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IN A FLOWING MEDIUM

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the
Degree Doctor of Philosophy in the Graduate School of
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by


***

The Ohio State University
1966

Approved by

Glenn O. Schwab
Adviser
Department of Agricultural Engineering
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VITA

May 14, 1939 Born - Hamilton, Ohio

1963 .................. B.A.E., M.S., The Ohio State University, Columbus, Ohio (combined degree program)

1963 .................. Teaching Assistant, Department of Agricultural Engineering, The Ohio State University, Columbus, Ohio

1964-1965 .................. Graduate Fellow, Natural Resources Institute, The Ohio State University, Columbus, Ohio

1965-1966 .................. Assistant Instructor, Department of Agricultural Engineering, The Ohio State University, Columbus, Ohio

PUBLICATIONS


FIELDS OF STUDY

Major Field: Engineering

Studies in Applied Mathematics. Professors William J. Davis and Ross D. Brazee

Studies in Colloid Chemistry. Professor Quentin Van Winkle

Studies in Theoretical Physics. Professor Wave H. Shaffer

Studies in Diffusion Theory. Professor Ross D. Brazee
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CHAPTER I

INTRODUCTION

Water is one of our most important resources. For us today, water is as necessary for life and health as it was for our prehistoric ancestors. Like air, water is bound up with man's evolution—and doubtless his destiny—in countless ways. One of the basic conditions for life on earth is that water be available in the liquid form.

Every organic process can occur only in a watery medium. The embryo floats in a liquid from conception to birth. Breathing, digestion, glandular activities, heat dissipation, and secretion can be performed only in the presence of watery solutions. Water acts as a lubricant, helps protect certain tissues from external injury, and gives flexibility to the muscles, tendons, cartilage, and bones.

The "Water Problem"—the problem of how to have water in adequate quantity and of adequate quality, available at reasonable cost, when and where needed—is one of world-wide importance. As population, irrigation, and industrialization increase, the water problem is becoming increasingly serious.

One of the primary problems in clarification of water by rural users who must treat their own domestic supply is the removal of small colloidal particles from suspension. Colloidal particles are difficult to remove with slow or rapid sand filters, and with other mechanical
filtration techniques. This difficulty limits the degree of clarification which can be attained. A method which has been investigated to help alleviate this problem involves the electrochemical process known as electrophoresis.

Electrophoresis may be defined as the movement or migration of suspended particles in a dc electric field. Utilizing this principle, negatively charged colloids are removed from suspension by migration in an electric field and subsequent deposition on the anode.

The purpose of the research reported in this account was to gain further understanding of the electrophoretic process for charged colloidal particles suspended in a flowing medium. Theoretical investigations were made, followed by some pertinent verifying experiments.
CHAPTER II

LITERATURE REVIEW

In this chapter, only research which directly applies to the subject of this dissertation will be reviewed. Literature which was utilized in the development of the theoretical and experimental portions of this work will be discussed under those headings.

Boyd (1963) has utilized the electrochemical process of electrophoresis as a method for the economic removal of colloidal and particulate suspension from heavy water at the Hanford Plutonium Recycle Test Reactor. In this method, electrophoresis was coupled with standard filtration and ion exchange processes to effect the complete removal of the following contaminants:

1. Oil in colloidal suspension,
2. Oil in emulsion,
3. Finely divided particles of dust and rust in suspension, and
4. Metallic ions.

Economic studies showed that utilization of this process reduced the cost of removal of items 2, 3, and 4 above by a factor of four over any previous method used at PRTR. It was the only process found in an extensive study that would remove colloidal suspensions of oil from the heavy water. The other processes studied which failed to overcome the problem included all combinations of filtration (filter sizes as low
as 0.45 microns), ultrasonic vibrations, charcoal adsorption, and chemical flocculation.

Kucha (1964) investigated the electrophoretic removal of clay colloids from water as a method of clarification. A parallel-plate configuration was utilized for the stainless-steel electrodes. The suspensions consisted of single distilled water and a bentonite clay. "Natural" water was also tested. An economic analysis of this method of clarification was made and the results were compared with those for conventional methods of municipal water treatment. Kucha concluded that (1) the practicality of the electrophoretic method decreased as suspension conductivity increased, and (2) the application of electrophoresis as a method of clarifying turbid water was too problematic to be practical. In the author's opinion, Kucha's conclusions are somewhat in jeopardy because he utilized stainless-steel electrodes of low corrosion resistance. These electrodes corroded to the extent that in some instances iron concentrations as high as 0.6 milligrams per liter were measured in the effluent suspension. High iron concentrations will increase the suspension conductivity and thereby increase the amount of electrolysis occurring in the system. A high degree of electrolysis will appreciably reduce the efficiency of the electrophoretic method.

Cooper, Mees, and Bier (1965) conducted an experimental investigation regarding the utilization of forced-flow electrophoresis as a method for water purification. The specific method of forced-flow electrophoresis, developed by Bier (1959), is somewhat similar to electrodialysis in that it involves the utilization of electrophoresis in combination with membrane filtration. It differs in that the water passes through the filter while the charged colloids are attracted away
from the filter by electrophoretic transport. The removal of bacteria, insecticides, algae, and colloidal clays from raw waters was investigated. On the basis of their experimental study, Cooper, Mees, and Bier (1965) concluded that at least two areas of potential application of this method should be considered. They are as follows:

1. Concentration of micro-organisms or dilute solutions of certain organic chemical compounds for purposes of identification and/or quantitative analysis, and
2. Removal of colloids and supra-colloids from surface waters.

It is added that although both applications may conceivably involve plant scale installations, the latter probably holds the greatest promise.

Hiler (1963) (1965) investigated an electrokinetic method for removal of colloidal clays from suspension. Theoretical equations for the movement of individual charged colloidal particles in an electric field were developed for movement between (1) two parallel flat plates and (2) a rod and a concentric cylinder. Experimental tests were made with a model consisting of a stainless-steel rod and cylinder as the positive and negative electrodes, respectively. Suspensions prepared from both colloidal kaolin and Wyoming bentonite were studied. Tests were made at influent concentrations of 25, 100, and 250 milligrams per liter for electric field strengths of 50, 150, and 250 volts per centimeter. Additional tests were made to determine the effects of rate of flow and volume of flow of suspension through the system. Pertinent conclusions of Hiler's investigation were:

1. The principle of electrophoresis can be successfully utilized in removing kaolin and bentonite from suspension.
(2) The theoretical removal of colloid from suspension differed from the actual removal in most cases. These differences were attributed primarily to the fact that actual values of electrical charge of the clay particles could not be determined.

(3) For a given influent concentration of suspension, the effluent concentration increased with an increasing flow rate of suspension through the system.

(4) The percentage reduction in effluent concentration compared to influent concentration of suspension increased with increasing electric field strength up to a given value of field strength which depended on properties of the suspension.

(5) Electrolysis of water molecules and heat transfer losses caused a reduction in efficiency of the system at high electric field strengths.

(6) The efficiency of removal of colloid from suspension decreased with an increase in deposition of clay on the rod (anode).

(7) More clay was deposited near the ends of the rod than in the central portion of the rod.

(8) The percentage removal of colloid from suspension was statistically equivalent for the two clays investigated.

(9) The electrokinetic system can be cleaned by reversal of the electric current flow through the system.

Hiler (1963) (1965) indicated that discrepancies between theoretical and experimental results could be at least partially attributed to the fundamental theoretical assumptions which were inherent in the single-particle approach. They were as follows:

1. Homogeneous suspension,
2. Laminar flow,
3. Equal charges on all particles, and
4. No particle interaction, i.e., isolated particles.

The first two assumptions were considered reasonably valid in this
study; however, the last two were probably not valid. One recommenda-
tion for future research in this area was as follows:

The theory of the movement of charged, colloidal clay particles in an electric field should be investigated further. The presently accepted theory leaves much to be desired when applied to electrophoresis of small, colloidal clay particles. The application of diffusion theory to the movement of clay particles in an electric field may be a better approach because with this type of analysis the whole colloidal system rather than a single particle can be considered.
The purpose of the research presented in this chapter was to investigate basic theoretical relationships for the electrokinetic movement of colloids in flowing fluid suspension. The essential basis of these considerations was the theory of stochastic processes whereby one seeks a description of a phenomenon in terms of the probability distributions of position and/or velocity at a later time, starting from given initial distributions. In this manner, although possible particle interactions are neglected, particle concentrations can be considered on a probabilistic basis rather than deterministically. Equations will be developed for both "pseudo-laminar" and turbulent flow conditions. For the pseudo-laminar case\(^1\), theories of Brownian diffusion form the basis for these considerations; the background for the turbulent flow case is provided by theories of turbulent diffusion. It is intended that these equations may be utilized to predict colloid concentration at position \(x\) at time \(t\) for a given influent concentration.

