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A Chemical Interpretation of Surface Phenomena in Silicate Minerals

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Abstract

In this report, the oxygen-silicon ratio for a representative series of silicate minerals is correlated to the degree of adsorption on the surface of the mineral when it is immersed in water. Experiments are conducted to prove that there is a corresponding increase in adsorption with increasing oxygen-silicon ratio. The behavior of the minerals in an electric field is investigated using zero point of charge as a parameter.

Equipment for these zero point of charge experiments consists of a moving boundary cell, a mass transport cell, two cataphoresis cells, and a streaming potential cell. Finally, a theoretical model is developed to explain the increase in zero point of charge with increasing oxygen-silicon ratio. A comprehensive bibliography on electrokinetic properties of silicates has been included at the end of the paper.

Introduction

In recent years great interest in surface chemistry has produced a number of methods to study the surface of minerals and to observe the phenomena occurring at their interfaces. Several such methods are discussed in this paper.

Before undertaking a description of the surface phenomena of minerals, some terms must be defined. The most important of these are *zero point of charge*, *particle mobility*, and *zeta potential*. *Zero point of charge* of a mineral whose potential-determining ions are H^+ and OH^- is defined as the point on the pH scale at which the mineral possesses no surface charge and the adsorption of H^+ and OH^- is nil. *Particle mobility* is the velocity of mineral particles in the presence of an electric field. It is usually expressed in microns per second per volt per centimeter. *Zeta potential* is the potential a mineral particle assumes when placed in an electric field. It is responsible for a constant reforming of the diffuse surface layer of the mineral particle.

A rather complete study of the surface chemistry of the oxide minerals has been undertaken by Parks (1965). However, a similar study had not been made for the silicate minerals. Two previous papers by the authors attempted to remedy this situation (Deju and Bhappu, 1965a,b). In these papers it was demonstrated that the reaction between the silicate mineral particles and acidic water involves mainly an exchange of metal ions for hydrogen ions on the surface of the solid, leading to an increase in pH of the aqueous

phase. Also, the degree of reaction was found to depend on the oxygen-silicon ratio of the silicate structure, being greatest for the olivines. It was then theorized that upon the fracturing of a silicate mineral, the oxygen-metal bond, which is almost entirely ionic in character, will break more easily than the stronger oxygen-silicon bond, resulting in a greater number of unsatisfied negative forces on the surface. Thus, an increase in the degree of adsorption of hydrogen ions occurs as the oxygen-silicon ratio increases.

A correlation between oxygen-silicon ratio and other electrophoretic properties will be further pursued in this paper from both the theoretical and experimental points of view. It is believed that this study may supply pertinent information on the behavior of silicate minerals in froth flotation systems.

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Equipment Electrokinetic Studies

MOVING-BOUNDARY CELL

Moving-boundary methods were among the earliest to be used for the determination of electrophoretic mobilities. The Burton cell is a moving-boundary method, such boundary being measured with a traveling telescope. When the Burton cell is used, it is essential to have osmotic equilibrium between the suspended particles and the supernatant liquid. Also, careful consideration must be given to the type of supernatant liquid used in the experiment.

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 may cause errors due to diffusion not detectable with the telescope. A very complete discussion of the Burton cell is given by Alexander and Johnson (1949).

MASS-TRANSPORT CELL

Long and Ross (1965) developed a method for determining electrophoretic mobilities in an effort to

obtain an instrument 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 1. This cell is made of machinable Plexiglas and is very simple in design and construction. For

mobility measurements, the main circuit components are two electrode probes, a Leeds and Northrup Speedomax G. Recorder with a voltage-divider circuit, and a d-c voltmeter.

