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COAGULATION IN ESTUARIES

James K. Edzwald

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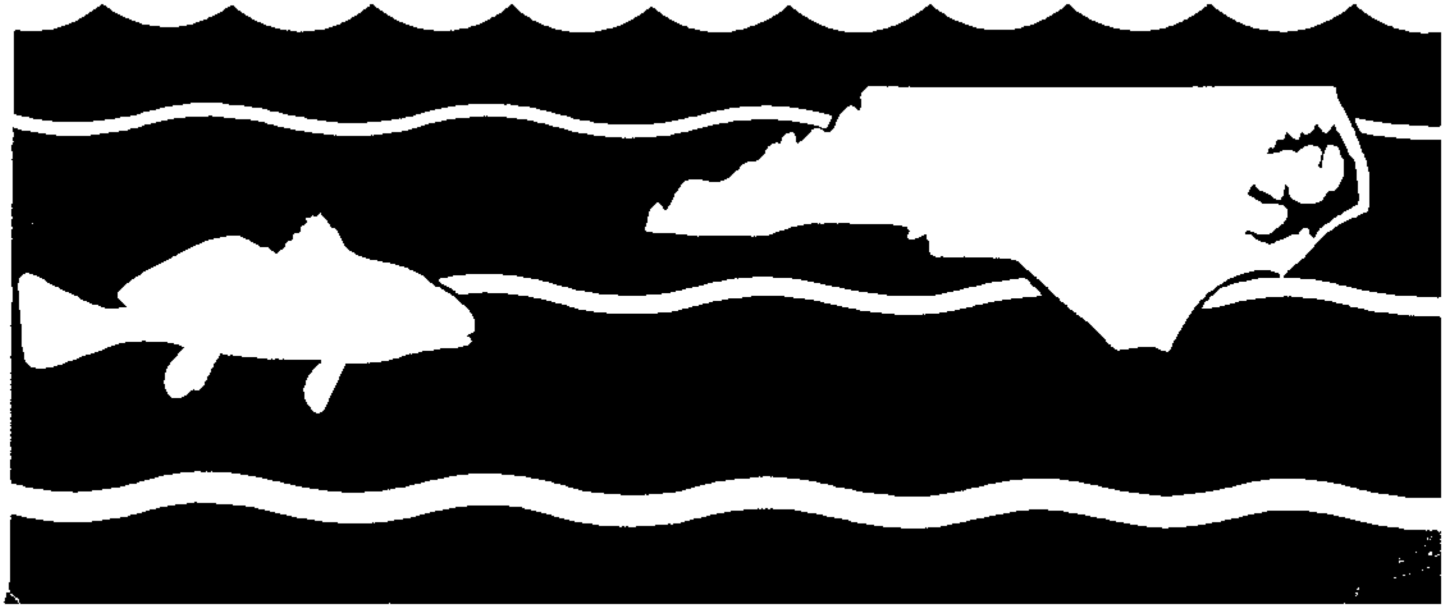

COAGULATION IN ESTUARIES

by

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ABSTRACT

JAMES KENNETH EDZWALD. Coagulation in Estuaries. (Under the direction of Professor CHARLES R. O'MELIA.)

A conceptual model describing the coagulation of clay minerals in estuaries has been proposed and tested. Conceptually it was postulated that clay suspensions are destabilized by compression of the electrical double layer when these suspensions are transported from fresh waters into estuaries. Operationally, it was postulated that the stability factor (α) depends on the chemistry of the system.

The coagulation rates of three clay minerals (kaolinite, illite, and montmorillonite) were determined in the laboratory in solutions at various ionic strengths. In addition, the coagulation rates of selected sediments collected from the Pamlico Estuary of North Carolina were determined. Stability values (α) were evaluated from the kinetic coagulation data using Smoluchowski's equation for orthokinetic flocculation. Finally, the effects of coagulation on water quality in estuaries were considered.

