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Streaming potentials in diatomite filtration of water

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STREAMING POTENTIALS IN DIATOMITE FILTRATION OF WATER

by

Charles Sylvan Oulman

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Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Head of Major Department

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Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1963

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INTRODUCTION

Production of Streaming Potentials

An electric potential called a streaming potential is produced when water is filtered through a porous media such as diatomite. Such media normally have a negative surface charge. Potentials of several hundred millivolts may be generated across a filter when using water of high purity. Streaming potentials produced depend on many factors including the kind of particles in the porous medium and on the ions in the water. Streaming potentials are lowered in magnitude or may even be reversed in sign by the presence of certain ions in the water being filtered. The reversal of streaming potential is believed to be caused by precipitates of metal hydroxides becoming concentrated near the surface of the diatomite. As the surface of the diatomite becomes coated with this positively charged material, the surface charge of the particle is changed from negative to positive.

Surface Charge of Diatomite

Most substances develop a negative surface charge when they are immersed in water. In the middle of the Nineteenth Century, Quincke (1) determined that this was true for platinum, gold, copper, iron, graphite, quartz, feldspar, manganese, asbestos, emery, clay, porcelain, air bubbles, oxygen bubbles, hydrogen bubbles, sulfur, shellac, silk, cotton, starch, paper, lycopodium, carmine, ivory, turpentine oil, carbon disulfide and carbon dioxide.

The surface charge of particles can be determined in several ways. Quincke used electrophoretic methods for determining that the substances listed were negatively charged. Electrophoresis is the movement of a charged particle in an electric field. In practice, two electrodes are immersed in a suspension of the particles and an electric potential is applied across the electrodes through an external circuit. Negatively charged particles migrate to the anode and positively charged particles migrate to the cathode.

Electrophoretic measurements demonstrating that diatomite is negatively charged are described below (6):

> "Dr. C. E. White has demonstrated the presence of negative charges on certain particles of diatomaceous earth suspended in distilled water. A platinum electrode was placed in either arm of a glass U-tube containing the suspension. When a direct current was sent through the U-tube at a potential of 110 volts, there was a migration of diatomaceous particles away from the negative and toward the positive electrode. After ten minutes of such electrolysis, the liquid near the negative electrode was almost free from suspended matter and nearly clear, whereas the positive electrode was covered with the deposited siliceous particles."

The surface charge of diatomite has also been studied by streaming potential measurements. Most manufactured grades of diatomite have a negative charge according to these measurements while a few have a positive charge (29). Those grades of diatomite having a positive charge were specially prepared by a patented process (9) in which an adherent coating of an electropositive substance such as an aluminum salt or a ferric salt is applied to diatomite.

Effect of Surface Charge on Filtration

Streaming potentials and electrophoresis are two of several phenomena known as electrokinetic phenomena. Electrokinetic phenomena are those concerned with movement of charged bodies in an electric field. Usually, electrokinetic phenomena pertain to movement of solid particles through a liquid in which they are suspended or the movement of liquid through a porous medium or capillary. Following is a list of electrokinetic phenomena and brief descriptions of each:

1. Electrophoresis -- the movement of particles through a liquid across which an electric potential has been applied.
2. Sedimentation or migration potentials -- electric potentials produced by particles during sedimentation or when moved in some other way through a liquid.
3. Electroosmosis -- the movement of liquid through a porous medium or capillary across which an electric potential has been applied.
4. Streaming potentials -- electric potentials produced by liquids moving through a porous medium or capillary.

Ruth (37) has written at length about the way in which streaming potentials and electroosmosis might affect filtration. He suggests that streaming potentials developed in a filter could cause an electroosmotic counter flow of water in the filter medium. This reverse flow would tend to increase the head loss of filtration by reducing the size of pore available for flow. With increasing head losses, the streaming potentials would increase still more with the result that head losses in filtration would continue to increase whether or not the filter medium was becoming clogged with particulate matter. He concluded that:

> "It is difficult to avoid the conclusion that electrokinetic phenomena play a large part in the success or failure of filtration as a method of separation."

At the University of Illinois the head loss in both sand and diatomite filters filtering distilled water was found to build up over a period of time (26, 45). Several techniques that would tend to dissipate a streaming potential were found effective in reducing the head loss. One method consisted of stopping filtration for a period of time. During the rest period, electroosmosis would dissipate the streaming potentials built up during filtration. Another method consisted of applying an opposing electric potential for a short time to neutralize the streaming potential. Both methods had a similar effect in that the head loss was much lower following the treatment than it had been before. The build up of head loss was attributed to "electrokinetic blocking". No measurements of streaming potentials were made to confirm this, however.

The following statements taken from the Illinois research group's final report (19) indicates that they did not place much stock in the idea that "electrokinetic blocking" was an important factor in the build up of head loss in practical filtration applications:

> "This investigation has demonstrated that electrokinetic phenomena play a considerable role in building up the head loss across a filter during the filtration of distilled water."
>
> "The investigation tended to indicate that as the conductivity of the water increased the effects due to streaming potential and electroosmosis would decrease. In fact, some doubt has been expressed as to whether the phenomena even exist using the raw water ordinarily filtered in the field."

Since streaming potentials are high when distilled or deionized water is being filtered and low when natural water is being filtered, the head loss increase, as it is affected by electroosmosis, can be expected to differ greatly from one source of water to another. Hence, the surface charge of diatomite affects the increase of head loss in water that is relatively free of mineral impurities and may complicate the process of extrapolating filtration results from one place to another.

The surface charge of the diatomite may also affect the kind of particles that are removed in the filtration process.

Colloidal sols of ferric and aluminum hydroxide are coagulated by diatomite (7). Thus, instead of clogging the interstices of diatomite filter cakes, and thereby decreasing the permeability, as colloidal particles might be expected to do. These positively charged particles, when present in amounts less than 8 per cent of the weight of the dry cake, tend to separate the particles of diatomite and make the cake more permeable.

On the other hand, Cummins (9) claims that diatomite coated with electropositive materials has the ability to flocculate electronegative suspensions. According to his patent description:

> "Because of the flocculating of electronegative impurities in aqueous solutions, the diatomaceous filter aid provided with an electropositive coating of aluminum hydroxide or the like is particularly effective in the filtration of liquids in which there is a high proportion of such impurities. Thus, the filter aid is effective in the filtration of glue and of turbid river water."
>
> "Filtering a turbid river water in comparable manner, first with a conventional filter aid and second, with the same filter aid electropositively coated, and observing the filtrates with a Tyndallometer, there was noted a more pronounced Tyndall effect in the filtrate from the conventional filter aid than from the electropositive aid."

The removal of color and bacteria in addition to that of turbidity is increased by coating filter aids with aluminum and ferric hydroxide (2):

> "Use of diatomaceous silica filter aids for direct filtration has generally been confined to surface waters of relatively low turbidity. This is due to the fact that such filter aids effects turbidity

> reduction by substantially mechanical means, the degree of removal of any specific particle size distribution being a function to the porosity or grade of filter aid used.
>
> "By contrast, filter aids in which the individual particles have been coated with a surface active coating, such as aluminum or ferric hydrate, have substantial adsorptive activity. Their use not only results in a much higher degree of clarification but also effects substantial color and bacteria removal. Interestingly, coated filter aids seem best adapted to more turbid supplies than can be effectively clarified by uncoated filter aids."

Evidence shows that electropositive coatings improved the performance of a filter aid used for filtering a New Jersey river water in the following ways (2):

1. Turbidity removal was about 50 to 70 per cent without the coating and about 80 to 95 per cent with the coating.
2. Color removal was about 30 to 50 per cent without the coating and about 70 to 85 per cent with the coating.
3. Bacterial removal was about 70 to 85 per cent without the coating and about 90 to 95 per cent with the coating.

Thus, some colloidal particles too small to be removed by mechanical straining are removed by mutual coagulation in those cases where the filter aid and the colloids carry opposite surface charges. These same colloidal particles might pass through the interstices of a filter cake in which the filter cake and the colloids had the same surface charge.

Source of Surface Charge

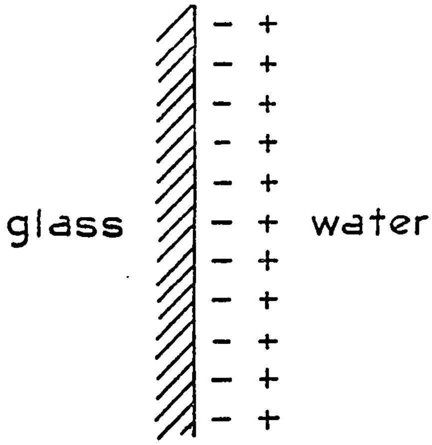
Particles of diatomite suspended in water behave as if they are electrically charged even though the suspension is electrically neutral. Many attempts have been made to describe the nature of the charge on particles in contact with water. One of the earliest attempts was that of Quincke who postulated the presence of negative charges on the surface of glass in contact with water and positive charges in the water layer next to the glass wall (1). See Figure 1.

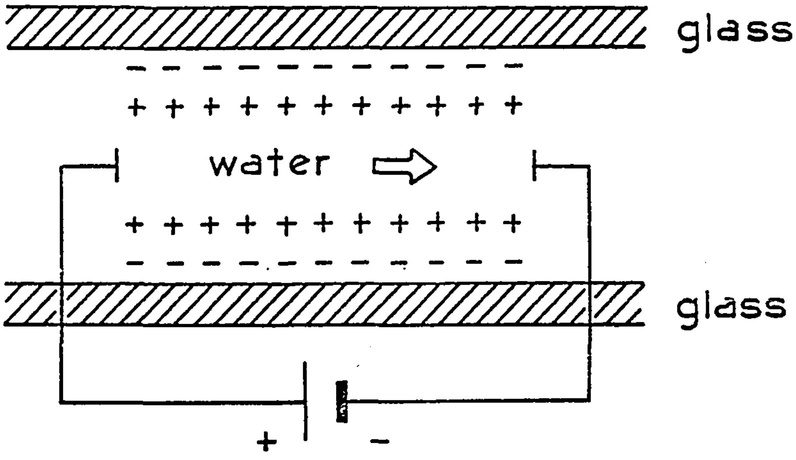
This provided a satisfactory basis for explaining electroosmosis. An electric potential applied across a capillary filled with water displaces positively charged water toward the negative electrode. The rest of the water in the capillary is dragged along with the positively charged water layer because of internal friction. See Figure 2.

Helmholtz elaborated mathematically on Quincke's idea of the existence of the electric double layer of charges which is now called the Helmholtz double layer. He assumed that the thickness of the double layer, although small, was not vanishingly small and that the layer of charged water molecules in contact with the wall was not movable. Hence, there is a potential difference between the negative charge associated with the glass and the positive charge associated with the water. Because neither the glass nor the water is charged unless they are in contact with each other, and

Figure 1. The electric double layer at a glass-water interface according to Quincke

Figure 2. A diagram representing electroosmosis in a glass capillary filled with water


glass
water


glass
water
glass
+
–

collectively they are neutral when they are in contact, there must be as many negative charges on the surface of the glass as there are positive charges in the water layer. In order that electrical neutrality be maintained, the entire electrokinetic potential drop would take place between the particle surface and the layer of charged water molecules next to the wall which Helmholtz assumed were not movable. See Figure 3.

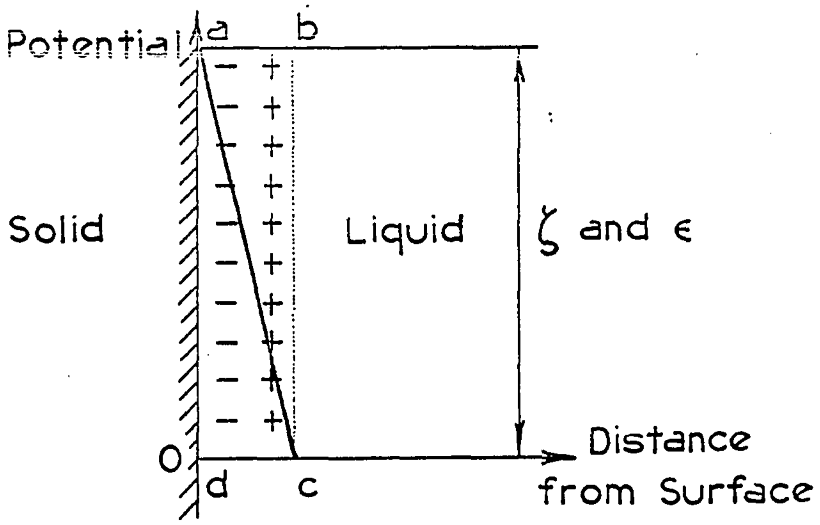
An attempt was made later to connect the electrokinetic or zeta potential with the electrochemical or Nernst potential. The Nernst potential (ϵ) is the total drop in potential between the particle and the solution. According to the Helmholtz double layer theory, the Nernst potential would be the same as the zeta potential (ζ). See Figure 3. It was later demonstrated that the zeta potential of glass in solutions of KCl, $BaCl_2$, $La(NO_3)_3$ and $Th(NO_3)_4$ was different from the Nernst potential. The zeta potential differed not only in magnitude and sign but also by having maximum and minimum values depending on the concentration of the solutions (44).

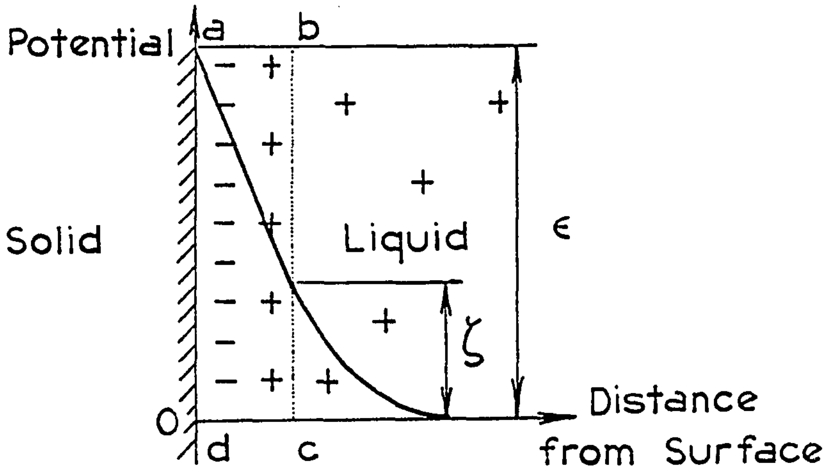
The present theory about the charge distribution in the vicinity of a solid phase in contact with a liquid phase is based on ideas advanced by Gouy and Stern (44). According to Gouy, thermal diffusion tends to overcome in part the electrostatic attraction between charged ions in the liquid phase and on the surface of the solid phase. Instead of a fixed layer of charges in the liquid phase next to the solid

Figure 3. A diagram showing the potential drop across the Helmholtz double layer at a solid-liquid interface

Figure 4. A diagram showing the relationship between the zeta potential and the Nernst potential at a solid-liquid interface

Figure 5. A diagram showing that the sign of the zeta potential may be opposite to that of the Nernst potential at a solid-liquid interface


Potential
a
b
Solid
Liquid
ζ and ε
0
d
c
Distance from Surface


Potential
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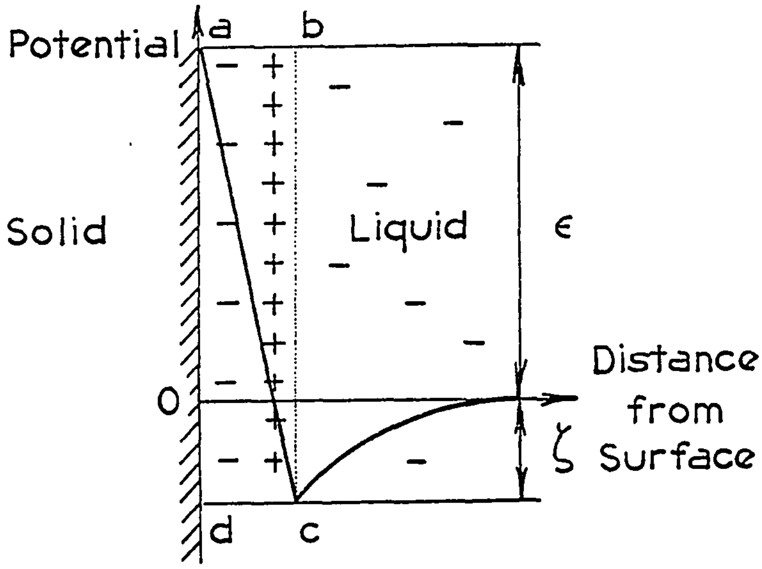
Potential
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b
Solid
Liquid
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0
Distance from Surface
ζ
d
c

phase as Helmholtz assumed, Gouy postulated a diffused layer in which the electrical density falls off exponentially with distance from the surface of the solid phase.

Stern's ideas represent a compromise between the positions taken by Helmholtz and Gouy. Stern recognized that some ions may be strongly adsorbed on the surface of the solid phase and be held immobile as Helmholtz had assumed. The rest of the ions near the surface are attracted electrostatically by the charged surface but are also affected by thermal diffusion which tends to distribute them in the way that Gouy had assumed. Thus, the zeta potential is the potential drop between the surface of the immobile liquid layer adsorbed on the surface of the solid phase (bc in Figures 4 and 5) and the movable liquid layer in the liquid phase. Figure 4 shows the relationship between the zeta potential and the Nernst potential at a solid-liquid interface. Figure 5 shows how the sign of the zeta potential may be opposite to that of the Nernst potential at a solid-liquid interface. This can be done by crowding more positive charges into the fixed layer than are needed to balance the negative surface charge.

The diffuse layer can be divided into two additional layers (42). The outer layer is relatively loosely held by electrostatic attraction and can be displaced by hydrostatic forces. The inner layer which is more firmly held cannot be displaced by hydrodynamic forces but can be displaced by electric forces. Thus, the zeta potential of a solid in contact with a liquid may not be the same when determined by streaming potential measurements as it is when determined by electroosmosis or electrophoresis.

This has been demonstrated using glass as the solid and solutions of $ThCl_4$, $AlCl_3$ and $FeCl_3$ as the liquid (25). The isoelectric ion concentration was lower for streaming potentials than for electroosmosis or electrophoresis. In other words, less salt was needed to lower the zeta potential to zero as measured by streaming potential methods than was needed when the measurements were made with electrophoretic or electroosmotic methods.

Since filter aids are affected by hydrodynamic forces in filtration rather than by electric forces, streaming potential measurements should yield information that is more pertinent about the zeta potential than information obtained by electrophoretic or electroosmotic methods.

Zeta Potential and Streaming Potentials

The electrokinetic potential or zeta potential is a derived property of the immobile surface of a wetted particle. It is a potential that would produce electrokinetic effects similar to those observed if it existed across the plates of a condenser equivalent to the diffuse layer surrounding the particle.

The relationship between zeta potential and streaming potentials can be derived by means of a condenser analogy which was introduced by Smoluchowski (3). The following derivation is based in part on information contained in standard physics and physical chemistry texts (4, 10, 40).

Considering a portion of a particle having an area A in contact with water, the diffuse layer of ions surrounding this particle is equivalent to an electric condenser whose plates are separated by a distance t. The water between the plates is assumed to have a dielectric constant D which is the same as the dielectric constant of pure water. The charge on each of the plates per unit area is σ and the potential between the plates is ζ. Hence, the charge q on one of the plates is

$$q = \sigma A$$

and on the other oppositely charged plate is

$$q' = \sigma A$$

where

$$q' = q.$$

The electric force of attraction between two point charges q and q' is

$$F = \frac{kqq'}{t^2}$$

where k is a proportionality constant equal to 8.98776 x 10^9 newton meter^2 per coulomb^2. The magnitude of the electric field intensity, X, may be expressed in terms of either the zeta potential

$$X = \frac{\zeta}{t}$$

or the force F on a test charge q' exerted by the field set up by charge q

$$X = \frac{F}{q'} .$$

The electric field intensity can therefore be expressed in terms of the size of the charge q setting up the field and the distance t between the charges

$$X = \frac{kq}{t^2}$$

or in terms of the unit charge

$$X = \frac{k\sigma A}{t^2}\ .$$

Since the electric field of a condenser is set up by charges distributed over the plane surfaces of its plates rather than by point charges, it is necessary to differentiate the equation to give

$$dX = \frac{k\sigma\cos\alpha dA}{t^2}$$

where α is the angle between the line joining a point in one of the condenser plates with the differential element dA of charged surface in the other condenser plate and a line normal to the planes of the condenser plates. If t is assumed to be very small compared to the dimensions of the condenser plate, the condenser plate can be assumed to be infinite in extent and the differential equation can be integrated between $\alpha = 0$ and $\alpha = \pi/2$. When this is done, the electric field intensity of one plate is found to be

$$X_1 = 2\pi k\sigma\ .$$

Since the condenser has two plates with equal and opposite charges, the fields of each will reinforce each other and the electric field intensity in a vacuum for the whole condenser will be

$$X = 4\pi k \sigma .$$

In a liquid whose dielectric constant is D,

$$X = \frac{4\pi k \sigma}{D} .$$

Therefore,

$$\zeta = \frac{4\pi k \sigma t}{D} .$$

During filtration, positive ions in the diffuse layer are displaced with respect to negative ions in the fixed layer due to hydrodynamic forces. These hydrodynamic forces can be expressed in terms of Stokes' law

$$F = \frac{\eta A v}{t}$$

where v is the velocity of the moving water and η is its viscosity. The motion of these ions constitutes a streaming current. The electric field set up by this streaming current is

$$X = \frac{F}{q'}$$

or

$$X = \frac{F}{\sigma A} .$$

Thus,

$$\sigma XA = \frac{\eta Av}{t}$$

or

$$\sigma = \frac{\eta v}{tX} .$$

If the conversion of hydrodynamic energy to electrical energy is complete, the power consumed in moving water over the surface of the particle will be equal to the electrical power generated, and

$$PAv = EI$$

or

$$PAv = \frac{E^2}{r}$$

where r is resistance, P is pressure, I is streaming current and E is the streaming potential. The streaming potential is related to the electric field intensity by means of the mean electric flow path s by

$$X = \frac{E}{s}$$

or

$$E = Xs.$$

Therefore,

$$PAv = \frac{EXs}{r}$$

or

$$v = \frac{EXs}{PAr} .$$

The zeta potential can be expressed in terms of the streaming potential as

$$\zeta = \frac{4\pi kt}{D} \cdot \frac{\eta}{tX} \cdot \frac{EXs}{PAr} = \frac{4\pi k\eta E}{DP} \cdot \frac{s}{Ar} .$$

If resistivity, R, is defined as

$$R = \frac{Ar}{s} ,$$

then

$$\zeta = \frac{4\pi k\eta E}{DRP} .$$

This equation was used for calculating the zeta potential of diatomite from measured values of E, P and R and from values of η and D calculated from the temperature of the filtrate.

Further refinements in the equation can be made to account for the effect on zeta potential caused by electrical conductance along the surface of particles of diatomite in the filter cake (22):

$$\zeta_T = \frac{4\pi k \eta E}{DP} \cdot \left(\frac{1}{R} + \frac{4\lambda_S}{\phi} \right)$$

where ζ_T is the true zeta potential, ϕ is the mean particle diameter and λ_S is the specific surface conductance of the particles.

If the true zeta potential (ζ_T) is equated to the zeta potential calculated by the more approximate equation (ζ), the following relationship is found to exist:

$$\frac{1}{\zeta} = \frac{1}{\zeta_T} + \frac{4\ \lambda_S\ R}{\zeta_T\ \phi}$$

If the zeta potential of diatomite is found to vary with the resistivity of the solution being used in testing it, the cause of the variation could be caused by surface conductance, the resistivity of the solution or the kind of ions in the test solution. If the variations with resistivity of the solution are due to surface conductance only, the results should be correlated with the last equation given above. The true zeta potential can be calculated in this case from the intercept of the curve ($1/\zeta_T$) if the reciprocal of the apparent zeta potential ($1/\zeta$) is plotted as a function of the resistivity.

Further, the surface conductivity of the diatomite will be given by the slope

$$\frac{4\lambda_S}{\zeta_T \phi}$$

the mean particle size of the diatomite and the true zeta potential.

Objectives

It has been stated that streaming potentials produced by filtering water through diatomite affect the build up of head loss in diatomite filters and that the electric charge of diatomite as it is related to the zeta potential may determine the kind of particles that can be successfully removed on diatomite filter cakes. Further, it is reported that certain electropositive materials such as aluminum hydroxide can be coated on diatomite thus changing the zeta potential from negative to positive. There is no record that these reports have been verified by either measuring streaming potentials produced during filtration or by calculating zeta potentials from streaming potential data.

Streaming potential cells for testing many different materials such as silk, linen, ivory, glass, sand, wood, sulfer, talc, graphite, charcoal, platinum, etc., have been devised (5, 24, 32). None of these seemed to be suitable for testing diatomite filter aids, however, because a filter cake of diatomite could not be formed in these cells in the same way that filter cakes are formed in a diatomite filter. Therefore, a small diatomite filter equipped with electrodes was designed and built for use as a streaming potential cell. The objectives of the studies made using this streaming potential cell have been:

1. To determine the zeta potential of several representative grades of flux calcined diatomite filter aids used in water filtration from streaming potential measurements,
2. To determine the effect of electropositive materials on the zeta potential of flux calcined diatomite filter aids, and
3. To determine the effect of chemically treated water on the zeta potential of diatomite filter aids.

MATERIALS

Diatomite

Origin and occurrence

Diatomite is the fossil remains of diatoms, microscopic plants closely related biologically to brown algae. Diatoms extract silica from water and secrete it to form a shell-like envelope called a frustule. Because silica is practically inert, the fossil frustules of diatoms have remained unchanged for thousands of years while the organic and metallic compounds associated with the life cycle have long since decomposed and been leached away.

Large beds of diatomite are found throughout the world covering hundreds of square miles and some are up to 5000 feet in thickness. These beds of diatomite bear witness to the fact that diatoms were the principal form of life (33) during long periods of time. Some fossil frustules are known to be more than 25 million years old, yet their frustule patterns are nearly identical to those of their living descendants. The brown, yellow and black slimes found on submerged weeds and on stagnant pond bottoms are masses of living diatoms. They are found in fresh water as well as in salt water and in hot springs as well as in the waters of the Arctic and Antarctic. They are still one of the most abundant forms of life (27).

More than 12,000 different frustule patterns have been identified, many having intricate substructures which are visible only under an electron microscope. Typical shapes of frustules found in the diatomite used in this study are shown in Figures 6, 7, 8 and 9. Also associated with deposits of diatomite are sponge spicules and cilia of animals that are not of diatomaceous origin. One such cilia is shaped like a turtle shell, Figure 10. This form is affectionately referred to as "Myrtle" and distinguishes California diatomite of marine origin from that of any other location (33).

Frustules are composed of two halves which telescope over each other like the top and bottom of a Petri dish. Concerning methods of reproduction used by diatoms one author (13) wrote:

> "There appear to be several methods of reproduction, the commonest of which is brought about by the separation of the individual, longitudinally, into two along the median dividing line. The bottoms of a box are formed back to back along this line, push outwards, slip snugly into the upper and lower valves of the parent, thus forming two new boxes which separate, and each repeats the process, and so on. This method of formation is the origin of the name diatom, from two Greek words meaning, 'to cut through'."

