A Mathematical and Experimental Model of the Electrical Properties of Silicate Minerals

by Raul A. Deju and Roshan B. Bhappu

STATE BUREAU OF MINES AND MINERAL RESOURCES NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY

CAMPUS STATION   **SOCORRO, NEW MEXICO**

A MATHEMATICAL AND EXPERIMENTAL MODEL OF THE ELECTRICAL PROPERTIES OF SILICATE MINERALS

Raúl. A. Dejú and Roshan B. Bhappu
New Mexico Institute of Mining and Technology
Socorro, New Mexico

INTRODUCTION

The electrical phenomena occurring at the water-solid interface have been the subject of almost constant investigation for the past two centuries. The first breakthrough was accomplished by Reuss[1] who found that if a potential is applied across a porous plug of wet clay, separating two portions of water, then a flow of water occurs from one side of the plug to the other. This phenomenon has been termed electro-osmosis.

About 40 years later, Wiedemann[2] made quantitative measurements of electro-osmosis in his mass flow rate studies. Then Quinke[3] discovered that, if a liquid is forced through a porous plug of wet clay, a potential is created. This potential is now called streaming potential.

All of the above investigations were experimental in nature and the quantiative results derived from them were arrived at in an empirical fashion.

The development of the theory of electrical phenomena at the water-solid interface did not begin until the time of Helmholtz[4] who based his theory on the existence of electrically charged layers of opposite sign at the water-solid boundary.

Since the early works of Helmholtz, theoretical investigations on the electrical properties of interfaces have received detailed consideration from many investigators; results indicate that a quantitative treatment presents many difficulties. In most cases, only useful approximations have been derived.

In this paper, the authors show the results of a new, modified model of the water-solid interface. The terminology that will be used in describing the electrical layers that extend between the solid particle's surface and the bulk of the water has been modernized. The model is then tested by experimental means and its electrical properties are related to other properties of the water-solid system.

THEORETICAL CONSIDERATIONS

When a potential differential is externally applied to a liquid containing charged particles, it causes a migration of the particles to the pole having a charge opposite to that of the particles. If the particles are ions, the phenomenon is called ionic conduction; in the case of mineral particles, it is called electrophoresis. Here we will be concerned only with electrophoresis and other electrical properties of a colloidal suspension of a mineral.

Generally, a mineral particle in suspension has a charge on its surface. This surface charge, together with the ions in solution near the surface to maintain electroneutrality, forms a series of electrical layers around the mineral particle. The ions responsible for the surface charge are termed surface-charge ions. The potential at the surface of the mineral will be designed by ψ_o. Some of the ions near the surface of the mineral are anchored within a layer directly adjacent to the surface. These ions, which are said to be in the Stern layer, are strongly held to the surface. The potential of the periphery of this layer is called zeta potential $(\psi \zeta)$. The remaining ions are loosely held by electrostatic forces and constitute the diffuse layer of counter ions that extends deep into the solution. The surface layer and the Stern layer are grouped into what we call the dipole layer. Figure 1 is a representation of these layers.
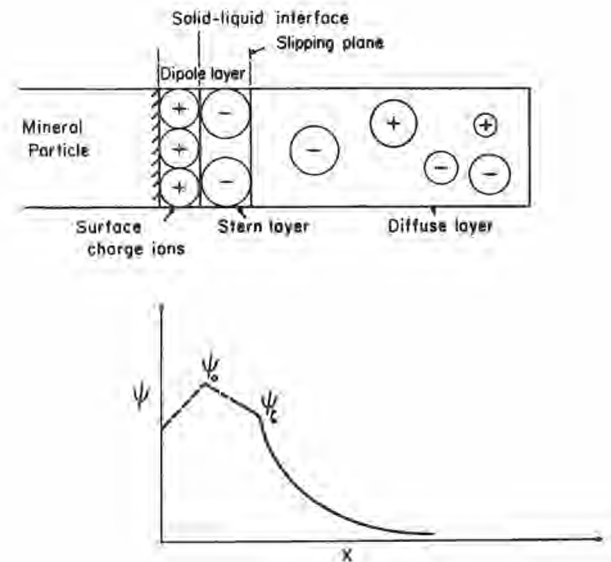

Fig 1. A Model of a Particle Surface and Its Surrounding Electric Layers

The diffuse layer is very important but difficult to treat; therefore, it has not been as extensively

treated in the literature as the other two layers.

