Streaming Potential Studies

Andrew L. Mular

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STREAMING POTENTIAL STUDIES

BY

ANDREW L. MULAR

A THESIS

SUBMITTED TO THE DEPARTMENT OF MINERAL DRESSING

IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN METALLURGICAL ENGINEERING

MINERAL DRESSING OPTION

MONTANA SCHOOL OF MINES

BUTTE, MONTANA

MAY 20, 1956
PROFESSOR D. W. MACGLASHAN,
DEPARTMENT OF MINERAL DRESSING
MONTANA SCHOOL OF MINES
BUTTE, MONTANA

DEAR PROFESSOR MACGLASHAN:

THE FOLLOWING THESIS ON "STREAMING POTENTIAL STUDIES" AUTHORIZED BY YOU IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE BACHELOR OF SCIENCE IN METALLURGY, MINERAL DRESSING OPTION, IS HEREWITH SUBMITTED.

THE WORK CLOSELY PARALLELS THAT OF PREVIOUS LITERATURE SURVEYS OF THIS TYPE, AND DOES NOT CONTAIN ANY EXPERIMENTAL DATA GATHERED IN YOUR LABORATORIES.

IT IS HOPED THAT THOSE STUDENTS WHO MAY LATER UNDERTAKE STUDIES IN ELECTROKINETICS WILL OBTAIN BASIC INFORMATION FROM THIS COMPILATION, AND THUS AVOID EXTRANEOUS LITERATURE STUDIES.

RESPECTFULLY SUBMITTED,

A. L. MULAR

A. L. MULAR
PREFACE

The application of streaming potential to mineral-dressing is comparatively recent. Although colloidal chemists, for some time, have been familiar with streaming potential and the electrical double layer, A. M. Gaudin, Richards Professor of Mineral-Dressing, M. I. T., and D. W. Fuerstenau, his assistant, were the first to publish a series of experiments dealing directly with streaming potential applied to flotation. The apparatus described in this thesis was used by Fuerstenau and was developed by him especially for this type of investigation. Much of the early information regarding the essential principles of streaming potential was obtained from papers published by O. Stern, H. R. Kruyt, D. C. Grahame, J. Th. Overbeek, and others. Whenever possible, their works were referred to.

This thesis is not of an experimental nature, nor is it intended to be original work. It is a compilation of data and information regarding streaming potential and its application to the mineral-dressing field. It will be used as a reference by students who wish to study adsorption on mineral surfaces. Much of the information concerning adsorption study through streaming potential measurements was taken from Dr. Fuerstenau's thesis.

I would like to express my appreciation to Mrs. Loretta B. Peck, librarian, for her assistance in obtaining hard-to-get articles; Dr. A. J. Smith, Mathematics Department Head, for clarifying mathematical derivations; Professor D. W. MacGlashan, Mineral-Dressing Department Head, for allowing additional study time and providing constructive comments. They have helped make this paper an aid to a better understanding of adsorption in flotation.
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SELECTIVE FLATATION HAS BECOME INCREASINGLY IMPORTANT TO MINERAL ENGINEERS AS A CONCENTRATION METHOD FOR LOW-GRADE ORES. THE ORES ARE TREATED IN FINELY GROUND STATES WITH ORGANIC REAGENTS WHICH EFFECT THE CONCENTRATION OF THE VALUABLE MINERAL. ADSORPTION, THE INCREASE IN IONIC CONCENTRATION AT A MINERAL-LIQUID INTERFACE, IS THOUGHT TO BE AN ESSENTIAL MECHANISM WHEREBY ACTIVATED MINERAL PARTICLES, DURING A FLATATION OPERATION, ARE SELECTIVELY SEPARATED FROM GANGLUE MATERIAL AND NON-ACTIVATED MINERALS. THE COLLECTOR ION ORIENTS ITS POLAR END TOWARDS THE MINERAL SURFACE; THE NON-POLAR END OF THE COLLECTOR ATTACHES ITSELF TO AN AIR BUBBLE, AND THE MINERAL IS BROUGHT TO THE SURFACE. THIS PREFERRED ORIENTATION MAY BE CAUSED, IN PART, BY ELECTROSTATIC FORCES ACTING AT THE SOLID-LIQUID INTERFACE.

YIELDS PRECISE RESULTS, BECAUSE ALL OF THE QUANTITIES INVOLVED IN COMPUTATIONS CAN BE MEASURED WITH GREAT ACCURACY. SURFACE CONDUCTANCE IS IMPORTANT, BECAUSE THE PHENOMENON INTRODUCES SERIOUS ERROR IN STREAMING POTENTIAL VALUES.

ZETA POTENTIAL, OBTAINED WITH STREAMING POTENTIAL APPARATUS, IS USEFUL AS A FLOTATION RESEARCH TOOL. FOR INSTANCE, GAUDIN AND FUERSTENAU, USING STREAMING POTENTIAL TECHNIQUES, HAVE MEASURED THE ZETA POTENTIAL OF QUARTZ AS A FUNCTION OF pH AND CONCENTRATION. 3 THEY HAVE PROVIDED EVIDENCE THAT HYDROGEN AND HYDROXYL IONS FUNCTION AS POTENTIAL-DETERMINING IONS IN WATER. VARIOUS ELECTROLYTES AFFECT ZETA POTENTIAL BY COMPRESSION OF THE DOUBLE LAYER, WHEREAS ACTIVATORS SUCH AS BARIUM AND ALUMINUM FUNCTION AS COUNTER IONS AND ARE SPECIFICALLY ADSORBED. DODECYLAMMONIUM ACETATE IS ADSORBED TO THE QUARTZ SURFACE IN THE FORM OF AMINIUM IONS UNTIL, AT A CERTAIN CONCENTRATION IN THE DOUBLE LAYER, THE ADSORBED COLLECTOR IONS BEGIN TO ASSOCIATE INTO PATCHES OF IONS CALLED HEMI-MICELLES. 4