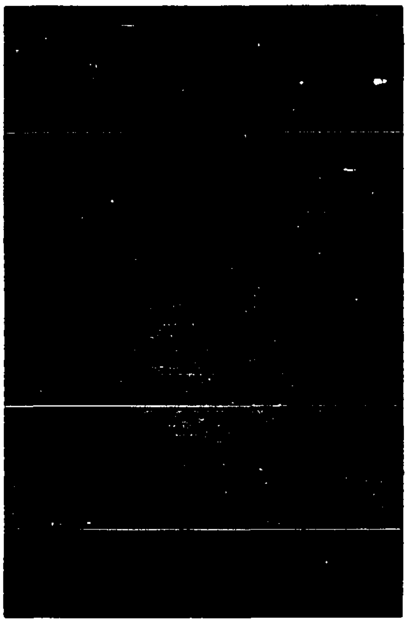
One of the old frustule-halves remains with one of the new diatoms and the other remains with the second. It is possible then that a living diatom may be wearing a frustule-half which is several million years old (13). It is estimated that diatoms divide as often as once in eight hours but the average rate is once in twenty-four hours.

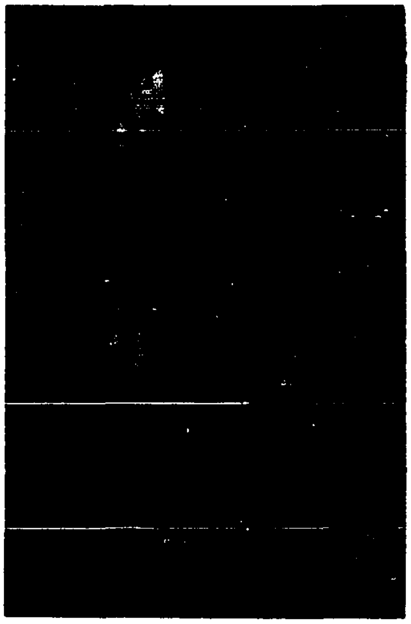
Figure 6. (Top left) Disk-shaped frustule from Dicalite Speedex (500x)

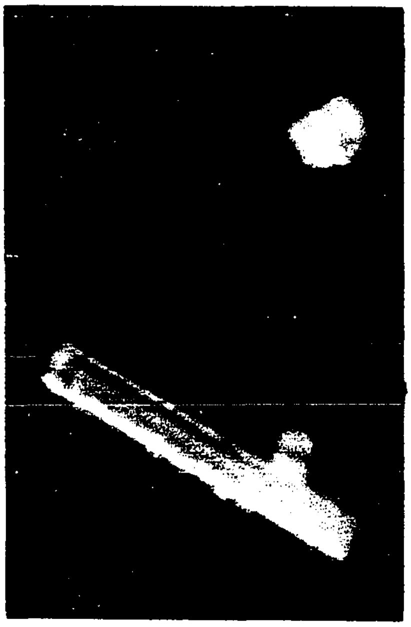
Figure 7. (Top right) Fragment of a large disk shaped frustule from Dicalite Speedex (500x)

Figure 8. (Lower left) Elongated frustule from Celatom FW-20 (500x)

Figure 9. (Lower right) Box-shaped frustule from Celatom FW-20 (500x)







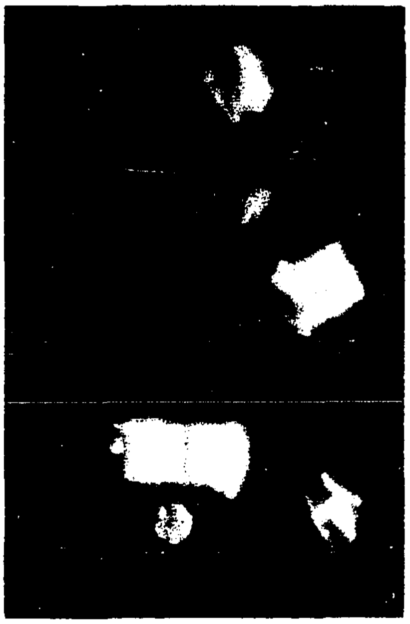
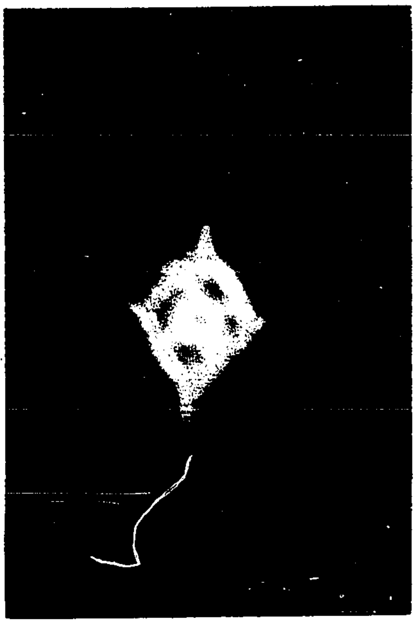


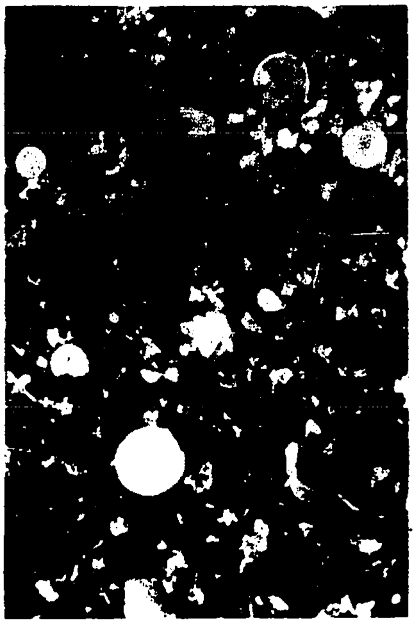
Figure 10. (Top left) Cilia called "Myrtle" from Celite 535 (500x)

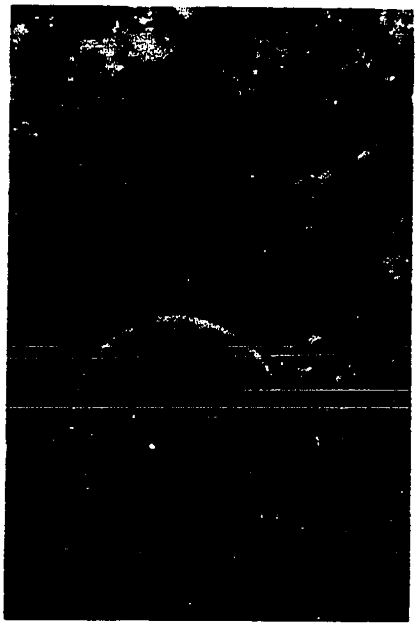
Figure 11. (Top right) Strewn sample of Celite 503 in a water mount (100x)

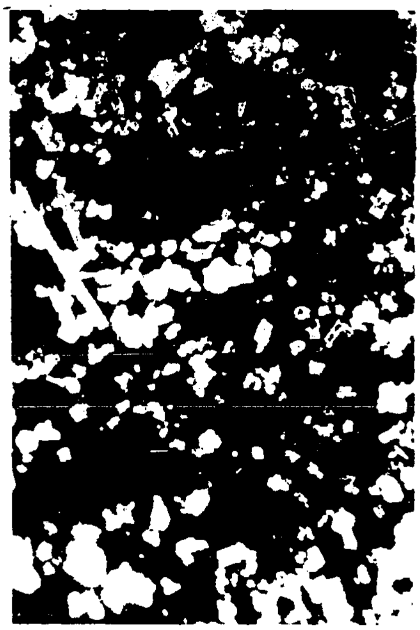
Figure 12. (Lower left) Strewn sample of Dicalite Speedex in water mount (100x)

Figure 13. (Lower right) Strewn sample of Celatom FW-20 in water mount (100x)









Processing by the manufacturer

The United States produces and consumes more diatomite than any other country. Although diatomite occurs in almost every state and has been mined in at least 13, California has led in production since 1910. Since 1958, diatomite has been produced commercially in only three other states -- Nevada, Oregon and Washington (28). Diatomite is also mined throughout the world, the principal foreign producers being Denmark, West Germany, France, Great Britain and Algeria.

Diatomite is a soft mineral composed of the fossil frustules of diatoms loosely cemented together. It occurs as strata of solid rock ranging from a few feet to thousands of feet in thickness. Hand quarrying with saws and picks was used in the past but mining is now done with power shovels or scraper carryalls using open pit techniques.

Three general grades of processed diatomite are produced by the various manufacturers. These grades are called natural, calcined or pink and flux calcined or white. The natural grades are processed by drying, comminuting and air classifying the crude diatomite into various particle size ranges. Freshly mined crude diatomite contains about 30 to 50 per cent moisture (17). Flash drying methods are used to lower the moisture content and comminution takes place as the diatomite is blown through the process pneumatically with hot gases (28). The calcined grades are processed similarly but in addition are heat treated in direct-fired rotary kilns.

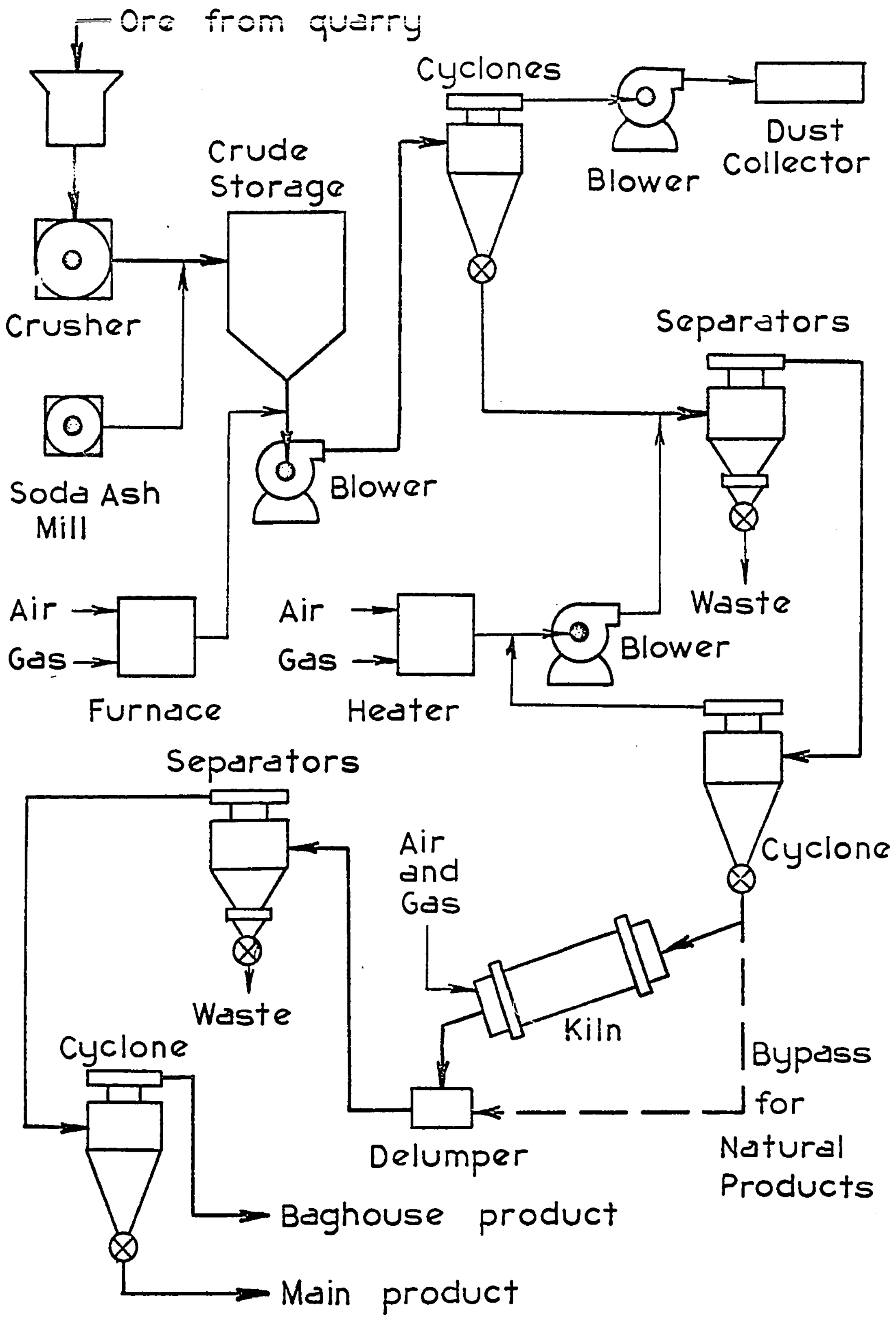
Flux calcined grades are calcined with the addition of about 3 to 10 per cent of a fusible alkali salt such as soda ash, sodium chloride or caustic soda, Figure 14.

Properties of Diatomite

Crude diatomite consists of loosely cemented frustules of diatoms and has a low apparent density because of the void space within the box-like structure of the frustules. Unmilled diatomite weighs only 20 to 30 pounds per cubic foot. As a loosely packed, milled powder it weighs 5 to 12 pounds per cubic foot. In a filter cake compacted by wetting, it weighs about 14 to 17 pounds per cubic foot. The true density of opaline silica of which diatomite is composed is about 131 pounds per cubic foot, so 87 to 89 per cent of the filter cake is void space available for holding water.

Since diatomite is essentially an opaline silica containing various contaminants such as clay minerals, iron, alkalies and alkaline earths, the physical and chemical properties are essentially the same as those of silica except as they are modified by the impurities. Unprocessed diatomite has a hardness between 4 and 6½ on the Mohs' scale and is softer than opal (28). Uncontaminated diatomite should melt at or below 1600° C, the temperature at which silica melts. Diatomite of average quality contains enough clay, however, to produce sintering at 800° to 1000° C. Some diatomite containing lime melts rather sharply at 1150° to 1250° C (6)

Figure 14. Flow sheet for processing diatomite


Ore from quarry
Cyclones
Blower
Dust Collector
Crude Storage
Crusher
Separators
Soda Ash Mill
Blower
Waste
Air
Gas
Furnace
Air
Gas
Heater
Blower
Separators
Cyclone
Air and Gas
Waste
Cyclone
Kiln
Bypass for Natural Products
Delumper
Baghouse product
Main product

while others can be heated to 1400° C with little visible change.

The impurities in diatomite are made relatively insoluble by the calcining process. Calcined grades of diatomite are insoluble in acid and are only slightly soluble in alkali. The pH of water containing calcined diatomite is about 7.0. Flux calcined diatomite, however, will raise the pH of water to about 9.5 (14). This is due to the alkali used as a flux in processing.

The color of pure diatomite is white but organic matter changes the color of the natural grades to brown or even green (6). Iron present changes the color to pink when diatomite is calcined. Flux calcining with a fusible alkali again whitens diatomite.

Grades of diatomite used in this study

Ten grades of diatomite filter aid manufactured by three different companies were used in this study. Eight of the grades were flux calcined filter aid and two were filter aids that had been coated with electropositive materials or contained materials which would give the filter aid an electropositive coating.

The Johns-Manville Corporation supplied six of the grades of filter aid used. Four were flux calcined filter aids: Celite 503 (Figure 11), Celite 535, Celite 545 and Celite 560 listed in order of increasing coarseness. The first two are suitable for filtering drinking water while the latter two are suitable for filtering swimming pool water. Two electropositively coated filter aids, Sorbo-Cel and Celite 545 Mix B, were also supplied by Johns-Manville. Sorbo-Cel is a specially processed filter aid which was developed for removing oil from steam condensate (2). Celite 545 Mix B is a mixture of Celite 545 and some electropositive material (probably alum) which coats the particles of diatomite when the mixture is added to water.

The Great Lakes Carbon Corporation supplied two of the grades of flux calcined diatomite used: Speedex (Figure 12) and Dicalite 4200. Speedex is recommended for filtering drinking water (14) and Dicalite 4200 would be suitable for filtering swimming pool water (15).

The Eagle-Picher Company supplied two grades of flux calcined diatomite filter aid: Celatom FW 20 (Figure 13) and Celatom FW 60. Celatom FW 20 is recommended for filtering drinking water and Celatom FW 60 for filtering swimming pool water (11).

Filter aids may be compared on the basis of "bomb filter tests" (8) in which the clarity of the filtrate and the amount of filtrate produced in a given period of time is determined for a filter aid filtering a specific solution at a specified temperature. Table 1 gives comparative filter aid flow ratios based on bomb filter tests made using 60° Brix raw sugar solution at 90° F (2, 12). The natural grade of diatomite filter aid is assigned a relative flow ratio of 1 and serves as a rough standard.

Table 1. Relative flow ratios of filter aids used in this study

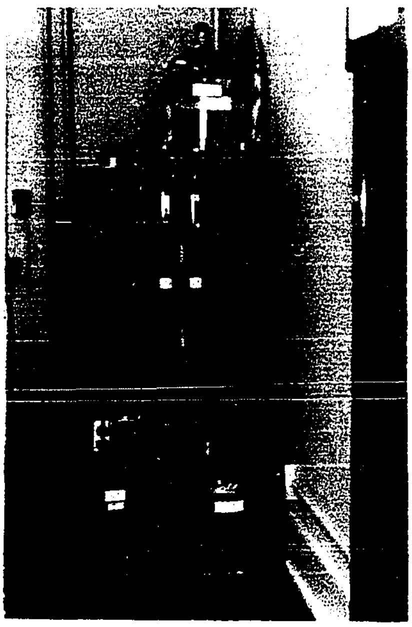
Relative flow ratio	Eagle-Picher Company	Johns-Manville Corporation	Great Lakes Carbon Corporation
7		Sorbo-Cel	
10	Celatom FW 20	Celite 503	Speedex
25		Celite 535	Dicalite 4200
30	Celatom FW 60	Celite 545	
55		Celite 560	

Water

All of the water used in this study was either distilled or deionized. Distilled water was prepared with a Barnstead Water Still Model ELH-2 and was collected in a 25 gallon aluminum storage tank manufactured by Precision Scientific Company. The water fed to the still was softened with a Culligan Soft Water Service zeolite softener, Figure 15. The tap water on campus has a hardness of about 310 mg/L as $CaCO_3$. This softening pretreatment prevents hard scale formation in the still as well as excessive foaming which could lead to a reduction in the quality of the distilled water.

Figure 15. Zeolite water softener, Barnstead water still and distilled water storage tank

Figure 16. Ion exchange columns



The ion exchange equipment that was used consisted of two columns, a cation exchanger and an anion exchanger, connected in series, Figure 16. Each column had an inside diameter of about 1.75 inches and was filled to a depth of about two feet with resin. The first column contained Amberlite IR-120 and the other contained Amberlite IRA-410. Both are synthetic ion exchange resins manufactured by the Rohm and Haas Company.

Amberlite IR-120 is a nuclear sulfonic-acid (styrene beads) cation exchanger with a total capacity of 4.6 meq/gram; Amberlite IRA-410 is a quaternary strong base (styrene beads) anion exchanger with a total capacity of 3.9 meq/gram. The Amberlite IR-120 was regenerated with a 10 per cent solution of HCl (25 pounds of 30 per cent HCl per cubic foot of resin) and the Amberlite IRA-410 with a 4 per cent solution of NaOH (12 pounds of NaOH per cu ft of resin) according to the manufacturers recommendations (35, 36).

Distilled and deionized water was stored in 5 gallon stoppered soft glass bottles used only for this purpose. No attempt was made to exclude carbon dioxide from the water.

Chemicals

All standard chemicals used in this study were either J. T. Baker Chemical Company "Baker Analyzed" Reagent, Allied Chemical and Dye Corporation "Baker and Adamson Quality"

Reagent or Millinckrodt Chemical Works Analytical Reagent grade chemicals.

The cationic polyelectrolyte used was UCAR Resin C-149 manufactured by the Union Carbide Chemicals Company. Beryllium perchlorate used was provided by Mr. A. L. Baetz of the Analytical Chemistry Group at Iowa State University.

APPARATUS

Filter Plant

First filter

The first streaming potential filter was designed to be operated as a pressure diatomite filter with the filter element lying in a horizontal plane. Plexiglass was used in constructing the filter so streaming potentials produced during filtration would not be dissipated through the filter housing, Figures 17 and 18. At the flow rates used, 0.9 to 2.25 gpm per sq ft, the velocity of the water approaching the filter elements, 0.12 to 0.30 fpm, was not great enough to keep diatomite in suspension in an upward flow of water. According to the Johns-Manville Corporation, a vertical flow of 4.5 fpm is needed to insure even deposition of filter aid in the filter cake (21). Therefore, it was necessary to operate the filter with a downward flow of water through the filter element. The filter did not work well when operated with a downward flow of water because air became trapped beneath the filter element and could not be removed completely.

This filter, however, was used in several runs before the design was abandoned. During these runs, data were taken which demonstrated that streaming potentials could be measured while water was being filtered through a diatomite filter cake. It was found that the streaming potentials changed rapidly with changes in the flow rate. The zeta potentials

Figure 17. Line drawing of the first streaming potential filter

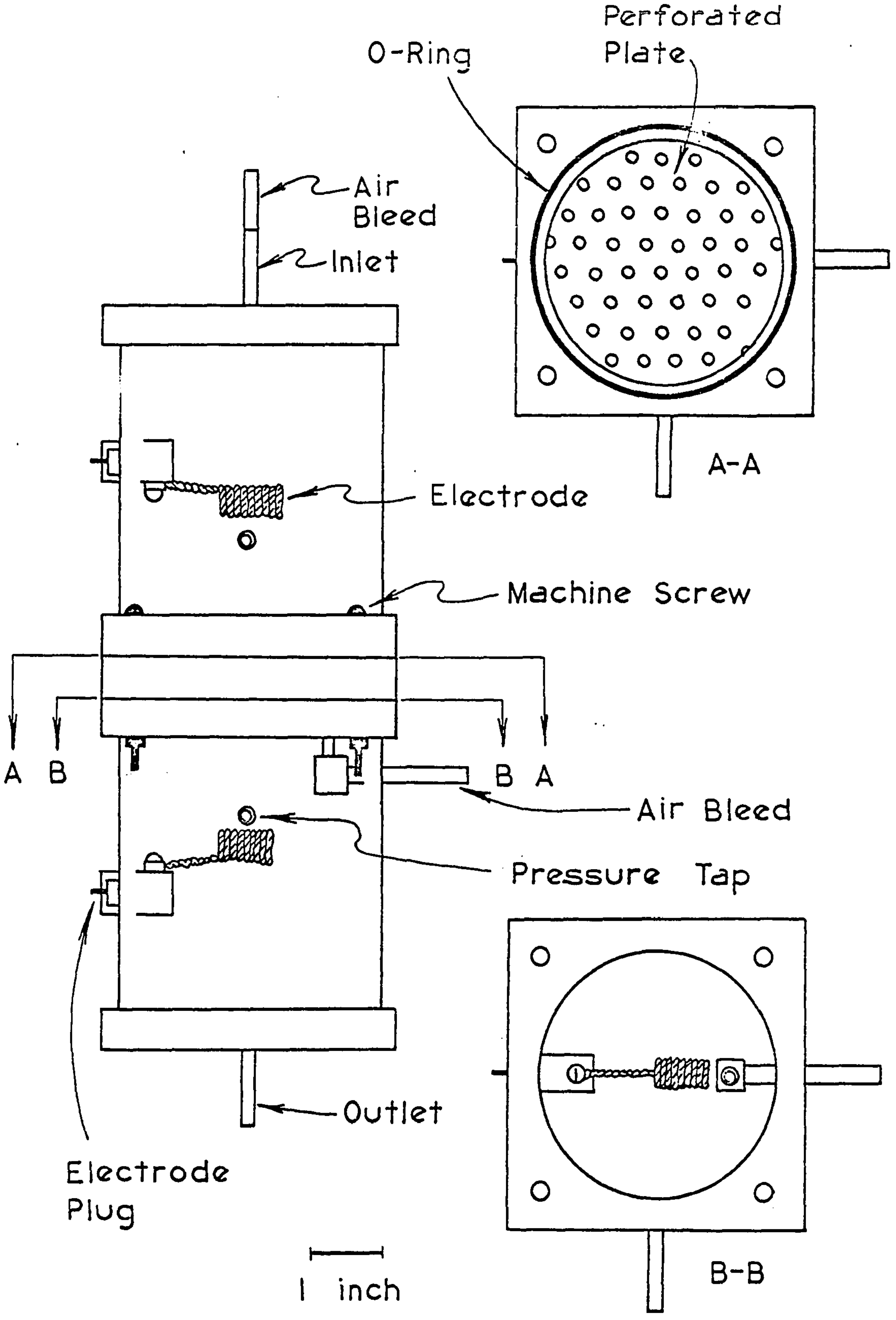
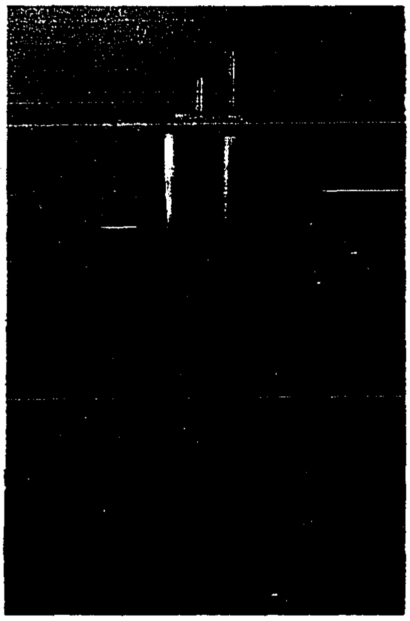
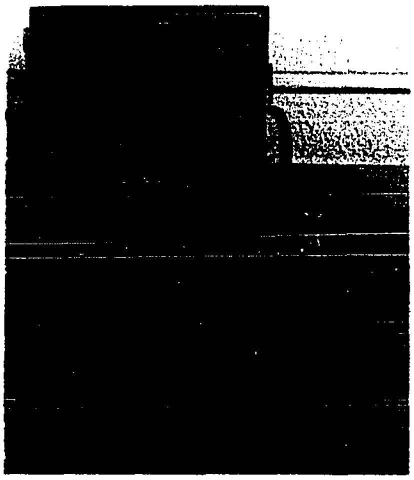

Perforated Plate
O-Ring
Air Bleed
Inlet
Electrode
Machine Screw
A
B
B
A
Air Bleed
Pressure Tap
Outlet
Electrode Plug
1 inch
A-A
B-B

Figure 18. First streaming potential filter

Figure 19. Conductivity bridge and cell





of diatomite were not calculated from these measurements of streaming potentials during these filter runs because no measurements of pressure loss or of resistivity of the filtrate were made.

Second streaming potential filter

The second streaming potential filter was designed to be operated with its filter element in a vertical plane, Figure 20. As with the previous filter, the velocity of the water approaching the filter element was not high enough to hold diatomite in suspension. Therefore, the flow was brought into the inlet chamber tangentially so as to impart a rotary motion to the diatomite suspension in this chamber. According to calculations made before the filter was built, the suspension in the chamber would rotate with a velocity of 0.16 to 0.64 rps. This rotation can be observed when the cake is being formed and it is sufficient to hold the diatomite in suspension without scouring the surface of the filter cake as it forms.

