance of the liquid circulation inside the capillaries.

This resistance depends upon the conductivity
of the liquid circulating inside the capillaries, the cross section and the length of the capillaries.

The porosity and permeability give an importance of the pore size and allow us to get an idea of the surface conductance, in comparison to the bulk conductivity of the liquid inside the capillaries.

The tortuosity (the square root of the ratio:

\[
\frac{\text{length of the path of water in the porous plug}}{\text{length of the specimen}}
\]

can be of importance as far as the law of liquid flow inside the specimen is concerned.

II - STREAMING POTENTIALS

A calculation of the streaming potential can be based upon the following considerations. The difference of pressure applied to the end of a capillary (or to both sides of a porous plug) causes a flow through the capillary. This liquid stream carries along with it part of the charge of the "double layer" (a detailed conception of this physical phenomenon will be given below) and so is the bearer of an electric convection current.

As a consequence of this transport of charge, a potential difference arises between the ends of the capillary, which causes a conduction current through the capillary directed oppositely to the convection current.
In the stationary state, the convection current, which is proportional to the pressure difference \( P \), just counterbalances the conduction current which is proportional to the potential difference \( E \). Consequently the streaming potential \( E \) is proportional to the pressure \( P \). The factor of proportionality can be determined by a reasoning given below.

The electro-kinetic phenomena are based on the properties of the double layer and the \( E \) potential.

The electrical double layer consists of excess ions (or electrons) present on the solid phase and an equivalent amount of ionic charge of opposite sign distributed in the solution phase near the interface.

The charge on the solid "wall" is treated as a surface charge smeared out uniformly over the surface. The space charge in the solution is considered to be built up by unequal distribution of point-like ions. The solvent is treated as a continuous medium influencing the double layer only through its dielectric constant.

The Coulomb interaction between the charges present in the system is described by Poisson's equation

\[
\nabla^2 \varphi = -\frac{4\pi \rho}{\varepsilon} \tag{1}
\]

between the potential \( \varphi \), which changes from a certain value at the interface to zero in the bulk of the
solution and the charge density

\[ \varepsilon \] is the dielectric constant

\[ \nabla^2 \] Laplace operator.

1- ZETA POTENTIAL -

It appears that, in all modes of calculation the electrical potential in the slipping plane between the fixed and the flowing liquid is determinative for the electro-kinetic phenomena.

This potential is usually called the Zeta-potential \((\xi)\).

2- DERIVATION OF THE FORMULA -

In the case of water pressed through a glass capillary, the wall is negatively and the liquid positively charged. These positive charges are carried with the liquid (convection of electric charge); if the length of the capillary is "1", the radius of the circular section \((r)\), the velocity of the liquid in the capillary is given by:

\[ u(r) = \frac{P}{4 \eta t} \left( r^2 - r^2 \right) \]

\[ \frac{d\omega}{dr} = \frac{-Pr}{2 \eta t} \]

\(P\) hydrostatic pressure through the capillary

\(\eta\) viscosity of the liquid.

The gradient of the velocity at the wall is

\[ \left( \frac{d\omega}{dr} \right)_{r=r} = \frac{-Pr}{2 \eta t} \]
The diffuse electric charge in the liquid is situated in the immediate neighborhood of the wall; the thickness of the diffuse layer is very small in comparison with the radius of the capillary; therefore, in the calculation of the transport of electric charge by convection, the wall of the capillary may be considered to be flat.

The velocity of the liquid in the immediate neighborhood of the wall, at a distance \( x \) from the wall will be

\[
\psi(x) = \left( \frac{d\psi}{dx} \right)_{x=0} x = \frac{P_2}{2\pi L} x
\]

The electric charge carried away per second amounts to

\[
I_1 = 2\pi \eta \int_0^\infty \psi(x) \psi(x) dx = -2\pi \eta \int_0^\infty \frac{P_2}{2\pi L} \frac{d^2\psi}{dx^2} x dx
\]

\( \varepsilon_2 \) : dielectric constant of the liquid

\[
I_1 = -\varepsilon_2 \frac{P_2}{4\pi L} \left[ x \frac{d\psi}{dx} \right]_0^\infty + \varepsilon_2 \frac{P_2}{4\pi L} \int_0^\infty \frac{d^2\psi}{dx^2} dx
\]

\( \xi_2 \) : Zeta potential of the double layer.

This transport of charge will cause an electric potential difference \( E_1 \) between the two ends of the capillary, which will give rise to a current of conduction \( I_2 \) given by:

\[
I_2 = \sqrt{\varepsilon_2 \frac{P_2}{L} \pi \eta^2}
\]

stationary state \( I_1 - I_2 \) will and therefore

\[
\frac{E_1}{P} = \frac{\varepsilon \xi_2}{4\pi \eta L}
\]
specific electric conductivity of the liquid.

This is the Helmholtz-Smoluchowski equation: the length $l$ and the radius $r$, of the capillary do not appear in the final equation.

ASSUMPTIONS UPON WHICH THE STREAMING POTENTIAL FORMULA IS BASED.

a) $\varepsilon$ the dielectric constant of the liquid in the region of an interface is assumed to be equal to that of the liquid in bulk. Measurements of the dielectric of water in the presence of an electric field show that for water can be lowered from a value of 80 to a value of 1 by placing the water in an electric field of the order of 500,000 volts per centimeter.

Helmholtz and Quincke estimated the distance across an interface to be of the order of $10^{-5}$ centimeter, that is the thickness of the molecule. If the $\varepsilon$ potential were then of an order of 0.2 volts, it is easily seen that the liquid in the interfacial layer is being acted upon by an extremely high electrical field and its dielectric constant might be greatly reduced.