---

\(^1\)This case refers to velocities at which random velocity fluctuations are of low enough magnitude to be unimportant.
Chandrasekhar (1943) has presented an excellent review of the theories of Brownian movement. His writings form the background for much of the presentation in this section.

Modern Brownian motion theory for a particle immersed in a fluid generally starts with the Langevin equation, which may be written:

\[ \frac{dv}{dt} = -\beta v + A(t) + K(x) \quad , \tag{1} \]

where \( x \) is the position and \( v \) the velocity of the particle. The effect of the medium is assumed to be separable into two parts, a dynamic friction, \(-\beta v\), and a rapidly fluctuating term \( A(t) \). The principal assumptions regarding the fluctuating term, \( A(t) \), are (1) \( A(t) \) is independent of \( v \), and (2) \( A(t) \) varies rapidly compared with the variations of \( v \). This second assumption implies that time intervals of duration \( \Delta t \) exist such that during \( \Delta t \) the variations in \( v \) that are to be expected are very small indeed, while during the same time interval \( A(t) \) may undergo several fluctuations. Alternatively, we may say that though \( v(t) \) and \( v(t + \Delta t) \) are expected to differ by a negligible amount, no correlation between \( A(t) \) and \( A(t + \Delta t) \) exists.

Regarding the frictional term \(-\beta v\) it is assumed in this section that this is governed by Stokes' law which states that the frictional deceleration of a spherical particle of radius \( a \) and mass \( m \) is given by \( \frac{6\pi \rho a v}{m} \), where \( \rho \) denotes the coefficient of viscosity of the surrounding fluid. Hence it follows that \( \beta = \frac{6\pi \rho a}{m} \quad . \tag{2} \)

\(^2\)A glossary of symbols is given following the Appendix.
The last term, $K(x)$, in equation (1) represents the acceleration caused by any field of force acting on the particle.

Chandrasekhar (1943) gives a convenient formulation of the properties of $A(t)$. If we define a new vector $B(\Delta t)$ as

$$B(\Delta t) = \int_t^{t+\Delta t} A(\tau) d\tau ,$$

then the probability density for the values of $B(\Delta t)$ is

$$W[B(\Delta t)] = \left( \frac{1}{\pi \alpha q \Delta t} \right)^{\frac{3}{2}} \exp \left( -\frac{|B(\Delta t)|^2}{4q \Delta t} \right) ,$$

where $q = \frac{\beta kT}{\mu}$. The absolute temperature of the fluid is $T$, and $k$ is Boltzmann's constant.

The Langevin equation is valid only for a single particle. However, it is quite important in that it provides the basis for derivation of equations in which an entire ensemble of particles can be considered.

Let $\Delta t$ denote an interval of time which is long compared with the periods of fluctuations of the acceleration $A(t)$ occurring in the Langevin equation but short compared with intervals during which the velocity of a Brownian particle changes by appreciable amounts. Then the increments $\Delta x$ and $\Delta v$ in position and velocity which the particle suffers during $\Delta t$ are

$$\Delta x = v \Delta t ; \quad \Delta v = - (\beta v - K) \Delta t + B(\Delta t) .$$

Assuming that the Brownian movement can be idealized as a Markov process it is possible to derive the probability distribution

$$W(x, v, t+\Delta t)$$
governing the probability of occurrence of $x$ and $v$ in

---

3A Markov process is a process which possesses the characteristic that what happens at a given instant of time $t$ depends only on the state of the system at time $t$. 

phase space at time \( t + \Delta t \) from the distribution \( W(x, v, t) \) at time \( t \) and a knowledge of the transition probability \( \psi(x, v, \Delta x, \Delta v) \) that \( x \) and \( v \) suffer increments \( \Delta x \) and \( \Delta v \) in time \( t \). For the conditions of equation (5), Chandrasekhar (1943, p. 34) writes

\[
W(x, v, t + \Delta t) = \int W(x - \Delta x, v - \Delta v, t) \psi(x, v, \Delta x, \Delta v) d(\Delta x) d(\Delta v) ,
\]

where

\[
\tilde{W}(x, v; \Delta x, \Delta v) = \psi(x, v; \Delta v) \delta(\Delta x_1 - v_1 \Delta t) \delta(\Delta x_2 - v_2 \Delta t) \delta(\Delta x_3 - v_3 \Delta t).
\]

In equation (7), the \( \delta \)'s denote Dirac's delta function and \( \psi(x, v; \Delta v) \) the transition probability in the velocity space. Utilizing equations (5), (6), and (7), Chandrasekhar (1943, p. 35) derives the following partial differential equation:

\[
\frac{\partial W}{\partial t} + v \cdot \text{grad}_x W + K \cdot \text{grad}_v W = \beta \text{div}_v(Wv) + q \nabla_v^2 W.
\]

Equation (8) is the Fokker-Planck equation in phase space. It is a fundamental equation for the description of Brownian movement in terms of probability distributions. The terms arising from Brownian motion occur on the right-hand side of equation (8), while on the left-hand side the usual Stokes operator \( \frac{D}{Dt} \) is acting on \( W \).

All of the physically significant questions regarding Brownian movement can be answered by solving equation (8) with the appropriate boundary conditions. However, if one is interested only in time intervals that are very large compared with the "time of relaxation" \( \beta^{-1} \) and space intervals of the order of \( \left( \frac{q}{\beta^2} \right) \), the Fokker-Planck equation in phase space can be utilized to derive an equation in configuration space (\( x \)) which is independent of velocity space. Chandrasekhar
(1943, p. 41) notes that if one starts with an arbitrary initial distribution $W(x,v,0)$ at $t = 0$, it is to be expected that a Maxwellian distribution of the velocities will be established at all points after $\Delta t \gg \beta^{-1}$ and for $\Delta x \gg \left( \frac{a}{\beta^3} \right)^{\frac{1}{2}}$. Thus, with these restrictions, one can write

$$W(x,v,t) \approx \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp \left( - \frac{m|v|^2}{2kT} \right) P(x,t). \quad (9)$$

Utilizing equations (8) and (9), Chandrasekhar (1943, p. 41) derives the following equation:

$$\frac{\partial P(x,t)}{\partial t} = \text{div} \left( \frac{q}{\beta^2} \text{grad}_x P(x,t) - \frac{K(x)}{\beta} P(x,t) \right). \quad (10)$$

Equation (10) is often called the Smoluchowski equation. The term $P(x,t)$ is a probability density function for position $x$ at time $t$.

It should be noted at this point that the coefficient $\frac{q}{\beta^2}$ of the first term on the right-hand side of equation (10) is precisely the diffusion coefficient for Brownian particles which was first derived by Einstein (1905).

Note once again that equation (10) is valid only if effects that happen in time intervals of the order of $\beta^{-1}$ and space intervals of the order of $\left( \frac{a}{\beta^3} \right)^{\frac{1}{2}}$ are ignored. For clay-water systems, characteristic values of these constants are $\beta^{-1} \approx 10^{-6}$ seconds and $\left( \frac{a}{\beta^3} \right)^{\frac{1}{2}} \approx 10^{-6}$ centimeters. Thus, equation (10) with appropriate boundary conditions will be utilized for the pseudo-laminar flow case where random velocity fluctuations are negligible.
In this section a description of the electrokinetic movement of charged colloidal particles in a turbulent medium is sought. Portions of the work presented in this section are based on theories of turbulent diffusion first proposed by Batchelor (1949) (1952).

Throughout this section it is presumed that diffusion is taking place in a spatially homogeneous turbulence of stationary character; however, no restrictions are placed on the directional characteristics. In these considerations, the diffusion of some transportable property, which at some initial instant is possessed by fluid particles within a specified tagged volume, is treated. It is assumed that the diffusion property confers no new dynamical properties upon the transporting fluid.

In turbulent diffusion theory, two types of analysis have been defined, viz., Eulerian and Lagrangian. In the Eulerian analysis, one investigates the probable concentration of the diffusion property at fixed points of space at different instants of time. In the Lagrangian analysis, the inquiry is concerned with the probable distribution of the diffusing property with respect to points which follow the fluid motion. The contents of this chapter deal primarily with the Eulerian type of analysis.

Suppose that at time \( t = t_0 \) the fluid within a certain region of space of volume \( V \) possesses with unit intensity the property that is being diffused; this defines the marked fluid. Then the problem is to find the distribution of average intensity or concentration of this property at subsequent times. This is equivalent to finding the
probability \( P(x,t) \) that the point defined by the position vector \( x \) lies within the marked fluid at time \( t \), and the initial condition gives

\[
P(x,t) = \begin{cases} 1 & \text{for } x \text{ inside } V \\ 0 & \text{for } x \text{ outside } V. \end{cases} \tag{11}
\]

The volume of the marked fluid is the same at all times; thus it follows that

\[
\int P(x,t) dV(x) = V, \tag{12}
\]

where \( dV(x) \) is an element of volume at position \( x \) and the integration is over the entire space.