PURPOSE OF STUDY

THIS PAPER WILL DISCUSS BASIC PRINCIPLES RELATED TO THE THEORY OF THE ELECTRICAL DOUBLE LAYER AND STREAMING POTENTIAL, AND WILL DESCRIBE, IN DETAIL, APPARATUS FOR MEASURING STREAMING POTENTIAL. ALSO, IT WILL INVESTIGATE ZETA POTENTIAL AS A METHOD OF DEDUCING ADSORPTION MECHANISM ESSENTIAL TO FLOTATION. EVENTUALLY, THE MINERAL-DRESSING DEPARTMENT AT MONTANA SCHOOL OF MINES WILL CONDUCT EXPERIMENTS USING STREAMING POTENTIAL APPARATUS, AND IT IS HOPE THAT THIS THESIS WILL SERVE AS A REFERENCE TO THOSE WISHING TO GAIN A FUNDAMENTAL CONCEPT OF ZETA POTENTIAL AND STREAMING POTENTIAL.
STREAMING POTENTIAL

To lack a basic knowledge of the double layer precludes an understanding of zeta and streaming potentials, so that an examination of the Stern theory is in order.

To begin, most mineral particles dispersed in water are found to migrate under the influence of an electric field, indicating that the particles bear a negative or a positive charge. In the case of sols (colloidal suspensions of fine particles) it has been shown \(^2\) that the hydrophobic type, which includes most of the sols of the elements, their oxides, and salts, must (in the absence of protecting colloids) contain an electro-

---

**Figure 1.**

\[
\begin{array}{c|c|c}
\text{Ag}^+ & \text{I}^- & \text{H}^+ \\
\hline
\text{Ag}^+ & \text{I}^- & \text{H}^+ \\
\text{Ag}^+ & \text{I}^- & \text{H}^+ \\
\text{Ag}^+ & \text{I}^- & \text{H}^+ \\
\text{Ag}^+ & \text{I}^- & \text{H}^+ \\
\text{Ag}^+ & \text{I}^- & \text{H}^+ \\
\end{array}
\]

\text{AgI-H}_2\text{O Interface (After Weiser)}
LYTE TO INSURE THEIR STABILITY. (ALTHOUGH ONE MAY HAVE A STABLE HYDRO-
PHILIC SOL WITHOUT THE PARTICLES HAVING A CHARGE, THE SOL IS STILL INFL-
UENCED WITH RESPECT TO STABILITY BY ELECTROLYTE ADDITION—I.E., CHARGE
STILL AFFECTS THE SOL.) INTENSIVE STUDY OF THESE PHENOMENA BY COLLOIDAL
CHEMISTS HAS LED TO THE CONCEPT OF THE ELECTRIC DOUBLE LAYER.

THE DOUBLE LAYER IS BEST ILLUSTRATED BY AN EXAMPLE SUCH AS AgI PARTICLES
IN WATER. IF WE ASSUME THAT THE PARTICLES BEAR A NEGATIVE CHARGE, THE
CONSTITUTION OF THE IMMEDIATE VICINITY OF A SINGLE PARTICLE IS SHOWN IN

FIGURE 1. ACCORDING TO WEISER, AT SOME ACTIVE SPOT OF THE SURFACE,
IODIDE IONS ARE ADSORBED BY THE SILVER IONS OF THE LATTICE, THEREBY SET-
TING UP A DOUBLE LAYER. THE ATTACHED IODIDE IONS CONSTITUTE THE INNER
PORTION OF THE LAYER, AND HYDROGEN IONS, THE OUTER PORTION. THE OUTER
PORTION IS THOUGHT TO BE DIFFUSE, AND THE IONS HELD BY ELECTROSTATIC AT-
TRACTION OF THE INNER LAYER. HOWEVER, BECAUSE OF THE HIGHER KINETIC ENERGY,
THE DIFFUSE LAYER CAN EXERT SUFFICIENT FORCE AGAINST THE ATTRACTION OF THE
INNER LAYER TO INFLUENCE AN ELECTRODE AND SO MAY BE DETECTED POTENTIO-
METRICALLY. THAT PART OF THE DIFFUSE LAYER IN JUXTAPOSITION WITH THE INNER
LAYER IS THOUGHT TO BE FIXED AND NOT TO MIGRATE WITH THE MAIN PORTION.
HENCE, IN FIGURE 1, EVERYTHING TO THE LEFT OF THE BROKEN LINE WILL MOVE TO
THE ANODE UNDER ELECTRICAL STRESS, WHEREAS THE HYDROGEN IONS IN THE OUTER-
MOST PART TO THE RIGHT OF THE BROKEN LINE WILL MOVE TO THE CATHODE. THE
 ADSORBED IONS WHICH CONSTITUTE THE INNER PART OF THE DOUBLE LAYER ARE CALLED
THE POTENTIAL-DETERMINING IONS; THE IONS WHICH CONSTITUTE THE OUTER PART
OF THE DOUBLE LAYER ARE TERMED COUNTER IONS.
The concept of the electric double layer, originating with Helmholtz, is essentially the work of Gouy and Chapman\textsuperscript{5}, who proposed that the mineral has a charge on its surface (excess electrons or ions) and an equivalent opposite charge congregated diffusely about it. A proportionality between surface charge density and surface potential was established, which indicated that the double layer behaved as a flat condenser. However, the balancing charges of the diffuse layer were considered to originate from the surface out into the body of the medium. Stern\textsuperscript{5,6} postulated that the first ionic layers of the diffuse layer could not approach the mineral surface any closer than a distance delta (1 or 2 angstroms) from it. He also suggested that some ions would be specifically adsorbed (adhere directly to the surface by chemical bonding or van der Waal attraction) and proposed that these ions were also a distance delta away. Kruyt\textsuperscript{5} pointed out, however, that if ions are specifically adsorbed, they will be a distance delta from the wall, whereas the next layer of ions will be a distance greater than delta from the wall. In the case of specific adsorption, Graham chose to make a distinction by referring to the inner and outer Helmholtz planes of the double layer (actually a triple layer now). Accordingly, ions which are not specifically adsorbed are assumed to be separated from the surface by a solvent sheath. The locus of the electrical centers of a layer of adsorbed ions is called the inner Helmholtz plane (IHP); the locus of electrical centers of solvated ions near the surface is called the outer Helmholtz plane (OHP). Except in the case of large specifically adsorbed ions, the OHP is farther from the surface than the IHP. In their diagrams of the interface, Gaudin and Fuerstenau\textsuperscript{4} prefer
TO CONSIDER SPECIFICALLY ADSORBED IONS AS PART OF THE SURFACE.