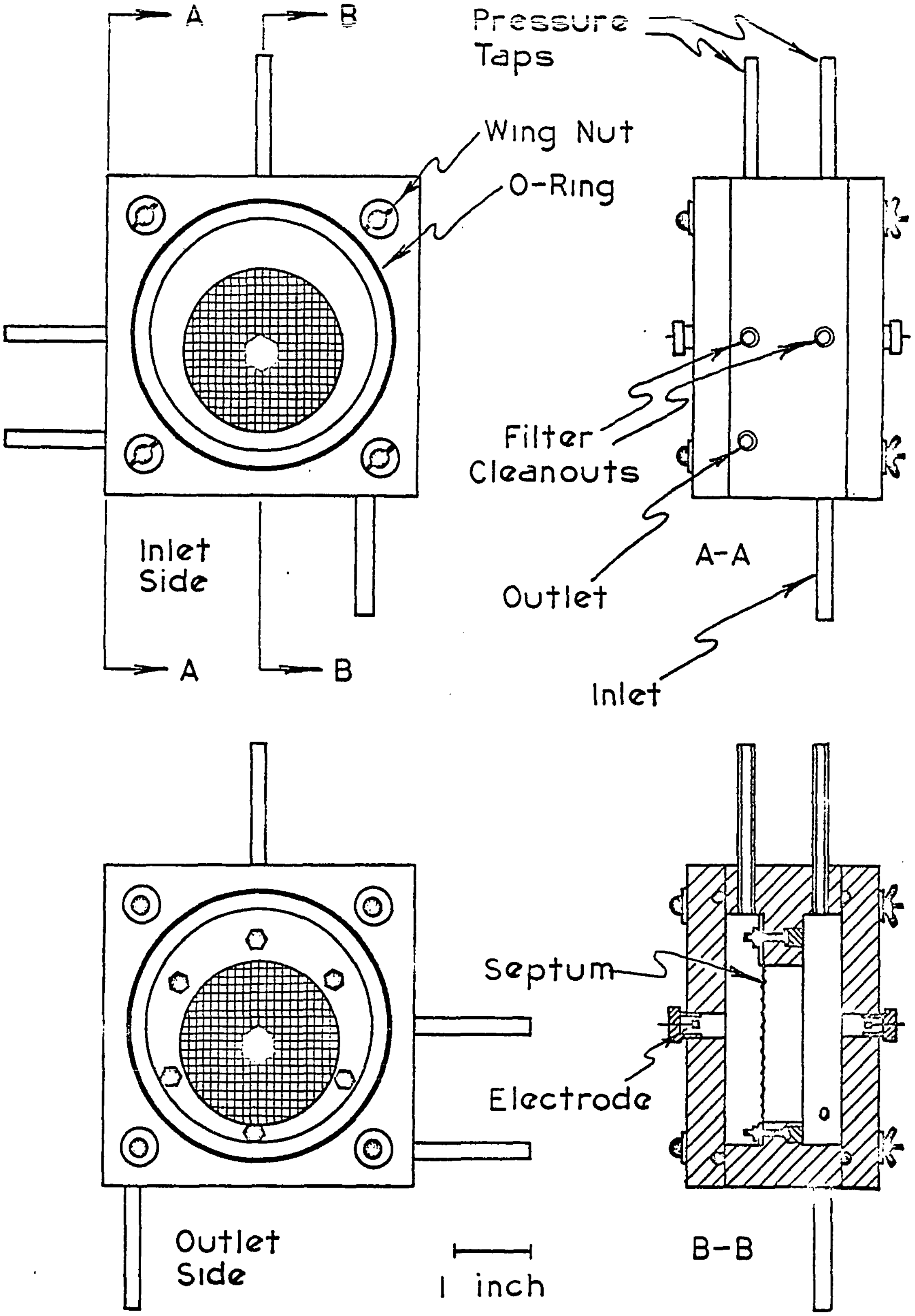
The electrodes used in the filter for sensing streaming potentials are reversible silver-silver chloride electrodes. They were made from 24 gauge (0.020 inch) fine silver wire and were plated with silver chloride (41). The rat-tail end of the completed electrode was slipped through a hole in the end of a brass pipe plug so that the helical portion of the electrode was nestled within the plug and the tail of the electrode was soldered to the exterior of the plug. The electrode assemblies were screwed into the inlet and outlet cover plates of the filter, Figure 20. Since the brass plug as well as the silver-silver chloride electrode was in contact with the water in the filter, the plug also acted as a part of the electrode and the electrode for this reason was not actually reversible. Nonreversible electrodes have caused problems for others working with streaming potential measuring equipment and it is usually necessary to find some way of operating the apparatus in such a way that the difference in potential between the nonreversible electrodes does not affect the desired results (18).

Difficulties with air entrapment under the filter element were corrected by the new design. The new filter element consists of a plastic filter cloth supported on brass "window screening." The filter element is held in place with a brass ring attached to the filter housing by six brass machine screws whose heads are counter sunk into the inlet face of the filter housing and insulated with rubber cement so they will not serve as electrical pathways which would dissipate streaming potentials. The filter element is stiffened with a cross piece made of number 16 galvanized wire to prevent bulging.

Other filter components

The streaming potential filter has been incorporated with other components into a filter plant, Figures 21 and 22.

Figure 20. Line drawing of the second streaming potential filter


A
B
Pressure Taps
Wing Nut
O-Ring
Filter Cleanouts
Outlet
A-A
Inlet Side
A
B
Inlet
Septum
Electrode
Outlet Side
1 inch
B-B

Two 10 gallon galvanized iron garbage cans painted on the inside with an epoxy resin coating were originally used for water supply tanks. The epoxy resin coating peeled after a few months of use and the garbage pails began to rust so these containers were replaced with two 8 gallon polyethylene waste cans.

The connecting tubing used in the system consisted of ¼ inch O. D. glass tubing, ¼ inch I. D. Tygon tubing and ¼ inch O. D. copper tubing. Tubing in these small diameters was needed, especially where diatomite was being carried in suspension, to provide high enough velocities to prevent diatomite from settling out in the lines. Brass plug valves were used for shut-off valves and a needle valve was used for controlling the rate of flow through the filter.

An Eastern Industries model B-1 centrifugal pump constructed of stainless steel was used to produce flow in the system. The pump has nearly straight line flow characteristics between a flow rate of zero at a shut-off pressure of 17 psig and a flow rate of 7 gpm when pumping against no head. The maximum flow that can be measured in the system with the flow meter is 2.55 gpm per sq ft of filter area which corresponds to a flow rate of about 0.056 gpm. Thus, the pump is delivering nearly the shut-off pressure throughout the entire range of flows being used for filtration. Because of the low flow conditions, however, the temperature

Figure 21. Filter plant and recording potentiometer

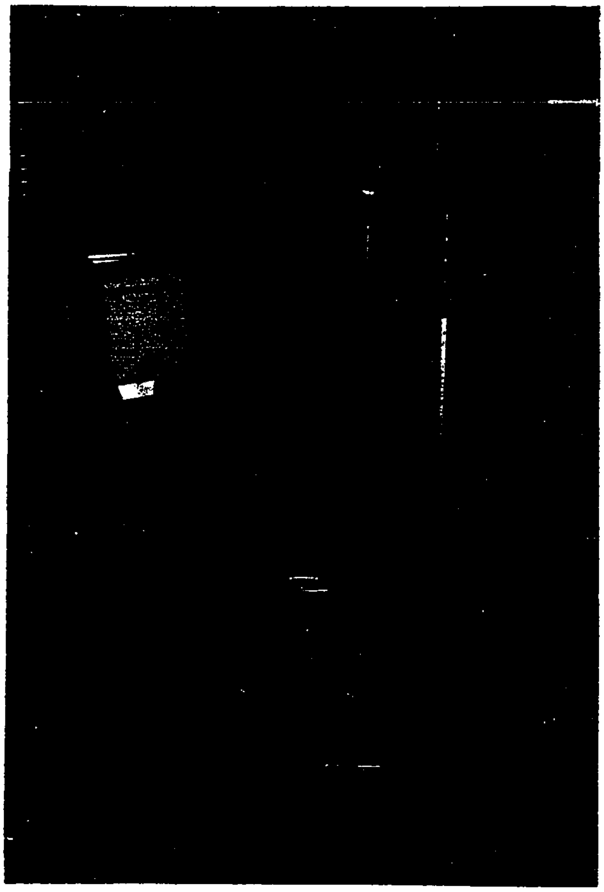
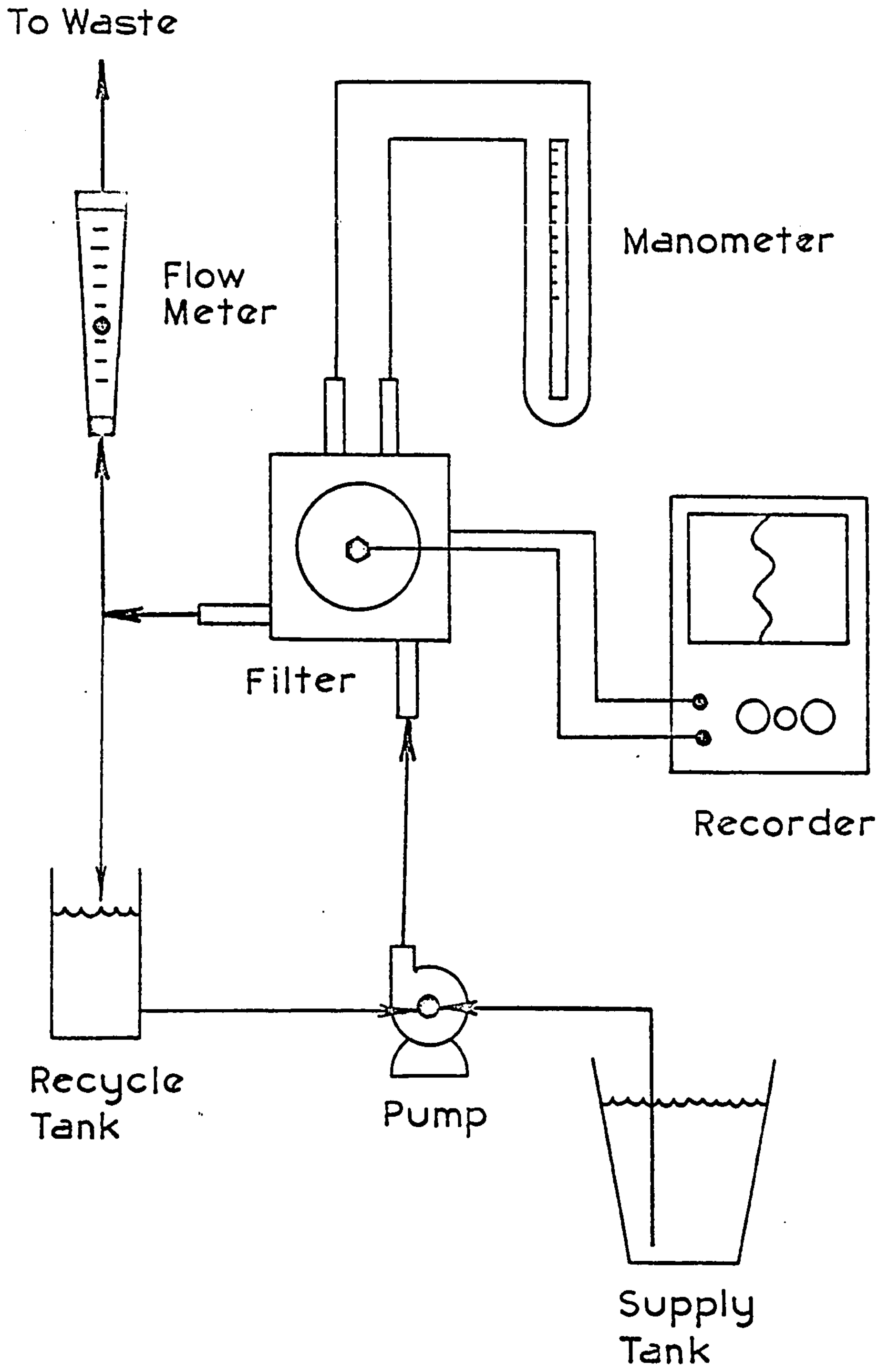


Figure 22. Diagram of filter plant and recording potentiometer


To Waste
Flow Meter
Manometer
Filter
Recorder
Recycle Tank
Pump
Supply Tank

of the water is increased about 3° C in passing through the system.

The rate of flow of filtrate being run to waste is measured with a Fischer and Porter Company precision bore Flowrater, model number 2F-$\frac{1}{4}$-20-5/70. This flow meter was calibrated for filter flow rates which vary linearly between 0.75 gpm per sq ft which corresponds to a reading of 8 on the flow meter and 2.55 gpm per sq ft which corresponds to a reading of 20.

Pressure loss through the filter cake is measured with a manometer in which bromoform, $CHBr_3$, is used as the manometer fluid. Bromoform has a density of 2.85 grams per cc at 25° C. Therefore, a reading of 10 cm of bromoform is equivalent to a pressure loss of 0.607 foot of water.

Care must be exercised in using the manometer because bromoform is a solvent for plexiglass. Since bromoform has anesthetic properties similar to chloroform, "shooting" the manometer is also hazardous to the operator who must tear down the filter and clean out the bromoform before it dissolves the plastic housing. Bromoform was selected because it is electrically nonconducting and because it has a low density. Thus, it is a sensitive manometer fluid that will not provide an electrical pathway through which streaming potentials can be dissipated.

A recycle tank through which flow from the filter can be recirculated back to the filter is used to get diatomite into the filter. The tank is 3 inches in diameter and 6 inches deep and is constructed of plexiglass.

Recording Potentiometer

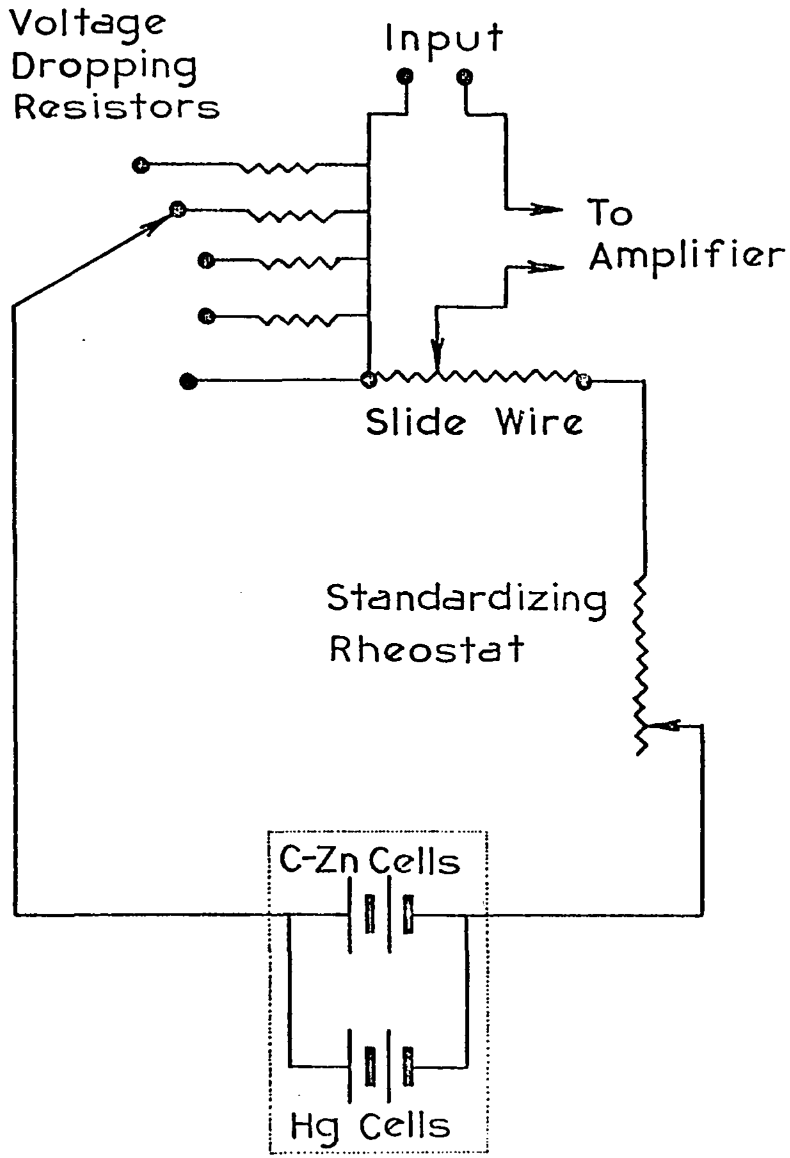
A recording potentiometer model MR manufactured by E. H. Sargent and Company was used for measuring streaming potentials, Figure 21. It is a servo-mechanism potentiometer pen-writing recorder which is provided with controls for measuring current and voltage over a wide range of values, for adjusting or suppressing the zero point and for varying the chart speed and direction (23).

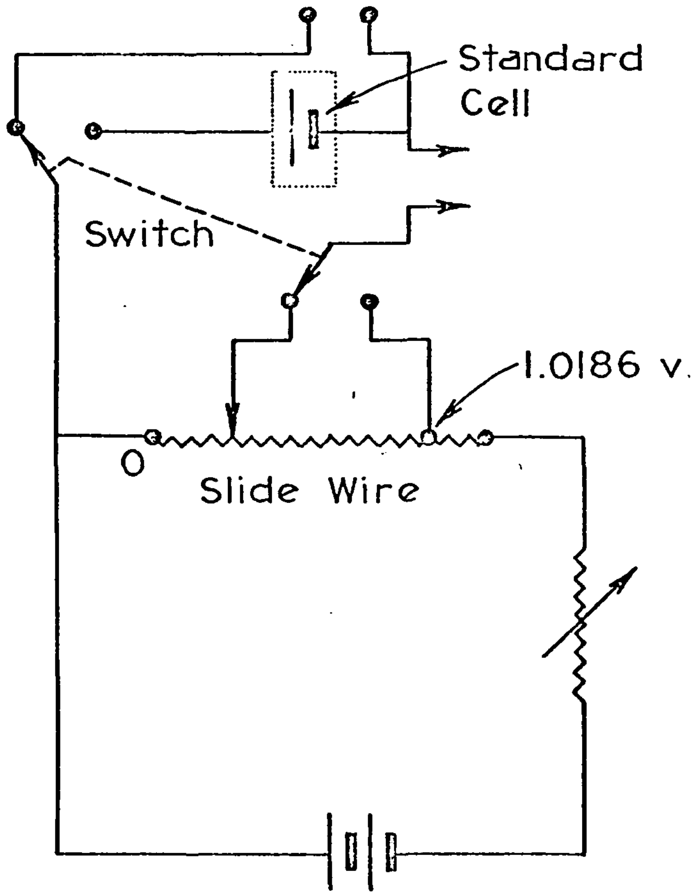
Input potentials are balanced against the instrument battery supply by means of a three turn helical slide wire. The battery supply consists of carbon-zinc dry cells in parallel with mercury cells. A mercury cell has an amalgamated zinc anode and a mercuric oxide cathode imbedded in an immobilized electrolyte containing sodium hydroxide. Mercury cells have an extremely constant cell potential of about 1.3 volts until they are nearly discharged and are therefore useful for supplying a reference voltage while delivering a moderate current. The carbon-zinc cells supply most of the current while the mercury cells maintain a constant output voltage from the parallel combination.

The slide wire is in series with a standardization adjusting rheostat and voltage dropping resistors, Figure 23. The voltage dropping resistors are precision resistors mounted

Figure 23. (Left) Potentiometer slide wire with range selection by voltage dropping resistors

Figure 24. (Right) Diagram of manual standardization circuit in the recording potentiometer


Voltage Dropping Resistors
Input
To Amplifier
Slide Wire
Standardizing Rheostat
C-Zn Cells
Hg Cells


Standard Cell
Switch
1.0186 v.
0
Slide Wire

on a selector switch which provides a variety of operating ranges for the potentiometer slide wire by dropping the potential across the slide wire from that of the mercury cells to the amount indicated on the selector switch.

A standardization circuit provides a means of adjustment to correct the potential supplied by the instrument voltage supply for variations caused by aging of the dry cells, temperature variations, etc. When the standardization switch is depressed, the external input circuit is opened and an internal circuit is closed making a cadmium amalgam standard cell the source of the input signal. Also, contact is made with a fixed point on the slide wire corresponding to the voltage of the standard cell which is 1.0186 volts. The standardization adjusting rheostat is then adjusted manually until the unbalanced signal is zero as is indicated when the motor driven pen stops moving, Figure 24.

The recorder has several other features that add to its usefulness. Damping is controlled by manual adjustment of a rheostat that controls the power output of the amplifier. The chart paper may be driven either forward or backward at chart speeds ranging from 1/3 to 12 inches per minute by means of interchangeable driving gears. A neutral position in the chart drive is provided that unrolls or rerolls the chart paper at a speed of 20 feet per minute.

Conductivity Bridge and Cell

A Freas type conductivity cell was used for making resistivity measurements. The cell consists of a small glass bottle with two platinum electrodes, each 1 centimeter square rigidly separated a distance of 1 centimeter by glass spacers. The electrodes are supported by wire leads which are sealed into the closed ends of two hollow arms which protrude into the cell through the shoulders of the bottle. These arms are partially filled with mercury through the openings outside of the cell and leads from the measuring circuit are immersed in the mercury to complete contact with the electrodes (39).

A conductivity bridge manufactured by Industrial Instruments, Inc., model RC-16B2 was used for measuring the resistance of water in the conductivity cell, Figure 19. This is a line-operated bridge having a potentiometer and an electron-ray tube null indicator capable of measuring resistances between 0.2 and 2,500,000 ohms. A frequency switch provides a choice between a 60 cps and a 1000 cps input to the bridge (38).

The cell constant was determined by measuring the resistance of a 0.01 M KCl solution at 27.0° C. The specific resistance of this solution is not given in the tables (16) for this temperature so it was extrapolated from values given for 23.0, 24.0 and 25.0° C. The measured resistance of the solution was found to be 256 ohms and the cell constant was computed to be 0.375 cm^{-1}.

PROCEDURES

Streaming Potential Filter Runs

Filter runs made with the streaming potential filter followed a uniform pattern. At the beginning of a filter run the supply tanks were filled with distilled water or the solution which was to be filtered. Some of this solution was flushed through the supply lines to purge air from the system and to wash out any residue solution remaining from previous filter runs. The recycle tank was then drained and washed down to remove any diatomite that remained from previous filter runs. This tank was filled again from the supply line until the pump suction was submerged by about one-half inch of water.

The valves were then set so that water would be drawn from the supply tanks. The pump was turned on and a valve was opened which put the filter under pressure. The hose clamp on the drain hose from the inlet chamber of the filter was opened repeatedly to flush several changes of water through the chamber and into a beaker. This served to remove any filter aid residue that remained in the inlet chamber from the previous filter run as well as any air bubbles that may have come out of solution and collected on the filter element. Following this, the valves on the outlet side of the filter were opened to run water through the flow meter and to waste. Water was wasted in this way for a few minutes to flush out the whole system thoroughly and put the electrodes in the filter in contact with the solution to be filtered. The valves were then closed beginning near the outlet and working back to the pump. Then the pump was turned off.

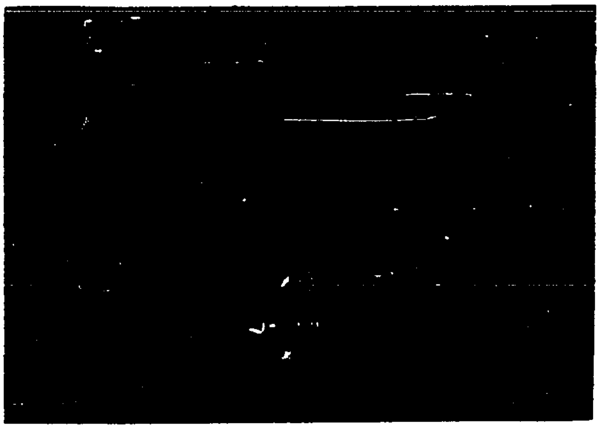
Next, a predetermined amount of diatomite was weighed out on a trip balance having a capacity of 5 grams and was mixed with 250 ml of the solution in the system, Figure 25. The slurry was mixed for 10 minutes before introducing it into the filter system. Shortly before the slurry was to be introduced into the system, the pump was turned on and the valves were set to circulate water through the recycle tank. There is no flow meter in this part of the system, but the flow was adjusted to recycle the flow at a rate of approximately 2.5 gpm per sq ft.

Following this, the recording potentiometer is turned on, set for the expected full scale range of potentials, standardized and damped. The position of the pen is shifted to one side of the chart or the other by suppressing the zero point depending on whether the filter aid being tested is expected to have a positive or a negative zeta potential.

After the diatomite had been mixed with the test solution for 10 minutes, the slurry was poured into the recycle tank, Figure 26. The sides of the beaker were washed down into the tank to get all of the diatomite into the system. The flow was recirculated for 10 minutes to get as much of the

Figure 25. Materials for preparing the diatomite slurry

Figure 26. Diatomite slurry being added to the recycle chamber



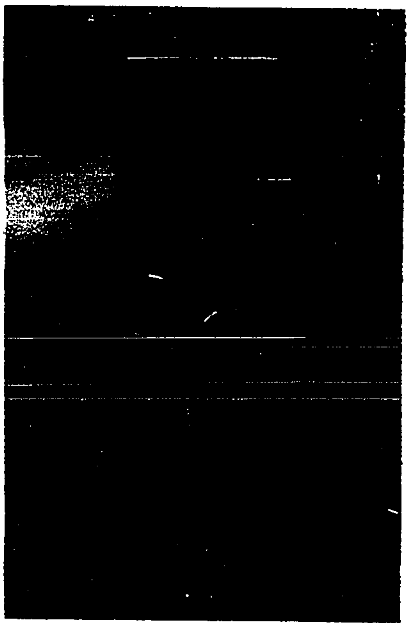
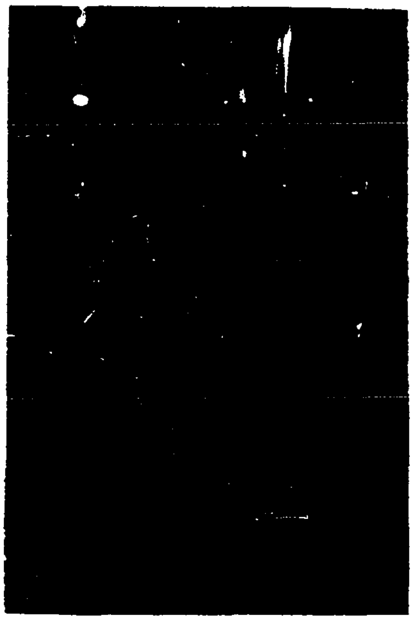
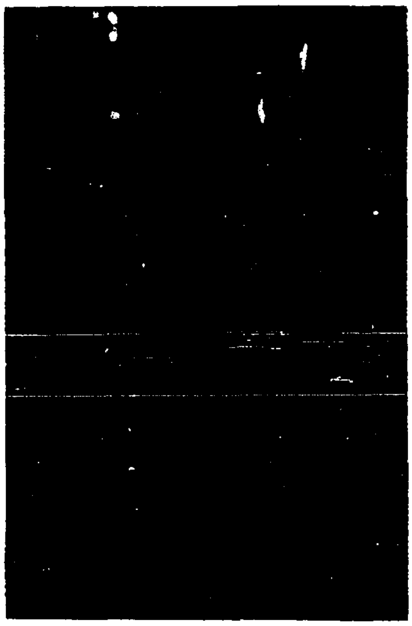


Figure 27. Appearance of a well-formed cake in filter

Figure 28. Cake which has dropped away from the septum at the end of the filter run





diatomite as possible out of the recycle tank and into the filter to form the filter cake. During this period, the contents of the recycle chamber were stirred intermittently to prevent the diatomite from settling out.

If the recirculation rate were set correctly, the filter cake was uniform in thickness and its surface was smooth, Figure 27. If the rate were set too high the surface became scoured and took on an irregular spiral pattern. Too low a rate permits diatomite to settle out in the inlet chamber making the cake thicker at the bottom than at the top.

After recirculating the flow for 10 minutes, the water in the recycle tank was relatively free of diatomite with the grades used in this study. Following this period of forming the cake, the valves were reset to run the filtrate to waste through the flow meter and to pump from the supply tanks instead of the recycle tank. The wash rate was adjusted to give a flow rate of 2.25 gpm per sq ft. Following this, the hose clamps were carefully removed from the manometer leads.