Let us now introduce the probability density function \( Q(x,t;t_0) \) of the displacement \( x \) of a fluid particle over the time interval \( t_0 \) to \( t \). If the form of this probability density function can be established, the spatial distribution of the mean concentration of the property carried by the fluid particles can be determined, and there is a possibility of obtaining a differential equation for the propagation (in time) of this mean concentration. The probability that a fluid particle at time \( t \) will lie within a volume element \( dV(x) \) whose center is at position \( x \) relative to the initial position of the particle is \( Q(x,t) dV(x) \). Hence the mean concentration for a finite volume of marked fluid is

\[
P(x,t) = \int P(x',t_0) Q(x-x',t;t_0) dV(x') , \tag{13}
\]

where \( x' \) is the initial position of the particle. Equation (13) can be written alternatively as

\[
P(x,t) = P(x,t_0) * Q(x,t;t_0) , \tag{14}
\]
where the asterisk denotes convolution and $X = \mathbf{x} - \mathbf{x}'$ is the particle displacement.

It is convenient at this point to introduce the Fourier transforms of the probability density functions in equation (14). Define the Fourier transforms

$$G(\mathbf{\epsilon}, t) = \int \mathbf{p}(\mathbf{x}, t) e^{i\mathbf{\epsilon} \cdot \mathbf{x}} \, d\mathbf{x}$$

(15)

and

$$H(\mathbf{\epsilon}, t) = \frac{1}{V} \int \mathbf{q}(\mathbf{x}, t; t_0) e^{i\mathbf{\epsilon} \cdot \mathbf{x}} \, d\mathbf{x}$$

(16)

where $\mathbf{\epsilon}$ is a wave number vector. Then an alternative form of equation (14) is

$$G(\mathbf{\epsilon}, t) = G(\mathbf{\epsilon}, t_0) \, H(\mathbf{\epsilon}, t)$$

(17)

Thus the diffusion of a marked fluid relative to a fixed point is determined by the initial location of the marked fluid and by the probability density function of the displacement of the fluid particle.

On the basis of experimental evidence\(^4\), it is presumed that the distribution of displacements $X(t)$ is Gaussian. This result can be expressed as

$$H(\mathbf{\epsilon}, t; t_0) = \exp\left\{ -\frac{1}{2} \mathbf{\epsilon}_i \mathbf{\epsilon}_j \overline{X_i(t)X_j(t)} \right\}$$

(18)

where the overbar denotes expectation [see Cramer (1946, p. 311)].

Equations (17) and (18) permit deduction of the fact that

---

\(^4\)For pertinent references, see Batchelor (1949).
$G(\varepsilon, t)$ satisfies the differential equation

$$\frac{\partial G(\varepsilon, t)}{\partial t} = -\mu_{ij} \varepsilon_i \varepsilon_j G(\varepsilon, t), \quad (19)$$

so that by equation (16),

$$\frac{\partial P(x, t)}{\partial t} = \mu_{ij} \frac{\partial^2 P(x, t)}{\partial x_i \partial x_j}, \quad (20)$$

where

$$\mu_{ij}(t) = \frac{1}{2} \frac{\partial x_i(t) x_j(t)}{\partial t} \quad (21)$$

Hence, $P(x, t)$ satisfies a partial differential equation with a tensorial diffusion coefficient $\mu_{ij}$ which is dependent upon the dispersion tensor $X_i X_j$. For isotropic turbulence, the right-hand side of equation (20) becomes the ordinary Laplacian.

In order to define the diffusion coefficient $\mu_{ij}$ more explicitly, it is convenient to introduce the Lagrangian correlation coefficient $R_{ij}(\tau)$ and the Lagrangian time scale $L_t$. They are defined as follows:

$$R_{ij}(\tau) = \frac{u_i(t) u_j(t+\tau)}{u_i u_j}; \quad (22)$$

$$L_t = \frac{1}{2} \int_0^\infty [R_{ij}(\tau) + R_{ji}(\tau)] \, d\tau \quad (23)$$

The term $u$ refers to fluid velocity while $u'$ is the root-mean-square fluid velocity, $\sqrt{\overline{u'^2}}$. With these definitions, $\mu_{ij}$ can be written as

$$\mu_{ij}(t) = u'_i u'_j \int_0^t \frac{1}{2} [R_{ij}(\tau) + R_{ji}(\tau)] \, d\tau \quad (24)$$

It has been shown [Hinze (1959), Chapter 5] that

for $t \ll L_t$, \quad $\mu_{ij} = \overline{u_i u_j} \, t$ \quad (25)

while for $t \gg L_t$, \quad $\mu_{ij} = u'_i u'_j L_t$
Thus far a plausible description for the turbulent motion of a fluid particle with no external force fields acting has been achieved. This description is incomplete for the electrokinetic system of this study because the action of the external force fields has not been considered. The problem at this point then is to bring the external field forces into equation (20) in a compatible manner.

In recent years, the fundamental ideas and techniques of the theory of Brownian motion have been applied to the phenomenon of turbulent diffusion [Obukhov (1959), Lin (1960a) (1960b), Lumley (1961), Chadam (1962)]. Chadam (1962) has shown that the motion of a particle in a turbulent fluid is governed by a Langevin equation similar to that arising in theories of Brownian motion. The generalized Fokker-Planck equation [equation (8)] for Brownian movement also is based on the Langevin equation [equation (1)]. The Smoluchowski equation [equation (10)] is a special case of the Fokker-Planck equation and has a structure similar to that of the turbulent diffusion equation (20). Thus it does not seem unreasonable that the external force could be introduced into the structure of the turbulent diffusion equation in a manner similar to that of the Smoluchowski equation.

Chadam (1962) has shown that the Lagrangian motion of a fluid particle is governed by

\[ \frac{du(t)}{dt} + \beta u(t) = A(t) , \quad u(t) = \frac{d[x(t)]}{dt} , \]

where \(x(t)\) and \(u(t)\) are the position and velocity of the particle, respectively, in the Lagrangian sense. The random accelerations \(A(t)\) must satisfy
(a) $A(t)$ is a stationary random process;

(b) $E(t)u(t) = 0$;

(c) $\int_0^\infty \frac{A(t+\tau)A(t)}{t^2} d\tau = \int_0^\infty R(\tau) d\tau = \int_0^{t^*} R(\tau) d\tau = B$

and (d) $E(t) = 0$.

Suppose an ensemble of particles starts at $t = t_0 = 0$ with $x_0 = 0$ and a velocity $u_0$. The motion of these particles is governed by equation (26). The solution of this equation is then given by

$$u(t) = u_0 e^{-\beta t} + e^{-\beta t} \int_0^t e^{\beta \tau} A(\tau) d\tau ,$$

$$x(t) = \frac{u_0}{\beta} (1 - e^{-\beta t}) - \frac{1}{\beta} e^{-\beta t} \int_0^t e^{\beta \tau} A(\tau) d\tau + \frac{1}{\beta} \int_0^t A(\tau) d\tau .$$

Now using techniques characteristic of Brownian motion, Chadam (1962) has shown that as $t \to \infty$

$$\overline{x(t)^2} = 2B \left( t - \frac{3}{2\beta^2} \right) \approx 2 \frac{B}{\beta^2} t .$$

This result agrees with the original results of Taylor (1921) considering turbulent diffusion by continuous movements. Taylor, however, considered random velocities obtaining

$$\overline{x(t)^2} = 2Dt ; \quad D = \int_0^\infty u(t+\tau) u(t) d\tau ,$$

where $D$ is a diffusion coefficient. From equation (28) and (29), it follows that

$$D = \frac{B}{\beta^2} .$$

From the theory of Brownian motion [Einstein (1905)], recall that

$$D = \frac{4}{\beta^2} .$$
Thus, for Brownian movement, it follows that

\[ \langle x(t)^2 \rangle = 2Dt = 2 \frac{q}{\beta^2} t \quad . \quad (32) \]

Hence, in a mathematical sense, it follows from equations (30) and (32) that

\[ B = q. \quad (33) \]

This is the important relation which is necessary to effect the passage from the Smoluchowski equation for Brownian movement to the appropriate turbulent diffusion equation.

Now substituting \( B \) for \( q \) in the Smoluchowski equation (10), one obtains the following equation for turbulent diffusion of particles under the influence of an external force field:

\[ \frac{\partial P(x,t)}{\partial t} = \text{div}_x \left( \frac{B}{\beta^2} \text{grad}_x P(x,t) - \frac{K(x)}{\beta} P(x,t) \right) . \quad (34) \]

Utilizing equations (29) and (30) and letting \( D(t) \) be the conventional \( \mu(t) \) for turbulent diffusion, one can rewrite equation (34) in tensorial notation as follows:

\[ \frac{\partial P(x,t)}{\partial t} = \mu_{ij} \frac{\partial^2 P(x,t)}{\partial x_i \partial x_j} - \frac{1}{\beta} \frac{\partial}{\partial x_j} \left[ K_j P(x,t) \right] , \quad (35) \]

for \( i, j = 1, 2, 3 \).