Gouy[5] assumed that the ions in the liquid phase followed a Boltzmann distribution function up to the surface of the particle. This assumption is rather inaccurate when applied close to the particle's surface. In the present treatment, we have assumed that a Boltzmann function governs the distribution of ions up to the boundary between the Stern and the diffuse layers. The result we obtain is

$$\Psi = \Psi_\zeta \exp(-\kappa x) \qquad (1)$$

where ψ is the potential at a distance x from the boundary between the dipole and the diffuse layer and κ is the Debye-Huckel function.

This model gives us an approximation to the potential as a function of distance. The potential drops exponentially as we move outwardly from the plane separating the Stern and the diffuse layers.

Complications in the Thoery

There are many complications in the detailed theory of the electric layers, especially for particles moving within an electric field [Kruyt(6), Overbeek[7], Irving[8]]. The effective viscosity in the diffuse layer is affected because the ions in it are also moving as a result of the field applied. This gives rise to <u>electrophoretic retardation.</u> Briefly, since net charge in the fluid region close to the surface is opposite in sign to that of the surface, these ions, on the whole, move relative to the solution in a direction opposite to that of the surface. In turn, these ions entrain solvent with them (for example, through their hydration shells and atmospheres) so that there is a local motion of the medium opposing the motion of the charged particle or surface. Therefore, a more realistic model of the electric layers as a particle moves within an electric field must also include a consideration of the local medium velocity.

There is also a relaxation effect which exists due to the dipole layer lagging somewhat behind because of the motion of the particle; again, the effect is one of retarding the motion of the particle. Deryagin and co-workers(9) studied this relaxation effect and showed that differential diffusion of ions in the vicinity and toward the surface of a moving particle may give rise to an added contribution to the electrical potential which is independent of and perhaps superposed on the zeta potential.

Another point to consider is that the dipole-layer region is a source of conductance as well as the surface of the particle. This conductance is difficult to evaluate.

The Zeta Potential Equation

The diffuse layer satisfies Poisson's equation

$$\nabla^2 \Psi = -\frac{4\pi p}{D}$$

where V^2 is the Laplace operator, ψ is the potential at a point located a distance x from the outer boundary of the Stern layer, p is the space-charge per unit-volume at that same point, and D is the dielectric constant of the medium.

Let us further assume that the liquid under consideration is undergoing laminar flow. Let us call its viscosity μ and let us assume that μ and **D** are uniform throughout the mobile part of the diffuse layer, and assume that the bulk of the potential drop in the diffuse layer takes place in a distance which is small when compared to the curvature radius of the surface.

On the basis of these assumptions, we obtain

$$v_B = \frac{ED\,\Psi_\zeta}{4\pi\mu} \qquad (2)$$

A possible use of this equation is in determining the so-called zeta potential. We can define zeta potential as the electrical potential in the slipping plane between fixed and flowing liquid, that is, the potential at the outer edge of the Stern layer. In order to determine the zeta potential, we measure the electrophoretic velocity y_e under a certain electric field of strength, E, and knowing D and μ for the case under consideration we can determine $\psi\zeta$.

EXPERIMENTAL

In recent years, a great interest in the study of surface chemistry has resulted in a number of methods to study the surfaces of minerals and to observe the phenomena occurring at their interfaces. These methods involve electrokinetic and/or adsorption measurements. This section is concerned mainly with electrokinetics.

The quantity which is measured in electrokinetic studies is electrophoretic mobility, that is, the velocity at which a given particle moves when a suspension of these particles is placed within an electric field. The electrophoretic mobility, as shown in the previous section, depends on the strength of the field, the viscosity of the fluid, the dielectric constant of the fluid, and the zeta potential. The zeta potential is highly dependent on some of the ions present in the dipole layer. Such ions are usually termed <u>potential-determining</u> ions. In the case of experiments with silicate minerals to be described in this paper, the potential-determining ions are H+ and OH. Thus, zeta potential is a function of the pH of the solution in which the particles are immersed.

The isoelectric point of charge of a given solid sample whose potential-determining ions are H^+ and OH^- can be defined as that point on the pH scale at which the sample possesses zero net-surface charge and the adsorption densities of H^+ and OH^- are equal. At the isoelectric point-of-charge both the electrophoretic mobility and the zeta potential are zero.

