

Electrokinetic Measurements of Colloidal-Laden Flow Through a Sand Column¹

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The flow of colloidal-laden water into or through porous media occurs repeatedly in nature. With water infiltration into soil, seepage through deeper aquifers and drainage into tile drains, retardation of flow caused by clogging of pores is not desirable. In other instances, however, with sealing of reservoir bottoms or irrigation canals and filtration of raw water for domestic use, retardation of flow becomes an indication of effectiveness. Further complications arise when the surface of a porous media is subject to extended periods of inundation. When this happens there is evidence of bacterial growth assisting the clogging process.

In this study (7), electrokinetic measurements were made to determine the reaction of a sand column to the inflow of colloidal-laden flow at different pH levels, periods of operation, and depths within the column.

An electrokinetic effect occurs when one layer of the electric double layer surrounding a particle moves relative to the other. Four electrokinetic phenomena are possible, but only two were used in this study. One, electrophoresis, is the movement of a suspended solid in a liquid by means of an applied electrical force; the other, streaming potential, is a potential which is established when an applied mechanical force moves a liquid relative to a stationary surface.

Literature Review

Ever since Helmholtz and Smoluchowski presented their theoretical treatment of the properties of the electric double layer as reported in a translation by Bocquet (4), numerous investigators in soil science, colloidal chemistry, biology, medicine, and other disciplines have applied the theory of electrophoresis to their research. In their classical presentation of electrophoresis, Helmholtz and Smoluchowski considered a two-phase system in which some ions would move with a suspended particle in an electrical field toward one pole while other ions, the counter-ions, would migrate toward the opposite pole. An electrical potential, the zeta-potential, was thereby established at the boundary between the two phases which was proportional to the particle velocity and the viscosity of the fluid and inversely proportional to the applied electric field strength and dielectric constant of the fluid.

Clay colloids which are suspended in a fluid, when energized, migrate toward the positive pole because they normally carry a net negative charge. This charge as stated by van Olphen (12) is brought about in two different ways: (1) imperfections within the interior of the crystal lattice of a particle which gives a net positive or a net negative lattice charge, and (2) preferential adsorption of certain ions on the particle surface. The charge on montmorillonitic clay particles originate

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both from lattice imperfections and ion adsorption. The face surface is negatively charged mainly by an isomorphous replacement of trivalent aluminum by divalent magnesium ions. The charge on the broken edges of a clay crystal depends upon the pH of the surrounding solution. In acid solutions, both the silica and alumina surfaces may carry a positive charge. In alkaline solutions, the alumina surfaces will likely be negatively charged. In total, however, the net charge on the clay particle is negative.

Early development of the electrokinetic phenomena was summarized by Abramson (1). Recently, Black (3) has reviewed the application of electrokinetic theory to coagulation for the period of 1923 to 1960. In coagulation, other than by gravity, movement of colloidal particles in suspension is mainly brought about by Brownian movement (thermal effect) and van der Waals forces (molecular cohesive forces); stabilization is due primarily to particle hydration (attraction of solvent molecules) and particle zeta potential. When a colloidal sol is moving through a porous media, Hunter and Alexander (9) concluded that movement of colloidal particles and the resulting filtration is also accomplished by diffusion into areas where the shear rate is low.

Surprisingly little use of the electrokinetic concept of streaming potential, also developed by Helmholtz and Smoluchowski, has been made until recently. When a liquid is forced through a capillary tube or porous diaphragm by an external pressure, the counter-ions are forced to flow with the liquid. A convection current is established which causes a potential difference called streaming potential across the tube or diaphragm. Some recent studies all since 1960 dealing with the flow of clay colloidal sols through porous media in which streaming potential measurements were made are those by Curry, Barker, and Strack (6), Hunter and Alexander (9), Ives (10), and Jordan (11). Ives (10) also summarized the work of these investigators as well as some others, notably foreign.

Experimental Procedure

The electrokinetic properties of a colloidal clay-silica sand system were studied in the laboratory by introducing a bentonite clay suspension onto a 20-inch silica sand column.

The silica sand used in the column was a graded silica sand ranging from 300 to 700 microns with an effective size of 0.35 mm. and a uniformity coefficient of 1.43. Before use, the sand was washed with detergent, rinsed, dried and acid leached.