Equation (35) with the appropriate boundary conditions will be utilized for the case where turbulent flow conditions are encountered. It should be noted at this point, however, that the structure of \( \beta \), the viscous resistance coefficient, may not necessarily be the same for the turbulent case as it was for the Brownian case.

An important consideration for the turbulent flow case at this point is that of particle-fluid coupling. This problem has been
attacked by applying methods of solving stochastic differential equations [Bartlett (1955)] to a typical turbulent Langevin equation. It has been shown that

\[ (p) \phi(\omega) = \frac{\beta^2}{\omega^2 + \beta^2} \phi(\omega) \]  

(36)

where \( \omega \) is frequency and \((p)\phi(\omega)\) and \(\phi(\omega)\) are the spectral density functions for the particle and the fluid, respectively. From equation (36), it follows that the condition for "perfect" coupling,

\[ (p)\phi(\omega) = \phi(\omega) \]  

is

\[ \omega^2 \ll \beta^2 \]  

(37)

This condition is quite easily met for clay-water systems for which \( \beta^2 \approx 10^{12} \text{ sec}^{-1} \), when \( \beta \) is defined as in equation (2).

Application to Problem

In this section, equations (10) and (35) for the pseudo-laminar and turbulent flow conditions, respectively, will be applied specifically to the electrokinetic movement of colloids in flowing fluid suspension. It is assumed here that all other external force fields are negligible in comparison with the electric field. Preliminary calculations indicate that this assumption is quite valid for the conditions of this investigation. Let us note that the probability density \( P(x,t) \) can be interpreted physically as the concentration \( c(x,t) \) at position \( x \) at time \( t \).

For the acceleration \( K(x) \) of charged colloidal particles in an

\footnotesize{References: Csanady (1963), Hinze (1959, p. 354).}
electric field $E(x)$, one can write

$$\kappa(x) = \frac{\sigma E(x)}{m}, \quad (38)$$

where $\sigma$ is electric charge density and $m$ mass density of the colloidal particles. Making this substitution into equations (10) and (35) for the electric field acting in the $x_1$-direction, one can write

$$\frac{\partial c(x,t)}{\partial t} = \frac{q}{\beta^2} \frac{\partial^2 c(x,t)}{\partial x_1^2} - \frac{\sigma}{m \beta} \frac{\partial}{\partial x_1} [E(x_1)P(x,t)] \quad , \quad (39)$$

$$i = 1, 2, 3,$$

$$\frac{\partial c(x,t)}{\partial t} = \mu_{ij} \frac{\partial^2 c(x,t)}{\partial x_i \partial x_j} - \frac{\sigma}{m \beta} \frac{\partial}{\partial x_1} [E(x_1)P(x,t)] \quad , \quad (40)$$

$$i, j = 1, 2, 3.$$

Thus, equations (39) and (40) for the pseudo-laminar and turbulent flow cases, respectively, may be utilized to describe the electrokinetic movement of an ensemble of charged colloids in flowing fluid suspension.
CHAPTER IV

EXPERIMENTAL INVESTIGATION

The objective of this portion of the study was to verify the theory presented in the previous chapter. A parallel-plate electrode configuration was utilized in the experimental model. The suspension studied was prepared from colloidal kaolin and deionized water. Mass concentration of colloid was measured at various points in the system both in situ on a continuous basis and by withdrawing samples. Both determination methods involved light transmittance measurements. Charge concentration was measured indirectly at various points in the system by utilizing potentiometric determinations. The following flow and/or turbulence characteristics of the medium were measured with a hot-film anemometer and spectral density analyzer: (a) velocity profile, (b) spectral density, and (c) root-mean-square (rms) velocity of turbulence.

Materials

Water

The suspensions for this investigation were prepared in water which was deionized first in a large two-bed deionizer and then brought to final quality by passage through a small mixed-bed deionizer. The specific conductivity of this water was maintained between 1.0 and 2.0 micromhos per centimeter.
Clay

The clay suspensions were prepared with colloidal kaolin. This clay, with the trade name "Kaolin NF Colloidal", was obtained from the Mallinckrodt Chemical Works, St. Louis, Missouri. The cation exchange capacity of this clay was very low, ranging from three to five milliequivalents per 100 grams. Specifications of this clay, as presented by the producer, are shown in Table 1. A particle-size distribution for this clay was given by Hiler (1963). The mean particle "radius" was found to be 0.3 micron. Hiler (1963) (1965) also showed an electron micrograph of this clay. The electrophoretic mobility of this clay was determined to be 4.0 microns per second per volt per centimeter [Hiler, (1963)] .

Table 1. Kaolin Specifications

<table>
<thead>
<tr>
<th>Test</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Fine, soft white or yellowish-white power</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless to a faint clay-like odor</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>15.0% maximum</td>
</tr>
<tr>
<td>Identification</td>
<td>To pass NF a test</td>
</tr>
<tr>
<td>Carbonate</td>
<td>To pass NF test</td>
</tr>
<tr>
<td>Acid-soluble substances</td>
<td>2.0% maximum</td>
</tr>
<tr>
<td>Iron</td>
<td>To pass NF test</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.001% maximum</td>
</tr>
</tbody>
</table>

Source: Personal communication with Mallinckrodt Chemical Works.

aNF refers to National Formulary. Standards for chemical quality control of various substances are established by National Formulary.
Experimental Model

As mentioned earlier, a parallel-plate electrode configuration was utilized in the experimental model. The experimental model is shown in Figures 1 and 2. The model was located in a large chamber which was blackened on the inside for maximum light absorption; also, a grounded wire screen was fastened to the inside of the chamber for electrical shielding purposes (see Figure 2). All of the equipment utilized in this study was located in a laboratory where the temperature could be controlled to within one Centigrade degree. Because of this small variation, the environmental temperature was considered to be constant in the analysis of the data.

The electrodes for the experimental model were made from type 304 stainless steel. This electrode material was chosen specifically because of its superior corrosion resistance characteristics. The dimensions of each of the two electrodes were 76 centimeters long, five centimeters wide, and 0.32 centimeter thick.

The experimental model itself was constructed from one-half inch "Plexiglas G" clear sheets. This material was chosen for its minimal light absorbance and reflectance characteristics.

The entrance and exit sections of the experimental model were designed to effect smooth transitions to and from uniform flow conditions, respectively. As shown in Figure 1, a screen of 0.15 centimeter grid size was placed across the center of the entrance section. The purpose of this screen was to enhance breakup of jets which may pass into the entrance section.

As illustrated in Figure 1, the suspension passed from a large
Figure 1. Schematic Diagram of Experimental Arrangement
Figure 2. Experimental Model
supply to the initial constant head device and up through the parallel-plate experimental model. Utilizing an external power supply, a dc electric field was set up between the stainless-steel electrodes. The negatively charged clay was deposited on the positive electrode (anode). The rate of flow of suspension through the system was controlled to the desired value by the position of the outlet. From the outlet, the water passed to a graduated container from which the total volume and rate of flow through the system could be measured. Temperature was recorded continuously at the inlet and outlet positions as shown in Figure 1. Taps were placed at various locations on the experimental model for withdrawing samples and for the insertion of various sensors.

Sensors

Four different types of sensors were utilized in this study. These sensors were selected for the measurement of the following parameters: (a) mass concentration of colloid in situ on a continuous basis; (b) mass concentration of colloid by withdrawing samples; (c) charge concentration of colloid; and (d) turbulence characteristics of the flowing medium. Each of these sensors will be discussed together with the necessary instrumentation to implement their use.

Mass concentration - in situ

One of four devices constructed for determination of mass concentration of colloid in situ on a continuous basis is shown in Figure 3. The principle utilized with this sensor is that light transmittance through a colloidal suspension is proportional to the colloid
Figure 3. Device for Determination of Mass Concentration In Situ

Figure 4. Device for Withdrawing Samples
concentration of suspension. This principle is formulated in the Lambert-Beer law,

\[ I = I_0 e^{-\nu sc} \]  \hspace{1cm} (41)

where \( I \) and \( I_0 \) are the intensities of transmitted and entering light, respectively, \( \nu \) is an absorption constant, \( s \) is the length of the light path through the suspension, and \( c \) is the concentration of suspension. The primary components of an individual sensor were (a) a lamp, (b) two blackened light tubes, and (c) two photovoltaic cells whose voltage output was proportional to the intensity of light reaching them. The purpose of the blackened light tubes was to provide collimated light beams for measurements. In the device shown in Figure 3, there are three individual sensors. Two photocells were utilized differentially with each sensor to compensate for any fluctuation in current through the lamp filament. A regulated dc power supply was used to energize the lamps. General Electric number 1815 lamps with a candlepower of 14 candles at 14 volts and 0.20 ampere were utilized in each sensor. The photovoltaic cells were International Rectifier model B2M.