According to the theory of Gouy on the existence of a diffuse double layer, which postulates a much greater distance between the centers of electrical charge than that estimated by Helmholtz, it seems probable that the electrical
field extant in interfacial regions may not be high enough to entirely eliminate \( \varepsilon \) from the equation.

b) \( \eta \) the viscosity of the liquid is assumed to remain a constant for dilute salt solutions and to be equal to that of the pure liquid in the bulk.

Helmholtz's equation also leaves out of consideration any effect due to slippage of the liquid layer along the surface of the solid, assuming all motion to be between two liquid layers, where \( \eta \) would be the only factor. LAMB, however introduces a term, \( \frac{1}{\beta} \) into all the equations of Helmholtz, where \( \beta = \) the coefficient of slippage at solid-liquid interface and linear magnitude of this slippage.

c) The flow of liquid.

As to the flow of liquid one postulates a purely laminar flow, with a coefficient of viscosity, having the same value throughout the whole system.

There have been some differences of opinion concerning the boundary conditions of the movement of the liquid. In considerations using Perrin's condenser layer, the liquid is assumed to be at rest in a plane coinciding with the charge on the wall.

Helmholtz and especially Lamb have taken account of the possibility of a slip along the wall, but no
experimental evidence in favour of such a slip has ever been found.

In 1928, Reichardt showed in his doctoral thesis that it is not necessary to assume that the entire liquid flow be laminar in order that the displaced ions be moved with constant velocity parallel to the wall. The basis of his presentation was that a film exists at any liquid-solid interface whose flow is always laminar even if the flow in the interior of the liquid is turbulent; therefore, the necessary criterion is that the flow be established or be developed so as to cause the steady state.

Bocquet, Sliepcevich, Bohr, in a recent paper have checked experimentally this theory and found that the Helmholtz-Smoluchowski equation for the streaming potential is valid for both laminar and turbulent flow.

The specific conductivity factor found in the equation refers to that of the liquid. In the derivation of the streaming potential formula it will be remembered that the solid phase is assumed to have a negligible amount of conductivity. Also any surface conductivity is disregarded.

The surface conduction is the extra conductivity along the capillary.

This surface conductivity has for its origin:
- The double layer contains more ions than the bulk of the liquid. These excess ions cause the surface conductivity by their motion in the electrical field.

- The effect of this surface conduction is important when the bulk resistance of the fluid inside the capillaries is small. The pore size of the specimens can play an important role and contribute to minimize or increase the surface conduction.

It is not difficult to make the necessary corrections for the surface conductance, if the streaming potential is determined by a capillary of radius (r).

In the case of a porous plug (assemblage of capillaries in parallel) the return current is proportional to \( \pi r^2 \lambda + 2 \pi r \lambda_j \) instead of \( \pi r^2 \lambda \) and the corrected equation for the streaming potential becomes:

\[
\frac{E}{P} = \frac{E \xi}{4 \pi \xi \left( \lambda + \frac{2 \lambda_j}{r} \right)}
\]

\( \lambda \): bulk conductivity of the liquid

\( \lambda_j \): specific surface conductance.
III - STREAMINGS POTENTIALS AND THE ONSAGER'S PRINCIPLE

The Onsager's principle deals with irreversible phenomena. According to Onsager's theory the "forces" are causes which can give rise to the occurrence of irreversible phenomena.

These forces are denoted by \( X_i \) \((i = 1, 2, 3 \ldots n)\)

These forces cause certain irreversible phenomena. These are called together "fluxes" or sometimes flow or current.

They are symbolized by \( J_i \) \((i = 1, 2, 3 \ldots n)\)

The irreversible phenomena can be expressed by phenomenological relations of the general type.

\[
J_i = \sum_{k=1}^{n} \mathcal{L}_{ik} X_k \quad (i = 1, 2, 3 \ldots n)
\]

\( \mathcal{L}_{ik} \) \((i, k = 1, 2, 3 \ldots n)\) are the phenomenological coefficients

Onsager's fundamental theorems states that provided a proper choice is made for the "fluxes" \( J_i \) and "forces" \( X_i \), the matrix of phenomenological coefficients is symmetric, i.e.

\[
\mathcal{L}_{ik} = \mathcal{L}_{ki} \quad (i, k = 1, 2, 3 \ldots n)
\]

These identities are called the Onsager reciprocal relations.
In electro-kinetic effects, the "fluxes" are the electrical current \( I \) and the flow of water \( J \); the "forces" are the streaming potential \( \Delta \phi \) and the pressure gradient \( \Delta P \).

The phenomenological equations are:

\[
I = L_{11} \Delta \phi + L_{12} \Delta P \quad (1)
\]

\[
J = L_{21} \Delta \phi + L_{22} \Delta P \quad (2)
\]

\[
L_{12} = L_{21}
\]

The streaming potential is defined as the potential difference corresponding to unit pressure difference in the stationary state with zero electrical current.

\[
\left( \frac{\Delta \phi}{\Delta P} \right)_{I=0} = -\frac{L_{12}}{L_{11}}
\]

\( L_{11} \) is an electrical resistance

\( L_{12} \) is connected to the \( \xi \) potential and the double layer properties

\[
L_{11} = \frac{1}{\lambda + (2 \lambda - 1)} \quad \text{surface conduction}
\]

The streaming potential can then be derived directly from the Onsager's equations.

The second Onsager's equation

\[
J = L_{12} \Delta \phi + L_{22} \Delta P
\]

shows the liquid flow through a capillary does not depend only on the pressure gradient \( \Delta P \) but also on the streaming potential \( \Delta \phi \).

\( L_{22} \) is the hydrodynamical resistance of the
specimen.

$\Lambda_x$ is connected to the $\Xi$ potential and the double layer property.