One-half percent clay colloidal suspensions were prepared using Wyoming bentonite and deionized water. An analogous uniform suspension was first produced by passing a hydrated suspension from which the larger particles had been removed through a cation exchange resin for replacing exchangeable cations with hydrogen ions and through an anion exchange resin for replacing exchangeable anions with hydroxyl ions. The pH of the suspension was adjusted to 5.1, 7.0, 7.8 and 8.4 levels by the addition of NaOH. Final clay suspensions were then produced that had hydrogen saturated clay at pH less than 7.0 and sodium saturated clay at higher levels.

A transparent acrylic cylinder, 4 inches in diameter, was fitted with inflow and outflow head controls, manometer taps, extraction ports, and platinum electrodes. The cylinder was also connected to a flow meter and manometer board. Streaming potential measurements were made with a high input impedance (10^{14} ohms) vacuum tube voltmeter. Both the cylinder and voltmeter were shielded with brass screening to stabilize subsequent voltage readings. A Briggs cell, as originally developed by Briggs (5), was used for the determination of the mobility of colloidal particles. Other equipment included a pH meter, a microscope, a conductance cell, a spectrophotometer, and numerous electrical components. All apparatus and instruments were contained in a small room which was thermostatically controlled at $29 \pm 1.0^\circ\text{C}$.

After silica sand was compacted uniformly into the cylinder, flow was begun with deionized water until a steady rate occurred. An inflow rate of the clay suspension at one of the four pH levels was then maintained at 30 milliliters per minute by periodically adjusting the height of the outlet to the sand column. This rate was continued for 60 hours or until over twenty inches (the height of the sand column) head was needed to maintain the flow rate.

The zeta potential of the clay particles was calculated using a working form of the Helmholtz-Smoluchowski equation for electrophoresis with the Briggs cell:

$$\zeta_0 = \frac{1.129 \times 10^9 \eta}{D} \frac{d}{t} \frac{A}{IR}$$

where ζ_0 is the particle zeta potential in millivolts, η is the viscosity of the fluid in poises, D is the dielectric constant, d is the distance in centimeters over which a particle moves, t is the time in seconds for the particle to move this distance, A is the cross-section of the Briggs cell in square centimeters, I is the applied current to the electrodes of the cell in amperes, and R is the specific resistance of the suspension in ohm-centimeters. The zeta potential of the clay particles was determined by periodically extracting samples of the interflow along the column, by making other measurements necessary to the solution of the above equation, and by observing the mobility of the particles in a Briggs cell under an applied voltage.

The zeta potential of the colloidal clay-silica sand column was calculated using a working form of the Helmholtz-Smoluchowski equation for streaming potential:

$$\zeta_s = \frac{11.55 \times 10^9 \eta K \Delta E}{DP}$$

where ζ_s is the column zeta potential in millivolts, η is the viscosity of the fluid in poises, K is the electrical conductivity of the fluid in the porous medium in mhos per centimeter, ΔE is the streaming potential in millivolts, D is the dielectric constant, and P is the pressure difference across the column in centimeters of water. Platinum electrodes consisting of 2-inch square 52-mesh platinum screen were placed at the top, bottom, and 3/16-inch below the surface of the silica sand column. The zeta potential of the silica sand column or portions of the column was then determined by measuring the streaming potential between any

two electrodes with the voltmeter and making other measurements necessary to the solution of the above equation. The equation involving the streaming potential is valid for porous media with intricate networks so long as the basic assumptions which were used in developing this equation, notably laminar flow and negligible conductivity through the solids, occur (4).

Results

The zeta potential of the column as determined by the streaming potential measurement changed upon the addition of a clay suspension as shown in Figure 1 for $\text{pH} = 7.0$. For all four pH levels the initial zeta potential values when only deionized water flowed through the column were approximately the same. These values were -133 millivolts for the total column, $+850$ for the top $3/16$ inch, and -200 for the bottom $19\ 13/16$ inches. At $\text{pH} = 7.0$, the zeta potential for the total column approached an isoelectric condition (zero zeta potential) in about 10 hours and afterwards remained steady. This was not the case for the other pH levels. At $\text{pH} = 5.1$, the total column zeta potential increased to -50 millivolts becoming steady after about 20 hours; for both $\text{pH} = 7.8$ and $\text{pH} = 8.4$, the column zeta potential increased rapidly to around $+200$ millivolts in about 10 hours and then reversed to a value at the end of 60 hours of around $+100$ millivolts.