One of these mass concentration devices as attached to the experimental model is shown in Figure 5. The experimental model with the instrumentation for the mass concentration \textit{in situ} determination is shown in Figure 7. The signals from the photocells passed to a programming board where various sequential arrangements could be accomplished. From the program board, the signals passed into a magnetic reed-switch scanner which was wired so that its output represented the difference between the outputs of the two photocells of each sensor.
Figure 5. Device for Mass Concentration In Situ Determination Attached to Experimental Model

Figure 6. System for Withdrawing Samples Showing Needles, Tubing, Flasks, and Manifold
Figure 7. Experimental Model with Instrumentation for Mass Concentration In Situ Determination
The values from the 12 sensors were scanned at a rate of approximately two sensors per second. A small dry-cell battery was also connected to scanner to provide a mark point. The scanner output was connected to a voltage-to-frequency converter which furnished the input to a counter. Individual values from each sensor and from the mark point were displayed on the counter and simultaneously printed on paper tape.

**Mass concentration - sampling**

The system for withdrawing samples for determination of mass concentration of colloid is shown in Figures 4 and 6. The primary components of this system included (a) 18-gauge hypodermic needles, (b) 0.27 centimeter inside diameter intramedic tubing, (c) tubing clamps, (d) 50 milliliter flasks, (e) a manifold, and (f) a vacuum pump. Prior to sampling, a vacuum was placed on the system up to a point near the end of the needle where the tubing was clamped. A sample of colloidal suspension was withdrawn by removing the clamp for a specified time. The sampling rate was approximately four milliliters per second; a sample of approximately 12 milliliters was necessary for the mass concentration determination. This determination was made with a Coleman model 14 spectrophotometer. The principle involved in this case was the same as that for the mass concentration in situ measurement.

The measurement of mass concentration by withdrawing samples was employed primarily to serve as an independent point check of the light-tube determinations. Also, one obtains somewhat better space resolution by withdrawing samples; the time resolution, however, is much better with the light-tube determination.
**Charge concentration**

An indirect determination of charge concentration was achieved by measuring the electrical potential between various points in the electric field and the grounded electrode. One of three identical sensors utilized for this determination is shown in Figure 8. These sensors were fabricated from shielded coaxial cable. They were four feet long and had a capacitance of 65 picofarads. The bare wire at the tip of the cable was insulated against charge leakage back through the cable by cementing the inner insulation of the coaxial cable to the glass tube around the cable with epoxy. The potential between each sensor and the grounded electrode was measured with an electrometer. Three electrometers were used to permit simultaneous potential measurements at three points.

**Turbulence**

Turbulence and flow characteristics of the flowing water were measured with a constant-temperature hot-film anemometer of which the sensor portion is shown in Figure 9. The most important part of this sensor is the small tungsten wire upon which is deposited the sensitive platinum film. The film sensor is coated with quartz to facilitate its use in water. The temperature of the tungsten wire was kept constant at 66° C in water at a temperature of 23° C. Velocity fluctuations of the flowing water were sensed by measuring the bridge-unbalance voltage which resulted from the anemometer's maintenance of the wire temperature at a constant value.

The hot-film anemometer was utilized either solely or in conjunction with other instrumentation for determination of the following
Figure 8. Sensor for Charge Concentration Determination

Figure 9. Sensor for Determination of Turbulence and Flow Characteristics
fluid characteristics: (a) velocity profile, (b) spectral density, and (c) rms velocity of turbulence. Anemometer signals were tape recorded and analyzed to determine spectral density and rms velocity by utilization of the respective instrumentation arrangements shown schematically in Figures 10 and 11. For calibration of the system shown in Figure 11, an oscillator replaced the three inputs to the initial operational amplifier and an rms voltmeter was in parallel with the circuit.

Testing Procedure

In the primary series of tests in which colloid concentrations (mass and charge) were determined, the input conditions to the experimental model remained constant for all tests. An influent clay concentration of 60 milligrams per liter was passed through the system at a rate of 250 milliliters per minute. The specific conductivity of influent colloidal suspension was maintained between one and two microhmhos per centimeter. The electric field strength between the parallel-plate electrodes was 100 volts per centimeter. The total volume of flow of suspension through the system for each test was eight liters. The temperature of the influent suspension and the room temperature were maintained at 23° C. The temperature of effluent suspension was also 23° C for all tests. Four replications of this series of tests were made. Mass concentration measurements both in situ and by withdrawing samples were made during one group of tests while charge concentration was measured during another series.

The locations of the light-tube devices and the sampling locations are shown in Figure 12. Samples were withdrawn after one liter and six liters of suspension had passed through the model. A continual record
Figure 10. Schematic Diagram of Instrumentation for Spectral Density Analysis
All resistors are one megohm.

dc

Input Signal
Correction for Mean

(dc Power Supply through Potentiometer)

Figure 11. Schematic Diagram of Instrumentation for rms Velocity Determination
Figure 12. Location of Light-Tube Sensors and Sampling Locations on Experimental Model
for the light-tube devices was recorded on the printer throughout each
test run. A preliminary test in which the voltage to the electrodes
was off indicated that gravitational sedimentation of colloid in the
experimental model was negligible. Calibration curves for the light-
tube devices and the spectrophotometer were also made in preliminary
tests.

The location of the potentiometric charge-concentration sensors
and the grounded electrode are shown in Figure 13. Voltages from these
sensors were recorded at 0.1 liter and at 0.5 liter intervals during
each test run.

For the turbulence measurements, no colloidal material was intro-
duced into the water since the particles tend to coat the sensor and
alter the heat exchange characteristic. The flow rate through the
system and the specific conductivity of the water were maintained at
the same values as for the previously discussed tests. A calibration
curve relating flow velocity and voltage output for the hot-film anem-
ometer was determined in the test column in a preliminary test. The
velocity profile of the flow was determined at the same locations as
measurements of charge concentration were made (see Figure 13). The
velocity profile was essentially flat at each of the three levels.

Signals of 10-minute duration for spectral density and rms velocity
determinations were recorded on magnetic tape at the locations shown in
Figure 13. The required duration of the signal was estimated from pre-
liminary measurements and stability considerations [Blackman and Tukey
(1958)]. At each of these locations, signals were recorded with the
film sensor wire (a) perpendicular to the direction of flow, (b) para-
llel to the flow direction, and (c) at angles of +45 degrees and
Figure 13. Locations of Charge Concentration and Turbulence Measurements on Experimental Model

- Charge Concentration Measurement
- Turbulence Measurement
- Tap Not Used
-45 degrees to the flow direction. Signals at these angles were necessary to evaluate the degree of anisotropy of the turbulence.

Results

The results obtained from the mass concentration in situ measurements are shown in Figures 14 through 17. Each of the curves represents an average of four replications. The differences among replications were not found to be statistically significant at the one percent level. The influent concentration for each of these tests was 60 milligrams per liter while the electric field strength was 100 volts per centimeter.

Mass concentration results obtained by sampling are shown in Table 2. Each of the values in this table also represents an average of four replications. This sampling was performed during the same tests in which the mass concentration in situ measurements were made. The differences among replications again were not found to be significant at the one percent level. The results were essentially identical after one liter and after six liters had flowed through the system.

The results of the potentiometric charge concentration determinations are shown in Figure 18. Since only three sensors were available, these nine measurements were made during three test runs. However, the influent conditions for each of these tests were the same as during the mass concentration determinations. As the charge concentration decreased between the potentiometric sensor and the grounded electrode, the electrical potential reading also decreased. This result would be expected theoretically. Thus, since the negative electrode was grounded, the results of this series of tests supported the mass concentration results.
Figure 14. Mass Concentration In Situ Results for Points a, b, and c
Figure 15. Mass Concentration In Situ Results for Points d, e, and f
Figure 16. Mass Concentration In Situ Results for Points g, h, and i
Figure 17. Mass Concentration *In Situ* Results for Points j, k, and l
Table 2. Mass Concentration Results by Sampling

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Concentration (mg./L.)</th>
<th>After 1 L.</th>
<th>After 6 L.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>59</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>57</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>57</td>
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<td></td>
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</tr>
<tr>
<td>18</td>
<td>36</td>
<td>36</td>
<td></td>
</tr>
</tbody>
</table>

See Figure 12 for sampling location on test column.

As mentioned earlier, the velocity profile measurements indicated that the velocity profile of fluid flow in the experimental model was flat, i.e., the velocity of fluid flow was constant across the column. Measurements were made to within one-half centimeter of the "Plexiglas" walls. Measurements closer to the walls were not made because of the possibility of mechanical damage to the delicate film sensor.

Root-mean-square velocity of turbulence determinations were made at locations 5, 10, and 15 on the experimental model. The rms velocity
Figure 18. Potentiometric Charge Concentration Results
of turbulence in the direction of fluid flow ($x_3$-direction) was found to be 8.0 centimeters per minute at location 5 while that at locations 10 and 15 was zero. By utilizing a procedure outlined by Hinze (1959, pp. 102-104), the rms velocity of turbulence in the direction of the electric field ($x_1$-direction) was found to be 5.8 centimeters per minute at location 5 and zero at locations 10 and 15. Turbulence characteristics of the flowing water could not be measured in the $x_2$-direction (mutually perpendicular to $x_1$- and $x_3$-directions) because of the physical arrangement of the experimental model. The work of Laufer (1951) provided many insights into both the rms velocity and the spectral density measurements.