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

$$m = MEAv_e t \quad (1)$$

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

This apparatus is most reliable for colloidal particles of high specific gravity. Comparison of the Long-Ross

- A - Recorder
- B - Electrodes
- C - Collection Chamber
- D - Migration Tube

- E - Reservoir
- F - Power Supply
- $R_1 - 10^3$ ohms
- $R_2 - 22 \times 10^6$ ohms

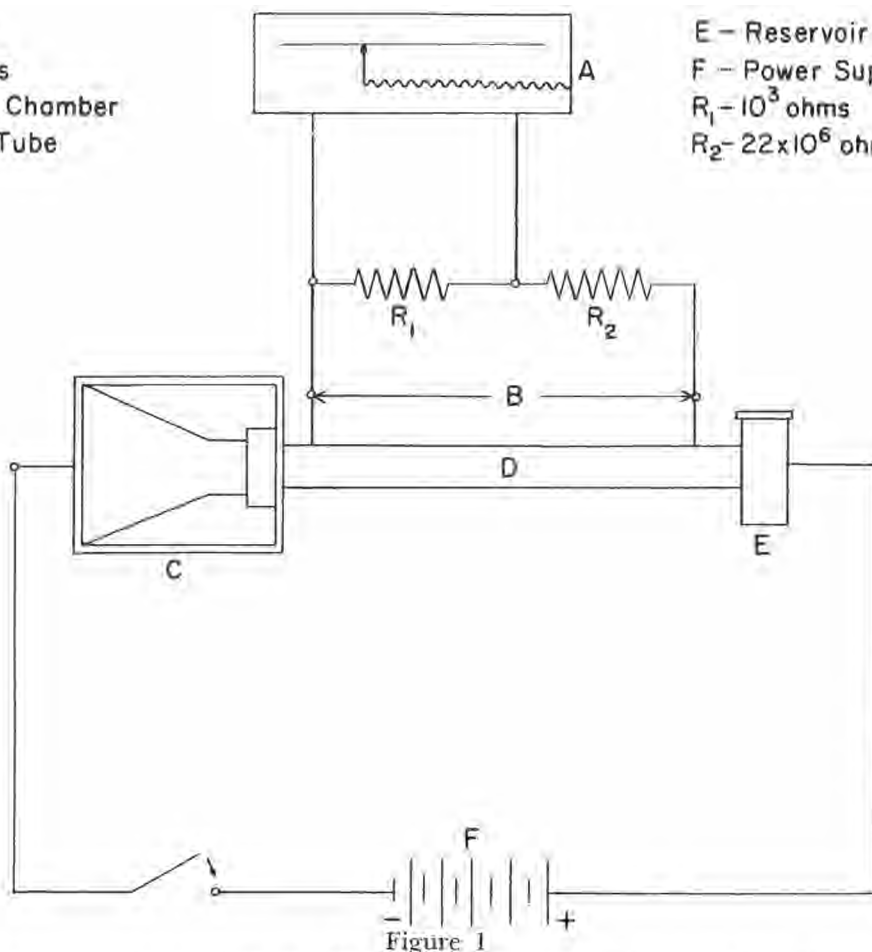


Figure 1
BATTERIES CONNECTED TO ELECTRODES. VOLTAGE DIVIDER CIRCUIT ATTACHED TO PLATINUM PROBES
(after Journal of Colloid Science, v. 20, 438-447 (1965))

method with the Burton Cell show mobility differences of no more than 4 per cent.