It was necessary in most filter runs to wash the cake at about 2.25 gpm per sq ft for about 10 to 15 minutes before a reasonably steady flow rate could be maintained. During this start up period, the flow rate had a tendency to decline abruptly unless the control valve was adjusted frequently to maintain the steady flow. The streaming potential built up gradually until a steady potential was established at about the same time that the flow became steady.

Because the electrodes were not reversible, the potential at the end of a filter run with no flow through the system was not necessarily the same as the potential indicated before the run began. Therefore, the actual streaming potential corresponding to a given flow rate could not be determined directly. Instead, the difference in streaming potential between that indicated for a flow rate of 2.25 gpm per sq ft and that indicated for a lower flow rate was measured. Since the relationship between streaming potential and head loss is linear, this procedure is satisfactory. (The apparatus can be modified by use of reversible electrodes to permit direct determination of streaming potentials).

Thus, a typical filter run was made according to the following schedule:

1. The filter cake was formed and the suspending liquid was recycled through the cake for 10 minutes.
2. The cake was washed for about 10 to 15 minutes with the test solution until a steady flow was established at a flow rate of 2.25 gpm per sq ft.
3. The flow rate was reduced to 1.05 gpm per sq ft, a reading of 10 on the flow meter, for about 2 to 3 minutes after which the flow rate was increased to 2.25 gpm per sq ft again for 2 to 3

minutes. This procedure was repeated for flow rates 1.35, 1.65 and 1.95 gpm per sq ft indicated respectively by readings of 12, 14 and 16. The streaming potentials corresponding to each of these flow rates were recorded during the run.

4. At each flow rate change the manometer was read to determine the head loss corresponding to each flow rate.
5. The flow rate at each flow meter setting was checked volumetrically by collecting filtrate for 1 minute in a graduated cylinder.
6. The conductivity and temperature of the filtrate and the water in the supply tank were checked midway through the run when the rate of flow was 2.25 gpm per sq ft.

The run was terminated by closing a plug valve in the vicinity of the flow meter. The manometer reading corresponding to this condition of no flow was determined after the cake had fallen from the filter element, Figure 28. Following this, the manometer leads were clamped off and the diatomite flushed out of the inlet chamber through the drain hose. Several liters of water were flushed through the chamber in short bursts during the flushing operation. By opening and closing the hose clamp quickly, the rapid change in pressure across the septum caused the filter cloth to vibrate which caused particles of diatomite to become dislodged from the cloth.

Resistivity Measurements

Measurements in conductivity cell

Resistivity measurements were made using a Freas type conductivity cell and a conductivity bridge. When the resistivity of the filtrate was measured, the cell was filled and emptied several times from the Tygon tubing waste line before a sample was retained for measurement. When the resistivity of the solution in the supply tank was measured, a 50 ml pipette used only for that purpose was used to transfer solution to the cell. Initially, the pipette was filled and drained several times with solution from the tank. Then, it was refilled and used to wash out the cell several times. Finally, a sample of the solution was transferred to the cell for measurement of its resistivity.

Measurement in the streaming potential cell

Some measurements of the resistivity were made in the streaming potential cell itself to determine the effect of the filter cake on resistivity (5). These measurements were not made on a routine basis, however. The measurements were made by connecting the conductivity bridge across the electrodes of the streaming potential filter while water was being filtered and measuring the electrical resistance. These measurements, made both before and after the cake was formed, indicated that the resistance was increased less than 4 per cent by the presence of the filter cake. Therefore, the surface conductivity of the cake was assumed to be negligible.

Methods of Coating Diatomite

Coating during filtration

One method used for coating diatomite with electropositive materials consisted of washing the cake with dilute solutions of aluminum and ferric salts after the cake had been formed on the filter element. The solutions were made so dilute that they did not coat the diatomite completely until the cake had been washed with the solution for 5 to 10 minutes. Thus, it was possible to measure the zeta potential of the diatomite in the cake using distilled water after washing the cake for a minute or two with the electropositive solution. It was found that, in most cases, the zeta potential was reduced somewhat by the treatment. By repeating the treatment several times, the reduction of zeta potential and any change of its sign could be followed with sufficient accuracy. The amount of solution needed to cause the measured change could be determined by the time and rate of washing with the given solution.

Coating before filtration

A more accurate way of controlling the amount of electropositive material used in coating diatomite would consist of coating the diatomite before it was introduced into the filter. This was done by making the electropositive material a part of the solution used in preparing the slurry of diatomite initially. By carefully controlling the amount of electropositive material used and by increasing the amount progressively in successive runs, it was possible to determine accurately the amount needed to lower the zeta potential to zero and the amount needed to reverse the sign and to produce the maximum positive zeta potential.

Interpretation of Data

Data from a streaming potential filter run consist of three interrelated elements: flow rate, pressure loss and streaming potentials. Streaming potentials were measured continuously with a recording potentiometer whereas pressure losses were measured visually and recorded manually when changes were made in the flow rate. The values of resistivity and temperature of the filtrate remained relatively constant throughout a filter run for a given solution being filtered. If more than one measurement were made of resistivity and temperature, the values were averaged.

A typical pen recording of streaming potentials measured during a filter run is shown in Figure 29. Differences in streaming potentials corresponding to each change of flow rate were determined by measuring the displacement of the pen trace recorded on the chart paper. The flow rate at the beginning

Figure 29. Typical pen recording of streaming potentials during a filter run

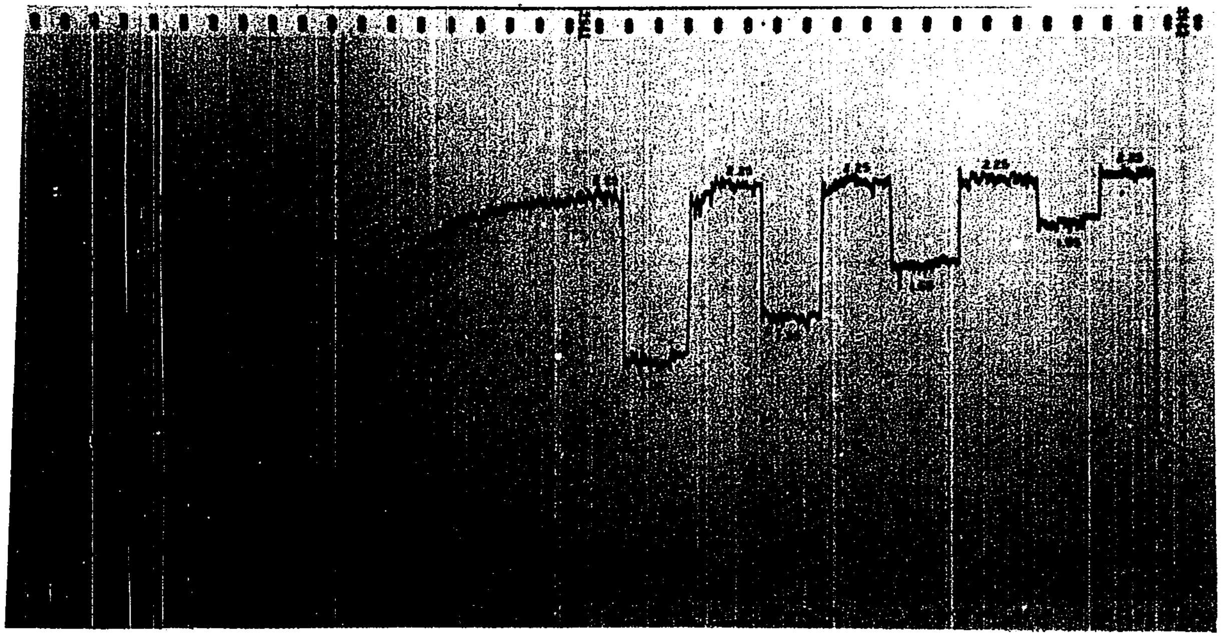
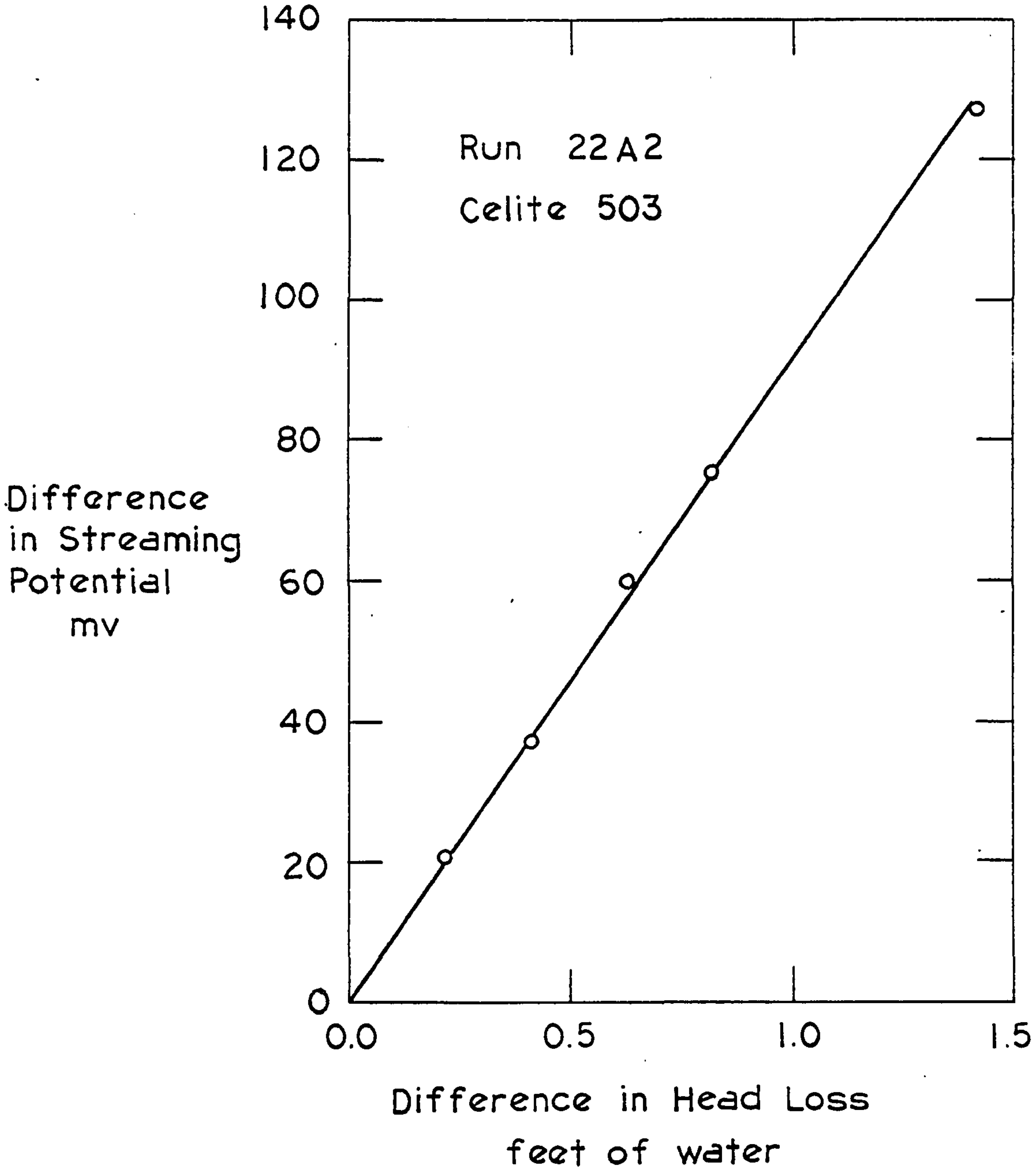

2.25
2.25
2.25
2.25

Figure 30. Typical curve showing difference in streaming potentials as a function of difference in pressure loss


Run 22A2
Celite 503
Difference in Streaming Potential mv
0
20
40
60
80
100
120
140
0.0
0.5
1.0
1.5
Difference in Head Loss feet of water

and end of each displacement was usually 2.25 gpm per sq ft and was always the higher flow rate of the two flow rates used. The difference in pressure loss corresponding to the flow rate change was computed for each change that was made to a lower flow rate including the last change where the flow was shut off. See Appendix.

At first the differences in streaming potential between the two flow rates were plotted against the corresponding differences in pressure loss to determine the ratio of streaming potential to pressure loss. A curve of this kind is shown in Figure 30 for the data from the pen recording shown in Figure 29. The data invariably gave a straight line plot. Plotting was later dispensed with and the ratio of streaming potential to pressure loss, E/P, was determined by averaging the ratio computed for each change in flow rate. The value of E/P was used in computing the zeta potential.

Numbering of Streaming Potential Filter Runs

General information

Streaming potential filter runs were numbered in an arbitrary manner. The original numbers used for several series of filter runs have been discarded and new numbers have been used to identify them. In general, however, runs are numbered in the order that they were completed. Thus, Run 1 was made before Run 17; Run 1B was made before Run 19B;

Run 1A1 was made before Run 25A1 and Run 8A1 was made on the same day as Run 8A6 but before it.

There are three exceptions to the order in which runs would appear to have been made:

1. Runs 1B through 35B were completed before Runs 1A1 through 25A1.
2. Runs 33B, 34B and 35B were made in that order but following Run 9B and before Run 10B.
3. No Run 16B was made.

Preliminary filter runs

Seventeen preliminary streaming potential filter runs were made between December 14, 1961 and February 20, 1962. These runs were made to gain general operating experience with the new filter and to determine some of the electrokinetic properties of several grades of flux calcined and electropositively coated grades of diatomite filter aid.

Initially, these runs were numbered with Roman numerals and lower case letters, as Ia through IIIj. These identifying numbers were changed to Arabic numbers when a progress report (29) covering this part of the study was prepared. Following is a key to the changes that have been made in numbering the preliminary filter runs:

New Number	Old Number	Remarks
1	Ia and Ib	Two parts of the same run
-	Ic	This run was never made
2	Id, Ie and If	Parts of the same run
3	Ig and Ih	Parts of the same run
4	Ii	
5-7	IIa - IIc	
8-17	IIIa - IIIj	

"B" series filter runs

The next series of streaming potential filter runs were made between May 29 and June 15, 1962 to determine the effect of solutions of 8 salts, NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, $AlCl_3$, $Al_2(SO_4)_3$, $FeCl_3$ and $FeSO_4$, on the zeta potential of 4 grades of flux calcined diatomite filter aids, Celite 503, Celite 545, Dicalite Speedex and Dicalite 4200. Thirty-two tests including each of the possible combinations of salt and filter aid were planned and the order in which the tests were to be run was randomly arranged in advance. Numbers from 1 through 32 were assigned to each anticipated test. After filter Run 9 had been made, however, three additional runs which had not been originally anticipated were made. These were assigned numbers from 33 through 35 to preserve the previously established numbering system. Run 33 was made to determine whether streaming potentials could be measured in tap water; Run 34 to determine whether streaming potentials could be measured in a solution containing 400 mg/L of $CaCl_2$; and Run 35 to determine whether streaming potentials could be measured in a solution containing 358 mg/L of Na_2SO_4. It was found that streaming potentials could not be measured in any of these solutions.

According to the plan, filter Runs 15 and 17 were to be made using a solution of the same salt, NaCl; filter Runs 16 and 20 were to be made using $MgCl_2$; and filter Runs 18 and 19 were to be made using $Al_2(SO_4)_3$. Since enough NaCl solution was left over after filter Run 15 was completed to make filter Run 17 immediately, filter Run 16 was skipped temporarily when its turn came up. Filter Runs 18 and 19 were made next and the series was terminated without making Run 16 so that other filter runs involving solutions of electropositive salts could be begun sooner.

The "B" was added to the numbers in this series after the "A" series had been completed. This was done to eliminate possible confusion with filter runs in the preliminary series.

"A" series filter runs

Seventy-seven filter runs were made between July 16, 1962 and October 29, 1962 to:

1. Study the changes in the zeta potential of flux calcined diatomite that was brought about by treatment with solutions of electropositive salts outside of the filter.

2. Test other chemicals that might reverse the streaming potential of flux calcined grades of diatomite. Beryllium perchlorate and cupric sulfate were tried without success. Ferric sulfate was effective in reversing the zeta potential. A cationic polyelectrolyte, UCAR Resin C-149, was tried and was found to be effective for reversing the zeta potential of diatomite.
3. Determine more precisely the zeta potential of diatomite in distilled water. The zeta potential, however, was found to vary in what appeared to be an erratic manner until a relationship with the water resistivity was indicated.

"C" series filter runs

Thirteen filter runs were made between December 8 and December 13, 1962, to determine whether resistivity of the water used in washing the filter cake during a streaming potential filter run had an important effect on the magnitude of the zeta potential of the filter cake. It was found that the results of these tests proved that the resistivity of the wash water did raise the zeta potential of the filter cake when either tap water or NaCl was used to lower the resistivity of deionized water used for washing the filter cake.

EXPERIMENTAL OBSERVATIONS

Zeta Potential of Flux Calcined Diatomite

Seventy-one filter runs were made in which diatomite was washed with distilled water or deionized water. The results from these runs were used in calculating zeta potentials for each of the grades of diatomite tested. Initially, it was assumed that the zeta potential of a filter aid would be the same in distilled water as it would be in tap water and that measurements made in one medium would apply in the other.

The results of these runs are given in Table 2 in order of decreasing zeta potentials calculated for each grade of diatomite. The values are also, by chance, arranged approximately in the order of increasing resistivity. The results in Table 2 appeared to indicate that the zeta potential of diatomite may be inversely proportional to the resistivity of the wash water used in testing the filter aid. This observation is reinforced by Figures 31 through 36 which show the zeta potential for each of six grades of flux calcined diatomite filter aid plotted as a function of the resistivity of the wash water. Figure 37 shows the zeta potential curves for each of the six grades plotted together. Figure 38 is a composite curve based on the results of all eight grades tested. The curve fitting was arbitrary. While these results do not prove that the zeta potential of a filter aid is increased by decreasing the resistivity or purity of the wash

Table 2. Zeta potentials of ten grades of diatomite determined by streaming potential measurements

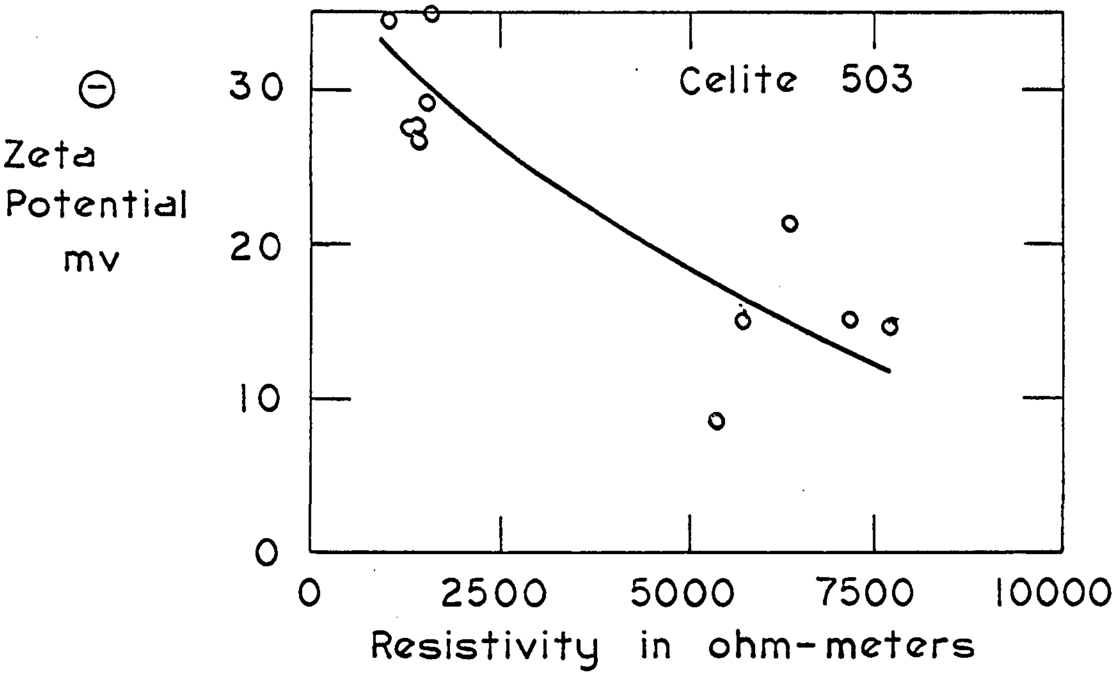
Grade of diatomite	Zeta potential, mv	Water temperature, °C	Water resistivity, ohm-meters	Run number
Celatom FW 20	-31.9	26.0	1534	23A4
	-28.5	26.0	1532	22A4
Celatom FW 60	-35.7	31.0	1305	24A2
	-33.6	26.0	1572	23A3
	-32.3	27.0	1360	21A2
Sorbo-Cel	+46.3	24.2	978	11
	+35.1	22.5	969	13
	+34.7	22.5	973	12
	+34.4	24.0	910	14
Celite 503	-34.8	26.0	1571	25A1
	-34.6	26.0	1033	7
	-29.2	27.6	1519	23A6
	-27.7	28.0	1290	5
	-27.6	25.0	1360	6
	-26.5	27.0	1441	22A2
	-21.4	28.3	6350	7B
	-15.3	29.0	5740	2B
	-14.8	27.2	7190	17B
	-14.5	28.9	7710	18B
	- 8.3	30.7	5350	3B
Celite 535	-37.0	26.0	947	8
	-33.7	25.0	1620	23A1
	-33.2	26.1	1360	21A1
	-28.8	27.4	1566	8A2
	-27.8	27.4	1550	8A1
	-26.8	26.4	2400	8A3
	-26.5	27.7	2260	7A2
	-26.3	28.0	2235	7A1
	-25.0	29.8	2440	20A2
	-24.4	30.6	2430	20A3
	-21.2	27.9	7900	5C1
	-19.9	22.6	8190	3C1
Celite 545	-47.2	27.6	684	19A2
	-45.7	27.9	682	19A1
	-39.5	26.0	969	9
	-34.1	28.2	3190	33B
	-32.6	28.2	3670	34B

Table 2 (Continued).

Grade of diatomite	Zeta potential, mv	Water temperature, °C	Water resistivity, ohm-meters	Run number
Celite 545 (cont.)	-26.4	28.0	4250	1B
	-25.9	29.3	2220	18A4
	-25.8	30.8	2500	18A3
	-25.5	29.1	2370	20A1
	-21.4	28.4	3540	35B
	-19.3	27.3	6970	12B
	-19.2	25.9	6990	11B
	-14.5	29.0	7100	6B
Celite 545, Mix B	+29.8	25.1	654	17
	+28.6	25.2	740	15
	+26.8	28.0	896	3
	+24.6	25.5	682	16
Celite 560	-45.1	24.2	963	11
	-41.0	25.3	1080	10
	-27.3	26.0	1510	4
	-25.3	28.1	2180	17A1
	-25.0	29.9	2500	18A2
	-23.8	29.0	2760	18A1
	-23.6	28.1	2220	17A2
Dicalite Speedex	-28.6	27.0	1491	23A5
	-28.1	26.8	1510	22A3
	-18.4	29.0	6640	8B
	-15.0	26.6	6360	10B
	-13.5	26.7	8800	14B
	-11.9	28.0	8450	15B
Dicalite 4200	-39.3	30.8	1111	24A1
	-33.6	25.3	1572	23A2
	-30.9	27.0	1386	22A1
	-25.3	28.1	6410	9B
	-23.3	28.6	4490	4B
	-18.7	27.6	6640	5B
	-18.1	30.0	6680	19B
	-15.9	27.3	8450	13B

Figure 31. Zeta potential of Celite 503 as a function of the resistivity of the wash water

Figure 32. Zeta potential of Celite 535 as a function of the resistivity of the wash water


⊖
Zeta Potential mv
30
20
10
0
0
2500
5000
7500
10000
Resistivity in ohm-meters
Celite 503

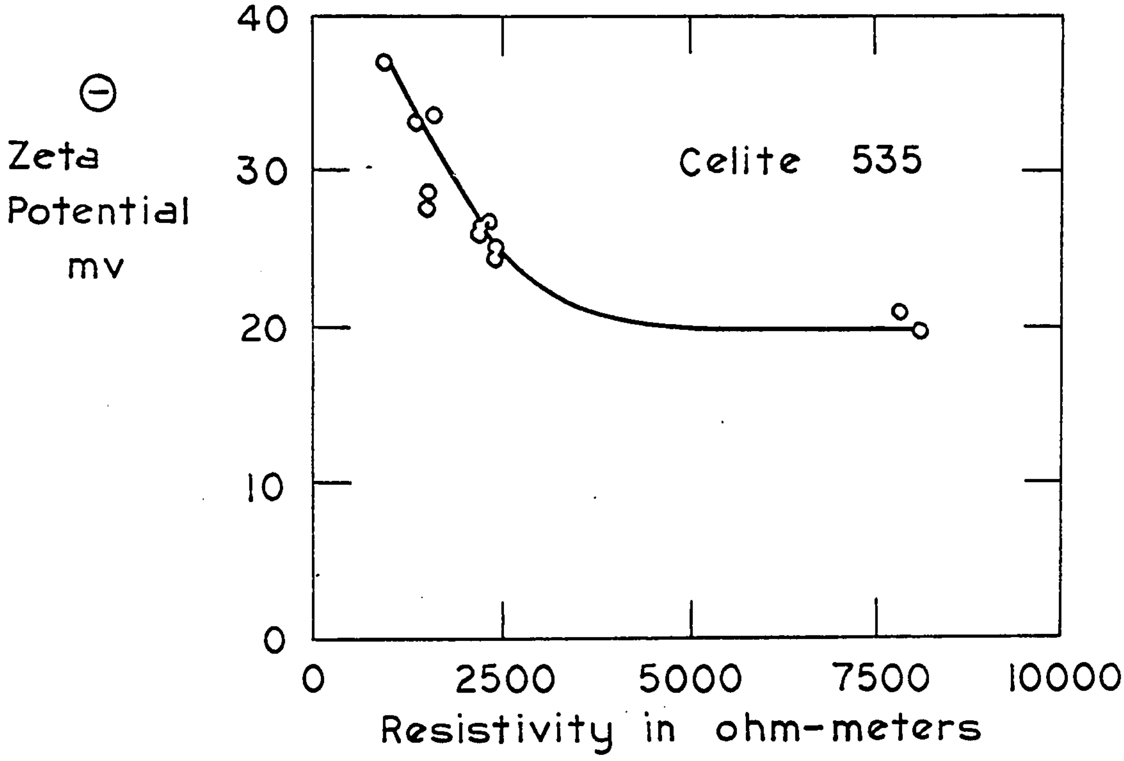
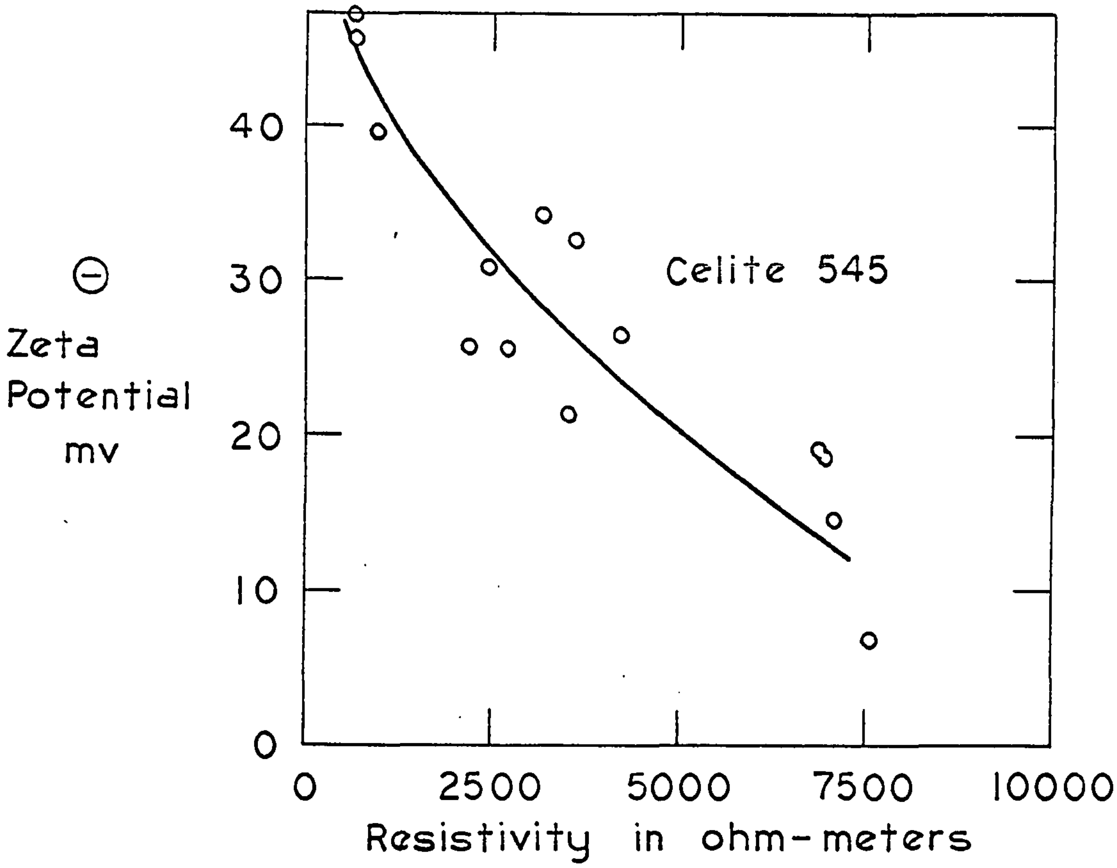