GRAHAME, WORKING WITH MERCURY, HAS SCHEMATIZED THE STRUCTURE OF THE DOUBLE LAYER AS FOLLOWS:

**Situation A**

No specific adsorption with negative charge on the mercury. (Gouy double layer with a gap between the charge on the surface and the counter ions.)

**Situation B**

Specific adsorption of anions with no charge on the mercury. (Negative charge in the IHP and a Gouy layer with positive charge.)

**Situation C**

Specific adsorption of anions with positive charge on the mercury. (Larger negative charge in the IHP and a positive charge in the OHP. The diffuse layer is positive as in B. A triple layer is formed.)

Figures 2, 3, and 4, illustrate the above situations at the mercury-liquid interface. (All after Grahame)
Figure 3.
Situation B

Figure 4.
Situation C
The above illustrations serve to provide a physical picture of the solid-liquid interface, so that the concept of zeta potential can now be easily presented.

**Zeta Potential**

Figure 5 illustrates the electrical distribution of the double layer. The fixed layer of counter ions is assumed to be in a plane at a distance delta from the surface. Specifically adsorbed ions are on the surface. If the electrolyte (the portion to the right of the broken line in Figure 5) is caused to move with respect to the particle, only that part of the ionic atmosphere which is not fixed by strong electric or chemical forces will move. The potential difference measured from the plane of movement out into the main body of moving liquid is called the zeta potential. This potential difference between the slipping plane (that plane where the moving ionic atmosphere shears the fixed ionic atmosphere) and the body of liquid can be measured by electrokinetic methods. Measurement of zeta potential is important to mineral-engineers, because of its effect in adsorption processes.

Four common methods are available for evaluating zeta potential: streaming potential, electro-osmosis, electrophoresis, and sedimentation potential. However, the method of streaming potential is preferred, because all experimental quantities can be measured with a greater ease and accuracy than when the other methods are used.
STREAMING POTENTIAL

Figure 6 represents a glass tube filled with fine particles immersed in a liquid medium. The space within the tube not occupied by the fine mesh particles can be thought of as a system or network of very fine capillary tubes. Since streaming potentials depend on the interrelation of mechanical and electrical phenomena at the solid-liquid interface, when a liquid is forced through the porous plug, it carries along with it the movable ions clustered about the porous medium in the plug. If the displaced cluster of ions possesses a surplus of charge, a streaming current is generated.
Furthermore, the transport of charge gives rise to a potential difference at the ends of the plug. Hence, a conduction current flows through the bulk of liquid. At steady state, the convection current just counter-balances the conduction current. The streaming potential is thus the voltage generated when the ionic convection current is converted into the galvanic conduction current. The streaming current may be compared to the current flowing through the interior of a battery between its terminals, whereas the conduction current would be the current flowing through the external circuit connected to the same battery.

Various investigators have developed an equation from theoretical considerations showing that the ratio of the streaming potential (E) to the pressure difference (P) is a constant (see Appendix I). The constant is directly proportional to the product of the dielectric constant (ε) and the
Zeta potential ($\zeta$), and inversely proportional to the specific conductance of the liquid ($\lambda$) and its viscosity ($\eta$). Thus, in the electrostatic system of units,

$$\zeta = \frac{4\pi \eta (\text{poises})}{\varepsilon (\text{esu}/\text{erg-cm})} \times \frac{\lambda (\text{statohm}^{-1}\text{cm}^{-1})}{E (\text{statvolt})} \times \frac{1}{p (\text{dynes/cm}^2)}$$

$$= \text{statvolts}$$

The following conditions must be satisfied if equation (I) is to be valid:

(A) Liquid flow through the plug must be laminar.

(B) Radius of curvature of the pores of the plug must be much larger than the thickness of the double layer.

(C) The conductance determining the conduction current should depend solely on the bulk conductivity of the liquid (i.e., surface conductance should be negligible).

Fuerstenau has shown that streaming potential is directly proportional to pressure differences up to 46 cm of mercury and is independent of the direction of flow of liquid. To satisfy condition (B), he has pointed out that if particles sized at 48/65 mesh are used, the average pore diameter (assuming sphericity) is 39 microns, compared with a double layer thickness of 1 to 2 microns. Therefore, both conditions (A) and (B) are satisfied.

However, surface conductance of the capillary system in the plug, caused by excess ionic charge in the double layer, must be considered.
**Surface Conductance**

Because of the conducting effect on potential measurements, particles which act as conductors cannot be placed in the streaming cell. Even non-conductors such as quartz will give rise to surface conductance. For instance, many researchers have found low values for $E/p$ in dilute electrolytes, an effect attributed to a low-valued zeta potential. Later investigations proved conclusively that low values for zeta are caused by surface conductance, for as bulk conductivity appreciably decreases the surface conductance predominates. This contribution increases the return current (conduction current) and depresses the streaming potential.