Since the rms velocity at locations other than point 5 was not detectable, the energy spectral densities at point 5 are the only ones of interest here. The energy spectral density versus frequency curve in the $x_3$-direction for location 5 is shown in Figure 19. The semilogarithmic plot of these data in Figure 20 is a straight line down to the noise level of the instrumentation. Thus, the appropriate form of equation to fit this curve can be written as

$$\phi(\omega) = \frac{\alpha}{2} e^{-\alpha\omega} \quad (42)$$

For the data presented in Figures 19 and 20, $\alpha$ is computed to be 1.39 seconds (see Appendix). The correlation function, $R(\tau)$, is the Fourier transform of the spectral density. Thus, taking the Fourier transform of equation (42), one obtains

$$R(\tau) = \frac{\alpha^2}{\alpha^2 + \tau^2} \quad (43)$$
Figure 19. Spectral Density Curve at Point 5 on Experimental Model
Figure 20. Spectral Density Curve at Point 5 - Semilogarithmic Plot
From the definition of the Lagrangian time scale of turbulence in equation (23), it follows that

$$L_t = \frac{\kappa \alpha}{2} \quad \cdots \quad (44)$$

For location 5, one then obtains $L_t = 2.18$ seconds. The author was unable to determine the Lagrangian time scale in the $x_1$-direction with a very high degree of confidence. However, the range of possible values that was obtained was close to that for the $x_3$-direction. Thus, it was assumed that $L_t$ was the same in the $x_1$-direction as in the $x_3$-direction. Since all concentration observations in the experimental model were at times greater than 40 seconds,¹ it follows from equation (25) that the appropriate form of the turbulent diffusion coefficient is

$$\mu_{ij} = v_i v_j L_t \quad \cdots \quad (45)$$

Evaluation of the theoretical equations for Brownian and turbulent diffusion (Equations 39 and 40, Chapter III) was achieved with an EAI Pace TR 48 analog computer. Finite difference approximation methods were utilized to obtain these solutions (see Appendix). Since the velocity profile in the direction of fluid flow ($x_3$-direction) was flat and the electric field acted in the direction perpendicular to the electrodes ($x_1$-direction), displacements in the $x_1$-direction only were considered. Fluctuations in other directions would tend to equalize because of the relatively small time scale of turbulence; this is not true, however, in the $x_1$-direction because in this case the positive electrode acts as an absorbing barrier. Thus, restricting our

¹This time was measured with $t = 0$ when a particle entered the electric field.
attention to $x_1$-direction displacement and assuming the electric field strength $E$ to be constant, equations (39) and (40) for Brownian and turbulent diffusion, respectively, become for Brownian diffusion,
\[
\frac{\partial c(x_1,t)}{\partial t} = \frac{q}{\beta^2} \frac{\partial^2 c(x_1,t)}{\partial x_1^2} - \frac{\sigma E}{m\beta} \frac{\partial c(x_1,t)}{\partial x_1} \quad (46)
\]
while for turbulent diffusion,
\[
\frac{\partial c(x_1,t)}{\partial t} = \nu x_1 \frac{\partial^2 c(x_1,t)}{\partial x_1^2} - \frac{\sigma E}{m\beta} \frac{\partial c(x_1,t)}{\partial x_1} \quad (47)
\]
It is assumed also in equations (46) and (47) that the viscous resistance coefficient $\beta$ for turbulent diffusion is equal to that for Brownian diffusion [see equation (2)]. The boundary conditions utilized with these equations were as follows:
\[
c(x_1,0) = c_0; \quad c(0,t) = 0, t>0; \quad c(L,t) = c_0, t>0. \quad (48)
\]
The locations $x_1 = 0$ and $x_1 = L$ were at the negative and positive electrodes, respectively, while $c_0$ was the influent concentration of suspension. As indicated previously, the rms velocity of turbulence at location 5 in the $x_1$-direction was 5.8 centimeters per minute while that at locations 10 and 15 were zero. The rms velocity is an indication of the degree of turbulence in that it is a measure of the velocity fluctuations about the mean velocity. Thus, on the basis of these decaying turbulence data, it was decided to utilize the turbulent diffusion equation (47) for colloid movement in the influent one-third of the test column and the Brownian diffusion equation (46) for colloid movement in the remaining two-thirds of the length of the test column.

Pertinent values of clay colloid and flowing fluid properties necessary for the solution of equations (46) and (47) with the boundary
conditions in equation (48) are shown in Table 3. It should be noted that the value of particle charge was not measured in this investigation but was obtained from pertinent literature. Utilizing the data

Table 3. Pertinent Values of Clay Colloid and Flowing Fluid Properties

<table>
<thead>
<tr>
<th>Clay (kaolin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle &quot;radius&quot;</td>
</tr>
<tr>
<td>particle charge$^1$</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flowing Fluid Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>dynamic viscosity of colloidal suspension$^2$</td>
</tr>
<tr>
<td>mean-square velocity</td>
</tr>
<tr>
<td>Lagrangian time-scale</td>
</tr>
<tr>
<td>absolute temperature</td>
</tr>
<tr>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>electric field strength</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

$^1$References: Perrier and Evans (1959); Jacobs (1963).


In Table 3, one then arrives at the analog computer solution shown in Figure 21. The time values on the abscissa refer to the time during which a given fluid element is in the electric field. Predicted concentrations at various points on the experimental model can be determined by consideration of the suspension flow velocity through the
Figure 21. Analog Computer Solution for Partial Turbulent and Partial Brownian Diffusion of Suspended Clay Colloids in an Electric Field
system and the location on the model of the points in question. The flow velocity through the system was 10.4 centimeters per minute. Suppose, for example, that one wished to determine the predicted concentration at location h on the experimental model (see Figure 12). This point is 2.5 centimeters from the negative electrode and 44.0 centimeters above the entrance of the suspension into the electric field. From Figure 21, the predicted concentration at \( t = 4.2 \) minutes and \( I = 5 \) would be 20 milligrams per liter. Note that for these considerations the time axis essentially replaces the \( x_3 \)-axis.

A comparison of theoretical and experimental results is shown in Table 4. The theoretical values were taken from Figure 21. The experimental values represent the constant values which were reached during the continuous mass concentration in situ measurements (see Figures 14 through 17). The agreement between the experimental and theoretical values is within the limits of experimental error except at locations c and i. The deviation at location c may be attributed to the boundary condition at \( x_1 = 0 \). It is assumed that at the negative electrode \( (x_1 = 0) \) there exists an instantaneous change in concentration from the initial concentration at \( t = 0 \) to zero concentration for \( t > 0 \). No instantaneous change such as this can occur in nature; however, away from \( x_1 = 0 \) and \( t = 0 \) the error introduced is insignificant. The fact that point c on the experimental model is nearest to \( x_1 = 0 \) in space and \( t = 0 \) in time explains, to a large extent, the discrepancy at this point.

It is of interest to examine the analog computer solutions for Brownian diffusion alone and for turbulent diffusion alone. These solutions are shown in Figures 22 and 23, respectively. Note that the
concentration decreases faster initially in the turbulent case than in the Brownian case but then levels out while the Brownian concentration decreases to zero more rapidly. From the practical standpoint, this observation indicates that it would be desirable to have turbulence present in the initial stages for most effective colloid removal. This result appears logical in that initially the turbulent fluctuations would move more particles to the "absorbing" positive electrode, thereby increasing the probability of capture, than would pure Brownian diffusion.