In the calculation of permeability and rate of flow, we will come back later on, on the value and importance of $\Lambda_x A^y$ term.
Fig I

By comparing the direction of the external voltage applied to the electrodes 1 and 2 and the streaming potential, the polarity of the streaming potential is easily determined.

position A reversible switch

position B

Fig II

wetbird

nylon cloth
IV - EXPERIMENTAL PART

The purpose of this study is to show electro-kinetic properties of sedimentary rock and the importance of streaming potentials in these rocks.

As was already noted in the previous part, the streaming potential depends upon the general properties of capillaries or porous plugs.

The pore size and permeability were found to be important factors. They determine the importance of surface conductance compared to the importance of the resistance of the liquid circulating inside the capillaries and the type of flow that may be expected inside the capillaries.

To eliminate the surface conductance which seemed to play an important role in the case of solid rocks of relatively small porosity, we ground the rocks and studied the streaming potentials in the ground particles of rocks. We then measured the potentials of these rocks.

1) EQUIPMENT

a) The equipment shown in fig. (1) was used to measure the streaming potential in cylindrical rocks.

The specimen is placed between two chambers filled with water. One chamber (pipe 1), is connected
to an air pressure pipe controlled by a gauge. Two platinum wire electrodes dip in the liquid one in each chamber.

The voltage created between these two electrodes is chopped and measured with an A-C voltmeter.

In order to know the polarity of the created voltage, the circuit (fig.II) is connected in series with the electrodes 1 and 2.

Many difficulties were encountered in setting up the equipment.

The first problem that had to be solved was an electrode problem.

- The first electrodes used were the two brass flasks A and B of the chambers - As soon as the measuring circuit was closed, a large polarization effect was noticed (several hundreth of a volt in a few seconds).

It was therefore decided to change the brass electrodes for a less polarizable metal.

It is known that the contact electrode-liquid can be represented as a resistance and a condensor in parallel. This circuit is in serie with the resistance of the voltmeter.

If the polarization resistance is small, the
condenser is shorted out - No problems of reading are then encountered.

If the polarization resistance is big, one must try to increase the time constant of the circuit to make the readings possible.

- The capacitance of the electrodes must be large - as well as the resistance of the voltmeter.

For this reason, a relatively large surface contact liquid-electrodes must be used.

- Platinum electrodes, two wires of \( \phi \frac{1}{2} \text{mm} \) length 30 mm were then used.

- An appreciable polarization was still noticed.

- The surface area of the electrodes was then increased by soldering two thin plates of platinum to the original platinum wires (length 30 mm - width 20 mm - thickness 1/10 mm).

However the solder complicates the cleaning procedure and again some polarization was noticed.

The electrodes were cleaned thoroughly with a standard cleaning solution (sulfuric acid + potassium dichromate) and then dipped in nitric acid for 15 minutes. Finally the electrodes were boiled in distilled water for one hour; the water was changed three times during that time.
The platinum wire electrodes originally used were finally adopted since a thorough cleaning minimizes the polarization effect.

- The circuit was kept closed only during the minimum time required for the measurements.

- The entire equipment was made of plastic except the parts A-B-C-D, which were in brass and insulated from the electrical circuit.

- The cylindrical surface of the specimens was painted with a waterproof paint, deposited in thin layers and dried in an oven at 90° c. for two days.

- Water leakage problems in the equipment were solved after several tries by means of grease and flax.

b) - In order to measure the streaming potential in ground rocks the equipment described in fig. III was used.

The pressure is obtained by a waterhead.

The ground rock is placed in a glass tube (φ 8 mm.) the ends of which are closed by two stoppers of nylon cloth.

The platinum wire electrodes are the same as those used in part 1).
2) - MEASUREMENT OF POROSITY

No special equipment was used.

The specimen is weighed when soaked with water and when dry after remaining one day in an oven at 110°C.

- The difference of weights gives the content of water, and the volume of the porous part of the specimen.

The porosity is the ratio of this volume over the total volume of the specimen.

3) - MEASUREMENT OF PERMEABILITY

The equipment described in section 1) is used to measure the permeability of the rock specimens.

A pipe of glass, $\phi$ / mm, is connected to the plastic pipe 2.

The pipe 1 is connected to an air pressure pipe at the pressure 30

The water level rise is measured on the glass tube.

- The rate of flow can be measured in \( \text{cm}^3/\text{s} \)

The permeability in Darcy's is given by the formula

\[
\kappa = \frac{Q \mu L}{\Delta P A}
\]

\( Q \): rate of flow in \( \text{cm}^3/\text{s} \)
\( \frac{Q}{t} \) = rate of flow in \\
\( \mu \) = viscosity of water in centipoises \\
\( P \) = pressure in atmosphere \\
\( l \) = length of the specimen

It has previously been shown that the liquid flow through a capillary does not depend only on the pressure gradient \( \Delta P \) but also on the streaming potential 

\[ J = L_{12} \Delta \varphi + L_{22} \Delta \varphi \]

The value of \( L_{12} \Delta \varphi \) and its importance in the determination of "J" rate of flow shall be treated later on.

4) - SURFACE CONDUCTION MEASUREMENT

The rock specimen after soaking in water (conductivity \( \lambda_1 \)) is placed under a high frequency potential of 5 volt amplitude.

The measured current passing through the specimen is \( \chi \mu A \)

A high frequency voltage is used to minimize the electrode impedance.

To the same specimen, after soaking in a saturated salt solution (conductivity \( \lambda_2 \)), when the same 5 volt potential is applied, the current passing through the specimen is \( \gamma \mu A \)
In both cases the current is passing through the specimen can be expressed by the relation written below

\[ i = \lambda \left( 2\pi r \lambda_d + \pi r^2 \lambda_b \right) \]

\( r \): radius of the pores

\( \lambda_d \): specific surface conductance for the rock sample

\( \lambda_b \): bulk conductivity of the liquid.