40
⊖
Zeta Potential mv
30
20
10
0
0
2500
5000
7500
10000
Resistivity in ohm-meters
Celite 535

Figure 33. Zeta potential of Celite 545 as a function of the resistivity of the wash water

Figure 34. Zeta potential of Dicalite Speedex as a function of the resistivity of the wash water


⊖
Zeta
Potential
mv
0
10
20
30
40
0
2500
5000
7500
10000
Resistivity in ohm-meters
Celite 545

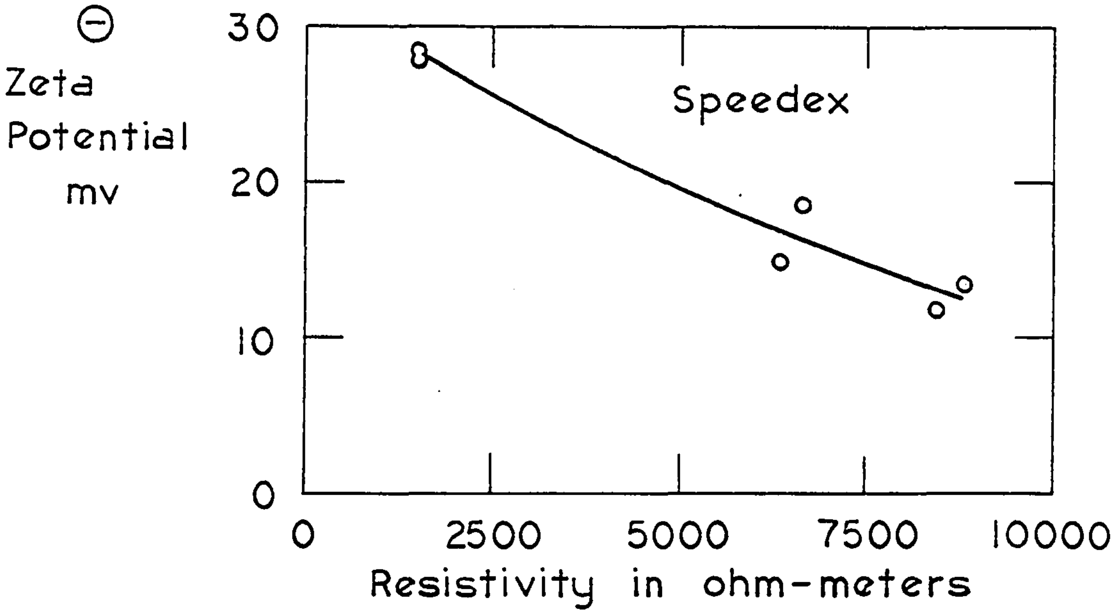
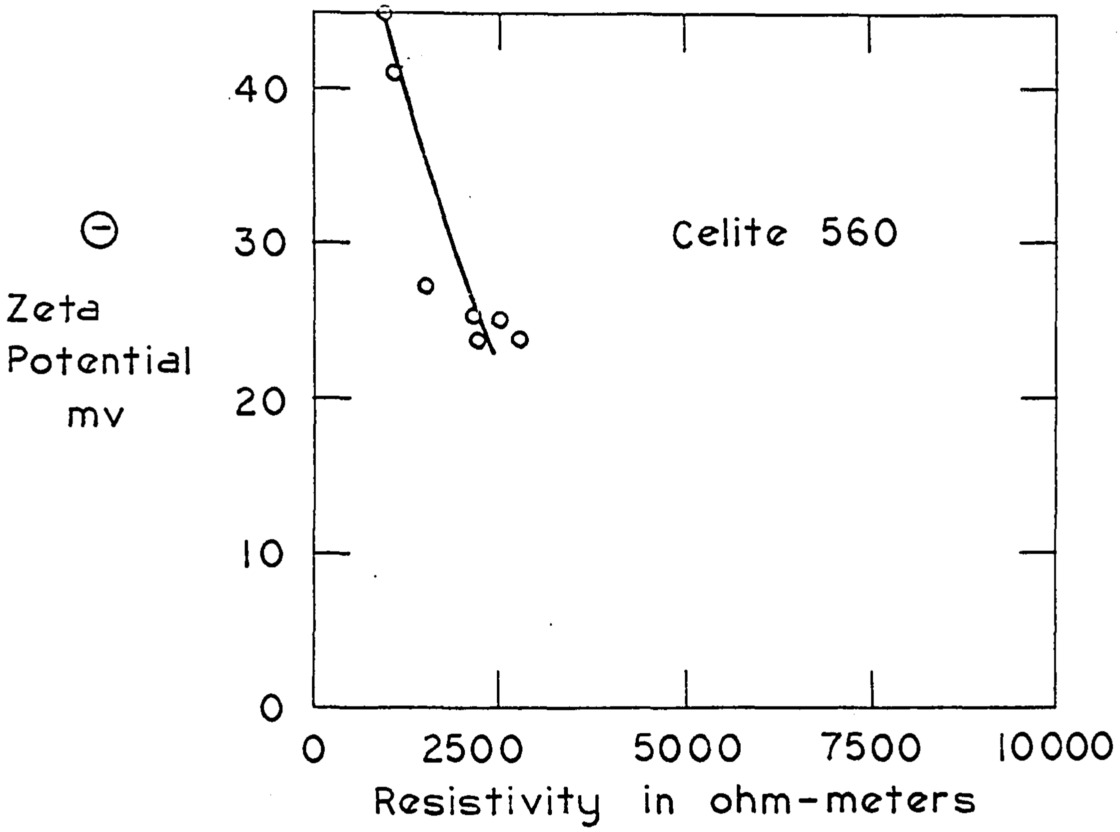

⊖
Zeta
Potential
mv
0
10
20
30
0
2500
5000
7500
10000
Resistivity in ohm-meters
Speedex

Figure 35. Zeta potential of Celite 560 as a function of the resistivity of the wash water

Figure 36. Zeta potential of Dicalite 4200 as a function of the resistivity of the wash water


⊖
Zeta
Potential
mv
40
30
20
10
0
Celite 560
0
2500
5000
7500
10000
Resistivity in ohm-meters

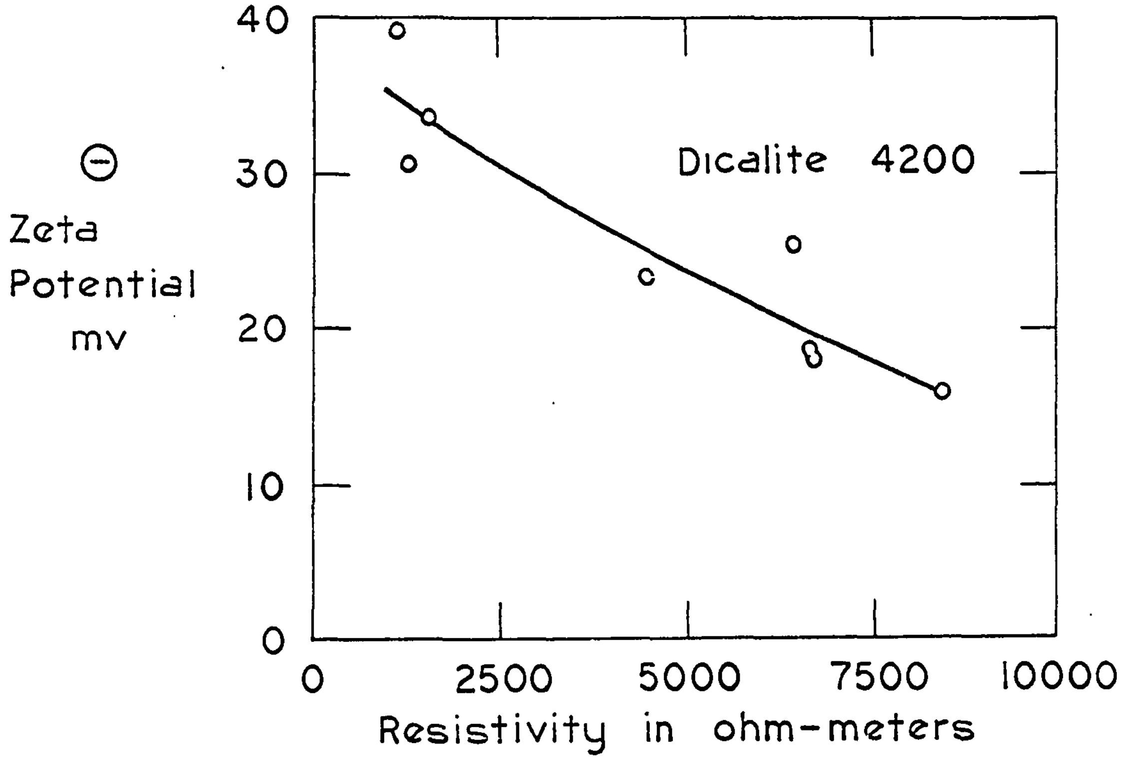
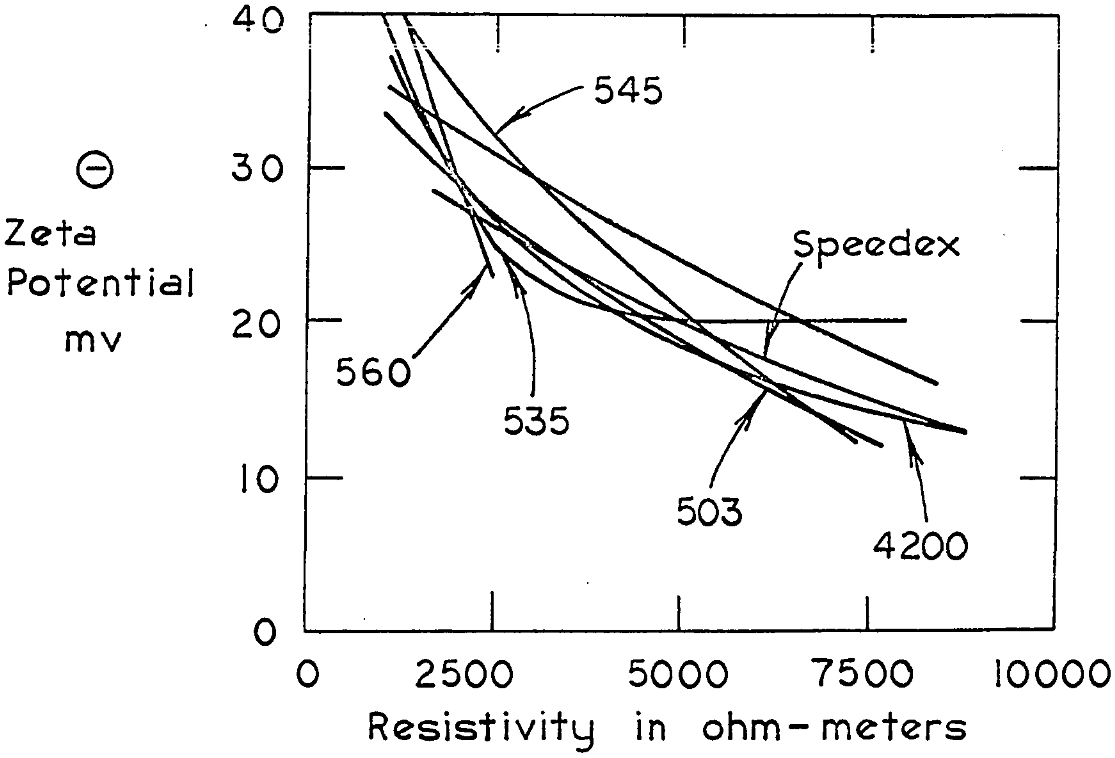
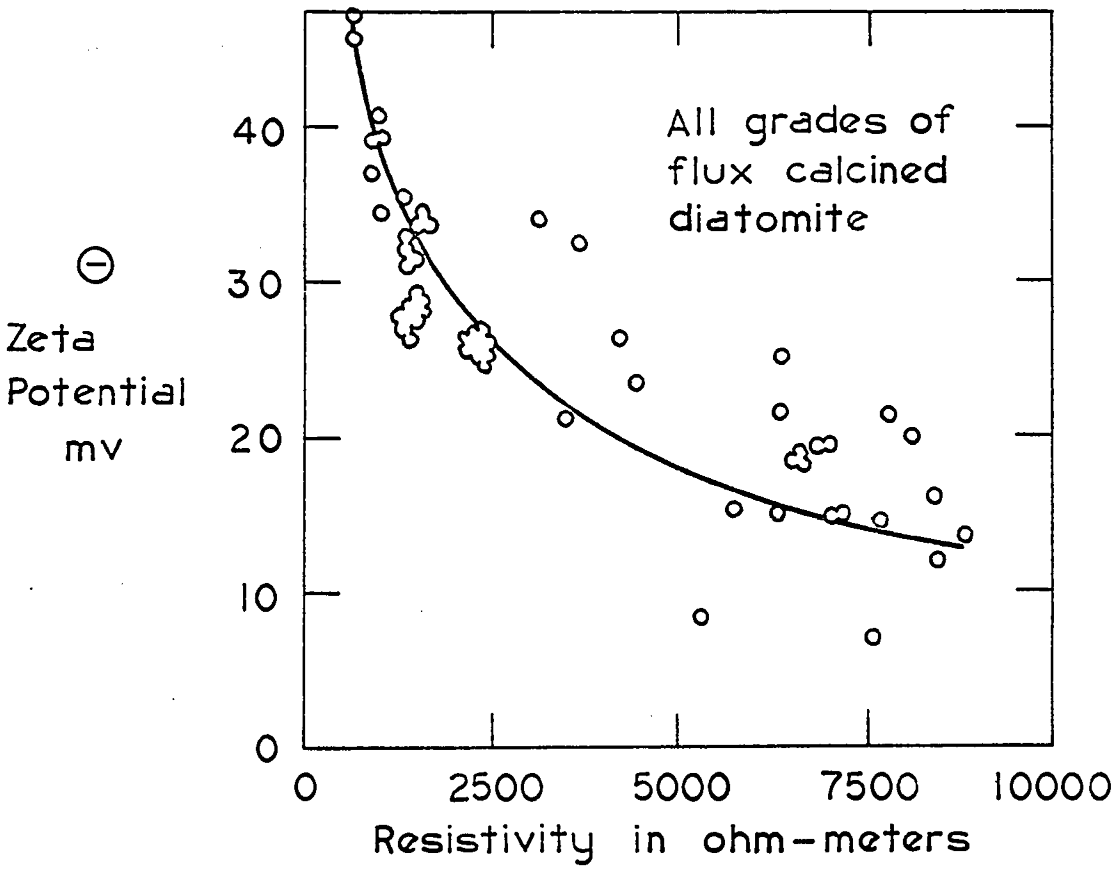

⊖
Zeta
Potential
mv
40
30
20
10
0
Dicalite 4200
0
2500
5000
7500
10000
Resistivity in ohm-meters

Figure 37. Zeta potential curves for six grades of flux calcined diatomite as a function of the resistivity of the wash water

Figure 38. Zeta potential of all grades of flux calcined diatomite tested as a function of the resistivity of the wash water


⊖
Zeta
Potential
mv
40
30
20
10
0
0
2500
5000
7500
10000
Resistivity in ohm-meters
545
Speedex
560
535
503
4200


⊖
Zeta
Potential
mv
40
30
20
10
0
0
2500
5000
7500
10000
Resistivity in ohm-meters
All grades of
flux calcined
diatomite

water, they strongly support this conclusion.

Table 2 also shows that the two electropositively coated grades of diatomite were actually positively charged when used in a filter cake. These filter aids are believed to have been treated with alum by the manufacturer. Electrophoretic measurements, however, showed that the direction of travel of Sorbocel in an electric field was the same as that of Celite 503. This would have indicated a negative zeta potential for Sorbocel using conventional techniques. If the positive zeta potential on Sorbocel as observed in this study were due to the adsorption of positive ions on the diatomite surface, the material causing the surface charge should not have been dislodged by either hydrodynamic or electric forces. The streaming potential tests indicate that the material causing the charge was not dislodged by hydrodynamic forces in the streaming potential apparatus. The electrophoresis tests, however, indicate that the material causing the charge must have been dislodged by electric forces in the electrophoresis cell in order for the diatomite to show up with a negative charge. Hence, the positively charged material affecting the Sorbocel and Celite 545 Mix B was probably a precipitate of $Al(OH)_3$ surrounding the particle rather than aluminum ions adsorbed on the surface.

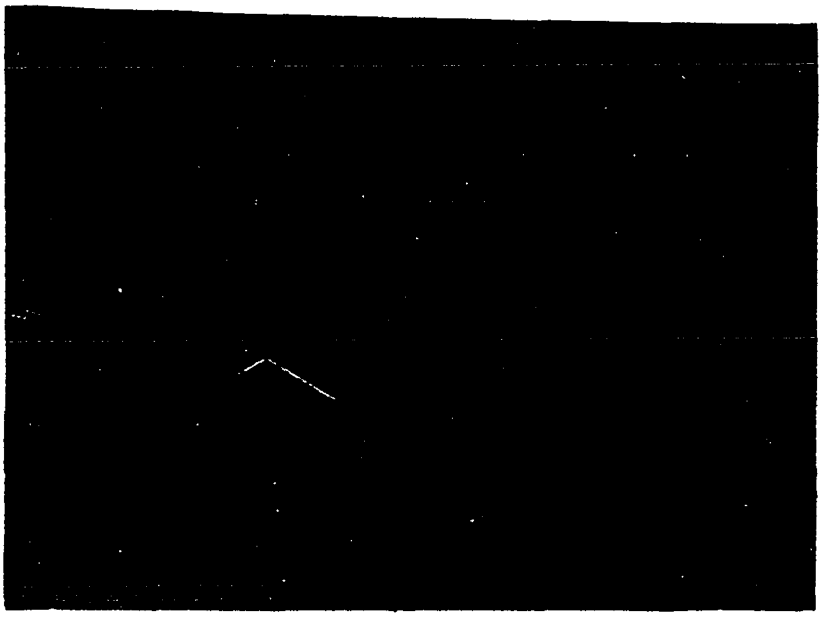
Effect of Several Salts on Zeta Potential

Nineteen filter runs were made to determine the effect on the zeta potential of flux calcined diatomite of washing the filter cake with dilute solutions of 9 different salts. Figures 39 through 47 show facsimiles made by tracing pen recordings from filter runs in which each kind of solution was used for cake washing. The most noticeable effect caused by washing the filter aid with a salt solution was an immediate drop in the streaming potential as the salt solution displaced the water in the filter. A second effect is observed by changing the flow rate while the salt solution is in the filter. The change in streaming potential with change in flow rate is greatly reduced over that observed with deionized water. These effects are the result of the lower resistivity of the salt solutions as compared with the resistivity of deionized water.

In Figure 39, for instance, the streaming potential dropped by about 60 per cent within a minute after the NaCl solution was admitted into the filter system. Subsequently, a change in flow rate from 2.40 gpm per sq ft to 1.35 gpm per sq ft produced only about 40 per cent as great a change in streaming potential when NaCl solution was being filtered as when deionized water was being filtered. Similar effects were caused by solutions of each of the other salts. Each solution contained 0.00005 mole per liter of salt except the

Figure 39. Pen recording of streaming potentials during filter Run 15B in which a Speedex filter cake was washed with a 0.00005 M NaCl solution

Figure 40. Pen recording of streaming potentials during filter Run 6B in which a Celite 545 filter cake was washed with a 0.00005 M Na_2SO_4 solution



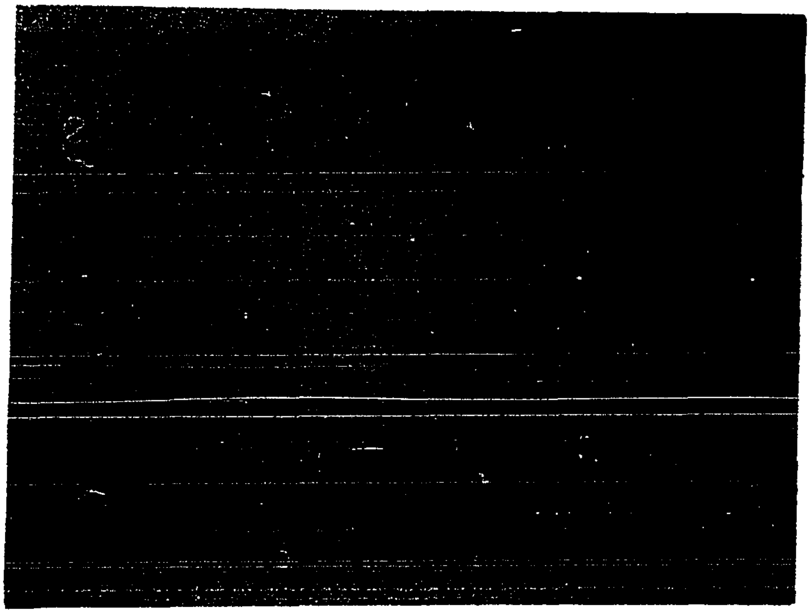
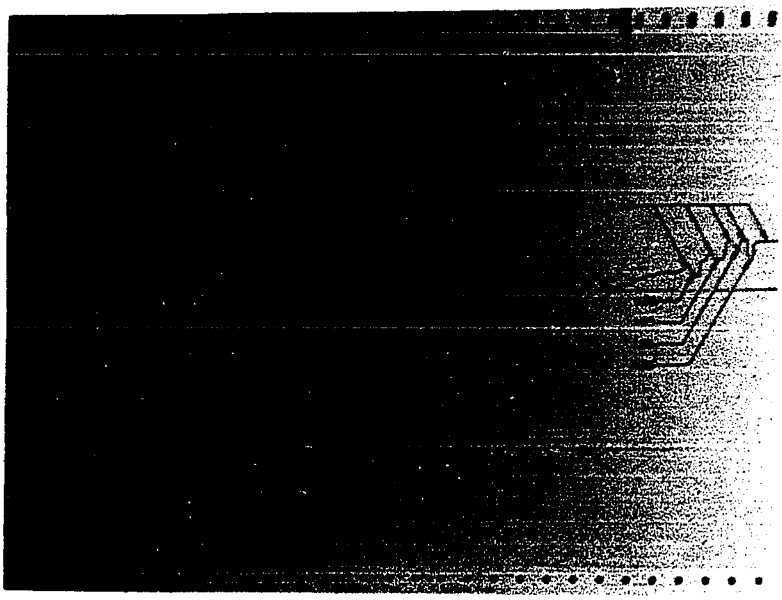


Figure 41. Pen recording of streaming potentials during filter Run 11B in which a Celite 545 filter cake was washed with a 0.00005 M $MgCl_2$ solution

Figure 42. Pen recording of streaming potentials during filter Run 10B in which a Speedex filter cake was washed with a 0.00005 M $MgSO_4$ solution

Figure 43. Pen recording of streaming potentials during filter Run 13B in which a Dicalite 4200 filter cake was washed with a 0.00005 M $AlCl_3$ solution

Figure 44. Pen recording of streaming potentials during filter Run 18B in which a Celite 503 filter cake was washed with a 0.00005 M $Al_2(SO_4)_3$ solution



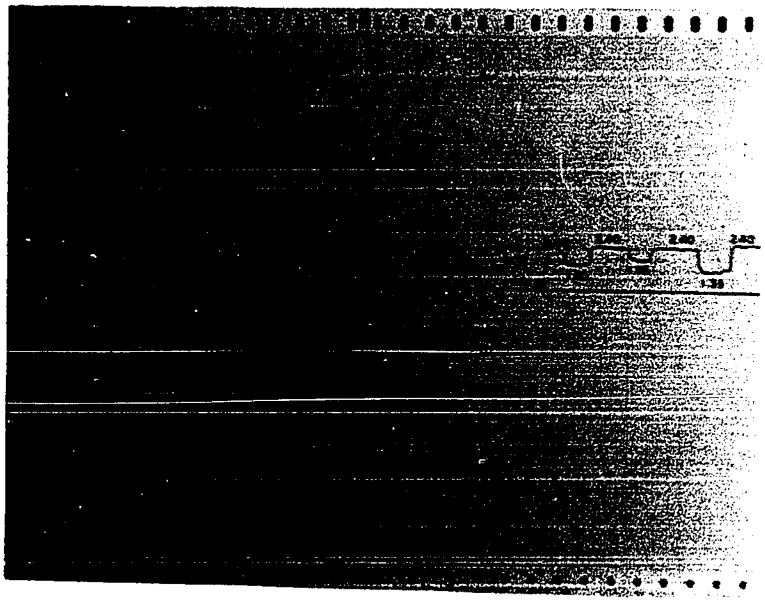

2.40
2.40
2.40
1.38

Figure 45. Pen recording of streaming potentials during filter Run 4B in which a Dicalite 4200 filter cake was washed with a 0.00005 M $FeCl_3$ solution

Figure 46. Pen recording of streaming potentials during filter Run 1A in which a Celite 545 filter cake was washed with a 0.00054 M $Fe_2(SO_4)_3$ solution

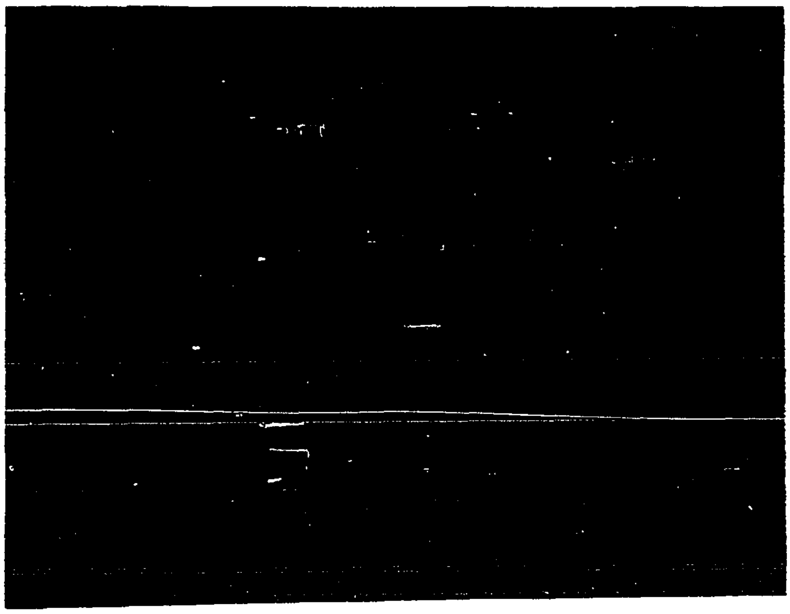
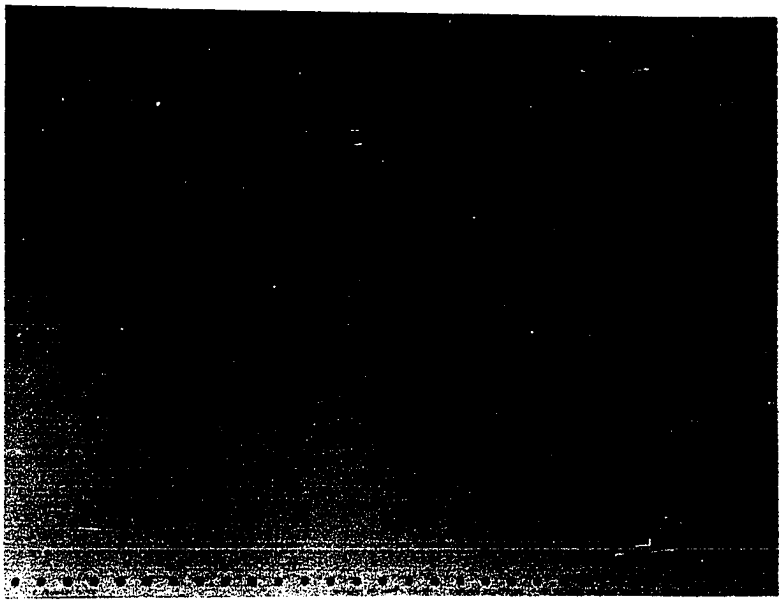


Figure 47. Pen recording of streaming potentials during filter Run 14B in which a Speedex filter cake was washed with a 0.00005 M $FeSO_4$ solution



$Fe_2(SO_4)_3$ solution which contained 0.00054 moles per liter.