Rutgers and DeSmet have proved that surface conductivity can account for as much as 60 per cent of the total conductivity for the narrowest capillary and lowest concentration. Fuerstenau, using 48/65-mesh quartz fractions, has pointed out that, in solutions which contain less than $1 \times 10^{-4}$ moles, NaCl per liter, surface conductance is present and, in dilute solutions, accounts for an 11 per cent depression of zeta. Values of zeta potential obtained for low-electrolyte concentrations must be treated cautiously.

Equation (1), page 11, corrected for surface conductance would be:

$$f = \frac{4\pi \eta \lambda}{\varepsilon} \left(1 + \frac{2 \lambda}{n \lambda} \right)$$

Still, the possibility of using conducting particles exists, provided suitable innovations are made. This subject is covered in the writer's Master of Science thesis.
WHERE $\lambda_s$, the specific surface conductivity is found from the relation:

$$\lambda_s = \frac{1}{2\pi \mu} \left( \frac{1}{R} - \frac{2\pi a^2}{l^2} \right)$$

Where $\lambda$ is the radius of the capillary, $I$ the conduction current, $R$ the resistance offered, and $l$ the length of the capillary.

It should be noted that the correction to equation (1) involves the radius of the capillary. A porous plug has numerous capillaries whose radii cannot be measured, indicating that in the case of a porous plug a correction is not feasible. However, if the total effective resistance of the plug is utilized to find the specific conductance, a fairly accurate value of zeta is obtained, because the effective resistance of the plug includes both the bulk conductance and the surface conductance. Figure 7 shows the effect of surface conductance in dilute solution. Curve A was calculated from the bulk conductance of the salt solutions. The value of zeta in curve B was obtained with values of the conductance determined from direct evaluation of the plug resistance (see specific conductance calculation method on subsequent pages). The appearance of the true curve probably looks like curve C.

**Blocking Effect**

Another source of false zeta potential values which may result from streaming measurements is attributed to flow differences in the body of the porous medium. Termed the "blocking effect" by Urban and White, a physical diagram of the phenomenon is pictured in Figure 8, which represents two of the
Figure 7.
Effect of Surface Conductance
(After Fuerstenau)

Figure 8.
Blocking Effect
(After White)
NUMEROUS CAPILLARIES IN A POROUS PLUG. IF THE STREAMING POTENTIAL BETWEEN
THE ENDS OF THE PORE AB IS GREATER OR REACHES ITS MAXIMUM MORE RAPIDLY
THAN THE PORE CD, A RETURN CIRCUIT IS SET UP THROUGH CD. BECAUSE POINT D
IS NEGATIVE TO POINT B, A CURRENT FLOWS AS INDICATED BY THE CURVED ARROW.
The plus sign to the right and the minus sign to the left indicate the
difference in potential set up across the two pores, provided the stream­
ing potential develops unhindered. Because of the pressure head, an
electro-osmotic flow opposes the flow of solution and discharges the pot­
etial difference across the pores. The return circuit through CD, by
opposing electro-osmotically the flow due to the pressure head, prevents
the normal passage of liquid through CD and thus deprives CD of an oppor­
tunity to develop any streaming potential.

LORENTZ, HOWEVER, IN HIS WORK WITH QUARTZ-ACETONE SYSTEMS, REFERRED TO
THE ABOVE AS THE ELECTROVISCOUS EFFECT AND SHOWED THAT THE EFFECT WAS
NEGLIGIBLE AND WITHIN THE LIMITS OF EXPERIMENTAL ERROR. NEVERTHELESS,
SHOULD STREAMING MEASUREMENTS ATTAIN AN UNUSUAL DEGREE OF ACCURACY, THE
EFFECT WILL HAVE TO BE ACCOUNTED FOR.

DESCRIPTION OF APPARATUS FOR STREAMING POTENTIAL MEASUREMENTS

AS INDICATED BY PREVIOUS DISCUSSION, THE ZETA POTENTIAL IS BEST EVALUATED
BY STREAMING POTENTIAL TECHNIQUES. DR. D. W. FUERSTENAU DESCRIBES AN
APPARATUS (SEE APPENDIX II), SENSITIVE, ACCURATE, DEPENDABLE, AND EASILY
HANDLED, WHICH IS ESSENTIALLY A MODIFICATION OF THAT USED BY BRIGGS, IN
HIS WORK WITH STREAMING POTENTIAL MEASUREMENTS ON CELLULOSE. BRIGGS,
Figure 9.
Diagram of the Streaming Potential Cell (after Fuerstenauf)
FIGURE 10.
The Assembled Streaming Potential Apparatus
(after Fuerstenau)
However, did not use an inert atmosphere and his method of determining the streaming potential was slightly different with respect to null point instrument. In addition, he utilized a single source of electrolyte, allowing it to flow through the porous plug without any provision for return flow.

Diagrams of Fuerstenau's apparatus, which consists essentially of the cell assembly, the flow system, and the electrical measuring equipment, are found on pages 16 and 17 (Figures 9 and 10).

Cell Assembly

The streaming potential cell consists of two standard ground joints (4) connected by a glass tube (5) about six cm long. The electrodes are made of 80-mesh platinum gauze welded onto a platinum grid (6) and are permanently mounted on the ends of the two standard joints. Each electrode is held in place by the tension of the platinum wire (7), which connects it to the tungsten seal (8) at the end of the cell.

The cell is filled with fine mesh particles. To prevent any particles from escaping through the holes of the electrodes, a layer of larger particles is packed next to each electrode. The bulk of the packing is thus held tightly in place between these two layers.

Flow System

The flow system consists of two 500-ml reservoirs (1), which are located at either end of the streaming potential cell. Two ball-and-socket joints (2) hold the reservoirs in place. A pressurized nitrogen source, connected individually to the solution reservoirs, forces liquid through the stream-
ing cell in either direction. Solution flow is stopped by means of a stopcock (3). One of the reservoir flasks has a large opening, so that thermometers or electrodes to measure solution pH can be inserted while nitrogen gas still circulates. The driving pressure is measured with either water or mercury manometers.