The most widely used electrokinetic-techniques are the moving-boundary cell, the mass-transport

cell, the streaming-potential cell, and the electro-
phoresis cell. This last cell is discussed later in the
experimental sections. The other cells are briefly
discussed for the sake of completeness.

Instrumentation

Moving Boundary Cell. Moving-boundary
methods were among the earliest procedures used for
the determination of electrophoretic mobilities. The
Burton cell uses a traveling telescope to measure the
moving boundary. With this technique, it is essential
to have osmotic equilibrium between the suspended
particles and the liquid. Also, careful consideration
must be given to the type of liquid used in the exper-
iment.

The Burton cell is highly reliable and has been
widely used. However, experiments with it are very
tedious and require several hours to complete. This
time factor can cause errors due to diffusion not
detectable with the telescope. A very complete dis-
cussion of the Burton cell is given by Alexander and
Johns on[10] .

Mass-Transport Cell. Long and Ross[11]
developed a method for determining electrophoretic
mobilities as a result of an effort to obtain an instru-
ment well adapted for fundamental research, while
retaining the main features of earlier mass-transport
cells.

The setup of the Long-Ross cell is shown in
Figure 2. This cell is made of an acrylic resin
(Lucite®, Plexiglas®), which is machinable. The cell
is simple in design and construction. For electro-
phoretic mobility measurements, the main circuit
components are two-electrode probes and a recorder
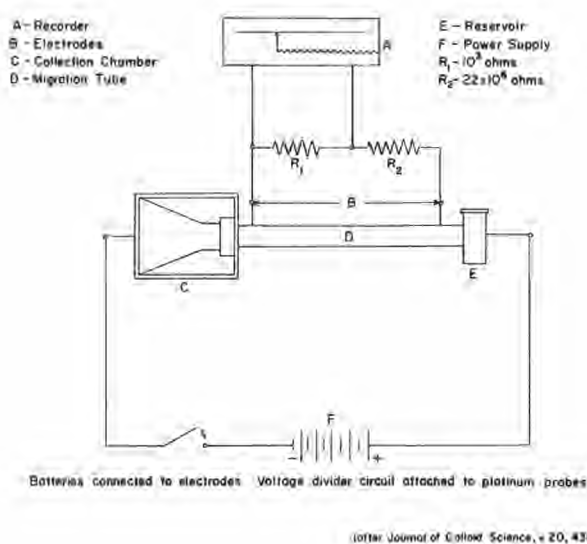with a voltage divider-circuit.

A – Recorder
B – Electrodes
C – Collection Chamber
D – Migration Tube
E – Reservoir
F – Power Supply
R_1 – 10^3 ohms
R_2 – 22x10^6 ohms

Batteries connected to electrodes Voltage divider circuit attached to platinum probes

(after Journal of Colloid Science, v 20, 438-447 (1965))

Fig 2. The Long-Ross Mass-Transport Cell

In this cell, the amount of solids transported
is given by the equation

$$m = MGAv_e t,$$ (3)

where M is the concentration of the solids (gm/ml),
G is the potential gradient (volts/cm), A is the area
of cross section of the migration tube (cm^2), . $_{ve}$ is the
electrophoretic mobility (cm sec^{-1}), and t is the time
(sec).

This apparatus is most reliable for colloidal
particles of high specific-gravity. Comparison of the
Long-Ross method with the Burton cell shows mobility
differences of no more than 4 percent.

Errors using this apparatus may be ascribed
to convection currents due to joule heating of the par-
ticles or of the supporting electrolyte, counterflow
effect, convection currents created by the gravita-
tional fall of particles, and thermal-conductivity
properties of and electrostatic charge effects on
Plexiglas®. The advantages of this method are many
more than its shortcomings, and reproducible
measurements of electrophoretic mobilities of dis-
persed particles can be easily made using the Long-
Ross cell.

Streaming Potential. Streaming potential is
also frequently used in measuring zeta potential and
isoelectric point-of-charge. This is an indirect way
of measurement. Zeta potentials ($\psi\varsigma$) can be calcu-
lated by determining the difference in potential
between the two ends of a porous plug of particles as
a liquid is forced through the plug. The equation that
relates zeta potential to streaming potential is given
by Gaudin and Fuerstenau[12]. For aqueous systems
at 25°C. this equation is

$$\psi_\zeta = 9.69 \times 10^4 \, \frac{S\lambda}{P}$$ (4)

where S is the streaming potential in millivolts, P is
the driving pressure in centimeters of mercury, and
X is the specific conductance of the solution contained
inside the plug in ohms^{-1} cm^{-1} .