We then get the system of equation

\[ x = \lambda \left( 2\pi r \lambda_d + \pi r^2 \lambda_b \right) \]

\[ y = \lambda \left( 2\pi r \lambda_d + \pi r^2 \lambda_b \right) \]

\[ \frac{x}{y} = \frac{2\lambda d}{2\lambda d + \lambda b} \]

Knowing the currents \( x \) and \( y \), as well as \( \lambda_d \) and \( \lambda_b \), we can compute \( \frac{2\lambda d}{\pi} \).

5) - **Tortuosity**

If \( L \) is the length of the specimen and \( L_c \), the length of the flow path, the tortuosity is defined as below

\[ \tau = \left( \frac{L_c}{L} \right)^2 = \text{tortuosity of the porous medium}. \]

The resistance of a homogeneous porous medium saturated with conducting fluid of resistivity \( \rho_a \), may be considered to be the resistance of a volume of fluid of length \( L_c \), area \( \phi A \), where \( L_c > L \) and \( L \) is the macroscopic length of a porous medium of porosity \( \phi \).
Thus, the resistance of a saturated porous medium is

\[ R_c = \frac{L \varepsilon}{\phi A} \]

However, the resistance of the volume of fluid of the same external dimensions as the saturated porous medium and measured using the same orientation of electrodes is:

**Fluid resistance:** \( R_c = \frac{L}{A} \)

Hence

\[
F = \frac{\text{Resistance of saturated porous medium}}{\text{Resistance of fluid}} \\
= \frac{\frac{L \varepsilon}{L}}{\frac{1}{\phi}} \\
= T^{\frac{1}{2}} \phi \\
T = F^2 \phi^2 \\
T^{\frac{1}{2}} = \frac{L}{L \varepsilon} = F \phi
\]

\( F \) can be measured easily as shown in section IV using a calibrated resistance in the AC measuring equipment.

The resistance of the fluid is easy to measure when the dimension of the specimen and the conductivity of the liquid are known.

The \( \phi \) porosity is known (see section II).
Five specimens of sedimentary rocks have been used in the experiments.

1- SPECIMEN A₁

a) **Origin:**
   - South Maunie field
   - Palestine sand (Mississipian)
   - White county (Illinois)

b) **Mineralogy:**
   - Quartz 90% - Mica

c) **Dimensions:**
   - Cylinder
   - length = 4 cm;
   - \( \phi = 2.8 \text{ cm} \).

d) **Porosity**

   Weight of specimen soaked with water: 59.99 g
   Weight of dry specimen: 56.87 g
   Weight of water: 0.312 g

   That is a volume of pore of 3.12 cm³

   Porosity = 13.3%

e) **Permeability**

   Under a pressure of 30 psi, the rise of water level, per minute in a tube of \( \phi = 1 \text{ mm} \) is 47 mm

   Rate of flow = \( 0.123 \times 10^{-3} \text{ cm}^3 / \text{s} \)

   **Permeability in Darcys**

   \( k = \frac{\phi h l}{\mu PA} \)

   \( \frac{\phi}{\mu} \) rate flow in \( \text{ cm}^3 / \text{s} \)

   \( \mu \) viscosity water in centipoises = 1
\[ P \text{ atmospheres} = 3 \times 0.069 \]
\[ L = 4 \text{ cm}. \]

Under a pressure of 30 psi, the rate of water level, per minute in a tube of \( \phi = 1 \text{ mm} \) is \( \frac{47}{5} \text{ mm} \)
rate of flow = \( 0.123 \times 10^{-3} \text{ cm}^3/\text{s} \)

f) **Resistivity measurement**

AC measurement.

- **Calibration of our measurement apparatus.**

For 5 volts, high frequency AC current, a resistance of 100,000 \( \Omega \) corresponds to a reading of 32.5 \( \mu \text{A} \)

1) Measurement with specimen soaked with tap water (conductivity \( \frac{1}{1925} \text{ \Omega}^{-1}\text{cm}^{-1} \))

Resistance of specimen soaked with water
\( 34200 \Omega \)

2) Measurement with specimen dipping in salt saturated water (conductivity \( \frac{1}{4.82} \text{ \Omega}^{-1}\text{cm}^{-1} \)).

We have recorded the variation of resistance versus time, until the specimen is completely saturated with liquid. See table I and corresponding curve for specimen A1

g) **Tortuosity**

Resistance of fluid : \( 1250 \Omega \)
Resistance specimen : \( 34200 \Omega \)

\( \text{porosity} : 13\% \)
\( T^{1/2} = 3.5 \)
a) **Origin:** 
slaughter field  
San Andreas (Permian)  
Cochron Co - Texas

b) **Mineralogy:** 
Dolomite - calcite

c) **Dimensions:** 
Cylindrical  
length : 4.8 cm.  
$\phi$ : 2.8 cm.

d) **Porosity:** 
Weight of specimen soaked with water: 81.66 g  
Weight of dry specimen: 80.37 g  
Weight of water: 1.29 g  
that is $1.29 \text{ cm}^3$  
Porosity $= 4\%$

e) **Permeability:** 
raise 26.5 mm in 70 minutes

$k \text{ Darcys} = 1.88$ Darcys

f) **Resistivity measurement:**
1) with specimen soaked with tap water ($L = \frac{l}{1925} \Omega \cdot \text{cm}^{-1}$)  
Resistance of specimen $59000 \Omega$