Electrical Equipment

A null technique is utilized to obtain precision measurements of the streaming potential. A counterpotential which originates in a Leeds and Northrup type K-2 potentiometer (17) is impressed through a high resistance (18).

A null point, detected through an Applied Physics Corporation vibrating reed electrometer (19)—a DC measuring instrument of extreme sensitivity—indicates that the streaming potential and the impressed potential across the \(10^{12}\) ohm resistance (18)—placed in series with the potentiometer and the streaming cell—are balanced. The range of the potentiometer is extended to 7.5 volts when four 1.5 volt batteries (20) are connected in series through switches (21) and (22). The cell assembly is connected to the electrical equipment through mercury wells (15) and a reversing switch.

Determination of Variables

In order for zeta potential to be evaluated from the streaming potential equation, values must be obtained for the following: 1) Plug Resistance, 2) Cell Constant, 3) Specific Conductance, 4) Dielectric Constant, 5) Viscosity of Electrolyte.
1) Determining the Resistance of the Plug

Two methods of measuring resistances of solutions in the plug have been discussed by Fuerstenau. The first, a 1000-cycle AC bridge, is made up of an impedance bridge—an audio amplifier and oscilloscope being utilized to determine the null point—and is applicable for resistance measurements in the low range (less than 1 megohm), since at lower resistances polarization of electrodes becomes appreciable. The second, a DC bridge which is used for resistances greater than 1 megohm because the device is easily incorporated into the streaming potential apparatus, is best described by Fuerstenau as follows:

"Figure 11 illustrates the DC bridge used to measure resistances greater than one megohm. A standard potential of about 1.5 volts (b) is applied to the bridge arm containing the plug filled with quartz particles (c) to balance the current through a calibrated megohm resistor (d) furnished by the potentiometer (a). This standard resistance is precision wound and has a 0.1 per cent accuracy. Zero deflection of the vibrating reed electrometer (e) across the 12-ohm resistance (f) is obtained by balancing the current through the streaming cell (c) under the potential from (b) against the current through the standard megohm resistance (d) under a potential (a). The ratio of the required potentials, b/a is equal to the resistance (c) in megohms."

To find the resistance of the plug, it is essential to measure the resistance across the plug while the liquid, against which the zeta potential is desired, is in the plug.
2) Determining the Cell Constant

The plug must be thoroughly cleaned of the experimental liquid. N/10 KCl solution, or a solution which has sufficient strength to eliminate all surface conductance effects of the porous plug, is streamed through the cell and the resistance is measured for this solution as described in 1. The cell constant is calculated from the relation:

\[ K = \alpha_s R \]

where \( K \) is the cell constant, \( \alpha_s \) is the specific conductance of the KCl, which has a standard value, and \( R \) is the resistance measured while the KCl solution is in the plug.

Once the cell constant is known, the specific conductance of the cell solution can be determined.
3) Determining Specific Conductance

The value obtained for the resistance of the plug while the experimental liquid flows through is used with the value for the cell constant obtained in 2). These values are substituted in equation (3), and the specific conductance of the cell is calculated. This method gives more accurate results, because both bulk conductance and surface conductance are included.

4) Determining the Dielectric Constant

In calculations involving zeta potential, it is assumed that \( \varepsilon \), the dielectric constant of the surrounding medium (water) is a constant. Recent measurements have shown that the dielectric constant, measured by placing water in an electric field of the order of 500,000 volts per centimeter, will vary from 80 to 1. Helmholtz has established the distance across the interface to be of the order of one angstrom unit. If zeta were 200 millivolts, then it is seen that the dielectric constant could easily be reduced, according to the distance across the interface and the zeta potential. However, because of the difficulties involved in measuring \( \varepsilon \), a standard value available in tables at normal temperature ranges will be applied to calculations.

5) Determining the Viscosity of the Electrolyte

Viscosity can be measured by either of the following methods: (a) the Falling Sphere Viscometer and (b) the Ostwald Viscometer, using the Westphal Balance.
Method (a) utilizes Stokes' law of spherical bodies falling in a viscous medium. However, some restrictions have been placed on the apparatus.

It is suggested that method (b) be utilized in the event that a more accurate method cannot be found. The method consists in placing a known volume of liquid in the viscometer (a constant temperature bath should surround the viscometer) and drawing the liquid into the bulb until the level of liquid is above a reference mark. The liquid is allowed to drain, and the time necessary for the liquid to fall to another reference mark is measured. The same procedure is repeated for a reference liquid of known density and viscosity (water preferably) and, after suitable density measurements with a Westphal balance, values can be substituted in the following equation:

\[
\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}
\]

From which the viscosity of the unknown is found. Here, \( \eta_1 \) and \( \eta_2 \) represent the viscosity of known and unknown respectively; \( d_1 \) and \( d_2 \) represent the densities; and \( t_1 \) and \( t_2 \) represent the times necessary to pass from one reference level to the other.

**Procedure for Use of Apparatus**

Because a standard operating technique has not been outlined in the literature, it seems plausible to list the following as a tentative method for taking a streaming reading. Changes will undoubtedly be made with experience.
CLEAN APPARATUS WITH CLEANING SOLUTION, FOLLOWED BY STEAM TREATMENT.

2. FILL PLUG WITH PARTICLES TO BE TESTED. (A STANDARD PROCEDURE OF "PACKING" THE PLUG WITH PARTICLES MUST BE ADOPTED. LORENTZ AND BRIGGS HAVE BOTH NOTED THAT PACKING THE PARTICLES DIFFERENTLY EACH TIME RESULTS IN ERRATIC E/P VALUES.)