To determine zeta potentials by this procedure,
it is necessary, experimentally, to measure driving
pressure, specific conductance, and streaming
potential. The error in zeta potential values measured
in this manner has been less than 1 percent. Further
discussion of streaming potential studies is given by
Fuerstenau[13] and Korpi( ).

Electrophoresis Cell. The apparatus used in
the electrophoresis experiments described below is
shown in Figures 3 and 4. The cell and glassware
were designed and built in the laboratories of the New
Mexico Bureau of Mines and Mineral Resources; the
projection apparatus was constructed by Rayoscope
Corporation; and the power supply unit was built by
Arthur H. Thomas Company.

This apparatus consists of three main parts; a
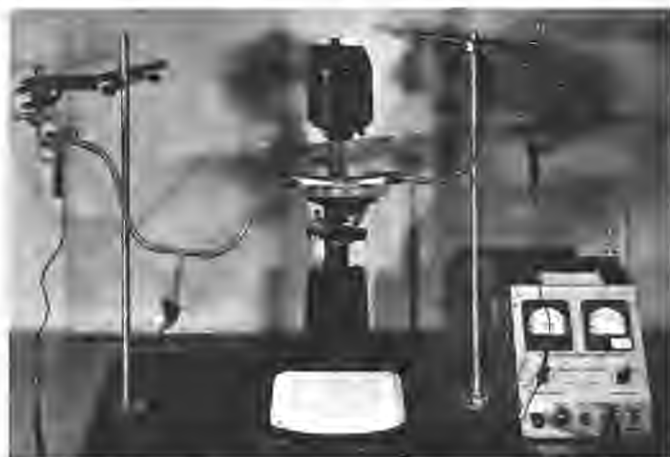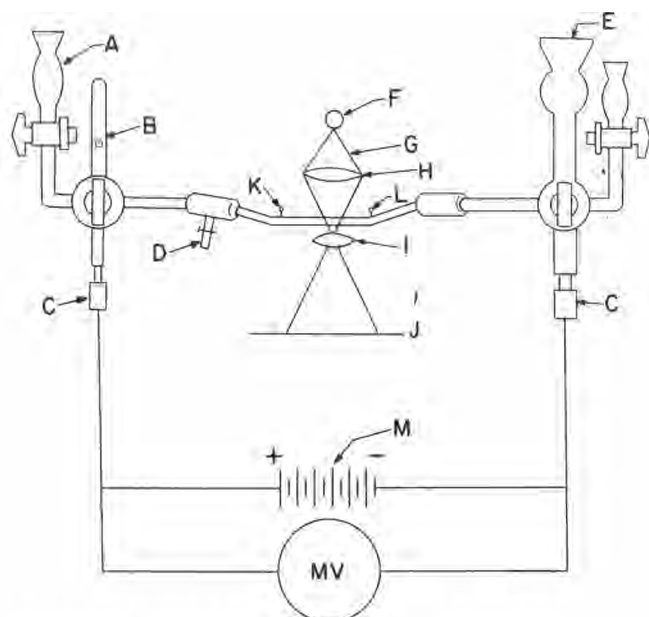power supply unit, a conducting unit, and an optical

Fig 3. Picture of Electrophoresis Cell

electrophoretic mobility when high accuracy is needed (the electrode separation can be determined extremely accurately) and an outer, removable set of electrodes for rapid, isoelectric, point-of-charge measurements.

The optical system consists of two parts: a projector and a lens filter-system. This modification, not previously used, allows the projection of the images of particles on a screen, thus eliminating the need for tedious microscopic observations. The heat adsorption and blue (color) filters added to the projector allowed the experimenter to minimize convection currents inside the cell. It was shown by Whitney and Blake[15] that suspended particles and not the glass itself are heated.

The author also developed a second, modified, electrophoresis cell based partly on the design by T. M. Riddick[16] (of Zeta-Meter Corporation) and based partly on the cell discussed above. This second electrophoresis cell is shown in Figure 5.

A – CuSO$_4$ or KCl reservoir
B – Drainage outlet
C – Cu-Zn electrode
D – Drainage outlet
E – Particles in solution
F – Light
G – Heat and color filters
H – Lens
I – Lens
J – Screen
K – Pt Electrode
L – Pt Electrode
M – Battery

Fig 4. Schematic of Electrophoresis Cell

system. The power supply used has a range of 0 to 300 volts d. c. and 0 to 50 mA d.c.