The coagulation kinetic data for the three clay minerals indicated an improvement in particle destabilization with increasing ionic strength (salinity). Particle destabilization was also improved when synthetic sea water solutions (containing divalent cations) were used for coagulation as compared to buffered NaCl solutions (containing only monovalent cations). The stability factor was observed to depend on the type of clay mineral, the ionic strength of the solution, and the composition of the destabilizing solution (type of counter-ions). The stability of the three clays is as follows: Illite $>$ Kaolinite $>$ Montmorillonite. These results support the hypotheses that the mechanism of particle destabilization is double layer compression and that the stability factor (α) depends on the solution chemistry.

The composition of the clay fraction of sediments collected from the Pamlico Estuary was determined by X-ray diffraction. Kaolinite was found as the dominant clay in the upper end of the estuary and decreased towards the mouth. Illite was found to occur in minor amounts in the upper end and increased towards the mouth. Montmorillonite was present in minor amounts and chlorite and a chlorite-like intergrade clay comprised the remainder of the clay fraction. The results of coagulation rate studies using Pamlico sediments indicated that the upstream sediments are relatively unstable (higher α values) as compared to the downstream sediments. The distribution of kaolinite and illite is explained by coagulation in which the least stable clays (higher α values) are deposited upstream of more stable clays.

The coagulation and deposition of clays in estuaries can affect water quality via adsorption and release of soluble pollutants. It is concluded from adsorbed phosphorus data that sediments (containing adsorbed P) entering the estuary in the fresh water inflow would lose phosphorus as they are transported through waters of increasing salinity to the mouth of the estuary. Depending upon the strength of the solid-solute interaction, coagulated materials could serve as a source or sink for a soluble substance in estuarine waters.

Key Words: Coagulation, Flocculation, Estuaries, Clay Minerals, Sediments

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CHAPTER I

INTRODUCTION

Natural waters contain dissolved species and undissolved or suspended substances. Most of the suspended substances are colloids. A large fraction of the colloids are clay minerals which have relatively large surface areas and exchange capacities. These clay minerals have the ability to concentrate appreciable quantities of soluble species on their surfaces. Soluble pollutants such as phosphates, trace metals, pesticides, and radionuclides may be removed by sorption processes from turbid fresh waters, transported to estuaries where fresh and salt water mix. The sorbed materials may be released to the saline water of the estuary. In this case suspended sediments act as a source of these pollutants. If the sorbed pollutants are not released during the coagulation (aggregation of suspended materials) and deposition of suspended sediments in estuaries, then the estuarine sediments serve as a sink for these pollutants. In this conceptual model, suspended materials (e.g. clays) transport soluble pollutants from fresh waters into estuaries. Conditions in estuaries are conducive for the coagulation and deposition of suspended sediments.

This investigation is concerned with the coagulation of clay minerals in estuaries. Coagulation in estuaries is of interest to geologists who study the distribution of clay minerals in estuarine sediments and to hydraulic engineers who are concerned with estuarine sedimentation and shoaling. Finally, environmental engineers and scientists are interested in the role of the coagulation process in affecting the fate of soluble adsorbable pollutants.

COAGULATION PROCESS

Colloidal and semi-colloidal particles carry an electrical charge, usually negative in natural waters, which influences their behavior in suspension; of these particles clay minerals are of primary importance. Colloidal suspensions are quite stable (i.e., they have little tendency for particle aggregation) in fresh waters due to the repulsion that exists between the electrical double layer surrounding the negatively charged particles. In conventional water treatment practice, the removal of suspended particles is accomplished by coagulation in which discrete colloidal particles are aggregated to such a size that gravitational sedimentation can readily be accomplished. Coagulation is a two step process (O'Melia (1969)): particle destabilization and particle transport. The destabilization step is concerned with eliminating or nullifying the repulsive energy barrier that exists between two particles. The second step - particle transport (flocculation) - is concerned with inducing interparticle contacts by: (1) Brownian motion of the colloidal particles, (2) effects of velocity gradients within the suspending liquid, or (3) differential settling velocities of suspended particles.