Table 4. Comparison of Theoretical and Experimental Results

<table>
<thead>
<tr>
<th>Location on Experimental Model&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Theoretical Concentration&lt;sup&gt;b&lt;/sup&gt; (mg./L.)</th>
<th>Experimental Concentration&lt;sup&gt;c&lt;/sup&gt; (mg./L.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>60</td>
<td>59</td>
</tr>
<tr>
<td>b</td>
<td>54</td>
<td>55</td>
</tr>
<tr>
<td>c</td>
<td>28</td>
<td>55</td>
</tr>
<tr>
<td>d</td>
<td>50</td>
<td>54</td>
</tr>
<tr>
<td>e</td>
<td>32</td>
<td>34</td>
</tr>
<tr>
<td>f</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>g</td>
<td>38</td>
<td>42</td>
</tr>
<tr>
<td>h</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>i</td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>j</td>
<td>26</td>
<td>24</td>
</tr>
<tr>
<td>k</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>l</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup>See Figure 12.
<sup>b</sup>See Figure 21.
<sup>c</sup>See Figures 14 through 17.
Figure 22. Analog Computer Results Considering Only Brownian Diffusion

\[
\frac{\partial c}{\partial t} = (6.7 \times 10^{-9}) \frac{\partial^2 c}{\partial x_1^2} - (8.4 \times 10^{-3}) \frac{\partial c}{\partial x_1}
\]
\[
\frac{\partial c}{\partial t} = (2.0 \times 10^{-2}) \frac{\partial^2 c}{\partial x_1^2} - (8.4 \times 10^{-3}) \frac{\partial c}{\partial x_1}
\]

Figure 23. Analog Computer Results Considering Only Turbulent Diffusion
CHAPTER V

DISCUSSION

A further observation concerning the comparison of theoretical and experimental results is pertinent at this point. Consider an equation of the form of equation (46) or (47) with the boundary conditions specified in equation (48). The form of such an equation would be

\[ \frac{\partial c(x_1, t)}{\partial t} = M \frac{\partial^2 c(x_1, t)}{\partial x_1^2} - N \frac{\partial c(x_1, t)}{\partial x_1}, \]

(49)

where \( M \) and \( N \) are constants. For the Brownian diffusion case in this study, the quotient \( \frac{N}{M} \) approximately equals \( 4 \times 10^5 \text{ cm}^{-1} \); for the turbulent diffusion case, one obtains \( \frac{N}{M} \approx 0.4 \text{ cm}^{-1} \). Now note the shapes of the solution curves shown in Figures 22 and 23. For small values of \( \frac{N}{M} \) (the turbulent case) the curves descend more rapidly in the initial stages than for large values of \( \frac{N}{M} \) (the Brownian case). For longer times, however, the curves for small values of \( \frac{N}{M} \) level off while the curves for large values of \( \frac{N}{M} \) decrease more rapidly. Thus the effect of the value of the ratio \( \frac{N}{M} \) can be seen. As mentioned earlier, the particle charge was not measured in the study but was obtained from literature. If, for example, the charge was larger the value shown in Table 3, then the coefficient \( N \) would be increased. The effect of increasing the value of \( \frac{N}{M} \) would be to decrease slightly the initial rate of descent of the curves in Figures 21 and 23 and to increase slightly.
the rate of descent of the curves in Figures 21 and 22 at longer times. If the particle charge was smaller than the value in Table 3, then the effect would be just the opposite of that discussed here.

A further observation concerning the boundary conditions in equation (48) is also pertinent. For the negatively charged colloids, the negative electrode could be considered ideally to be a reflecting barrier while the positive electrode could be considered ideally as an absorbing barrier. The last two boundary conditions in equation (48) are not those for ideally reflecting and absorbing barriers, respectively. The boundary condition for an ideally reflecting barrier with an external force acting on the system is

\[ M \frac{\partial c(0,t)}{\partial x} + N c(0,t) = 0 \]  

(50)

while that for an ideally absorbing barrier is

\[ c(L,t) = 0 \]  

(51)

The boundary conditions in equation (48) were utilized in preference to those in equations (50) and (51) because (a) the boundary layers were not investigated in this study, and (b) the author believed the conditions in equation (48) to be more nearly representative of the physical situation adjacent to the boundaries than those in equations (50) and (51).

The suspension concentrations determined by hypodermic needle sampling generally supported the mass concentration in situ results although the needle concentrations were higher in most cases than the

Reference: Chandrasekhar (1943).
light-tube concentrations. It is believed by the author that these concentrations were higher because of suspension which inevitably was in the needle and tube-locking assembly ahead of the clamp prior to sampling. Also, the samples possibly could have been withdrawn from a large enough sphere of influence in the test column so that the measured concentrations would have been greater than those at the tip of the needle. The sphere of influence quite possibly could be reduced by reducing the rate of withdrawal of samples. Visual observations of suspension concentration could not be made during the mass concentration tests because of the necessity of no light reaching the photocells from external sources. However, during the potentiometric tests, in which the influent conditions were identical with those of the mass concentration tests, it was visually observed that very low concentrations existed near the negative electrode in the upper half of the column. These observations support the light-tube results over those obtained by sampling.

It was intended originally that the potentiometric charge concentration determination could be utilized to develop an empirical charge-size relationship for the kaolin clay. A small sample of suspension would have been withdrawn from the area where the electrical potential was being measured. Then, a particle size distribution of the clay would have been determined from this sample by utilization of an electron microscope and flying-spot particle analyzer [Hiler (1964)]. It is the opinion of the author that a definite size-charge relationship exists for colloidal clays and further that charge density increases with decreasing size. This experiment was not pursued in the study, however, because it was felt that the electrical
potential measurements which could be made in the experimental model were not of high enough resolution for the results to be meaningful. An investigation of this type could be performed more accurately in a smaller model in which the fluid itself was quiescent.

The deposition of clay on the positive electrode was visually observed following each test run. Hiler (1963) (1965) utilized a rod and concentric cylinder electrode configuration and observed an "end effect" in which considerably more clay was deposited near the ends of the positive electrode than in the central portion. No "end effects" were observed with the parallel-plate electrode configuration utilized in this study.

Hiler (1963) (1965) and Kucha (1964) observed that much electrolysis of the water molecule occurred at high electric field strengths and/or high specific conductivities of suspension. The electric field strength and specific conductivity were regulated in this study so that electrolysis was not a problem.

From the practical standpoint of colloid removal from suspension for domestic water clarification, the results of this study indicate that very high quality water can be attained in a region near the negative electrode. Thus, a system in which the portion of the effluent near the negative electrode was removed while the remainder was recycled through the electrokinetic system would yield the best results.
CHAPTER VI

RECOMMENDATIONS FOR FUTURE RESEARCH

Recommendations for future research in the general area of interest of this investigation are as follows:

1. The structure of the viscous resistance coefficient $\beta$ for turbulent flow conditions warrants further study. This structure was not determined for turbulent flow conditions in this investigation.

2. Further experimental investigations should be conducted to test the theory developed in this study utilizing suspensions of various colloidal materials other than clay. Tests should also be performed in which (a) Brownian diffusion conditions prevail throughout the experimental model, and (b) turbulent flow conditions exist throughout.

3. The determination of charge-size ratios for various colloidal materials should be investigated, possibly utilizing methods mentioned in Chapter V.

4. Investigation of the effect of electrode material on electrokinetic removal of colloids from suspension would be of interest. Noncorrosive materials such as graphite and corrosive materials such as aluminum may offer promise.

5. A study of the effect of colloid concentration on electrokinetic colloid movement would be valuable. It is the opinion of the
author that this electrokinetic system will find greatest application as a "polishing filter" for low colloid concentration waters.

6. From the practical standpoint, research utilizing a unit similar to that of Boyd (1963) [see Chapter II] warrants consideration.

7. Research should be conducted on the electrokinetic movement of biological materials such as bacteria and algae in both flowing and still water. A study of the utilization of the electrophoretic principle for removal of materials in solution such as pesticides would also be valuable.
CHAPTER VII

SUMMARY AND CONCLUSIONS

This investigation involved the movement of liquid-suspended charged colloids in an electric field. Particular emphasis recently has been placed on the application of the electrophoretic process in water clarification for domestic water-treatment systems. The purpose of this research was to gain further understanding of the electrophoretic process for charged, colloidal particles suspended in a flowing medium. Theoretical investigations were made, followed by some pertinent verifying experiments.

The essential basis of the theoretical considerations was the theory of stochastic processes whereby one seeks a description of a phenomenon in terms of probability distributions of position and/or velocity at a later time, starting from given initial distributions. In this manner, particle concentrations can be considered on a probabilistic basis. Equations were developed for both "pseudo-laminar" and turbulent flow conditions. For the pseudo-laminar case, where random fluid-velocity fluctuations were unimportant, theories of Brownian diffusion formed the basis for these considerations; the background for the turbulent flow case was provided by theories of turbulent diffusion. These equations can be utilized to predict colloid concentration at position \( x \) at time \( t \) for a given influent concentration.
An experimental model was constructed to test this theory in which stainless-steel electrodes were utilized in a parallel-plate configuration. The suspensions studied were prepared from colloidal kaolin and deionized water. The influent concentration of suspension was maintained at 60 milligrams per liter. The flow rate of suspension was 250 milliliters per minute, while the electric field strength between the electrodes was 100 volts per centimeter. Mass concentration of suspension was measured at various points in the system both in situ on a continuous basis and by withdrawing samples. Both methods involved light transmittance measurements. Charge concentration was measured indirectly at various points in the system by utilizing potentiometric determinations. The following flow and/or turbulence characteristics of the medium were measured with a hot-film anemometer and spectral density analyzer: (a) velocity profile, (b) spectral density, and (c) root-mean-square (rms) velocity. Turbulence which was present in the influent section of the experimental model decayed to negligible amount approximately one-third of the way through the test column. The theoretical equations with appropriate boundary conditions were solved with an electronic analog computer to provide a comparison of theoretical and experimental results.