The conducting unit is composed of a series of glass tubes that allow the solution with the particles to pass through the observation region and then to drain at the other end of the unit. This conducting unit is supplied with two sets of electrodes: an inner, permanent, platinum electrode for measurements of

A – Rubber Bulb, 11ml. capacity
B – Foam Latex Plug
C – Electrode
D – Plexiglass Plugs
E – Drill Hole, 4.4mm. diameter
F – Type II UVA Plexiglass
G – Open Electrode
H – Light Source
I – Heat and Color Filters
J – Lens
K – Lens
L – Screen

Fig 5. Modified Electrophoresis Cell

Although less reliable than the electrophoresis apparatus above, it is more convenient for rapid, routine measurements of isoelectric point-of-charge. Measurement errors using this cell are caused mainly by the thermal conductivity properties of Plexiglas® and by convection inside the tube. Maximum deviation from results obtained with this cell has been approximately ± 3. 5 percent.

Experiments, Results and Discussion

Silicate minerals were chosen to test the different types of apparatus and theory described above

because of the following reasons:

1) Ready availability of samples of excellent quality,

2) High abundance of silicates in nature,

3) H+ and OW are potential-determining ions, and

4) A reasonable amount of literature pertaining to properties of silicates is available.

The samples studied are shown on Table 1. All samples were hand-picked and then dry-crushed in a ceramic ball mill and screened to obtain a minus 400-mesh-size fraction. The sized samples were then run through the electromagnetic separator to remove iron-bearing materials. Finally, the samples were crushed in an automatic mortar to obtain a size fraction 2 to 10 microns in diameter. Final particle sizes were determined to an accuracy ±1.5 percent using a Fisher subsieve-sizer. One gram of this size fraction of a mineral was mixed with about a gallon of deionized water. From this stock suspension, 10 samples of 100 milliliters each were taken, each having approximately the same degree of particle dispersion. Every sample was then adjusted to the desired pH with CI⁻ or NaOH, and its isoelectric point-of-charge was determined.

Results obtained for the isoelectric point-of-charge experiments are depicted in Table 1 and Figure 6. It can be determined from Table 1 that, for a series of very pure silicate samples, the oxygen-silicon ratio increases as the isoelectric point-of-charge increases.
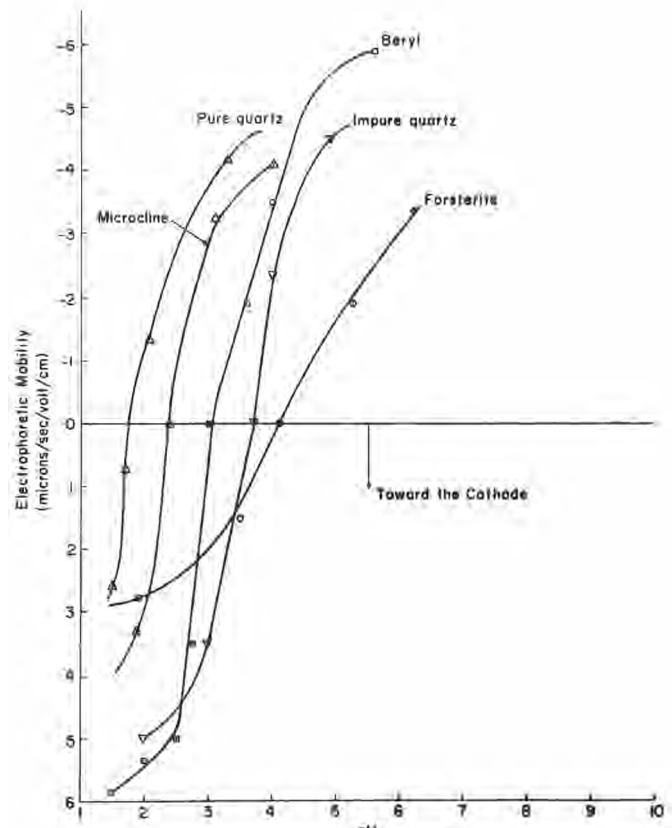

Fig 6. Results of Isoelectric Point-of-Charge Experiments

Table 1

The isoelectric point-of-charge was determined by observing the particles as they moved through the electrophoresis cells described previously. First, the velocity of the particles was statistically measured using 20 determinations. Then, the electrophoretic mobility was plotted as a function of pH to determine the isoelectric point-of-charge.