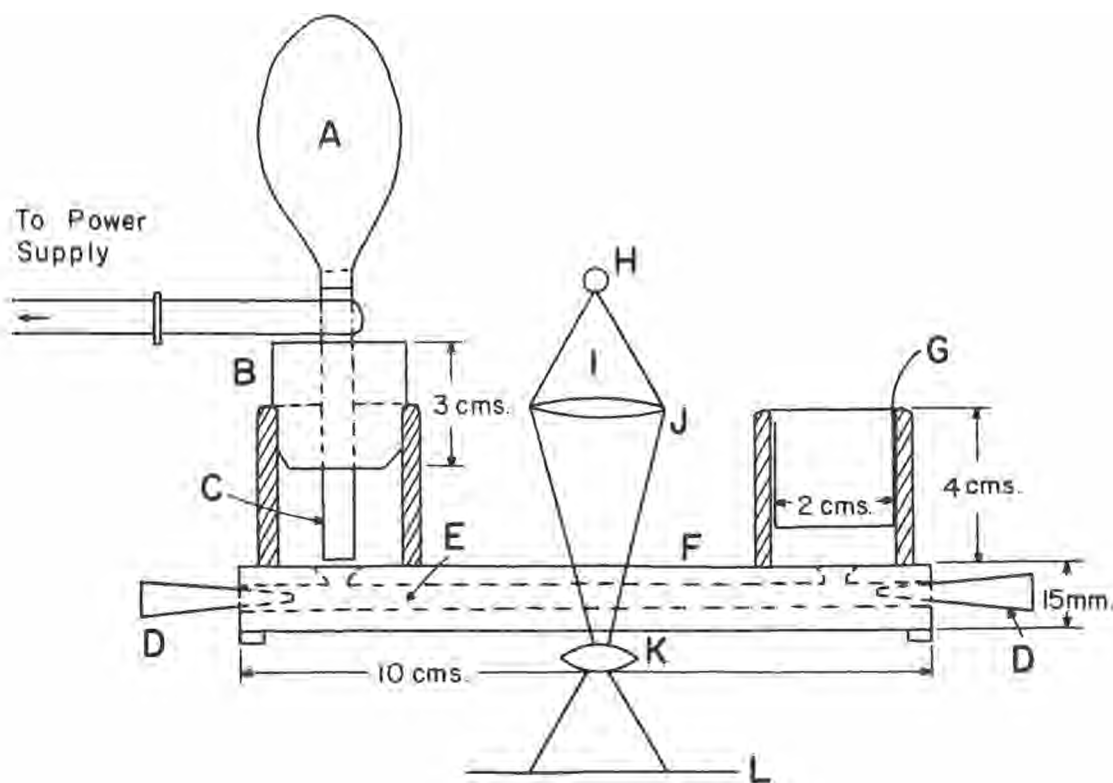
Errors using this apparatus may be due to formation of convection currents due to Joule heat, counterflow effect, mass transfer of supporting electrolyte, convection currents created by the gravitational fall of particles, and thermal conductivity properties of and electrostatic charge effects on Plexiglas and Teflon. The advantages of this method are many more than its shortcomings, and reproducible measurements of electrophoretic mobilities of dispersed particles can thus be easily made using the Long-Ross cell.

CATAPHORESIS CELL FOR ELECTROKINETIC STUDIES

In a previous paper, Deju and Bhappu (1965a) described a simple method for determining zero points of

charge using a potential across a cataphoresis cell and observing particle movement by means of a rayoscope optical system. This setup is simple in design and operation and extremely reliable. With care, reproducible results within 1.5 per cent accuracy may be obtained.

A new setup has been developed, based partly on the design by Zeta-Meter Corporation (Riddick, 1961) and partly on previous cataphoresis cells used at the New Mexico Bureau of Mines. This new, modified cell is shown in Figure 2. Although it is less reliable than the cataphoresis apparatus above, it is more convenient for rapid routine measurements of zero point of charge. Measurement errors using this cell are caused mainly by the thermal conductivity properties of Plexiglas and by convection inside the tube. Its maximum deviation from results obtained with the cataphoresis cell has been approximately ± 3.5 per cent for a total of 35 determinations.



- 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

Figure 2

STREAMING POTENTIAL

Streaming potential is also frequently used in measuring zeta potential and zero point of charge. This is an indirect way of measurement. Streaming potentials can be calculated 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 a zeta potential to streaming potential is given by Gaudin and Fuerstenau (1955). For aqueous systems at 25° C, this equation is

$$\bar{\zeta} = 9.69 \times 10^4 \frac{E\lambda}{P} \quad (2)$$

where E is the streaming potential in millivolts, P is the driving pressure in centimeters of mercury, and λ is the specific conductance of the solution contained inside the plug in ohms⁻¹-cm⁻¹.

To determine zeta potential 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 per cent. Further discussion of streaming potential studies is given by Fuerstenau (1956) and Korpi (1960).

Zero Point of Charge Studies

MATERIALS AND SAMPLE PREPARATION

Carefully selected hand-picked samples of the minerals investigated were 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 of ± 1.5 per cent using a Fisher subsieve sizer. One gram of this size fraction of a mineral was mixed with a gallon of deionized water. From this stock solution, 10 samples of 100 milliliters each were taken, each having approximately the same degree of particle dispersion. Every sample was then adjusted to a desired pH with HCl or NaOH, and its zero point of charge was immediately measured.