3. ASSEMBLE APPARATUS; CHECK ALL WIRING AND SWITCHES.

4. TURN ON NITROGEN TO ELIMINATE AIR IN APPARATUS.

5. TRANSFER CO₂-FREE SOLUTIONS TO BE TESTED TO APPARATUS WITHOUT EXPOSURE TO ATMOSPHERE.

6. PASS SOLUTION THROUGH PLUG FOR AT LEAST ONE HOUR.

7. REPLACE SOLUTION OF STEP 5 WITH NEW SOLUTION OF IDENTICAL CONCENTRATION.

8. CHECK POTENSIOMETER AGAINST A STANDARD CELL AND DETERMINE ZERO POINT OF VIBRATING REED ELECTROMETER.

9. APPLY PRESSURE FROM NITROGEN TANK.

10. BALANCE STREAMING POTENTIAL WITH POTENSIOMETER, USING ZERO VALUE OF THE VIBRATING REED ELECTROMETER AS NULL POINT. MAKE AT LEAST FOUR RUNS.

11. TAKE A SIMULTANEOUS PRESSURE READING AND PRESSURE CORRECTION.

12. DETERMINE PLUG RESISTANCE AT END OF RUNS.

THE ABOVE PROCEDURE IS BASED UPON OBSERVATIONS NOTED IN THE VARIOUS LITERATURE—PRINCIPALLY THOSE ARTICLES WRITTEN BY DR. FUERSTENAU.
ZETA POTENTIAL AND ADSORPTION

The value of zeta potential to the mineral engineer lies in its proper interpretation. For instance, the algebraic sign of zeta, values of which are obtained from streaming potential measurements, is indicative of conditions at a mineral-liquid interface. A negative sign or negative zeta potential implies that the particle surface carries a negative charge. If positive ions are attracted to the double layer and become counter ions, zeta might become less negative and, in the absence of specific adsorption, the double layer would be compressed. Should the positive ions become specifically adsorbed, zeta would probably change sign completely and become positive itself. (Here, it is not implied that the total surface charge is positive but rather that specific adsorption has occurred). Conversely, increased negativity of zeta (or decreased positivity—i.e., positive counter ions might be replaced by anions) implies that specific adsorption of anions has probably occurred.

DEDUCING ADSORPTION MECHANISMS

To date, Gaudin and Fuerstenau are alone in their application of streaming potential to flotation research. Using quartz-filled porous plugs, they have measured the streaming potential and have calculated the zeta potential of different electrolytes at various concentrations and pH values. From graphs of zeta versus pH and concentration (see Figures 12 and 13) these investigators have made the following deductions:
Figure 12
Zeta potential of quartz in solutions of four different electrolytes.
(After Fuerstenau)

Figure 13
Zeta potential of quartz as a function of pH for different concentrations of sodium chloride.
(After Fuerstenau)
1. Sodium ions function as surface-inactive counter ions. (i.e., their net effect is to merely compress the double layer and decrease zeta slightly.)

2. Increasing the concentration of HCl causes zeta to change continuously from negative to positive, indicating that hydrogen ions affect zeta more than sodium ions. Specific adsorption probably occurs, followed by dissociation.

3. NaOH addition increases the negativity of zeta; and since sodium ions are counter ions, the hydroxyl ion must be a potential-determining ion for quartz.

4. Barium and aluminum ions, since they reverse the sign of zeta, are specifically adsorbed (when in sufficient concentration), indicating that these ions are surface-active indifferent electrolytes (i.e., attracted to the surface by chemical and electrostatic forces). In this case, Graham's triple layer is formed.

5. In the absence of an activator (such as barium) sodium laurate addition serves to compress the double layer; whereas when barium ions are added, laurate ions associate with the barium (The barium ions are in the IHP; the laurate ions are in the QHP).

6. pH affects the adsorption of all other ions by quartz.

7. Dodecylammonium ions serve to compress the double layer much like sodium, except that at higher concentrations the sign of zeta is abruptly
changed from negative to positive. This effect is attributed to the formation of hemi-micelles, since the concentration of dodecylammonium ions is not large enough to change the sign of zeta by specific adsorption.

Deduction 7 is important in that the sign of zeta changed from negative to positive in the absence of specific adsorption. Hemi-micelles, patches or aggregates of paraffin-chained ions, are formed. Since this phenomenon results from mutual attraction of hydrocarbon ends of collector ions, excess positivity of zeta must necessarily arise from orientation of polar ends away from the mineral surface (i.e., some of the collector ions have their polar ends oriented towards the mineral surface. Collector ions from the solution will orient their nonpolar ends towards the nonpolar ends of the adsorbed collector ions. Thus the ions from the bulk liquid will have their polar ends pointing away from the mineral). More evidence is supplied by Gaudin and Fuerstenau in support of this hypothesis.

Conclusions

At this point, it would be well to summarize briefly the information thus far presented.

The electric double layer, illustrated by AgI particles in hydroiodic acid and water, consists of the Stern layer (which includes the IHF and OHP) lying adjacent to the surface charge on the particle and a Gouy diffuse
layer surrounding the Stern layer. Specifically adsorbed ions are situated in the IHP. If specific adsorption does not occur, the IHP is considered empty, and the Stern layer contains the OHP only. Adsorption is dependent, in part, upon zeta potential—the difference in potential measured from the zone of shear into the bulk of liquid. The zone of shear lies near the surface and is probably at the OHP.

Streaming potential, the potential difference measured between electrodes placed at each end of a porous plug, has been introduced as a method of finding the zeta potential. In order for the streaming potential equation to hold, flow of liquid must be laminar, pore size must be much larger than the thickness of the double layer, and surface conductance must be negligible. The third condition, surface conductance, resulting from a build up of charge in the double layer, can introduce serious error by depressing zeta potential in dilute solutions. In fact, the phenomenon can introduce as much as 60 per cent error. However, any error attributed to the blocking effect—the decrease in streaming potential as a result of electrosmotic flow in a reverse direction—can be regarded as negligible and within the limits of experimental error.