The zeta potential of the particles as determined from their observed mobilities in the Briggs cell varied with pH , generally increasing as the pH level of the solution increased. The zeta potential values did not change appreciably with column depth. The zeta potential tended to increase slightly in the first two inches and then a systematic propagation wave was exhibited which did not vary over 3 millivolts at any of the pH levels. The average particle zeta potential value at $\text{pH} = 5.1$ was -77 millivolts; at $\text{pH} = 7.0$, -52 millivolts; at $\text{pH} = 7.8$, -56 millivolts; and at $\text{pH} = 8.4$, -42 millivolts.

The column head loss as a function of column depth and period of operation for $\text{pH} = 7.0$ is shown in Figure 2. The total head loss increased rapidly and at the end of 40 hours was 15.2 inches of water. At the end of 45 hours, the flow through the column was stopped because the total head loss was approaching the limit imposed by the column length. In contrast to the high head loss at $\text{pH} = 7.0$, the total head loss for the column at the other pH levels after 60 hours of operation was only around 4 inches as shown in Figure 3.

Deposition occurred throughout the entire column for a short period of time after the clay sol was introduced onto the column surface. After this initial period, depending upon the pH of the solution, most of the remainder occurred in the top two inches of the column. At the end of the 40 hour period for $\text{pH} = 7.0$, the head loss in the first two inches was 13.5 inches out of 15.2 inches for the total column as shown in Figure 2. The total head loss for the column at $\text{pH} = 5.1, 7.0, 7.8$, and 8.4 were 2.9, 15.2, 2.3, and 3.9 inches, respectively; the head loss for the top two inches were 0.8, 13.5, 1.1 and 2.5 inches, respectively; and the head loss for the bottom 18 inches were 2.1, 1.7, 1.2, and 1.4 inches, respectively.