PROCEDURE

Particles were observed as they moved through the cataphoresis cell using a rayoscope optical system, and their velocities were statistically measured using 20 determinations. From the electrophoretic mobility data, the zeta potential was calculated using Henry's equation (Overbeek, 1959):

$$\zeta = \frac{V\pi\eta}{EDg(k, r)} \quad (3)$$

where ζ is the zeta potential, V is the velocity of the particle, E is the applied potential, η is the viscosity of the solution, $g(k, r)$ is a function of the reciprocal thickness of the double layer, r is the radius of the particle, and D is the dielectric constant. The procedure outlined above was applied to representative samples of silicate minerals. Results obtained for the zero point of charge experiments are shown in Table 1; Figure 3 shows these results in a graphic form.

Table 1. Results of Electrophoresis Experiments

Mineral	Formula	Location	History	O:Si ratio	Zero Charge (pH)	Specific Gravity
Forsterite	Mg ₂ SiO ₄	Twin Sisters Range, Wash.	very pure, dry crushed, iron-free sample, unleached	4:1	4.10	3.26-3.40
Enstatite	+Fe, Bronzite MgO · SiO ₂	Near Webster, Jackson County, North Carolina	very pure, dry crushed, iron-free sample, unleached	3:1	3.75	3.10-3.40
Augite	Ca(Mg·Fe)(SiO ₃) ₂ (Al·Fe) ₂ O ₃ _x	Mexico	very pure, dry crushed, iron-free sample, unleached	3:1	3.80	3.20-3.50
Augite	Ca(Mg·Fe)(SiO ₃) ₂ (Al·Fe) ₂ O ₃ _x	Mexico	bulk ore sample, dry crushed, unleached	3:1	4.45	3.20-3.50
Spodumene	Li ₂ O · Al ₂ O ₃ + SiO ₂	Harding Mine, Dixon, N. Mex.	very pure, dry crushed, iron-free sample, unleached	3:1	2.60	2.64
Beryl	3BeO · Al ₂ O ₃ + 6SiO ₂	Harding Mine, Dixon, N. Mex.	very pure, dry crushed, iron-free sample, cleaned with 1M HCl	-	3.00	2.63-2.91
Microcline	K ₂ OAl ₂ O ₃ + 6SiO ₂	Harding Mine, Dixon, N. Mex.	very pure, dry crushed, iron-free sample, unleached	2:1	2.40	2.54-2.57
Albite	Na ₂ OAl ₂ O ₃ + 6SiO ₂	Harding Mine, Dixon, N. Mex.	very pure, dry crushed, iron-free sample, unleached	2:1	2.00	2.61-2.64
Quartz	SiO ₂	Harding Mine, Dixon, N. Mex.	sample of high purity, cleaned by leaching in concentrated HCl and washed in conductivity H ₂ O	2:1	1.80	2.59-2.66
Quartz	SiO ₂	Brazilian crystals	sample of Brazilian hand-picked crystals, cleaned by leaching in concentrated HCl, 8 hrs. treatment in Soxhlet	2:1	1.50	2.59-2.66
Quartz	SiO ₂	Harding Mine, Dixon, N. Mex.	7-day leached sample, highly purified	2:1	1.40	2.59-2.66
Quartz	SiO ₂	Harding Mine, Dixon, N. Mex.	bulk sample, untreated	2:1	1.70	2.59-2.66