Another less obvious effect was the relationship between the zeta potential of the cake while being washed with the salt solution and the zeta potential while being washed with deionized water. See Table 3. The average of the ratio of zeta potential when filtering salt solution to that when filtering deionized water are as follows:

$NaCl$, 2.64
Na_2SO_4, 1.96
$MgCl_2$, 1.64
$MgSO_4$, 1.84
$AlCl_3$, -3.17
$Al_2(SO_4)_3$, -1.76
$FeCl_3$, -1.86
$FeSO_4$, 1.05.

The negative sign indicates a reversal of the zeta potential of the diatomite from negative to positive. These ratios were calculated by dividing the average numerical value of zeta potential for diatomite being washed with a given salt solution by the corresponding average value of zeta potential when the diatomite was being washed with deionized water.

The reversal of the sign of the zeta potential of $AlCl_3$, $Al_2(SO_4)_3$ and $FeCl_3$ is also evident in the recordings of the streaming potentials, Figures 43, 44 and 45. Changing the flow rate from a high flow rate (2.40 or 2.55 gpm per sq ft) to a lower flow rate (0.90, 1.35, 1.65 or 1.95 gpm per

Figure 48. Bar graphs showing relative zeta potentials of diatomite filtering deionized water and solutions of various salts

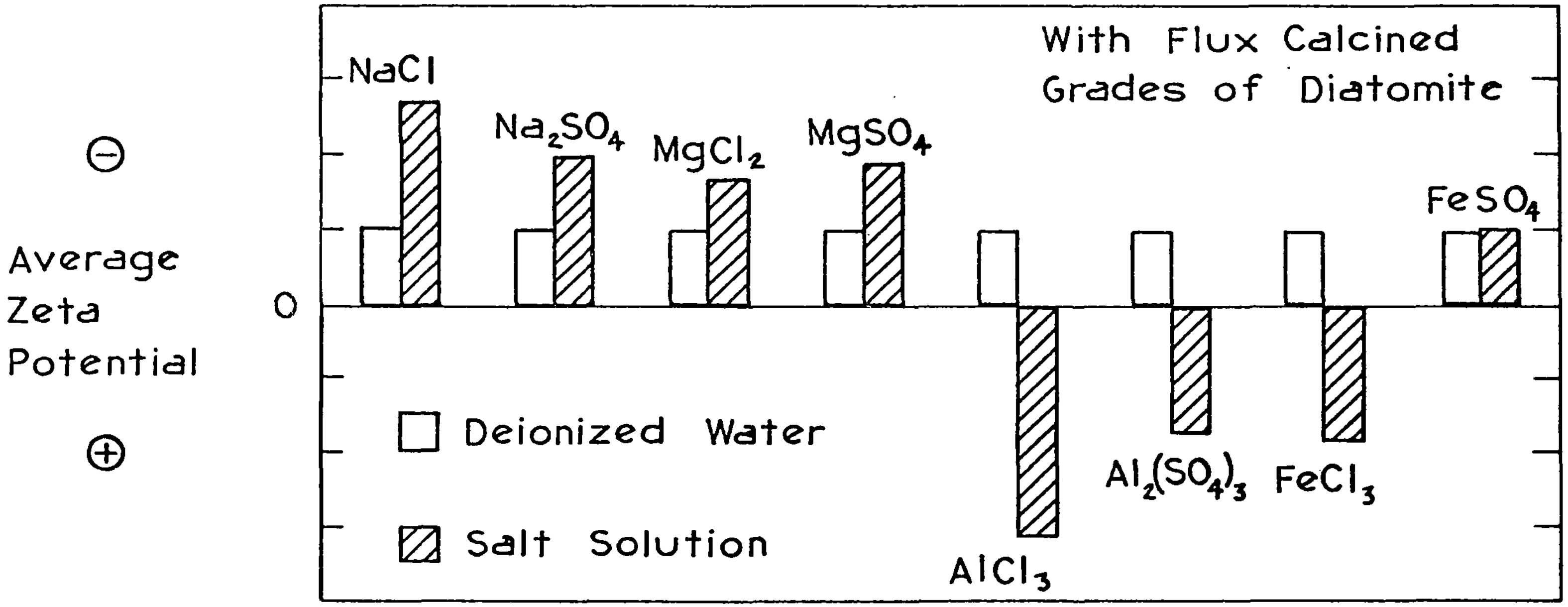

With Flux Calcined Grades of Diatomite
Average Zeta Potential
⊖
0
⊕
NaCl
Na_2SO_4
$MgCl_2$
$MgSO_4$
$AlCl_3$
$Al_2(SO_4)_3$
$FeCl_3$
$FeSO_4$
☐ Deionized Water
▨ Salt Solution

Table 3. Zeta potentials determined by streaming potential measurements of flux calcined diatomite in which deionized water and solutions of various salts (each 0.00005 M) were used as wash waters

		Deionized water as wash water		Salt solution as wash water		
Salt solution used	Grade of diatomite	Zeta potential, mv	Resistivity, ohm-meters	Zeta potential, mv	Resistivity, ohm-meters	Run number
NaCl	Speedex	-11.9	8450	-34.8	1200	15B
	Celite 503	-14.8	7190	-35.0	1200	17B
Na_2SO_4	Celite 545	-14.5	7100	-31.6	1190	6B
	Dicalite 4200	-25.3	6410	-44.0	1220	9B
$MgCl_2$	Celite 545	-19.2	6990	-31.4	590	11B
$MgSO_4$	Celite 503	-15.3	5740	-23.4	675	2B
	Speedex	-15.0	6360	-27.1	685	10B
	Celite 545	- 6.8	7600	-14.8	650	22B
$AlCl_3$	Celite 503	- 8.3	5350	+29.3	370	3B
	Speedex	-18.4	6640	+63.6	405	8B
	Dicalite 4200	-15.9	8450	+40.0	425	13B
$Al_2(SO_4)_3$	Celite 545	-26.4	4250	+30.7	670	1B
	Celite 503	-14.5	7710	+20.4	425	18B
	Dicalite 4200	-18.1	6680	+49.1	410	19B
$FeCl_3$	Dicalite 4200	-23.3	4490	+32.8	215	4B
	Celite 545	-19.3	6970	+44.5	225	12B
$FeSO_4$	Dicalite 4200	-18.7	6640	-15.0	695	5B
	Celite 503	-21.4	6350	-18.3	660	7B
	Speedex	-13.5	8800	-20.0	695	14B

sq ft) moves the pen in a direction opposite to that in which the pen moves while washing with deionized water. Thus, we have further evidence that the zeta potential of the cake has been changed from negative to positive.

The same thing takes place when the cake is washed with $Fe_2(SO_4)_3$ although it is not demonstrated in Figure 46. The surface charge reversal does not take place when a diatomite filter cake is washed with a solution of $FeSO_4$, however, as can be seen in Figure 47. Thus, the trivalent aluminum and ferric ions reverse the streaming potential of diatomite being washed with solutions in which they are present whereas the divalent ferrous and magnesium ions do not cause a reversal of streaming potential. Magnesium and sodium ions, as the ratios show, increase the zeta potential by making it more negative.

Reversal of Zeta Potential

Coating during filtration

<u>Solutions of aluminum salts</u> Diatomite whose zeta potential has been reversed by washing with solutions of aluminum salts is so permanently affected that its zeta potential and streaming potentials are found to be less negative when the filter cake is washed again with deionized water, Figures 43 and 44. Subsequent treatments with solutions of aluminum salts continue to decrease the negative zeta potential and streaming potentials until these potentials

finally become positive. Table 4 and Table 5 show the effects of repeatedly washing diatomite filter cakes with solutions of aluminum chloride and aluminum sulfate. The amount of aluminum salt solution brought in contact with the filter cake has been expressed as a percentage by weight that the weight of aluminum expressed as aluminum hydroxide in the contacting solution is of the weight of diatomite in the cake.

Less than 0.2 per cent by weight of aluminum hydroxide is needed to reverse the zeta potential of diatomite, Figures 49 and 50. The permanent change in the surface charge and a trend to demonstrate the permanent reversal of zeta potential is apparent in the pen recordings by the failure of streaming potentials to assume their former values after washing with the aluminum solutions, Figures 43 and 44.

Solutions of ferric salts This effect was not shown at first with solutions of ferric salts because the concentration of salt in the solution was too low. In Figure 45 it can be seen that the streaming potentials following washing with a solution of $FeCl_3$ appear to be as great or greater than they were before washing. Only slight trends toward a permanently lower zeta potential were found with these dilute solutions. A more concentrated ferric sulfate solution was used in Run 1A and this lowered the streaming potentials permanently. Additional washings reversed the streaming potential and the zeta potential by a small amount,

Table 4. Zeta potentials determined by streaming potential measurements of flux calcined diatomite coated during filtration of aluminum chloride solutions

Grade of diatomite	$Al(OH)_3$ to diatomite ratio,* per cent by weight	Zeta potential, mv	Run number
Celite 503	0.000	- 8.3	3B
	0.248	+ 8.7	
	0.372	+15.1	
	0.508	+19.0	
	0.645	+18.5	
Speedex	0.000	-18.4	8B
	0.086	-14.1	
	0.221	+ 5.6	
	0.422	+17.0	
	0.603	+21.8	
	0.889	+25.0	
Dicalite 4200	0.000	-15.9	13B
	0.089	- 4.2	
	0.151	+ 8.5	
	0.229	+19.6	
	0.352	+26.9	

*The amount of aluminum chloride brought in contact with the filter cake is expressed as the percentage ratio of the weight of aluminum hydroxide to the dry weight of diatomite.

Figure 46. Table 6 and Figure 51 show the way that the zeta potential was reversed by repeatedly washing the filter cake with $Fe_2(SO_4)_3$. Because the resistivity of the deionized water was not measured during this run and because the pressure loss was too great to measure after the first wash with $Fe_2(SO_4)_3$ solution, actual zeta potentials could not be calculated. Instead, relative values based on an assumed value of -30 for the zeta potential of Celite 545 and

Figure 49. Zeta potential (determined by streaming potential measurements of flux calcined diatomite coated during filtration of aluminum chloride solutions) as a function of the percentage ratio of the weight of aluminum hydroxide brought in contact with the filter cake to the dry weight of diatomite

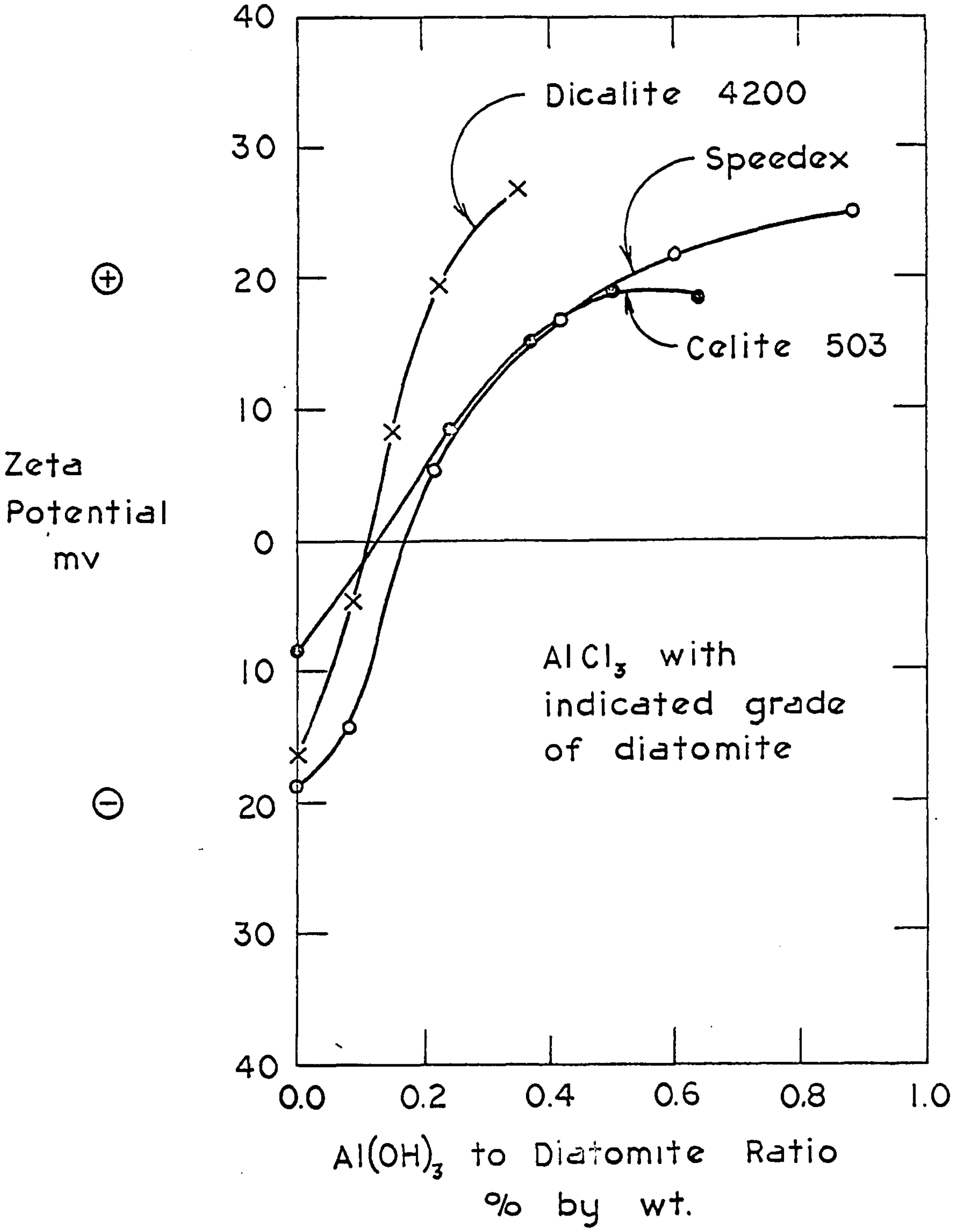

40
30
20
10
0
10
20
30
40
⊕
⊖
Zeta Potential mv
Dicalite 4200
Speedex
Celite 503
AlCl₃ with indicated grade of diatomite
0.0
0.2
0.4
0.6
0.8
1.0
Al(OH)₃ to Diatomite Ratio
% by wt.

Table 5. Zeta potentials determined by streaming potential measurements of flux calcined diatomite coated during filtration with aluminum sulfate solutions

Grade of diatomite	$Al(OH)_3$ to diatomite ratio,* per cent by weight	Zeta potential, mv	Run number
Celite 545	0.000	-26.4	1B
	0.086	-17.2	
	0.153	- 2.7	
	0.238	+13.0	
	0.340	+22.6	
	0.508	+30.0	
Celite 503	0.000	-14.5	18B
	0.113	- 8.7	
	0.252	+17.8	
	0.858	+31.4	
Dicalite 4200	0.000	-18.1	19B
	0.009	-19.8	
	0.041	-10.3	
	0.072	0.0	
	0.103	+13.2	
	0.249	+29.1	

*The amount of aluminum sulfate brought in contact with the filter cake is expressed as the percentage ratio of the weight of aluminum hydroxide to the dry weight of diatomite.

estimated head losses were calculated. They give an approximate idea of the change in zeta potential brought about by the electropositive material in the wash water.

Comparison of aluminum and ferric salts It may be seen by comparing Figures 49 and 50 with Figure 51 that only one tenth as much aluminum hydroxide is needed to reverse the zeta potential of diatomite to the same extent as ferric hydroxide. Only a small part of this difference is due to the

Figure 50. Zeta potential (determined by streaming potential measurements of flux calcined diatomite coated during filtration of aluminum sulfate solutions) as a function of the percentage ratio of the weight of aluminum hydroxide brought in contact with the filter cake to the dry weight of diatomite

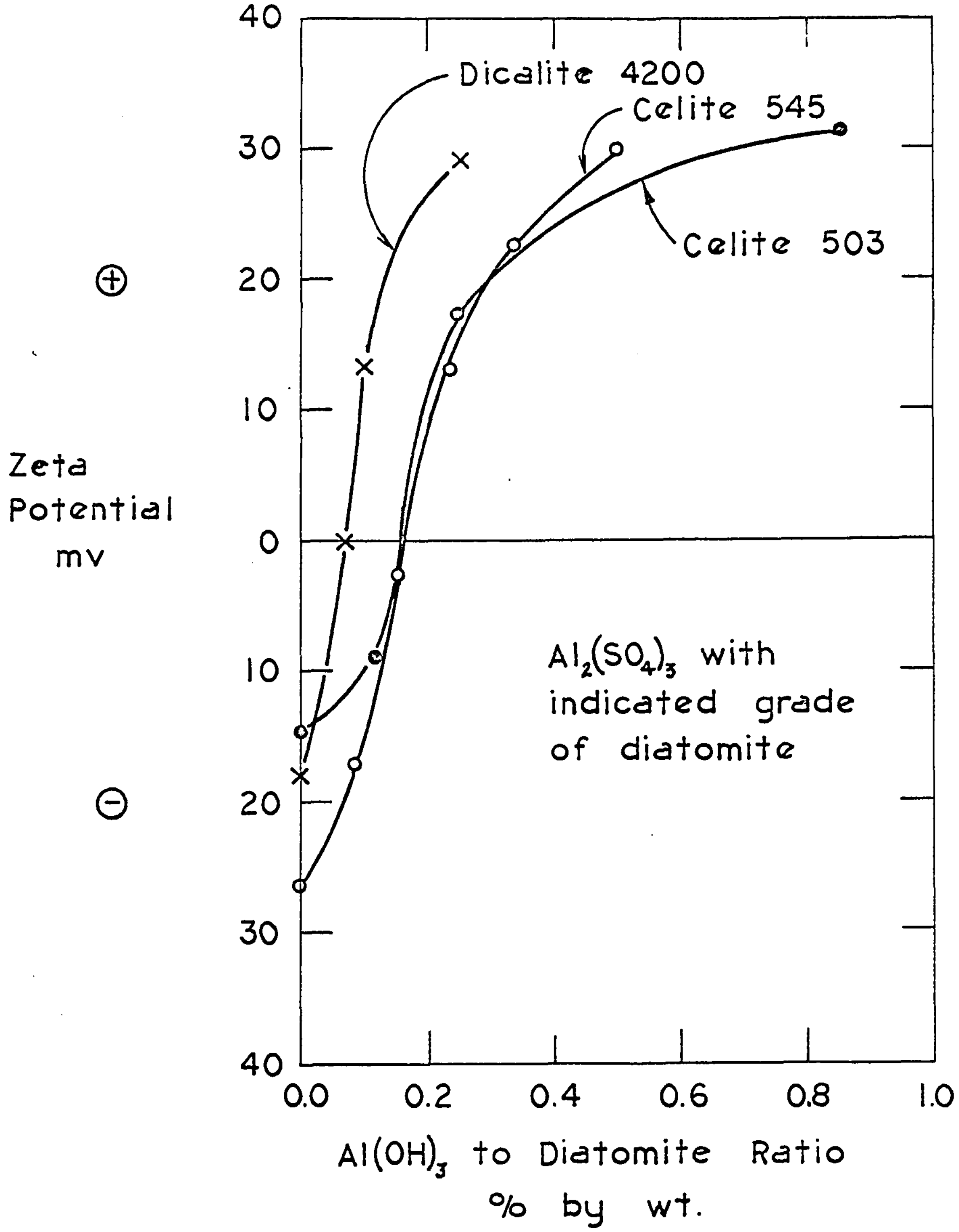

Dicalite 4200
Celite 545
Celite 503
⊕
⊖
Zeta Potential mv
40
30
20
10
0
10
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
$Al_2(SO_4)_3$ with indicated grade of diatomite
$Al(OH)_3$ to Diatomite Ratio % by wt.

Table 6. Zeta potentials determined by streaming potential measurements of Celite 545 coated in Run 1A during filtration of ferric sulfate solutions.

$Fe(OH)_3$ to diatomite ratio* per cent by weight	Zeta potential** mv
0.00	-30
1.05	- 2
2.43	0
3.44	+ 1
4.03	+ 1

*The amount of ferric sulfate brought in contact with the filter cake is expressed as the percentage ratio of the weight of ferric hydroxide to the dry weight of diatomite.

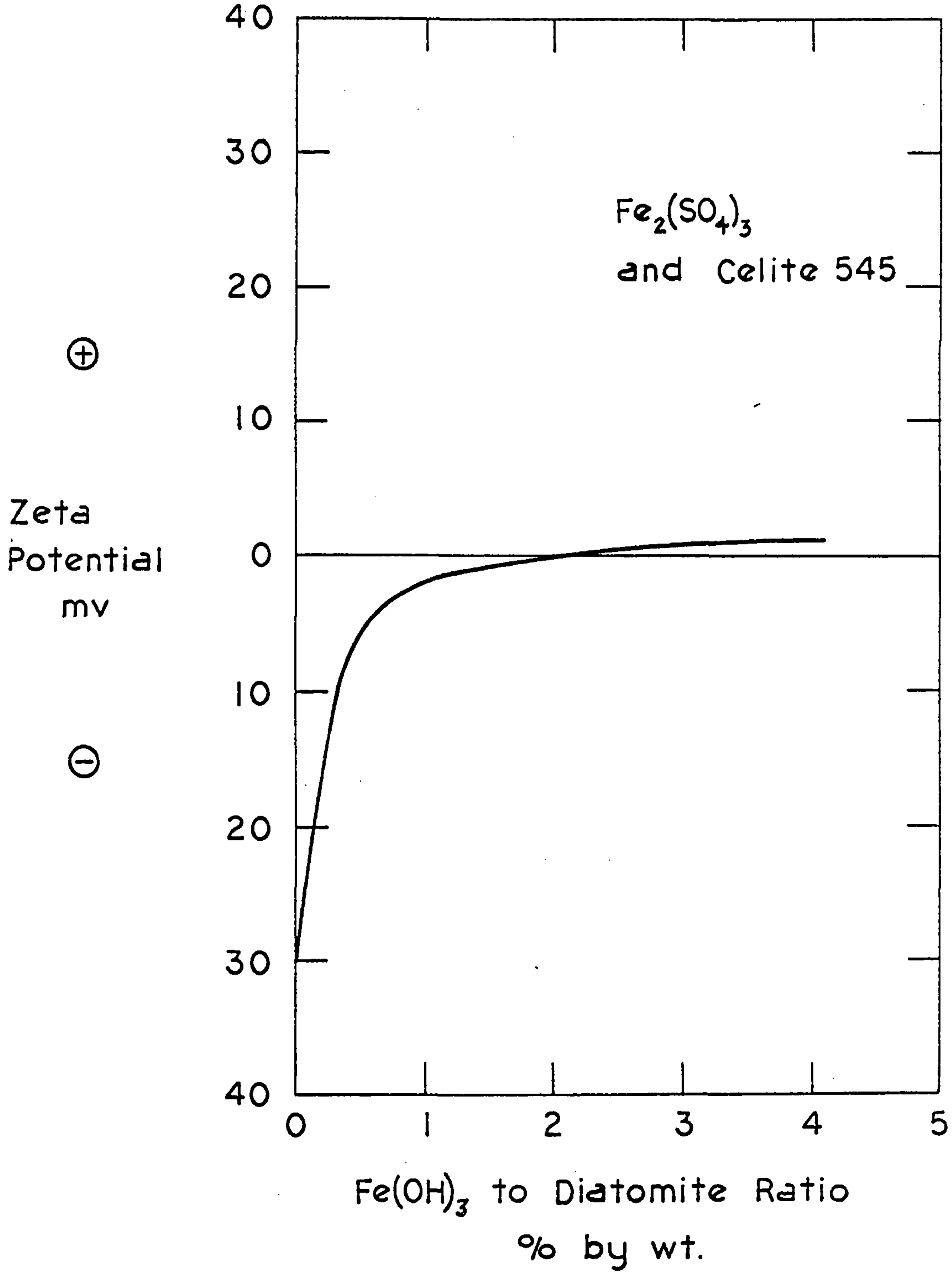
**Based on an assumed value of -30 for Celite 545 before coating.

lower formula weight of $Al(OH)_3$, 78 as compared with 107 for $Fe(OH)_3$. Further, diatomite coated with aluminum hydroxide can attain a much larger positive zeta potential than diatomite coated with ferric hydroxide. This is probably due to the presence of anions other than the hydroxyl ion that remain with the strongly electropositive ferric ion. The aluminum ion probably loses most of the anions that were associated with it as a salt and becomes more completely hydrated.

Coating before filtration

Aluminum salts Diatomite coated in the filter by washing with a solution of aluminum chloride does not make as efficient use of the electropositive material in the solution

Figure 51. Zeta potential (determined by streaming potential measurements of Celite 545 coated in Run 1A during filtration of ferric sulfate solutions) as a function of the percentage ratio of the weight of ferric hydroxide brought in contact with the filter cake to the dry weight of diatomite


40
30
20
10
0
10
20
30
40
⊕
⊖
Zeta
Potential
mv
$Fe_2(SO_4)_3$
and Celite 545
0
1
2
3
4
5
$Fe(OH)_3$ to Diatomite Ratio
% by wt.

as diatomite that is coated outside of the filter. When coated outside of the filter, diatomite was kept in contact with a solution of aluminum chloride in a beaker for a period of ten minutes before the slurry was poured into the recycle chamber to be pumped into the filter. While the cake was forming this same solution was recycled in a more dilute form through the diatomite filter cake for a period of ten more minutes. Only one-quarter to one-half as much aluminum hydroxide was needed to reverse the zeta potential of the diatomite in this way as was needed when the diatomite was coated in the filter. Compare Figures 49 and 52.