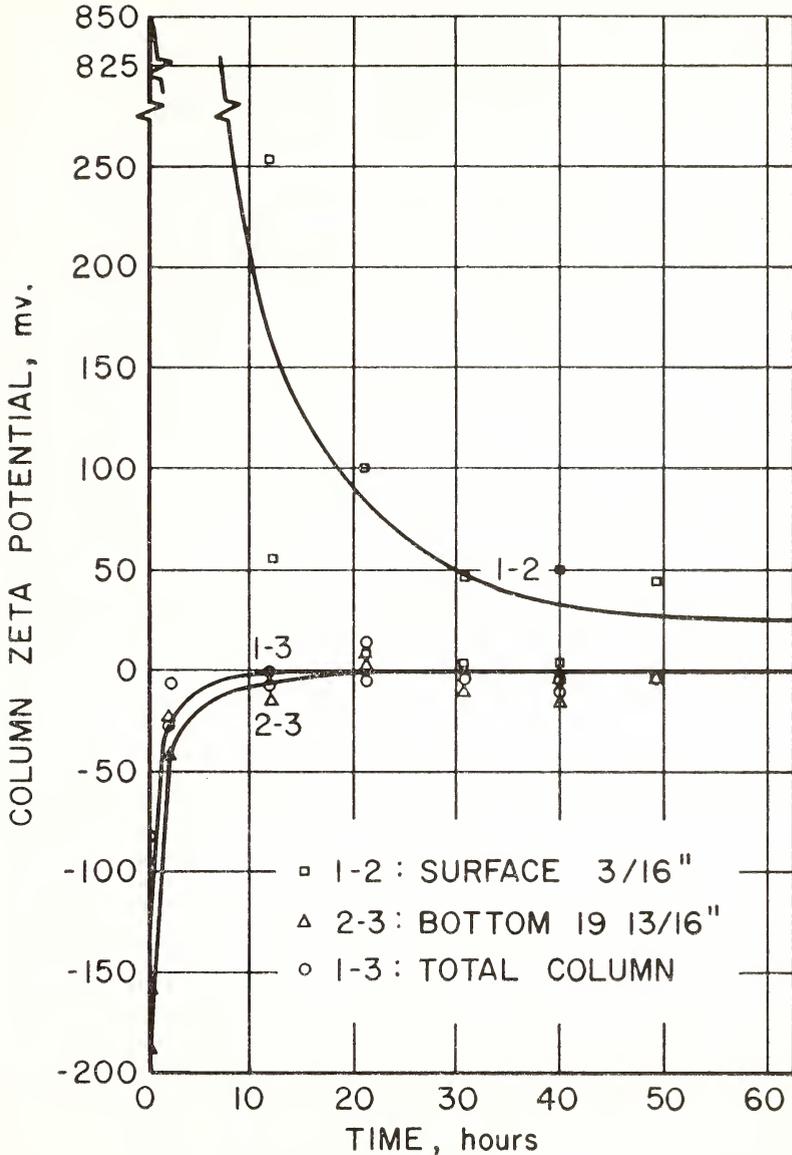


Figure 1. Column zeta potential from streaming potential measurements as a function of time at pH = 7.0.

Not to be expected, the column zeta potential for the top 3/16 inch carried a positive charge in all experiments. The performance of the top layer as shown in Figure 1 for pH = 7.0 was reasoned to be the result of biological activity. Studies by Allison (2) and later by Gupta and Swartzendruber (8) have shown the high reduction in hydraulic

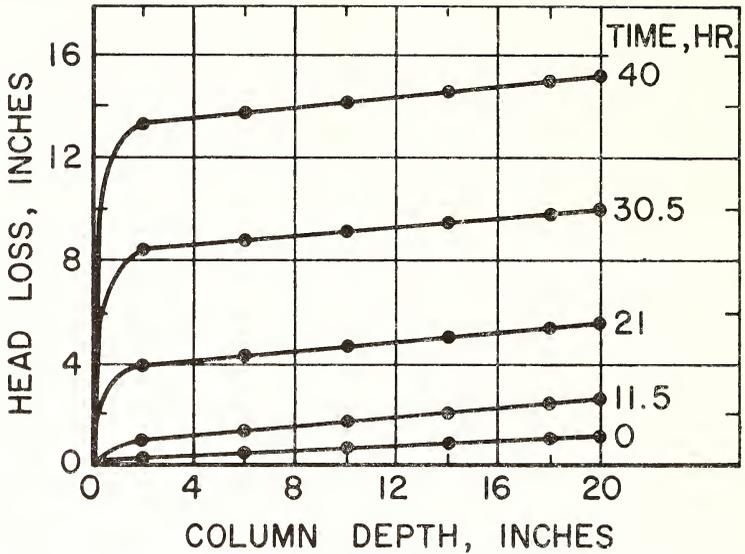


Figure 2. Column head loss as a function of column depth and period of operation at $\text{pH} = 7.0$.

conductivity of soil surfaces under prolonged submergence is due primarily to the accumulation of bacteria and their metabolic products in the surface layer. Quite recently Jordan (11) had hypothesized that under field conditions a positively charged schmutzdecke may be formed

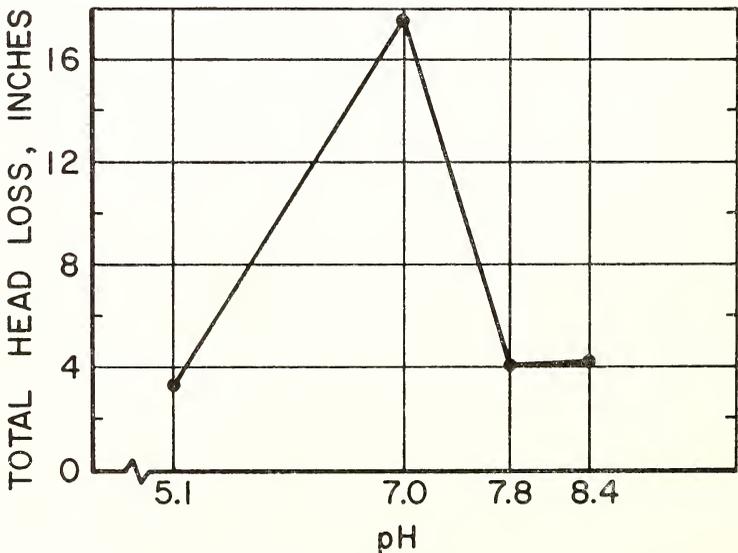


Figure 3. Total column head loss as a function of pH .

on a slow sand filter. To provide proof that bacteria accumulating in a surface layer may indeed be positively charged, one of the experiments in this study was followed by alternately dosing the column first with a disinfectant (0.1 percent phenol solution by weight) and then with deionized water. Although the magnitude of the zeta potential values varied, in all cases, the sign of the zeta potential became negative after the addition of the phenol solution and, in all cases, the sign of the zeta potential returned shortly to positive after deionized water was used. Further studies concerning this phenomenon are planned.