2) specimen in salt water  
see table (I) and curve for $A_2$

g) **Tortuosity:** 
Resistance of fluid : $1500 \Omega$  
Resistance specimen : $59000 \Omega$  
Porosity $= 4\%$  
$\sqrt{T} = 1.7$
3- SPECIMEN $A_3$

a) **Origins:**

West Seminde Field
San Andreas - Permian
Andrews Co - Texas

b) **Mineralogy:**

Quartz essentially

c) **Dimensions:**

Cylindrical

- $l = 45$ mm.
- $d = 28$ mm.

d) **Porosity:**

Weight specimen soaked with water: 68.66 g
Weight dry specimen: 63.17 g

That is $5.49 \text{ cm}^3\text{ water}$

Porosity = 20%

e) **Permeability:**

- raise 120 mm in two hours
- tube: 8 mm
- pressure 30 psi
- flow = $0.050 \text{ cm}^3/\text{s}$

$k = 1.7 \times 10^{-4}$ Darcy

f) **Resistivity measurement:**

1) specimen soaked with tap water ($L = \frac{1}{1325} \Omega^{-1}\text{cm}^{-1}$)

$R = 13600 \Omega$

2) salt water - see table I and curve

g) **Tortuosity:**

Resistance of fluid 1400 $\Omega$

Resistance specimen 13800 $\Omega$

Porosity 20%

$T^{1/2} = 2$
4- SPECIMEN A4

a) Origin: Red sandstone - Massachusetts

b) Mineralogy: Mica - quartz - hematite (very dispersed)

c) Dimensions

\[ l = 4.35 \text{ cm.} \]
\[ \phi = 2.8 \text{ cm.} \]

d) Porosity

Weight wet specimen: \(69.00 \text{ g}\)
Weight dry specimen: \(67.23 \text{ g}\)
Weight water: \(1.77 \text{ g}\)

that is \(1.77 \text{ cm}^3\) water.

Porosity = \(7\%\)

e) Permeability

Water level rise 334 mm in 55 minutes

tube 1 mm. pressure 30 psi

Flow: \(8 \times 10^{-5} \text{ cm}^3/\text{s}\)

Darcys = \(2.73 \times 10^{-7}\)

f) Resistivity measurement

1) Specimen soaked with tap water

\[ L = \frac{1}{1925} \text{ cm}^{-1} \]
\[ \mathcal{R} = 37,300 \Omega \]

2) Specimen soaked with salt water see table I and curve.

g) Tortuosity

Resistance of fluid \(1350 \Omega\)
Resistance specimen 37,300 $\Omega$
Porosity: 7%
$\pi^{1/2}/1.8$

5- SPECIMEN A5

a) Origin
   Unknown

b) Mineralogy
   Shale

c) Dimensions
   $l = 5.3$ cm.
   $\phi = 2.8$ cm.

d) Porosity
   Weight wet specimen: 90.51 g
   Weight dry specimen: 90.16 g
   Weight water: 0.35 g
   That is: 0.35 cm$^3$
   Porosity = 1%

e) Permeability
   Water level rise 7.1 mm in 131 minutes
   $\phi$ tube 1 mm. Pressure 30 psi
   Flow = $7.15 \times 10^{-7}$ cm$^3$/

   $k$ Darcy = $3.10^{-9}$ Darcy

f) Resistivity measurement
   1) Specimen soaked with tap water
      $L = \frac{1}{1925}$ $\Omega$ cm$^{-1}$
      $R = 50,000 \Omega$
   2) with salt water
      see table I and curve A5
g) **Tortuosity**

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<thead>
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\[ T^{1/2} = 3.2 \]
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<th>Conduction Solution (Ω·cm⁻¹)</th>
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</table>
VI - STREAMING POTENTIALS

The streaming potentials created in our rock samples were measured in order to compute an average potential for these rocks.

However we found that the surface conduction plays a very important role in these electro-kinetic phenomena.

- We then tried to make a correction for the surface conduction, in the evaluation of the $E_1$ potential.

- The role played by surface conduction in brought out by resistivity measurements of each specimen soaked in liquids of different conductivities. If the resistances of the sample do not vary proportionally with the specific resistivity of the liquids in which they soak, we have a proof of the role of surface conduction and a way to compute its influence.

I- A1 SPECIMEN

a) Rock specimen

The specimen after soaking in water (conductivity $\frac{1}{1925} \Omega \text{cm}^{-1}$) is placed under a high frequency potential of 5 volts amplitude.

The measured current passing through the
specimen is 95 μA

When a 5 volts potential is applied to the same specimen after soaking in a saturated salt solution of conductivity $\frac{1}{4.82} \Omega^{-1} \text{cm}^{-1}$, the current passing through the sample is 2400 μA

$$\frac{95}{2400} = \frac{\frac{2 \lambda_A}{r} + \lambda_1}{\frac{2 \lambda_A}{r} + \lambda_2}$$

If $\frac{2 \lambda_A}{r} = A$

$$\frac{95}{2400} = \frac{1}{\frac{19.15}{4.82} + A}$$

We get $A = 8.10^{-3} \Omega^{-1} \text{cm}^{-1}$

Total conductivity

$$(0.52 + 8.10^{-3}) \Omega^{-1} \text{cm}^{-1}$$

Or after conversion in the c.g.s.e.s. system:

$8.52 \times 10^{-3} \text{ cm} = 8.52 \times 9 \times 10^8 \text{ cgses units}$

We know from equation (9)

$$\mathcal{E} = \frac{E 4 \pi \eta (\lambda + \frac{2 \lambda_A}{r})}{\mathcal{P} \times \varepsilon}$$

$\mathcal{E}$ : coefficient of viscosity in poises for water.

$\varepsilon$ : the dielectric constant of water has been considered as having the value 80

$\mathcal{P}$ must be expressed in dyne/cm

$E$ = in millivolts

$\lambda + \frac{2 \lambda_A}{r}$ observed in $\Omega^{-1} \text{cm}^{-1}$ must be multiplied by $9 \times 10^8"$ to convert it into c.g.s.e.s. units.