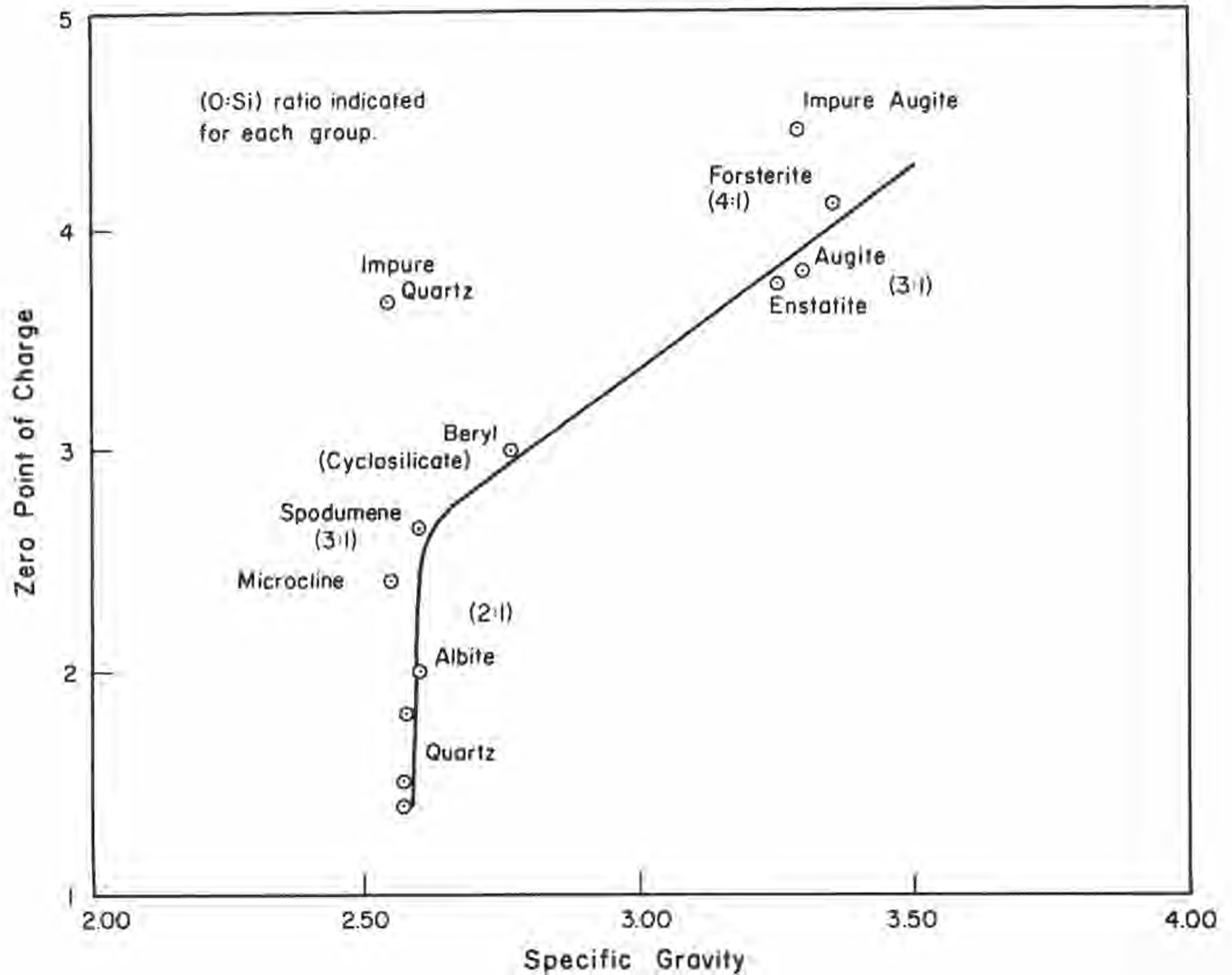


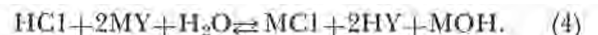
Figure 3
ZERO CHARGE VS. SPECIFIC GRAVITY OF SILICATE MINERALS

DISCUSSION OF RESULTS

From Table 1 it can be seen that for a series of very pure silicate samples, the oxygen-silicon ratio increases as the zero point of charge increases. Also, since specific gravity is approximately directly proportional to the oxygen-silicon ratio, it follows that zero point of charge is directly proportional to specific gravity for very pure silicate minerals. This relationship, however, will not hold for impure minerals of a high cationic content, as shown in Figure 3.

An important point that must be considered is the observed difference in zero point of charge between a leached and an unleached sample of the same mineral, as shown in Table 1. An explanation for this occurrence may be obtained by constructing a simple model of the reaction of these silicates immersed in an acid solution.