Discussion

The flow of a bentonite clay suspension through a silica sand column is highly complicated. The bentonite clay may carry both a net positive and a net negative charge on portions of its surface. The magnitude of these charges depends on the pH of the system. Adsorption, van der Waals forces, electrokinetic forces, and diffusion into low shear areas are the most probable mechanisms for the retention of clay colloids by a silica sand column. However, a colloidal clay-silica sand system may be further complicated by the accumulation of bacteria and their metabolic products in the interfacial zone between the porous medium and the ponded water above the medium. The effect of the accumulation of bacteria on the flow system may be pronounced but it is also likely to be erratic and difficult to predict.

There is strong evidence that these bacteria carry a net positive charge possibly as a food intake or anchorage mechanism in their largely, negatively charged environment. The net result may be to accentuate the electrokinetic forces in these regions. Actually the bacteria may be providing an electrical link between the net negatively charged silica sand and bentonite clay particles.

The zeta potential of the column changed because the column was altered by the retention of clay colloids and the accumulation of bacteria at the inlet portion of the column. Of the four pH levels investigated, filtration of the clay colloids was most effective at a pH = 7.0. This value satisfied best the amalgamated conditions for clogging imposed by the silica sand column, clay colloids, and bacteria. The greatest difference by far in the operation of the column at any of the pH levels occurred in the top two inches of the column when the pH = 7.0. At the end of 40 hours of operation, the head loss in the top two inches was 5 to 15 times greater than the head loss across this zone in experiments at other pH levels.

The zeta potential of the clay colloids in general increased (decreased in negative charge) as the pH of the suspension was increased. Rapid coagulation of colloidal sols usually take place shortly before the zeta potential has been completely neutralized. Although high base exchange capacity clays are easier to coagulate and may be done over a wider pH range, coagulation was not much of a factor with the range of zeta potential values used in this study. Also a relationship between the zeta potential of the clay colloids, remaining almost the same throughout the length of the column, and the zeta potential of the column was not found.

Summary

The operation of a colloidal clay-silica sand system was studied by introducing a bentonite clay suspension onto a 20-inch silica sand column. The purpose of this study was to investigate the effect of pH, period of operation, and depth within a column on the electrokinetic properties of the clay colloids and total colloidal clay-silica sand system. It soon became quite apparent that another ingredient to the system, the accumulation of bacteria and their metabolic products principally in the surface layer of the column, could not be discounted.

The zeta potential of the column changed because the column was altered by the clay colloids and bacteria which accumulated in the surface layer. The column zeta potential approached an isoelectric (neutral) condition quickly at a pH level of 7.0 thus indicating its propensity for rapid clogging. This was subsequently verified in terms of head loss. The total head loss for the column at pH = 5.1, 7.8, and 8.4 at the end of 60 hours was around 4 inches of water as compared to the head loss at pH = 7.0 at the end of 45 hours of nearly 18 inches. Almost all of this difference occurred in the top 2 inches of the column. pH control in systems where suspensions containing colloidal particles are introduced onto porous media is very important. The control level, however, would depend on whether the system is used to promote or inhibit the rapid clogging of pores.

The zeta potential of the clay colloids changed little regardless of where a sample was withdrawn from the column. In the range of zeta potential values used, the clay colloids had little tendency toward rapid coagulation. The dominant reaction therefore was that of the silica sand column and the accumulated bacteria to the clay colloids.

Perhaps the most important finding was that bacteria, at least of the type accumulating on soil surfaces, may exhibit a positive electrical charge. Whether this charge serves as a food intake mechanism, a method of anchorage, or some other function, the net result is to accentuate the electrokinetic forces in the regions influenced by bacteria. The positively charged bacteria may attract the net negatively charged clay colloids and bind them to the negatively charged silica sand. Electrokinetic forces thus augmented by the charge orientation of bacteria may well be the principal mechanism by which colloidal particles are retained in porous media.

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