Average for $E = 16$ millivolts (Table II)
**TABLE II**

**A1 SPECIMEN - Rock sample**

**Streaming potentials**

<table>
<thead>
<tr>
<th>Tests</th>
<th>Voltage at 0 psi</th>
<th>Voltage at 30 psi</th>
<th>Streaming Potential</th>
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</table>

**Average streaming potential**

16 ± 1 millivolts
### TABLE III

**A1 SPECIMEN - Ground rock**

**Streaming potential**

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<th>Tests</th>
<th>Voltage P=0cm water in millivolts</th>
<th>Voltage P=85cm w. in millivolts</th>
<th>Streaming potential in millivolts</th>
<th>Voltage P=0cm water in millivolts</th>
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</table>

**Average streaming potential**

$2 \pm 1 \text{ mv.}$

\[ + \quad \text{polarity} \quad - \]

\[ P \quad \text{Pressure} \]
b) **Ground specimen**

No evidence of surface conduction was noted. This has been checked by measuring the resistance of a glass tube filled with the ground specimen, impregnated with liquids of various conductivities.

\[
E = \frac{E 4\pi \eta \lambda}{\rho \varepsilon}
\]

\[E = 2 \text{mV}\]  

**Table III**

\[
\eta = 0.01 \text{ poises}
\]

\[\lambda = \frac{1}{2600} \text{ 9.10'' cgses units}\]

\[\varepsilon = 80 \text{ cgses units}\]

\[\rho = 85 \text{ cm water} = 85 \times 980.638 \text{ dynes/cm}\]

\[
E = \frac{2 \times 0.01 \times 9 \times 10^{-7} \times 4\pi}{2600 \times 85 \times 980.638 \times 80}
\]

\[= -14 \text{ millivolts}\]

---

**2- A2 SPECIMEN**

a) **Rock specimen**

Specimen after soaking in water (conductivity \[\frac{1}{1925} \Omega^{-1} \text{cm}^{-1}\])

Potential 5V A.C Current 55\mu A

Specimen after soaking in salt water (conductivity \[\frac{1}{4.82} \Omega^{-1} \text{cm}^{-1}\])

Potential 5V A.C Current 89\mu A

Determination of surface conduction:
### TABLE IV

A2 SPECIMEN - Solid rock

**Streaming potential**

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</table>

**Average streaming potential**

\[ 4 \pm 1 \text{ mv.} \]

**polarity**

+ --- - ---+ PRESSURE
### TABLE V

**A2 SPECIMEN - Ground rock**

**Streaming potentials**

<table>
<thead>
<tr>
<th>Test</th>
<th>Voltage p: 0 cm water</th>
<th>Voltage p: 8 cm water</th>
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<th>Voltage p: 8 cm water</th>
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</table>

**Average streaming potentials**

5 ± 1 mv.

---

**polarity**

![Pressure Diagram](image-url)
\[
\frac{55}{29} = \frac{1}{4.82} + A
\]

\[
A = 324 \cdot 10^{-3} \Omega^{-1} \text{cm}^{-1}
\]

\[
\xi = \frac{4 \pi \eta (\lambda + \frac{2 \lambda \lambda}{\rho})}{\rho \times \xi}
\]

\[
E = 324 \text{ millivolts}
\]

\[
\lambda + \frac{2 \lambda \lambda}{\rho} = (324 + 0.52) 10^{-3} \times 9 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}
\]

all other factors see p (17)

\[
\xi = -830 \text{ millivolts}
\]

b) Ground specimen

No surface conduction

\[
P = 80 \text{ cm} \text{ water} = 80 \times 980.638 \text{ dynes/cm}^2
\]

\[
E = 4.87 \text{ millivolts}
\]

others factors, see section about A1 specimen.

\[
\xi = -54 \text{ millivolts}
\]

3- A3 SPECIMEN

a) Specimen after soaking in water

(conductivity \( \frac{1}{1925} \) \( \Omega^{-1} \text{cm}^{-1} \))

Potential 5V, AC Current 235\( \mu \text{A} \)

Specimen after soaking in salt water

(conductivity \( \frac{1}{4.82} \) \( \Omega^{-1} \text{cm}^{-1} \))

Potential 5V, AC Current 2950\( \mu \text{A} \)
### TABLE VI

**A3 SPECIMEN - Solid rock**

**Streaming potentials**

<table>
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<th>Streaming Potential</th>
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</table>

**Average streaming potentials**

$18 \pm 1 \text{ mv.}$

**polarity**

---

**Pressure**
TABLE VII.

A3 SPECIMEN - Ground rock

Streaming potentials

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<tr>
<th>Test.</th>
<th>Voltage p=0psi</th>
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</table>

Average streaming potentials

$3 \pm 1 \text{mv.}$

polarity

$\text{+}$ $\text{-}$
\[
\frac{235}{2950} = \frac{1}{1925} + A
\]
\[
A = 1.76 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}
\]
\[
\lambda + \frac{2\lambda A}{\rho} = (1.76 + 0.52) \times 10^{-3} \Omega^{-1} \text{cm}^{-1} = 18.1 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}
\]
\[
\xi = -70 \text{ millivolts}
\]

b) **Ground rock**

No surface conduction

\[
P = 85 \text{ cm water} = 85 \times 980.638 \text{ dynes/cm}^2
\]
\[
E = 3 \text{ mV}
\]
other factors identical to the ones used for

\[
\xi = -16 \text{ millivolts}
\]

**4- A4 SPECIMEN**

a) **Rock specimen**

Specimen after soaking in water (conductivity

\[
\frac{1}{1925} \Omega^{-1} \text{cm}^{-1}
\]