An important point to consider is the observed difference in isoelectric point-of-charge between a leached and an unleashed sample of the same mineral, as shown in Table 1. An explanation may be obtained by constructing a model of the reaction of these silicates when they are immersed in an acid solution.

Let M+ be the metal cation, Y⁻ be the anionic part of the silicate sample; overbars represent surface products, and ions indicate species in aqueous phase. The surface reactions can be indicated by the equations:

$$H^+ + \overline{MY} \rightleftharpoons M^+ + \overline{HY} \tag{5a}$$

$$H_2O + \overline{MY} \rightleftharpoons M^+ + \overline{HY} + OH^- \tag{5b}$$
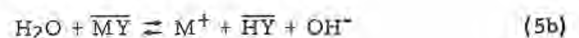
During this leaching process, a large number of the M^+ ions may leave the surface with an equivalent amount of H+ ions replacing them. The number of M +ions present on the surface will then be

substantially less than for the unleached sample, and the amount of OH- ions formed as an end product will also be much less. If the leached sample is denoted by A and the unleached sample by B, it follows that

$$[OH^-]_A < [OH^-]_B \qquad (6)$$

therefore,

$$[H^+]_A \text{ final} > [H^+]_B \text{ final} \qquad (7)$$

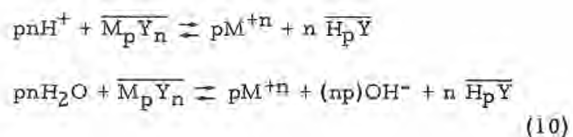Since for the silicates used, H+ is the potential determining factor, as shown by Dejú and and Bhappu[17, 18],

$$ip = \text{isoelectric point} = k/[H^+], \qquad (8)$$

where k is the proportionality constant. Thus Equation (6) becomes

$$ip_A < ip_B \qquad (9)$$

For this reason, the isoelectric point-of-charge of the leached and purified sample may be less than that of the impure sample, as is observed experimentally.

In reality, Equations (5a) and (5b) probably do not represent the only reactions occurring on the surface of the mineral. There may be an entire set of reactions simultaneously occurring, as indicated in general form by

$$pnH^+ + \overline{M_pY_n} \rightleftarrows pM^{+n} + n\,\overline{H_pY}$$

$$pnH_2O + \overline{M_pY_n} \rightleftarrows pM^{+n} + (np)OH^- + n\,\overline{H_pY} \qquad (10)$$

where n is the valence of M and p is the valence of Y in the silicate mineral.

The model discussed in the first section of this paper allows us to complete the picture of phenomena occurring at the silicate-solution interface discussed in the preceding paragraphs. By electrophoresis experiments, we measured the electrophoretic mobility of various silicate minerals (microns/sec/volt/cm). Thus, using Equation (2) and recalling that at 25°C D = 78.54 and μ = 0.00894 poises, we can obtain the value of the zeta potential of the minerals under consideration. By using values of the electrophoretic mobility at different pH values, we can obtain the zeta potential for different values of H+ concentration in solution. Then, using Equation (1), we can plot the potential as a function of relative distance (Kx), for several values of H^+ concentration. Such a plot is shown in Figure 7 in the case of beryl. Similar plots could be made for any of the minerals investigated. This type of plot gives us a quantitative view of the electrical potential surrounding a mineral particle in suspension. Such plots, together with the predicted type of chemical reaction between water and silicates and the concept of isoelectric point-of-charge, give us a picture of the phenomena occurring at the water-silicate interface.
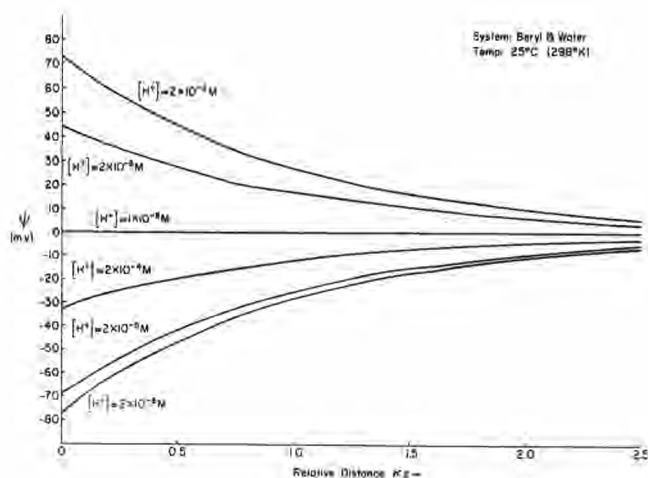