The results of the theoretical and experimental investigations indicated the following conclusions:

1. The theoretical equations developed in this study for pseudo-laminar and turbulent flow conditions provided a valid description of the electrokinetic movement of charged clay colloids suspended in flowing water.
2. The occurrence of turbulence enhanced colloid removal from suspension for small values of time which particles were in the electric field. However, for long times, pseudo-laminar flow conditions were superior to turbulent flow conditions for suspended particle removal.

3. The parallel-plate electrode arrangement provided a satisfactory system for the removal of charged clay colloids from suspension. Very low concentrations were quickly attainable in a region near the negative electrode. Thus, for the practical consideration of colloid removal from suspension for water supply clarification, a system in which water is removed for use only near the negative electrode while the remainder is recycled or wasted would be most desirable.

4. The mass concentration in situ method was the most desirable of the three concentration determination methods utilized in this study. This mode of measurement provided the advantages of an essentially continuous determination along with a minimal disturbance of the suspension.

5. The potentiometric charge concentration measurements supported the mass concentration results but were of insufficient resolution for detailed analysis.
Calculation of the Coefficient $\alpha$ for Determination of the Lagrangian Time-Scale of Turbulence $L_T$

The slope of the line shown in Figure 20 may be expressed as follows:

$$\alpha = -\frac{\ln \phi(f_1) - \ln \phi(f_2)}{f_2 - f_1}.$$ 

For a straight-line plot, one has

$$y = mx + b$$

so that for the semilogarithmic plot in Figure 20, it follows that

$$y = \ln \phi(f), \quad x = f, \quad \text{and} \quad b = \ln \phi(0) = \ln \phi_0.$$

Thus the equation for the line shown in Figure 20 is

$$\ln \phi(f) = \left(\frac{\ln \phi(f_1) - \ln \phi(f_2)}{f_2 - f_1}\right) f + \ln \phi_0$$

or

$$\ln \frac{\phi(f)}{\phi_0} = \left(\frac{\ln \phi(f_1) - \ln \phi(f_2)}{f_2 - f_1}\right) f.$$ 

Introducing the angular frequency, $\omega = 2\pi f$, it follows that

$$\phi(f) = \phi_0 e^{-\alpha \omega}.$$ 

Now, at the critical angular frequency, $\omega_c = \frac{1}{\alpha}$, one has

$$\frac{\phi(f)}{\phi_0} = \frac{1}{e} = 0.368.$$ 

From Figure 20, it can be seen that

$$\phi_0 = 345.$$ 

Note once again that $\phi(f)$ is expressed in arbitrary units so that $\phi_0$ here is not necessarily the number, three hundred forty five.
Introducing the value of $\phi_0$, one has, at $\omega_c = \frac{1}{\alpha}$,

$$\phi = (0.368)(345) = 127.$$  

From Figure 20, one can see that the value of $f_c$ corresponding to $\phi = 127$ is $f_c = 0.115$ cycles per second so that the critical angular frequency becomes $\omega_c = 0.722$ cps. From this value of $\omega_c$, it follows that

$$\alpha = 1.39 \text{ seconds}.$$  

Then, from equation (44), the Lagrangian time scale of turbulence is calculated to be

$$L_t = 2.18 \text{ seconds}.$$  

Methods Utilized for Obtaining Analog Computer Solutions

**Brownian diffusion, pseudo-laminar flow**

For this case, the appropriate equation is

$$\frac{\partial c}{\partial t} = \frac{q}{\beta^2} \frac{\partial^2 c}{\partial x_1^2} - \frac{\sigma E}{m \beta} \frac{\partial c}{\partial x_1}$$

while the boundary conditions are given in equation (48) (except now let $c_0$, the initial concentration, be R). Defining $M$ to be $\frac{q}{\beta^2}$ and $N$ to be $\frac{\sigma E}{m \beta}$, it follows, from the appropriate values in Table 3, that

$$M = 6.7 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}, \text{ and}$$

$$N = 8.40 \times 10^{-3} \text{ cm sec}^{-1}. $$
Letting $L$ be the distance between the electrodes and $n$ be the number of increments into which this distance is divided, one has $L = 5$ cm. and $n = 10$. Now, defining $\alpha = \frac{nM}{L^2}$ and $\gamma = \frac{nN}{L}$, it follows that $\alpha = 1.6 \times 10^{-6}$ and $\gamma = 0.0168$ sec.$^{-1}$. Define $\Delta x = \frac{L}{n}$ and let $i = 1, 2, \ldots, n = 10$. The term $i$ corresponds to $I$ in Figure 21.

By finite difference approximations, one has

$$\frac{\partial^2 c}{\partial x_1^2} \bigg|_{x_1=i} \approx \frac{1}{(\Delta x_1)^2} [c_{i+1} - 2c_i + c_{i-1}]$$

and

$$\frac{\partial c}{\partial x_1} \bigg|_{x_1=i} \approx \frac{1}{\Delta x_1} (c_i - c_{i-1})$$

so that

$$\frac{dc_i}{dt} = \frac{n^2M}{L^2} (c_{i+1} - 2c_i + c_{i-1}) - \frac{nN}{L} (c_i - c_{i-1})$$

or

$$c_i = \gamma[\alpha(c_{i+1} - (1 + 2\alpha)c_i + (1 + \alpha)c_{i-1})]$$

For $\alpha \approx 0$, this last equation reduces to

$$-c_i = c_i - c_{i-1}$$

In general then, the problem for solution on the analog computer for the pseudo-laminar case is as follows:

$$c_0 = 0$$
$$c_i = \gamma[\alpha(c_{i+1} - (1 + 2\alpha)c_i + (1 + \alpha)c_{i-1})] \text{ for } i = 1, 2, \ldots, 9$$
$$c_{10} = R$$
$$c_i \big|_{t=0} = R \text{ for } i = 0, 1, 2, \ldots, 10,$$

where $\alpha = 1.6 \times 10^{-6}$, $\gamma = 1.68 \times 10^{-2}$ sec.$^{-1}$, and $R = 60$ milligrams per liter.
Turbulent diffusion, turbulent flow

For this case, the appropriate equation is

$$\frac{\partial c}{\partial t} = v_{x_1}^2 L_t \frac{\partial^2 c}{\partial x_1^2} - \frac{\sigma E}{m \beta} \frac{\partial c}{\partial x_1}$$

while the boundary conditions again are given in equation (48). Now, letting $M = \frac{v_{x_1}^2}{x_1} L_t$ and $N = \frac{\sigma E}{m \beta}$, one has

$$M = 2.04 \times 10^{-2} \text{ cm}^2 \text{ sec}^{-1} \quad \text{and} \quad N = 8.40 \times 10^{-3} \text{ cm} \text{ sec}^{-1}$$

so that $\alpha$ and $\gamma$ now become

$$\alpha = 4.86 \quad \text{and} \quad \gamma = 1.68 \times 10^{-2} \text{ sec}^{-1}.$$ 

Except for these changes, the problem for solution on the analog computer for the turbulent case is the same as that for the pseudo-laminar case.
GLOSSARY OF SYMBOLS

$x$ - position vector
$t$ - time
$v$ - particle velocity vector
$u$ - fluid velocity vector
$\beta$ - viscous resistance coefficient; for Brownian diffusion, $\beta = \frac{6\pi \rho a}{m}$
$\rho$ - absolute viscosity
$a$ - particle radius
$m$ - particle mass

$A(t)$ - rapidly fluctuating acceleration due to Brownian motion
$K(x)$ - acceleration caused by external force field
$k$ - Boltzmann universal constant
$T$ - absolute temperature
$q$ - $\frac{3kT}{m}$

$P(x,t)$ - probability density function for position $x$ at time $t$

$V$ - volume of specified region of space

$Q(x,t; t_0)$ - probability density function for displacement

$\xi$ - wave number vector

$G(\xi, t)$ - Fourier transform of $P(x,t)$

$H(\xi, t)$ - Fourier transform of $Q(x,t; t_0)$

$i = \sqrt{-1}$

$\mu_{ij}(t)$ - $i$-$j$ component of turbulent diffusion tensor coefficient

$R_{ij}(t)$ - $i$-$j$ component of Lagrangian correlation tensor coefficient

$u'$ - $\sqrt{u^2}$
L_t - Lagrangian time scale of turbulence

\[ B = \int_0^\infty R(\tau) d\tau \approx \int_0^{\tau^*} R(\tau) d\tau \]

\( \tau^* \) - time above which \( R(\tau) \approx 0 \)

D - diffusion coefficient

f - circular frequency

\( \omega \) - angular frequency, \( \omega = 2\pi f \)

\( (p)\phi(\omega) \) - particle spectral density

\( \phi(\omega) \) - fluid spectral density

\( c(x,t) \) - concentration at position \( x \) at time \( t \)

\( \sigma \) - electric charge density

\( \mathbf{E}(x) \) - electric field strength

I - intensity of transmitted light

I_0 - intensity of entering light

\( \nu \) - absorption constant

s - length of light path through suspension
LITERATURE CITED