Potential \(5 \text{V AC}\) Current \(87 \mu\text{A}\)

Specimen after soaking in salt water

Conductivity \(\frac{1}{4.82} \Omega^{-1} \text{cm}^{-1}\)

Potential \(5 \text{V AC}\) Current \(1800 \mu\text{A}\)

\[
\frac{87}{1800} = \frac{1}{1925} + A
\]
\[
A = 0.010 \Omega^{-1} \text{cm}^{-1}
\]
\[
\lambda + \frac{2\lambda A}{\rho} = (10 + 0.52) \times 10^{-3} \Omega^{-1} \text{cm}^{-1}
\]
\[
\xi = -82 \text{ millivolts}
\]
### TABLE VIII
A4 SPECIMEN - Solid rock

**Streaming potentials**

<table>
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<tr>
<th>Test</th>
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**Average Streaming Potentials**

11 ± 1 mv.
### TABLE IX

**A4 SPECIMEN - Ground rock**

**Streaming potentials**

<table>
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<tr>
<th>Test.</th>
<th>Voltage p: 0 cm. water (millivolts)</th>
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</tbody>
</table>

**Average streaming potential**

5 ± 1 mv.
b) **Ground specimen**

No evidence of surface conduction

\[ \xi = \frac{E}{\rho \varepsilon} \]

\[ E = 5 \text{ millivolts} \quad \rho = 75 \times 980.638 \text{ dynes/cm}^2 \]

For other factors see previous calculation.

\[ \xi = -37 \text{ millivolts} \]

---

**5- A5 SPECIMEN**

a) **Rock specimen**

Specimen after soaking in water

Conductivity \( \frac{1}{1925} \) \( \Omega^{-1} \text{cm}^{-1} \)

Potential 5 V \( \text{AC} \)  Current \( 65 \mu A \)

After soaking in salt water  \( 2950 \mu A \)

Surface conductance determination

\[ \frac{65}{490} = \frac{1}{1925} + A \]

\[ \frac{1}{1925} + A \]

\( A = 31.1 \times 10^{-3} \)

\( \lambda + \frac{2\lambda A}{\rho} = 31.62 \times 10^{-3} \)

\[ E = 2 \text{ millivolts} \]

\[ \xi = -40 \]
TABLE X
A5 SPECIMEN - Solid rock
Streaming potentials

<table>
<thead>
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<th>Test</th>
<th>Voltage p: 0 p.s.i.</th>
<th>Voltage p: 30 p.s.i.</th>
<th>Streaming potential</th>
<th>Voltage p: 30 p.s.i.</th>
<th>Streaming potential</th>
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Average streaming potential
2 ± 1 mv.
### TABLE XI

A5 SPECIMEN - Ground rock

**Streaming potentials**

<table>
<thead>
<tr>
<th>Test</th>
<th>Voltage p. 0 cm water (millivolts)</th>
<th>Voltage p. 3 cm water (millivolts)</th>
<th>Streaming potential (millivolts)</th>
<th>Voltage p. 6 cm water (millivolts)</th>
<th>Voltage p. 9 cm water (millivolts)</th>
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<td>3</td>
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</tbody>
</table>

**Average streaming potential**

$3 \pm 1 \text{ mv.}$
b) **Ground rock**

No surface conduction

\[
\frac{\xi}{T} = \frac{E4\pi\eta\lambda}{\rho \varepsilon}
\]

\(E = 3\text{mv}\)
\(\rho = 85 \times 980.638 \text{ dynes/cm}^2\)

for other factors, see other specimens.

\[\xi = -15 \text{ millivolts}\]

As we can see our results are very divergent, even for \(\xi\) potentials of the same type of rocks.

In order to relate these results to the physical properties of our rocks, it would be good to come back again on the permeability factor from Onsager's equation.

As we have already noticed in the previous section, the flow of liquid passing through the porous rocks depends not only upon the pressure factor, but also upon the streaming potential set up.
VI- PERMEABILITY AND THE ONSAGER RELATIONS

\[ I = L_{11} \Delta \varphi + L_{12} \Delta P \]
\[ J = L_{21} \Delta \varphi + L_{22} \Delta P \]

Let us first try to find the dimension formulas of the coefficients \( L_{11}, L_{12}, L_{21}, L_{22} \), we want to compute

- \( I \) is a current
- \( \Delta \varphi \) a voltage
- \( \Delta P \) a pressure

Equation (1) can be written

\[
\frac{q}{T} = L_{11} \left( \frac{E}{Q} L \right) + L_{12} \frac{E}{L^2}
\]

\[
L_{11} = \frac{q^2}{F T L} \quad L_{12} = \frac{q L^2}{F T}
\]

\( J \) is a volume of water per second.

Equation (2) can be written

\[
\frac{L^3}{T} = L_{21} \left( \frac{FL}{Q} \right) + L_{22} \left( \frac{F L^2}{L^2} \right)
\]

\[
L_{21} = \frac{q L^2}{F T} \quad L_{22} = \frac{L^5}{T F}
\]

dimensionally \( L_{21} = L_{12} \)

Let us see now the importance of the term in the determination of \( J \), that is in the determination of the permeability of our specimens of rocks.

Let us consider the specimen A4

a) \( I = L_{11} \Delta \varphi \) when \( \Delta P = 0 \)

that is the case of our resistivity measurement, a voltage of 5 volts being applied at the ends of our specimen
J is a volume of water per second.

Equation (2) can be written

\[
\frac{L^3}{T} = L_{21} \frac{FL}{Q} + L_{22} \frac{F}{L^2}
\]

dimensionally

Let us now see the importance of the term in the determination of J, that is in the determination of the permeability of our specimens of rocks.

Let us consider the specimen A4. a)

that is the case of our resistivity measurement, a voltage of 5 volts being applied at the ends of our specimen.