Fuerstenau's apparatus for measuring streaming potential, a modification of that used by Briggs, is described. Methods for determining plug resistance, cell constant, specific conductance, dielectric constant, and viscosity are presented. The tentative procedure for using Fuerstenau's apparatus will probably change as experimental work progresses.
The sign of Zeta is important, in that much can be deduced concerning the mechanism of adsorption. A decrease in negativity implies double layer compression; a change in sign implies specific adsorption in some cases, and an increase in the negativity of Zeta implies that specific adsorption has occurred. The works of Gaudin and Fuerstenau have been summarized as evidence in support of the preceding statements.

Conclusions

Before Zeta potential can be applied to adsorption study, a thorough understanding of the electric double layer is necessary. Furthermore, D. W. Fuerstenau's apparatus (provided surface conductance is negligible) can be used advantageously, because ease in handling, equipment of high precision, and reverse flow are incorporated. Too, the combination conductivity cell and streaming cell provide for measurement of specific conductivity in such a way as to make errors compensating.

Recommendations

1. An apparatus capable of measuring the streaming potential of conducting particles should be constructed to enable the study of adsorption on oxide minerals.

2. Effects of surface conductance for a given porous plug should be studied and attempts made to establish a correction factor.
3. Nonconductors other than quartz should be used in the plug so that adsorption mechanisms on other minerals can be studied.

4. To eliminate surface conductance, a capillary made of the nonconducting material under investigation could be substituted for the porous plug. This idea should be expanded.

5. Mechanisms of adsorption of various commercial flotation reagents should be studied with the aid of streaming potential apparatus, and data should be correlated with flotation operations.

6. A study of electrocapillarity should be made, and attempts to correlate data taken from both streaming potential and electrocapillary phenomena should be the prime object.
APPENDIX I

DERIVATION OF STREAMING POTENTIAL EQUATION

If we have a uniform cross-section of a cylindrical plug with radius \( r \), the resistance \( R \), against the surface is \( R = \frac{\eta V}{d} \). The total shear \( \tau = \frac{dV}{d\theta} \).

Since a pressure difference exists during liquid flow, then \( P r a^2 = -\frac{dV}{dx} \) and \( \sigma = \frac{P}{a} \). Integrating both sides we have \( V_a = \frac{P \tau}{a} + C \).

At the surface of the plug where the radius is \( a \), the velocity is zero, so \( C = \frac{P \tau}{a} \) and \( V_a = \frac{P \tau}{a} \left( \frac{r^2}{a^2} - 1 \right) \) (A).

Assume we have a cylindrical-shaped volume (although it can be any shape), finite and enclosed in a bounded region of space, which is bounded by a piecewise smooth surface. Let \( P = P(x, y, z) \) be bounded and continuous in the interior of the surface, the point charge density. Let \( (\xi, \eta, \mu) \) be a variable point ranging over the volume.

Let \( \vec{R} \) be a vector from one point to the other, so that \( \vec{R} = (x - \xi) \hat{x} + (y - \eta) \hat{y} + (z - \mu) \hat{z} \)
where \( \vec{R} = \sqrt{(x - \xi)^2 + (y - \eta)^2 + (z - \mu)^2} \) and \( \vec{R} = \frac{R}{r} \) (a unit vector leaving the direction of \( \vec{R} \)). Then associated with every point \((x, y, z)\) in a quantity \( \psi \) as a function of \((\xi, \eta, \mu)\) defined as \( \psi(x, y, z) = \iint \frac{P(\xi, \eta, \mu)}{\vec{R}} \, dV \), continuous in the interior of the surface and called the potential function. Then \( \frac{dV}{dx} = \iiint \frac{P(x, y, z)}{\vec{R}} \, dV = \iiint \psi(\xi, \eta, \mu) \frac{\partial}{\partial x} dV \) -- the same being true (except for necessary letter change) for \( \frac{dV}{dy} \) and \( \frac{dV}{dz} \). Since \( \frac{dV}{dx} = \frac{dV}{dy} + \frac{dV}{dz} \) we can substitute so that

\[ \nabla \psi = \iiint \frac{\partial}{\partial x} dV \]
and because \( \nabla = -\frac{\vec{R}}{R^2} \) we have (the grad of \( \psi \))

\[ \nabla \psi = -\iiint \frac{\partial}{\partial x} \frac{\vec{R}}{R^2} dV \].

In our case, \( P(x, y, z) \) is interior to the surface, so we must solve the integral by letting \( I = \iiint \nabla \psi \, dS = \lim_{\sigma \to 0} \frac{1}{\sigma^2} \int \nabla \psi \cdot dS \) and
\[ \nabla \psi = \lim_{\Delta V \to 0} \sum_{V} \frac{[\psi(x, y, z) \Delta V]}{\Delta V} \]  
We can take our sum in any direction and use either summation, so

\[ I = \lim_{\Delta V \to 0} \sum_{V} \left\{ -\nabla \psi(x, y, z) \cdot \frac{\Delta V}{\Delta V} \right\} \]  
Since \((x, y, z)\) is interior
to the surface, then by Gauss's theorem, \(\int S \nabla \psi \cdot dS = 4\pi \). Then

\[ I = \lim_{\Delta V \to 0} \sum_{V} \left\{ -4\pi \int \nabla \psi \cdot dV \right\} = -4\pi \int S \nabla \psi \cdot dS \]  
By the divergence theorem

\[ \int S \nabla \psi \cdot dS = \int S \nabla \cdot dV \]  
and letting \(dV = d\psi \) then \(\int S \nabla \psi \cdot dS = \int \nabla \cdot dV \) dV.