Let M^+ be the metal cation and Y^- be the anionic part of the silicate sample. The surface reaction may be indicated by the equation



If the silicate sample is leached and purified, a large number of the M^+ ions may leave the surface. The number of them originally present on the surface will then be substantially less than otherwise, and the amount of MOH 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

$$[MOH]_A < [MOH]_B \quad (5)$$

Therefore,
$$[H^+]_{final A} > [H^+]_{final B} \quad (6)$$

Since for the silicates used, [H+] is the potential determining factor,

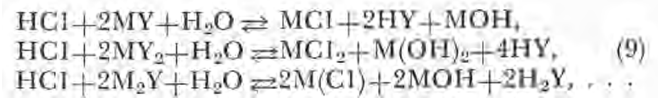
$$zpc = \frac{K}{[H^+]}; \quad (7)$$

thus (5) becomes

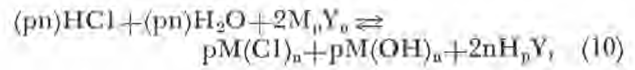
$$zpc_A < zpc_B \quad (8)$$

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

In reality, equation (4) will not be the only reaction occurring on the surface of the mineral. There may be an entire set of reactions simultaneously occurring, as indicated by the following:



All equations in this set are particular cases of a general chemical equation that can be written as



where p is the valence of Y and n is the valence of M. Further experimental evidence for this result for the case of iron has been presented in previous papers (Deju and Bhappu, 1965a,b).

Absorption Studies

MATERIALS AND PROCEDURE

Hand-picked fractions of the same samples used above were crushed and screened dry to obtain a —100+200-mesh size fraction. These fractions were dry-treated and purified to reduce the surface iron content to a minimum. A 10-gram sample of each mineral was placed in 100 milliliters of deionized water previously adjusted to a pH of 3.50 with HCl. The beaker containing the sample and the water was then placed in a nitrogen atmosphere. The changes in pH were followed with a Beckman Zeromatic pH meter and recorded on a Heathkit servo-recorder, as shown by Deju and Bhappu (1965b).

RESULTS AND DISCUSSION

Adsorption experiments using the above setup show that the adsorption of hydrogen ions by the mineral

surface increases as the oxygen-silicon ratio in the silicate structure increases; for example, olivines will adsorb more hydrogen ions than augite or quartz.

From the zero charge and the adsorption studies, a proportionality is observed between the oxygen-silicon ratio and the zero point of charge of the mineral. This occurrence can also be explained using equation (10). Assume that sample X has a higher oxygen-silicon ratio than sample Y. Then, from the adsorption it follows that

$$[\text{MOH}]_x > [\text{MOH}]_y \quad (11)$$

Thus,
$$[\text{H}]_x < [\text{H}]_y \quad (12)$$

and by equations (7) and (12) it is easily seen that

$$zpc_x > zpc_y$$

Therefore, as the oxygen-silicon ratio increases, the zero point of charge also increases.

Conclusions

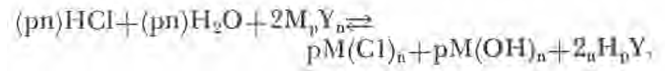
The most important methods for determining zero points of charge and other electrokinetic variables are electrophoresis, cataphoresis, moving boundary, and streaming potential.

Cataphoresis experiments seem to indicate that for representative silicate minerals there is an increase in the zero point of charge as the oxygen-silicon ratio increases.

Since specific gravity is so directly dependent upon the oxygen-silicon ratio, it can roughly be said that the zero point of charge of silicate minerals increases as the specific gravity values go up.

The authors have devised a theoretical model to explain the behavior of silicate minerals when im-

mersed in water. This model postulates that the reaction between the silicate mineral particles and water involves mainly an exchange of metal ions for hydrogen ions leading to an increase in pH of the aqueous phase. The model states that the actual reactions are defined by a set of equations derived from the general equation below:



The theoretical model described not only explains the adsorptive behavior of silicates but also explains the direct proportionality between the zero point of charge and the oxygen-silicon ratio.

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