Cationic polyelectrolytes Diatomite was also be coated outside of the filter with a solution containing a cationic polyelectrolyte. A cationic polyelectrolyte is an organic polymer used as a coagulant aid. Small amounts of a cationic polyelectrolyte will coagulate negatively charged colloids by neutralizing their charge. When greater amounts are added, the colloids may redisperse carrying a positive charge.

It was found that the zeta potential of Celite 545 was reversed from negative to positive by treatment with a very dilute solution of unknown concentration of a polyelectrolyte, UCAR Resin C-149. The filter aid was coated before filtration. Although the solution of polyelectrolyte was very dilute, the head loss characteristics of the diatomite filter cake were such that head losses could only be measured at low flows. From crude head loss and streaming potential measurements, the streaming potential to head loss ratio was estimated to be about 150 mv per ft of water. The resistivity of the wash water used in the test was about 1500 ohm-meters and the temperature of the water was about 25° C. Therefore, the zeta potential of the filter aid coated with the cationic polyelectrolyte was about +43 mv.

Displacement of Electropositive Coating

Further differences in the pen recordings can be seen by comparing Figures 43 through 46 with Figures 39 through 42 and with Figure 47. Immediately after washing with solutions containing aluminum or ferric salts, the streaming potential recording appears to become even more positive than when the salt solution was present in the filter. This sag in the curve represents a rapid change to a more positive potential. The sag becomes less pronounced as the zeta potential of the filter cake becomes more and more positive and fails to appear at all when the zeta potential of the filter cake is permanently reversed and the diatomite is completely coated.

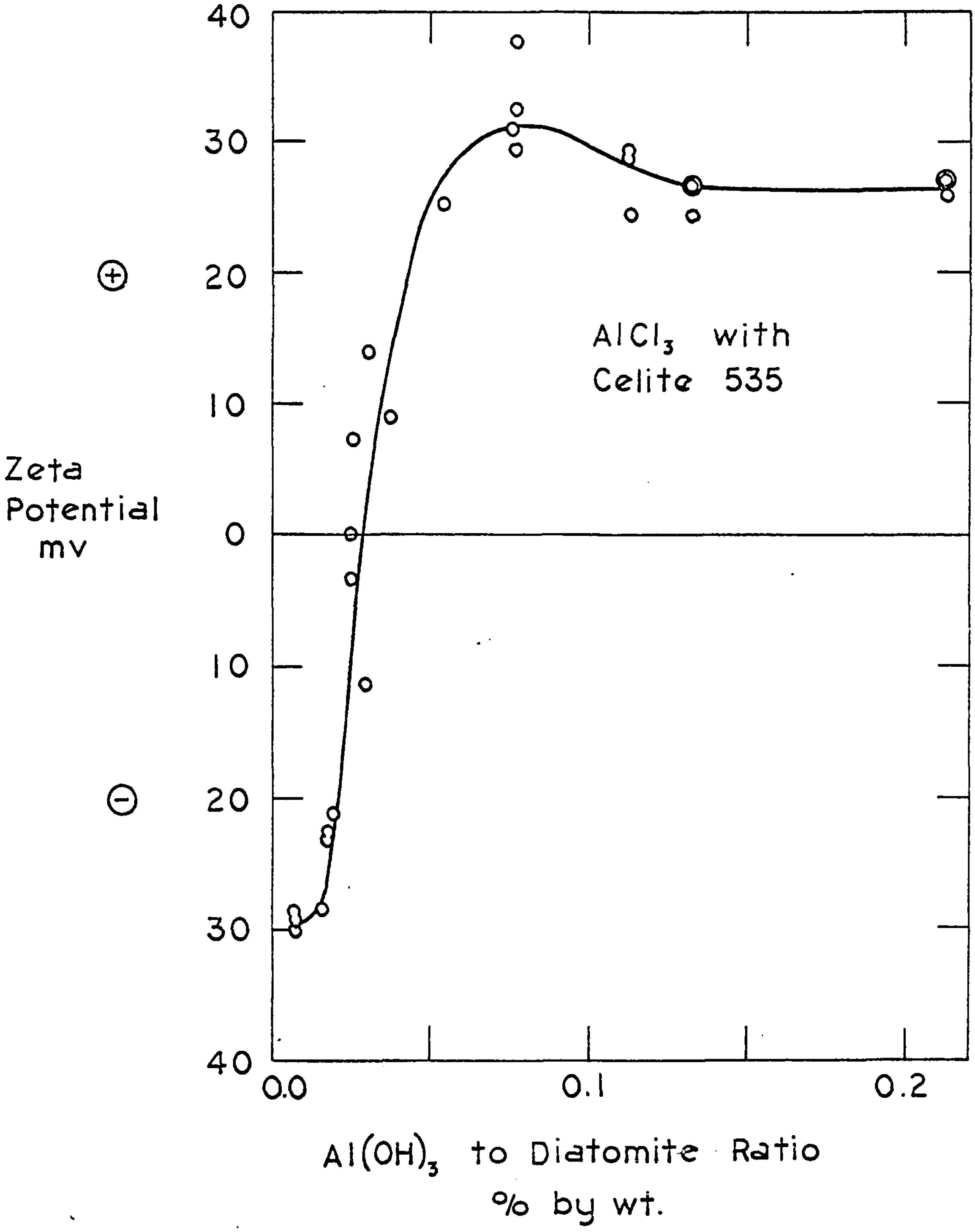
This sag may be caused by a concentration potential between the contents of the inlet and outlet chambers of the filter resulting from ferric hydroxide or aluminum hydroxide

Table 7. Zeta potentials determined by streaming potential measurements of Celite 535 coated before filtration in solutions of aluminum chloride

$Al(OH)_3$ diatomite ratio, per cent by wt.	Zeta potential, mv	Temperature, °C	Resistivity, ohm-meters	Run number
0.009	-28.9	28.0	1703	9A3
0.009	-30.0	28.0	1690	9A4
0.009	-29.3	28.0	1705	9A5
0.016	-28.4	25.5	1745	10A1
0.019	-23.9	26.2	1770	10A2
0.019	-22.5	26.3	1770	10A3
0.020	-21.1	26.3	1903	10A4
0.023	0.0	27.5	1600	9A1
0.023	- 3.3	27.5	1615	9A2
0.023	+ 7.1	26.4	1770	11A2
0.031	-11.3	26.3	2070	10A5
0.031	+14.1	26.4	1783	11A1
0.039	+ 9.2	26.8	1760	10A6
0.055	+25.2	26.7	1770	10A7
0.077	+31.0	28.4	1730	12A4
0.078	+29.4	27.3	1546	8A4
0.078	+37.8	28.1	1560	8A5
0.078	+32.6	27.8	1580	8A6
0.114	+24.5	28.3	2300	12A5
0.114	+29.5	28.1	1810	12A6
0.114	+28.8	27.3	1825	13A3
0.143	+26.7	28.7	1850	12A7
0.143	+24.5	28.4	1745	13A4
0.143	+26.7	28.3	1785	13A5
0.214	+27.3	28.4	1920	12A8
0.214	+27.3	27.4	1840	13A1
0.214	+26.0	27.5	1865	13A2

being washed from the cake as distilled water replaces the salt solution. When the ferric or aluminum hydroxide coatings are completely formed on the filter cake they are not so

Figure 52. Zeta potential (determined by streaming potential measurements of Celite 535 coated before filtration with solutions of aluminum chloride) as a function of the percentage ratio of aluminum hydroxide to the dry weight of diatomite with which it was brought in contact


40
30
20
10
0
10
20
30
40
⊕
⊖
Zeta Potential mv
AlCl$_3$ with Celite 535
0.0
0.1
0.2
Al(OH)$_3$ to Diatomite Ratio
% by wt.

susceptible to being displaced. Therefore, this effect is observed only when the coating is incompletely formed.

Zeta Potential and Resistivity

Early runs in which certain salts, NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$, were added to the deionized water used in the filtration runs indicated that the salts served to increase the negative zeta potential of the filter aids. These runs were not designed to tell whether the effect was due only to resistivity, surface conductance or to the kind of salt used in the water. The results shown in Figures 31 through 38 indicated that the water resistivity changes might be a major factor affecting the change in the zeta potential of the filter cakes.

To provide more information on the effect of resistivity, two series of filter runs were made for this purpose in which Celite 535 was used. In one series, NaCl was added to deionized water to decrease the resistivity. In the other series, tap water from the Iowa State University water supply was added to the deionized water to provide water of equivalent resistivity. The Iowa State University tap water has a hardness of about 310 mg/L as $CaCO_3$ of which about 104 mg/L is the calcium ion and 33 mg/L is the magnesium ion. Alkali is reported, as the sodium ion, at about 18 mg/L, chlorides at 20 mg/L, sulfates at 98 mg/L, with the remainder being primarily carbonates and bicarbonates (20).

The results of these streaming potential runs are given in Tables 8 and 9 and in Figures 53 and 54. The curve for Celite 535 in distilled and deionized water, Figure 32, falls between the curves for NaCl in deionized water and the one for tap water in deionized water. The water used in the filter runs pertaining to Figure 32 was taken from the distilled water supply tank shown in Figure 15. This tank is supplied by a zeolite water softener and a Barnstead Water Still. The water softener operates on a sodium cycle with brine prepared from NaCl being used for a regenerant. Therefore, most of the calcium and magnesium in the water being fed to the still has been exchanged for sodium and most of the contaminants in the distilled water are probably sodium chloride, sulfate or carbonates that have been carried over by entrainment in the vapor produced in the still. The fact that Figures 53 and 54 bear some resemblance to Figure 32 indicates that the resistivity of water used in streaming potential tests does affect the zeta potential of the filter aid being tested. The fact that there are marked differences in the zeta potential curves, however, in spite of the fact that the filter aid and the range of resistivities involved in the tests were the same indicates that resistivity of the wash water is not the only factor to be considered in

Table 8. Zeta potentials determined by streaming potential measurements of Celite 535 using solutions of sodium chloride in deionized water

Moles of NaCl per liter of water	Zeta potential, mv	Temperature, °C	Resistivity, ohm-meters	Run number
0.0001	-48.8	27.0	698	3C4
0.00004	-43.3	23.7	516	1C1
0.000023	-38.2	24.6	1132	2C1
0.0000126	-34.3	22.6	1890	2C2
0.0000104	-30.5	22.3	3550	3C2
0.0000054	-24.7	27.0	4540	3C3
0.0	-21.2	27.9	7900	5C1
0.0	-19.9	22.6	8190	3C1

Table 9. Zeta potentials determined by streaming potential measurements of Celite 535 using solutions of Iowa State University tap water in deionized water

Per cent tap water in wash water	Zeta potential, mv	Temperature, °C	Resistivity, ohm-meters	Run number
3.69	-32.3	28.4	251	5C2
1.845	-25.3	31.0	453	4C1
0.497	-22.0	27.9	1560	4C4
0.295	-19.2	28.0	2410	4C3
0.0626	-18.8	27.1	4720	4C2
0.0	-21.2	27.9	7900	5C1
0.0	-19.9	22.6	8190	3C1

determining the zeta potential of a filter aid. The kind of ions present in the water is probably the most important single factor as is evidenced by the fact that some salts seem to increase the negativity of the zeta potential of diatomite while other salts seem to have little if any effect while

Figure 53. Zeta potential of Celite 535 as a function of the resistivity of solutions of NaCl in deionized water

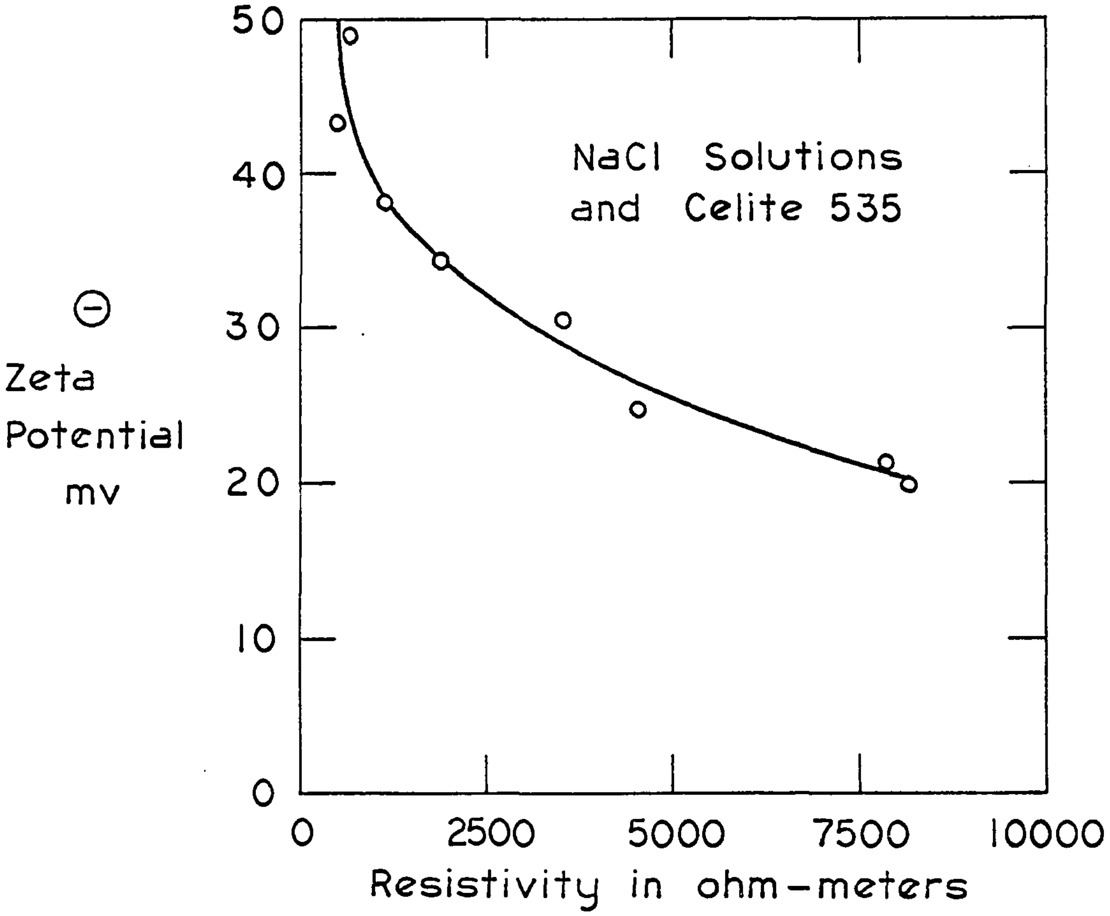
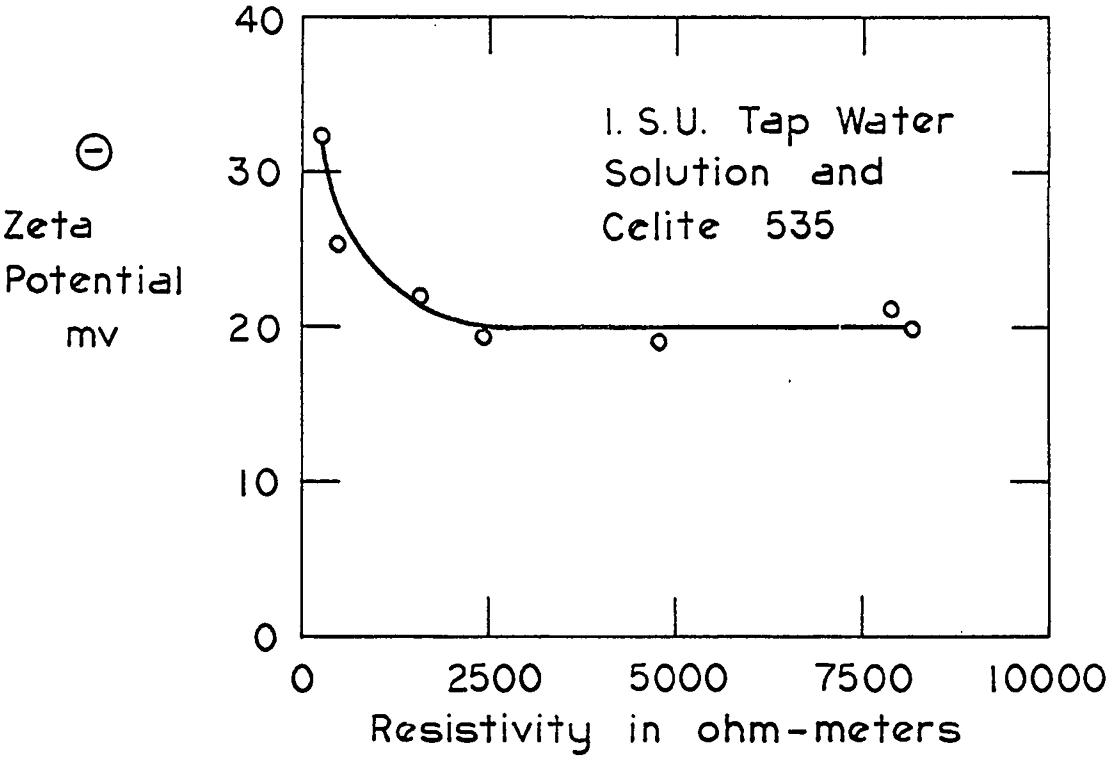

NaCl Solutions
and Celite 535
⊖
Zeta
Potential
mv
50
40
30
20
10
0
0
2500
5000
7500
10000
Resistivity in ohm-meters

Figure 54. Zeta potential of Celite 535 as a function of the resistivity of solutions of Iowa State University tap water in deionized water used as wash water


⊖
Zeta
Potential
mv
40
30
20
10
0
0
2500
5000
7500
10000
Resistivity in ohm-meters
I. S. U. Tap Water
Solution and
Celite 535

still others reverse the zeta potential from negative to positive.

Tables 10 and 11 give the reciprocals of the zeta potentials given in Tables 8 and 9 respectively. These data were used in plotting Figures 55 and 56 to determine whether surface conductance was also affecting the apparent zeta potential. For practical purposes a straight line can be plotted through the data points of Figure 55. This indicates that the true zeta potential of Celite 535 is about -50 mv and that the streaming potentials are being affected by conductance at the particle surface.

A mean particle diameter of 20 microns (21) was used in computing the specific surface conductance of Celite 535. This value, 1×10^{-9} ohms^{-1} has the same order of magnitude as was found (22) for Pyrex in 0 to 10^{-4} N KNO_3, ie, 0.7×10^{-9} to 4×10^{-9} ohms^{-1}; for Jena 16^{III} in 0 to 10^{-4} N KCl, ie, 0.6×10^{-9} ohms^{-1}; and for Pyrex in 10^{-4} N KCl, ie, 0.4×10^{-9} ohms^{-1}.

The data points shown in Figure 56 for a natural water and Celite 535 cannot be fit with a straight line. This indicates that other factors besides surface conductance are affecting the streaming potential measurements.

Figures 53 and 54 also demonstrate, as did Figures 31 through 38, that the results of streaming potential tests to determine the zeta potential of diatomite made by washing with deionized or distilled water are not directly related to those

Table 10. Reciprocals of zeta potentials in Table 8 for determining the effect of surface conductance on the streaming potential test results

Reciprocal zeta potential, mv^{-1}	Resistivity, ohm-meters
-0.0205	698
-0.0225	516
-0.0262	1132
-0.0309	1890
-0.0328	3550
-0.0405	4540
-0.0471	7900
-0.0502	8190

Table 11. Reciprocals of zeta potentials in Table 9 for determining the effect of surface conductance on the streaming potential test results

Reciprocal zeta potential, mv^{-1}	Resistivity, ohm-meters
-0.0310	251
-0.0395	453
-0.0455	1560
-0.0520	2410
-0.0530	4720
-0.0471	7900
-0.0502	8190

that would be obtained by measurements made in tap water. Accurate streaming potential measurements cannot be made in tap water in most cases, however, because the resistivity is so low that streaming potentials are extremely small. This is illustrated by the fact that a full scale range of 50 mv was needed in making Run 5C2 in which the wash water contained 3.69 per cent tap water in deionized water. Measurements can

Figure 55. Reciprocal of zeta potential of Celite 535 as a function of the resistivity of solutions of NaCl in deionized water

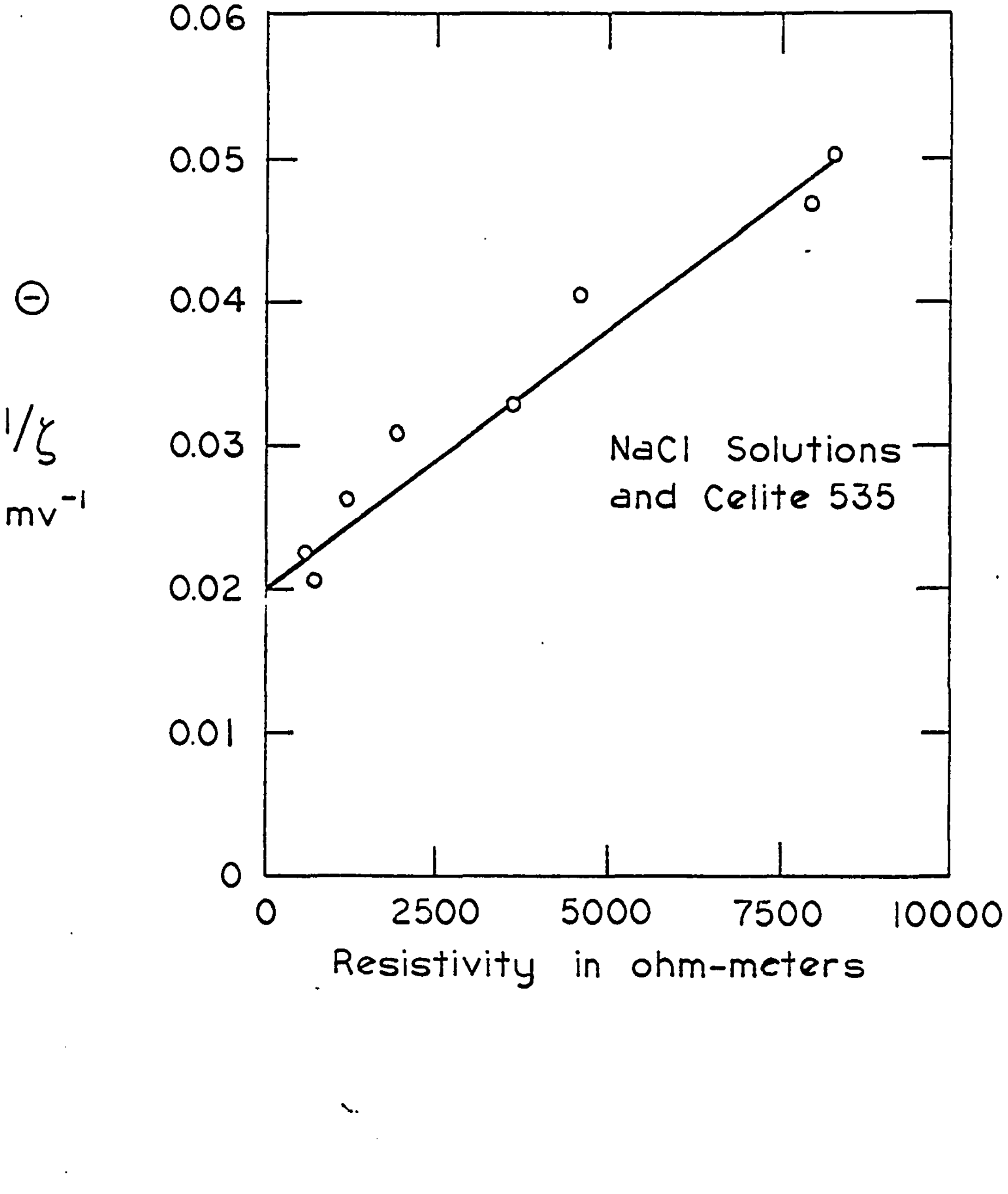
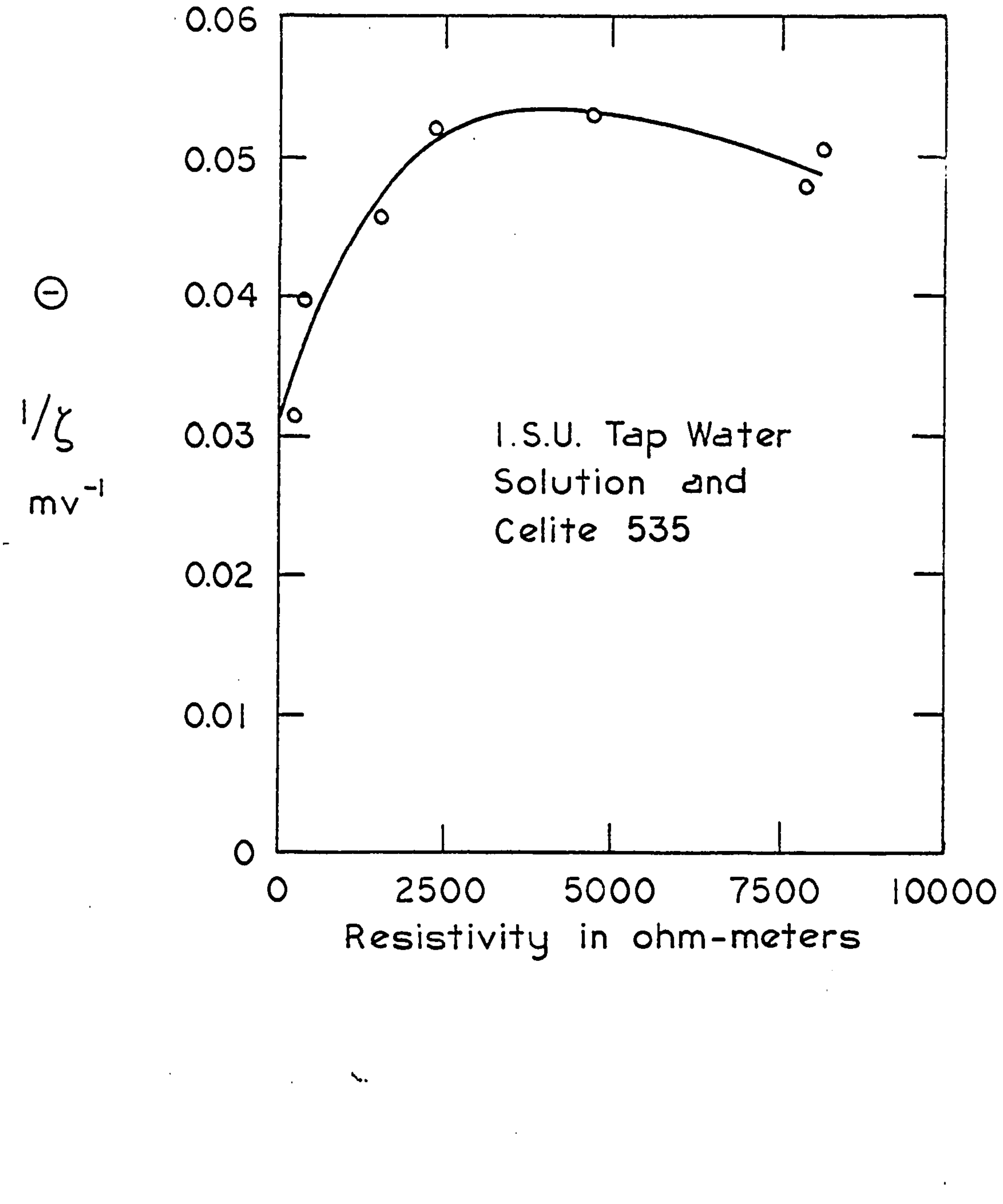

Θ
1/ζ
mv⁻¹
0.06
0.05
0.04
0.03
0.02
0.01
0
0
2500
5000
7500
10000
Resistivity in ohm-meters
NaCl Solutions
and Celite 535

Figure 56. Reciprocal of zeta potential of Celite 535 as a function of the resistivity of solutions of Iowa State University tap water in deionized water used as wash water


0.06
0.05
0.04
0.03
0.02
0.01
0
Θ
$1/\zeta$
mv^{-1}
0
2500
5000
7500
10000
Resistivity in ohm-meters
I.S.U. Tap Water
Solution and
Celite 535

be made with a full scale range down to 1.25 mv with the Sargent recorder but the practical limit is controlled by the amount of line broadening in the recording caused by erratic movement of the pen. This line broadening can be seen in Figures 41 and 42 as the broad line made when $MgCl_2$ and $MgSO_4$ solutions were being filtered. In Run 5C2 the line width amounted to about 2 mv while the range in streaming potential differences was only 3.8 to 21.9 mv.