\( L_{//} \) is merely the conductivity of the sample of rock.
\[ L_{\|} \text{ is merely the conductivity of the sample of rock.} \]

Resistance of the specimen \[ \frac{37500}{9} \times 10^{-11} \text{ cgs units} \]

\[ L_{\|} = \frac{37500}{9} \times 10^{-11} \text{ cgs units} \]

\[ = 2.4 \times 10^{-7} \text{ cgs units} \]

\[ I = 0 \quad \frac{\Delta \varphi}{\Delta P} = - \frac{L_{12}}{L_{\|}} \]

\[ \Delta \varphi = 11.35 \text{ millivolts} = \frac{11.35}{1000 \times 300} \text{ cgs units} \]

\[ \Delta P = 30 \times 68947 \text{ dynes/cm}^2 \]

\[ -L_{12} = -42 \times 10^{-5} \]

\[ J = 8 \times 10^{-5} \text{ cm}^3/\mu \]

We then have:

\[ 8 \times 10^{-5} = 16 \times 10^{-9} + L_{22} \Delta P \]

We thus see that the term \( L_{22} \Delta \varphi \) is small comparatively to \( J \)

and do not make any appreciable error by writing

\[ J = L_{22} \Delta P \]

All our determinations of permeability have been made under this assumption. We shall consider them true.
VII - DISCUSSION AND CONCLUSION

The important role played by surface conductance in electro-kinetic effects occurring in solid rocks is shown by these experiments.

This surface conductance effect seems to be an important factor in electro-kinetic measurements when the conductivity of the liquid is very low, or when the diameter of the pores is small.

The \( \xi \) potentials computed from the streaming potentials occurring in solid rocks lead to fairly good results when the "surface conduction" correction has been made.

<table>
<thead>
<tr>
<th></th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \xi ) rock sample</td>
<td>-93 mV</td>
<td>-830 mV</td>
<td>-70 mV</td>
<td>-82 mV</td>
<td>-40 mV</td>
</tr>
<tr>
<td>Porosity</td>
<td>14 mV</td>
<td>-34 mV</td>
<td>-16 mV</td>
<td>-37 mV</td>
<td>-15 mV</td>
</tr>
<tr>
<td>Porosity</td>
<td>13%</td>
<td>4%</td>
<td>20%</td>
<td>7%</td>
<td>1%</td>
</tr>
<tr>
<td>Permeability</td>
<td>( 38 \times 10^{-7} )</td>
<td>( 8.8 \times 10^{-7} )</td>
<td>( 1.7 \times 10^{-4} )</td>
<td>( 2.73 \times 10^{-7} )</td>
<td>( 3 \times 10^{-9} )</td>
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<tr>
<td>Tortuosity ( \frac{L}{L} )</td>
<td>3.5</td>
<td>1.7</td>
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<tr>
<td>Resistance on liquid: Tap water</td>
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<td>59000</td>
<td>13800</td>
<td>37300</td>
<td>50000</td>
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<tr>
<td>Resistance on liquid salt water</td>
<td>1350</td>
<td>36500</td>
<td>1100</td>
<td>1810</td>
<td>6.640</td>
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<tr>
<td>Surface cond. ( \frac{\sigma}{A} ) ( \Omega^{-1} \text{cm}^{-1} )</td>
<td>( 8.1 \times 10^{-3} )</td>
<td>( 324.1 \times 10^{-3} )</td>
<td>( 17.6 \times 10^{-3} )</td>
<td>( 10.1 \times 10^{-3} )</td>
<td>( 31.1 \times 10^{-3} )</td>
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<tr>
<td>Conduct liquid ( \frac{\sigma}{A} ) ( \Omega^{-1} \text{cm}^{-1} )</td>
<td>( 0.52 \times 10^{-3} )</td>
<td>( 0.52 \times 10^{-3} )</td>
<td>( 0.52 \times 10^{-3} )</td>
<td>( 0.52 \times 10^{-3} )</td>
<td>( 0.52 \times 10^{-3} )</td>
</tr>
</tbody>
</table>
The results are very close to those which have been obtained with ground quartz.

1- A5 has a very small porosity and small permeability. The factor of surface conductance is then very large as expected.

2- A1 and A3 are quartz samples. It is surprising to note that the surface conductance of A3 is big compared to A1, even though the porosity and permeability of A3 are bigger than that of A1.

It is possible that there are some additional minerals in one of the specimens which have caused this discrepancy in the results.

The $\xi$ potential we obtain are an average of the $\xi_j$ potentials of the different minerals composing each specimen.

- The tortuosity is a factor which could affect the type of flow of the liquid inside the capillaries.

However, even if the flow is turbulent, it has been proved to remain laminar in the double layer.

The shape of the crystals in the rock specimen could also be a factor influencing the type of flow.

- The $\xi$ potentials obtained from ground rocks show very big discrepancies with the $\xi_j$ potentials obtained
from solid rocks.

These discrepancies may be due to turbulent flow, or just to flaws in the equipment.

It is easy to see that since the value of streaming potentials are small, their importance will be small in the measurements of induced polarization effects.

The Onsager equation gives the following relationship:

\[ J = \mathcal{L}_{\|} \Delta \gamma + \mathcal{L}_{1/2} \Delta \varphi \]  

(1)

In the induced polarization effects, the value \( \frac{J}{\Delta \gamma} \) is measured.

\( \mathcal{L}_{1/2} \Delta \varphi \) seems to be a very small factor and practically \( \frac{J}{\Delta \gamma} = \mathcal{L}_{\|} \) can be employed.

However, when the Zeta potential of the rocks, as well as their surface conduction (easy to measure) is known, the necessary correction can be made according to equation (1).
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