Fig 7. Potential as a Function of Distance

SUMMARY AND CONCLUSIONS

A model of a mineral particle and its surrounding electric layers was developed. The electric layers surrounding a mineral particle in suspension were also closely studied, and a model of potential as a function of distance was constructed.

Phenomena, such as electrophoretic retardation, relaxation effects, and dipole layer conductance, are briefly discussed, and their possible effects on the above models are mentioned.

Beginning with the assumption that potential satisfies Poisson's equation in the diffuse layer, we arrived at a theoretical derivation of the equation

$$v_e = \frac{ED\Psi\zeta}{4\pi\mu}$$

The various instruments that are used for electrokinetic studies are briefly discussed. These are: the moving-boundary cell, mass-transport cell, streaming-potential apparatus, and the electrophoresis cell.

Experiments using the above instruments were performed with silicate minerals suspended in water. The isoelectric point-of-charge was determined by observing the particles as they moved in the presence of an electric field. Their velocity was then statistically measured.

Experiments showed that as the oxygen-silicon ratio increased, the isoelectric point-of-charge increased.

Experiments also showed that the isoelectric point-of-charge of a leached sample is less than that of an uncleaned sample. This same result can be

derived from knowledge of the surface reactions at the water-silicate interface.

Finally, electrophoresis experiments combined with the model described at the beginning of this paper permitted us to build a picture of the electric layers for each of the minerals under investigation.

REFERENCES

1. Reuss, F. F., Mem. Soc. Imperiale Natural Moscov, vol. 2, 1809, p. 327.

2. Wiedemann, G., Pogg. Ann., vol. 87, 1852, p. 321.

3. Quinke, G., Pogg. Ann., vol. 113, 1861, p. 513.

4. Helmholtz, H., Wied. Ann., vol. 7, 1879, p. 337.

5. Gouy, G., Ann. Phys., vol. 7, no. 9, 1917, p. 129.

6. Kruyt, H. R., Colloid Science, Elsevier Publishing Co., New York, 1952.

7. Overbeek, J. T., Advances in Colloid Science, Interscience Publishers, New York, 1959.

8. Frumkin, A., Journal of Colloid Science, vol. 1, 1946, pp. 277-291.

9. Deryaguin, B. V., Research in Surface Forces, two volumes, Consultants Bureau, New York, 1966.

10. Alexander, A. E., and Johnson, P., Colloid Science, Oxford University Press, London, vol. 1, 1949, p. 321.

11. Long, R. P., and Ross, S., "An Improved Mass Transport Cell for Measuring Electrophoretic Mobilities, " Journal of Colloid Science, vol. 20, 1965, pp. 438-447.

12. Gaudin, A. M., and Fuerstenau, D. W., "Quartz Flotation with Anionic Collectors, " Min. Eng., vol. 7, no. 1, 1955, pp. 62-72.

13. Fuerstenau, D. W., "Measuring Zeta Potential by Streaming Potential Techniques, " Min. Eng., vol. 8, no. 8, 1956, pp. 834-835.

14. Korpi, G. K., "Measuring of Streaming Potentials, " M.S. Thesis, Massachusetts Institute of Technology, 1960.

15. Whitney, W. R., and Blake, J. C., Jour. Am. Chem. Soc., vol. 26, 1904, pp. 1339-1387.

16. Riddick, T. M. "Zeta Potential New Tool for Water Treatment, " Chem. Era., vol. 68, no. 13, 1961, pp. 121-126.

17. Dejú, R. A., and Bhappu, R. B., "Design of an Apparatus for Determining Isoelectric Point of Charge, " N. Mex. Inst. Min. and Tech., State Bur. Mines and Mineral Resources, Circ. 79, 1965.

18. Dejú, R. A. , and Bhappu, R. B., "Surface Properties of Silicate Minerals, " N. Mex. Inst. Min. and Tec., State Bur. Mines and Mineral Resources, Circ. 82, 1965.