Now, \(\nabla \cdot dV = \nabla \cdot dV = d^2 \psi \) and so \(\int S \nabla \psi \cdot dS = \int S \nabla \cdot dV \) dV. Substituting,

\[ \int S \nabla \psi \cdot dV = \int S (4\pi \rho(x, y, z)) dV \]  
Since \((x, y, z)\) and \((x', y', z')\) both are point charges over the volume, then we have, after rearranging terms, \(\int S S \frac{\partial^2 \psi}{\partial x^2} + 4\pi \rho(x, y, z) dV = 0 \)

But for this to be true the integrand must be zero at the point so we can say

\[ \frac{\partial^2 \psi}{\partial x^2} + 4\pi \rho(x, y, z) = 0 \]  
and \(\frac{\partial^2 \psi}{\partial y^2} = -4\pi \rho(x, y, z) \). By definition, \(\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -4\pi \rho(x, y, z) \). Converting to cylindrical coordinates and including the permittivity of the medium we can write

\[ \frac{\partial}{\partial r} \left( \frac{\psi}{r} \right) + \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi \rho}{\varepsilon} \]  
(Poisson's Equation)

Because the linear potential gradient along the z-axis is zero, we can write:

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\psi}{r} \right) = -\frac{4\pi \rho}{\varepsilon} \]  
\(B\). The connection current \(i\) has a velocity such that

\[ i = \varepsilon \mu \frac{\partial \psi}{\partial t} \]  
\(C\). Substituting \((A) + (B)\) and solving \((B)\) for \(\psi\) first, we have

\[ i = \varepsilon \mu \frac{\partial \psi}{\partial t} \]  
and integrating by parts we have

\[ i = \frac{-\varepsilon}{\varepsilon \mu} \int \psi \left( \frac{\partial^2 \psi}{\partial r^2} + \frac{\partial^2 \psi}{\partial z^2} \right) \]  
Since \(R^2 = R_0^2\) we have \(i = 0 + \left[ \frac{-\varepsilon}{\varepsilon \mu} \int \frac{\partial^2 \psi}{\partial r^2} \right] \]

\[ i = \frac{-\varepsilon}{\varepsilon \mu} \int \psi \frac{\partial^2 \psi}{\partial r^2} \]  
Since over the region where \(\psi\) varies, \(R < R_0 < R_0^2\) then

\[ i = \frac{-\varepsilon}{\varepsilon \mu} \int \frac{\partial^2 \psi}{\partial r^2} \]  
where \(\psi = \psi \). Hence, \(i = \frac{-\varepsilon}{\varepsilon \mu} \frac{\partial^2 \psi}{\partial r^2} \). The conduction

current \(i = \frac{E}{R} = \frac{\pi R^2}{h} E = \pi R E \) \(D\). At steady state \(i = i\) therefore:

\[ \frac{E}{R} = \frac{\varepsilon}{4\pi \mu \lambda} \]  
the streaming potential equation.
APPENDIX II

A Method For Measuring Zeta Potentials By Streaming Potential Techniques 14

by D. W. Fuerstenau

Figure 9 (page 16) illustrates the streaming potential apparatus. "The streaming potential cell or plug consists of two 24/40 standard ground joints (4) joined with a piece of pyrex tubing 60 mm in length and 12 mm in diameter (5). The electrodes are made of bright platinum disks 19 mm in diameter and 1 mm in thickness through which 0.5 mm holes have been drilled (6). To the surface of each is welded a piece of 80 mesh platinum gauze. Each electrode is permanently mounted on the ends of the inner parts of the two standard joints by means of a platinum wire (7) which connects it to the tungsten seal at the end of the cell (8). For ease in cleaning and handling the apparatus, the streaming cell is fastened to the 500 ml reservoir flasks (1) by means of two 18/19 ball and socket joints (2). This particular arrangement permits passage of the solution in either direction through the plug of particles. Flow of solution can be stopped by means of a stopcock (3). One of the reservoir flasks has a large opening to permit the insertion of either a thermometer or a pair of electrodes for measuring pH of solutions within the system. In making the experiments, the plug is filled with 48/65 mesh particles, but a layer of 28/35 mesh particles is placed at each electrode to prevent any of the finer particles from passing through holes in the electrodes."

The assembled apparatus is shown schematically in Figure 10. "To eliminate
CO₂ from the solutions, all experiments are conducted in a nitrogen atmosphere. Nitrogen, which is used to drive the solutions through the plug, is passed through a bottle of concentrated KOH solution to remove the CO₂ (9).

A nine liter ballast reservoir is used to maintain a more nearly uniform pressure (10). A series of stopcocks controls the direction of flow of N₂ to the flasks (11). Tubes of ascarite prevent backflow of CO₂ into the system (12). The driving pressure, which can be set at any desired value, is measured with either a water manometer (13) or a mercury manometer (14).

The reservoir flasks have side arms for making pressure corrections for the difference in water levels in the flasks."

Streaming potentials are measured by the circuit illustrated in Figure 10 (page 17). "The electrodes from the plug are connected through mercury wells (15) to a reversing switch (16), which reverses the polarity of the electrodes dependent upon the direction of flow of solution through the plug. The streaming potential is measured with a Leeds and Northrup Type K-2 potentiometer (17). The proper choice of null instrument is important because equation (1) assumes that the current which escapes through the measuring instruments is negligible. An ordinary galvanometer cannot be used to determine the null point because it permits discharge of the electrodes to a significant extent. Therefore, the null point is determined by measuring the potential across a wax-coated 10¹²-ohm resistance (18) placed in series with the potentiometer and plug. The streaming potential is exactly balanced when the potential across the 10¹²-ohm resistance is at zero on the Applied Physics Corporation vibrating reed electrometer (19). To extend the range of the potentiometer, several calibrated ½ volt batteries (20) can be placed in series with the potentiometer by means of switches (21, 22)."
STREAMING POTENTIAL STUDIES

BY

ANDREW L. MULAR

A THESIS
SUBMITTED TO THE DEPARTMENT OF MINERAL DRESSING
IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
BACHELOR OF SCIENCE
IN METALLURGICAL ENGINEERING
MINERAL DRESSING OPTION

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
MAY 20, 1956