SUMMARY

Equipment and Measurements

The zeta potential of diatomite filter aids was determined from streaming potential measurements made with a small diatomite filter and a recording potentiometer. The filter was made from plexiglass which is electrically non-conducting; thereby limiting the extent to which streaming potentials are dissipated through the filter housing. The filter element was a plane vertical leaf 2 inches in diameter. Flow was brought into the inlet chamber of the filter tangentially so as to cause the contents of the chamber to rotate in a vertical plane thereby keeping the diatomite in suspension in the feed water until it was deposited on the filter element to form a filter cake.

Streaming potentials were measured and recorded with a recording potentiometer connected to two electrodes mounted in the filter, one in the inlet chamber and the other in the outlet chamber. Pressure losses across the filter cake were measured by means of a manometer containing bromoform as the manometer fluid. Flow rates were measured with a rotameter and controlled with a needle valve. The flow rates were checked periodically during each filter run with a graduated cylinder to be sure that the rotameter gave accurate results. The temperature and electrical resistivity of the filtrate were determined to provide information for calculating the zeta potential of the filter aid being tested. A Freas type conductivity cell and a conductivity bridge were used for measuring the resistivity of the filtrate.

Results of the Study

Some colloidal particles too small to be removed by mechanical straining during filtration are thought to be removed by mutual coagulation in those cases where the filter aid and the colloid carry opposite electric charges. The charge of a particle is related to its zeta potential and can be determined by several different methods. One method involves the measurement of the electrical potentials, called streaming potentials, which are generated when water is filtered through a porous medium consisting of the particles in question. This method was selected for studying the electric charge on diatomite because the test conditions are those that exist when a liquid is being filtered through diatomite.

One purpose of this study was to determine the zeta potential of flux calcined and electropositively coated grades of diatomite filter aids. The zeta potential of flux calcined diatomite was expected to have and did in fact have a negative sign. Electropositively coated grades of diatomite have been chemically treated with aluminum or ferric salts by a patented process which is supposed to impart a positive charge to the diatomite. The zeta potentials of these grades of filter aid were found to be positive and seems to be caused by a precipitate of aluminum or ferric hydroxide which surrounds or coats the particles in the filter cake.

Another purpose of this study was to determine the effect of ions in water on the zeta potential of diatomite. It was observed that some salts reverse the zeta potential of diatomite from negative to positive. Tests were made to determine what effects, if any, a number of typical salts in solution would have on the magnitude and sign of the zeta potential of diatomite. It is necessary to have this information to predict the way that diatomite might be expected to act in a naturally occuring water.

It was found that the zeta potential of diatomite is more negative in solutions of sodium and magnesium salts than in deionized water. Ferrous sulfate did not affect the zeta potential of the diatomite significantly. Ferric and aluminum salts reverse the zeta potential of diatomite from negative to positive.

The zeta potential of diatomite is increased as the resistivity of the water filtered through it is decreased. In other words, the zeta potential of diatomite filter aids is higher in magnitude in natural waters than it is in distilled or deionized water. Therefore, zeta potential measurements based on streaming potential tests made by washing the filter cake with deionized or distilled water are not directly related to those that would be obtained by measurements made in natural water. In most cases, streaming potential measurements cannot be made in tap water or chemically treated water because the resistivity is too low and as a result the streaming potentials are vanishingly small.

CONCLUSIONS

Several conclusions can be made about the use of streaming potential measurements for the determination of zeta potentials in studies of diatomite filter aids:

1. The determination of the zeta potential of a filter aid used as a filter cake can be determined from streaming potential measurements made during the filtration of distilled or deionized water through the filter cake.
2. The zeta potentials determined from streaming potential measurements using distilled or deionized water do not provide the same magnitude of zeta potential that would be obtained with natural waters.
3. The streaming potential method of determining zeta potentials cannot be used accurately with natural waters becuase the low resistivity of natural waters will produce vanishingly small streaming potentials.
4. The streaming potential method of determining zeta potentials is the only method which can accurately differentiate between negative and positive zeta potentials as they pertain to the effective charge on a filter cake. Streaming potential measurements

will not give the same information as electrophoretic measurements about zeta potentials of electropositively coated filter aids. The electropositive coatings are not easily displaced by hydrodynamic forces whereas they are displaced by electrical forces.

5. Streaming potential methods using distilled or deionized water are useful for determining the amount of chemical needed for reversing the zeta potential of diatomite filter aids. Since electrophoretic methods do not work for this purpose, streaming potential methods are the only practical method to use.

Several conclusions can also be made about the zeta potential of diatomite in chemically treated waters and about the way that filtration practice is affected in this respect:

1. The magnitude of zeta potentials of diatomite is related to the resistivity of the water in which the diatomite is suspended. Thus diatomite in water containing no sodium chloride may have a zeta potential of -20 mv whereas in water containing about 0.00001 moles per liter of sodium chloride it has a zeta potential of about -30 mv and in water containing about 0.0001 moles per liter of the same salt its zeta potential is about -50 mv. This is probably caused by surface conductance.

2. The magnitude and sign of the zeta potential of diatomite filter cakes is related to the kind of ions in the water. Thus, in general, sodium and magnesium salts tend to increase the negativity of the zeta potential while ferrous salts appear to have little if any effect. Aluminum salts, ferric salts and cationic polyelectrolytes on the other hand make the diatomite filter cakes strongly electropositive.
3. The zeta potential of diatomite can be permanently reversed by treatment with dilute solutions of aluminum salts either while the slurry is first being prepared before precoating the filter or while the solution is being filtered through the filter cake. Thus, electropositive filter aids can be prepared easily and cheaply as needed from standard grades of flux calcined diatomite available from any of the manufacturers. Where diatomite filters are used to filter an alum treated water, the diatomite will become electropositively coated without any special efforts to make it that way.
4. Ferric salts are probably ineffective for producing an electropositively charged diatomite either on a commercial basis or in the field where iron bearing waters are filtered. As diatomite becomes coated

with a precipitate of ferric hydroxide, the particles making up the filter cake become nearly electrically neutral. Mechanical straining is therefore responsible for most of the removal of iron that takes place in a diatomite filter after the slightly electropositive coating has been formed. This however, indicated that there are two modes of iron removal in diatomite filtration. The first involves a mutual coagulation of ferric hydroxide floc with diatomite. This can account for an iron removal of only 1.3 per cent by weight expressed as an iron to diatomite ratio in the cake. The remainder of the iron must be removed by mechanical straining.

DISCUSSION

The measurement of zeta potentials, particularly by means of electrophoresis, is receiving much attention in water treatment circles today as a possible method for controlling chemical dosages needed for coagulating water. Black in a paper on the application of electrophoresis to the study of water coagulation has written (30) that:

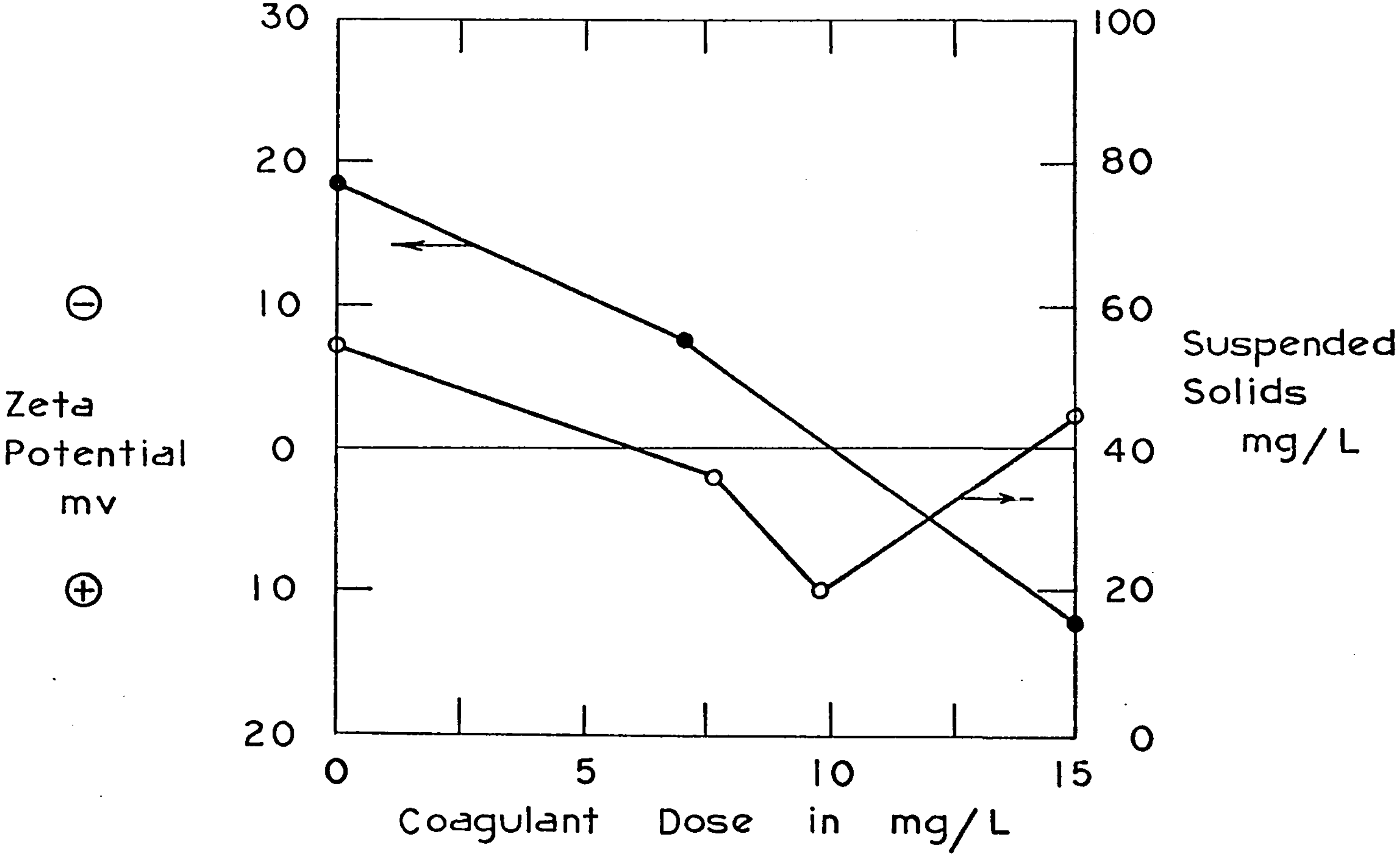
> "Coagulation with alum, as other coagulations, requires that a colloidal suspension be made unstable. The two factors related to the stability of colloidal suspensions are the zeta potential (sometimes incorrectly referred to as the "charge") and hydration. When coagulation occurs, the degree of hydration or the zeta potential, or both, are insufficient to maintain suspension stability. As the isoelectric point is approached, the zeta potential and hydration decrease and coagulation may occur."

In work to determine the effects of alum dosages on suspensions of clay in water using electrophoretic measurements, Black found (30) that:

> "1. For all clays, good coagulation occurred well before the isoelectric point was reached."
>
> "2. After the isoelectric point was reached, the zeta potential became positive and remained reasonably constant over the range of alum dosage employed."

Figure 57 has been redrawn from curves presented in a paper about coagulation theory (31). It shows the effect of chemical treatment on the zeta potential and suspended solids content of raw sewage. As is shown, the amount of solids remaining in suspension in this case is a minimum when the zeta potential is approximately zero.

Figure 57. Effect of coagulant dose on the zeta potential and suspended solids content of raw sewage


30
20
10
0
10
20
⊖
⊕
Zeta
Potential
mv
100
80
60
40
20
0
Suspended
Solids
mg/L
0
5
10
15
Coagulant Dose in mg/L

Riddick has advocated the use of electrophoresis as a control test to supplement the jar test in establishing coagulant dosages of alum and polyelectrolytes needed in treating a surface water (34):

> "To the writer, Zeta Potential Control is the only known technical means possible for optimum improvement of finished water quality. To face the situation squarely it is impossible to have Zeta Potential Control without increasing chemical costs."
>
> "However, if the facilities for Zeta Potential Control are properly installed--and the operation is reasonably meticulous--then the net result can be the translation from genuinely bad-to-mediocre quality--to a water of first quality throughout the year with no apologies required for summertime operation with its attending high algal content. Zeta Potential Control also enables substantially increased output from plants now operating at or greater than normal design capacity."

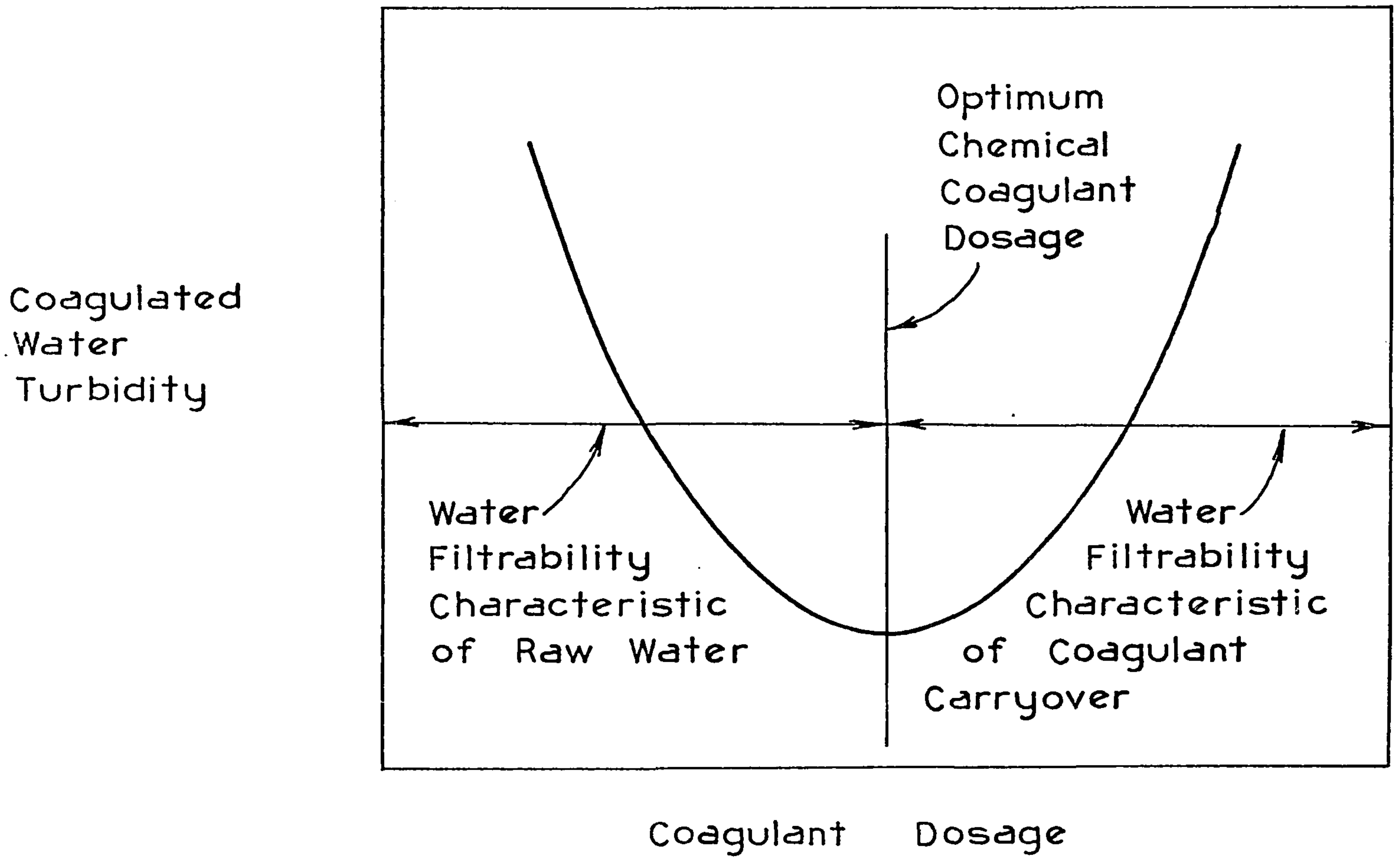
In explaining why conventional methods of treatment are not as effective as Zeta Potential Control, Riddick goes on to say (34):

> "In the field of water treatment, if we wish to effectively remove colloids it is necessary that we reduce the charge on the particle from its normal of -15 to -30 mv to a range of approximately zero, with a tolerance on either side of about plus or minus 5 mv. In my opinion, most of the taste and odor producing substances in water are not gaseous in nature, but are in colloidal form. Most reservoir and river waters have colloid concentrations ranging from tens of thousands, to millions per drop. If we wish to remove taste and odor, it is necessary to remove these colloids. They cannot be mechanically strained by any sand or diatomaceous filter and they pass the finest filter paper obtainable. This is readily demonstrated if one attempts to filter milk. These colloids are not removed by conventional coagulation as the charge on the floc is too high. They can only be removed by bringing the electric charge on the colloid to near zero, then by mechanical agitation creating innumerable individual physical contacts which result in agglomeration and build-up in size sufficient to promote settlement. The conventional employment of

> aluminum sulfate for coagulation does not remove these colloids, although it does remove most of the coarse turbidity. There is a logical reason for this which we will discuss later. Normal alum floc is electronegative with a charge of about -15 mv, and normal raw water colloids will more often range from -15 to -22 mv. In a floculation basin we induce mechanical movement. We are therefore attempting to bring the floc particle, and the coarse and the fine turbidity to adhere to, or become enmeshed in the floc. It is easy to pitch buck shot into an electric fan, but quite difficult to pitch pith balls or feathers. This is simply a matter of mass. Since average coarse turbidity has a mass of 1000 to 1,000,000 times the mass of the average colloid, the coarse turbidity is able to break through the repelling barrier of the Zeta Potential and achieve intimate and permanent contact with the floc. But the colloid, because of its relatively low mass, is unable to penetrate this barrier."

Coagulation, however, is seldom if ever used as the sole means for removing turbidity from a water. Even at the Waterford, N. Y. water treatment plant that Riddick provided with Zeta Potential Control, filters were used following chemical treatment and sedimentation (34). Figure 58 shows the relationship between coagulated water turbidity and coagulant dosage as they affect filtration. When coagulants are not used or when less than the optimum quantity is used, the load of turbidity to be removed by the filters is higher than when the optimum dosage is used and the filtrability of the water is related to the turbidity initially present. With surface waters, both the load of turbidity and the filtrability of the water can be highly variable. It is in the filtration of these waters that flux calcined diatomite has been least effective and it is here, also, that electropositively coated diatomite has been most effective (2).

Figure 58. Relationship between coagulated water turbidity and coagulant dosage


Optimum Chemical Coagulant Dosage
Coagulated Water Turbidity
Water Filtrability Characteristic of Raw Water
Water Filtrability Characteristic of Coagulant Carryover
Coagulant Dosage

When more than the optimum amount of coagulant is used, the load is increased again but the filtrability of the water is less variable. With "over-coagulated" water, the filtrability is characteristic of the coagulant floc that is carried over to the filters and since the filtrability of the coagulant floc is subject to prior study in the laboratory, filtration results are more predictable here than they are when "under-coagulated water" is being filtered.

As was pointed out earlier, mutual coagulation is believed to be responsible for the removal of turbidity in filtration if the particles in water contributing to its turbidity have a zeta potential opposite to that of the filter media. Since the zeta potential of most of the colloidal particles found in natural waters is negative, filter aids used in their filtration should have a positive zeta potential unless the particles can be removed effectively by simple straining. Diatomite filter aids can be given a positive zeta potential by either pretreating them with alum, or a cationic polyelectrolyte, before the filter cake is formed or by filtering a dilute solution of alum through the filter cake after it has been formed. This has been demonstrated in this study. Riddick suggests that alum is not effective in lowering the negative zeta potential of the finer colloids. However, this study indicates that alum is effective in actually lowering and even reversing the negative zeta potential of diatomite filter cakes. Therefore, pretreatment of natural waters using alum and/or cationic polyelectrolytes can be used to reduce the total suspended solids load to the filter while the remaining colloids still retain a negative charge. These can then be filtered effectively through a diatomite filter cake which has also received pretreatment to leave it with a positive zeta potential. Conversely, if the water treatment with alum is carried beyond the optimum, the remaining colloids will be left with a positive zeta potential and will be removed more effectively by a negatively charged diatomite filter cake.

There is a distinct possibility and even probability, however, that electrophoresis may be providing faulty information concerning the zeta potential of some colloids in the light of what Black has found. If clays which are characteristic of the colloidal particles found in most reservoir and river waters could be coagulated well before the isoelectric point was reached, then it is possible that they are acting like another silicate, glass, which becomes isoelectric for streaming potentials at lower concentrations of aluminum chloride than it does for electrophoresis (25). Further, clay colloids treated with alum may behave like electropositively coated diatomite which has a negative zeta potential to electrophoretic measurements and a positive zeta potential to streaming potential measurements. In other words, the application of an external charge may strip the colloid of its electropositive coating.

The observation by Riddick that coarse turbidity is coagulated by alum while colloids are apparently as difficult to coagulate as it is to pitch pith balls or feathers into an electric fan may be the result of his method of measuring zeta potentials. The fact that colloid removal with polyelectrolytes is superior to that with alum alone may not be pertinent at all to the problem at hand.

Another problem related to making coagulation and filtration studies in the laboratory is that of producing a "synthetic natural water" that has filtration characteristics similar to those that are found in the field. This has been the subject of much study in the Sanitary Engineering Laboratory of the Iowa Engineering Experiment Station. Another related problem concerns the addition of chemicals such as copper sulfate as a catalyst to effect the complete removal of iron from water as a hydrated oxide. There is a good possibility that the absence of certain ions in the former problem and the presence of certain ions in the latter problem may affect coagulation results, filtration results or both. The results of streaming potential measurements have shown that ions in water not commonly measured may increase or decrease the zeta potential of diatomite used in filter cakes.

Future research in these areas should be directed to finding answers for the following questions:

1. Does electrophoresis give information about the zeta potential of non-coagulated and coagulated

colloids suspended in water that is pertinent to their susceptibility for removal on filters? The optimum coagulant dosage for producing lowest coagulated water turbidity is less than the coagulant dosage required to produce a charge reversal on the clay colloids, as measured by electrophoresis. It is probable that the remaining colloids become positive to hydrodynamic forces and can be more effectively removed on a filter with a coagulant dosage significantly smaller than that required to cause a charge reversal using electrophoretic techniques.

2. How do the ions in water affect the removal of colloids and coagulant flocs on filters? If ions of various kinds and in various concentrations affect the zeta potential of diatomite filter cakes, the zeta potential of colloids and coagulant flocs are probably similarly affected. Whether they are made more electronegative or not will make some difference in determining how effective filtration will be in their removal.

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APPENDIX

A typical streaming potential pen recording, that for filter Run 22A2 was given in Figure 29. Additional data taken during that filter run are as follows:

Date: October 24, 1962

Electric resistance of water: 61,500 ohms at 23.3° C

Filter aid: 2.5 grams of Celite 503

Recording potentiometer: set for 250 mv range

Appearance of cake: good

Flow meter reading	Bromoform Manometer reading Left leg, cm	Right leg, cm	Filtrate resistance, ohms	Filtrate temperature, °C	Flow meter check, ml per min
18	14.3	37.5			
10	21.0	30.8			82
18	14.2	37.5			184
12	19.5	32.3			106
18	14.3	37.4			
14	17.7	34.0			133
18	14.2	37.5	54,000	27.0	
16	16.0	35.7			158
18	14.2	37.5			
0	25.9	25.9			

The dielectric constant, D, and the viscosity, η , of the filtrate are calculated from the filtrate temperature. The viscosity of water is given for different temperatures in the Handbook of Chemistry and Physics, 40th edition (16) on page 2156. For water at 27.0° C, η is 0.8545 centipoise or 0.8545×10^{-3} kilograms per meter-second. An equation for the dielectric constant of water is given in Critical Tables of Numerical Data, Physics, Chemistry and Technology (43) on page 78 of volume 6 as,

$$D = 80 - 0.4\,(T - 20),$$

where T is the water temperature in degrees centigrade. For water at 27° C, D is 77.2.

The resistivity, R, of the filtrate is calculated by dividing the electric resistance of the filtrate by the cell constant for the conductivity cell, 0.375 centimeters^{-1}. In this run, R is 144,100 ohm-centimeters or 1441 ohm-meters.

The head losses during filtration were computed as shown below:

Flow meter reading	Bromoform Manometer reading Left leg, cm	Bromoform Manometer reading Right leg, cm	Difference in readings, cm	Head loss,* ft H_2O
18	14.3	37.5	23.2	1.409
10	21.0	30.8	9.8	0.595
18	14.2	37.5	23.3	1.414
12	19.5	32.3	12.8	0.777
18	14.3	37.4	23.1	1.402

* (Difference in readings, cm) x 6.07×10^{-2} = ft of water

(continued)

Flow meter reading	Bromoform Manometer reading Left leg, cm	Right leg, cm	Difference in readings, cm	Head loss,* ft H_2O
14	17.7	34.0	16.3	0.990
18	14.2	37.5	23.3	1.414
16	16.0	35.7	19.7	1.195
18	14.2	37.5	23.3	1.414
0	25.9	25.9	0.0	0.000

The results of the flow meter check compared favorably with the results that would be expected according to the calibration of the flow meter:

Flow meter reading	Expected rate of flow, ml per min	Actual rate of flow, ml per min	Per cent difference from expected rate
18	186	184	1.1
16	161	158	1.9
14	136	133	2.2
12	111	106	4.5
10	87	82	5.8

The ratio of streaming potential to head loss, E/P, is needed for computing the zeta potential. It was determined as follows:

Flow rate change, meter readings	Head loss		Difference in head loss, ft H_2O	Difference in streaming potentials, mv	E/P mv per ft H_2O
	Average for higher flow, ft H_2O	Value for lower flow, ft H_2O			
18-10-18	1.412	0.595	0.817	75.0	91.8
18-12-18	1.408	0.777	0.631	59.5	94.3
18-14-18	1.408	0.990	0.418	37.0	88.5
18-16-18	1.414	1.195	0.219	20.5	93.6
18-0	1.414	0.000	1.414	127.0	89.9
				Total —	458.1
				Average —	91.6

The conversion factor from pressure loss in feet of water to the MKS units is 3000 kilograms per meter-second^2 per foot of water. Thus,

$$\zeta = - \frac{(4\pi)(0.8545 \times 10^{-3})(8.99 \times 10^{9})(91.6)}{(77.2)(1441)(3000)} = - 21.6 \text{ mv.}$$