Particle destabilization can be accomplished by four distinct mechanisms: (1) adsorption to produce charge neutralization, (2) adsorption to permit interparticle bridging, (3) enmeshment in a precipitate of a metal hydroxide, and (4) double layer compression. The first three listed mechanisms are utilized in the treatment of water and wastewater and are illustrated below. Particle destabilization is treated in depth in Chapter III. In water and wastewater treatment the particle transport step (flocculation) is frequently accomplished by mixing via mechanical stirring of the fluid with paddles.

Aluminum sulfate (alum) is commonly used as a coagulant in water and wastewater treatment. It is usually added in sufficient quantity to exceed the solubility of $Al(OH)_3(s)$. Colloidal particles present in the solution are removed by being enmeshed within the precipitate of the aluminum hydroxide ("sweep floc effect"). Hydroxo metal complexes are intermediates in the formation of $Al(OH)_3(s)$; these metal complexes are readily adsorbed at the colloid interface producing charge neutralization. In the last twenty years there has been an increase in the use of synthetic organic polyelectrolytes. These macromolecules are adsorbed to colloidal particles and accomplish particle destabilization and aggregation by interparticle bridging.

The conditions that exist in an estuary are conducive for coagulation. The result is that coagulation is a naturally occurring process in estuaries. These conditions and the mechanism of particle destabilization are presented in the following section.

HYPOTHESIS AND PURPOSE OF RESEARCH

It is postulated that clay suspensions are destabilized by double layer compression as these suspensions are transported from fresh waters into estuaries. Clay suspensions are destabilized by the salt water and mixing (particle transport) is provided by the interaction of the river inflow, tides, and winds. The repulsive energy barrier that exists between clay particles in fresh waters (low ionic strength) is reduced as the clays are transported into waters of increasing ionic strength (estuaries). The increase in the ionic strength of the system compresses the electrical double layer and permits van der Waals attractive forces to become effective at short-range interparticle distances.

A stable clay suspension is one in which the discrete particles show little or no tendency to agglomerate. Smoluchowski (1917) has quantified the coagulation process for the case of completely destabilized suspensions (rapid coagulation), i.e., complete discharge of the double layer. A stability factor (α) is introduced into Smoluchowski's equation to account for incomplete discharge of the double layer. The following equation is for orthokinetic flocculation and is discussed in detail in Chapter IV.

$$\frac{dn}{dt} = \frac{-4\alpha\phi G n}{\pi} \qquad [1\text{-}1]$$

Here n is the concentration of particles at time t, particles/cm^3; α is the stability factor, ϕ is the volume of colloidal particles per unit volume of suspension, and G is the root-mean-square velocity gradient, sec^{-1}. A completely destabilized suspension has a stability factor of 1; stable suspensions are characterized by $\alpha << 1$. Coagulation is a two step process in which α describes the degree of destabilization and G, n, and ϕ affect the frequency of particle collisions.

In addition, it is postulated that the stability factor (α) depends on the chemistry of the system. Thus, the stability factor depends upon the type of clay mineral, the ionic strength of the solution, and the composition of the destabilizing solution (type of counter-ions). The broad purposes of this research were (1) to determine (in the laboratory) the coagulation rates of three clay minerals in solutions at various ionic strengths (salinities), (2) to determine (in the laboratory) the coagulation rates of sediments collected from the Pamlico Estuary of North Carolina, and (3) to evaluate the role of the coagulation process in affecting the fate of soluble adsorbable pollutants.

SPECIFIC OBJECTIVES AND CONTENT OF DISSERTATION

The broad purposes or objectives of this investigation have been stated in the preceding section. The specific objectives of this research were the following:

1. To investigate the use of the Verwey-Overbeek, Derjaguin-Landau theory for the interaction of double layers as a theoretical tool for predicting stability factors (α).
2. To determine stability factors for three clay minerals (kaolinite, illite, and montmorillonite) from coagulation rate studies in the laboratory.
3. To investigate the effects of salinity and composition of the destabilizing solutions on the stability factor.
4. To determine the clay mineral distribution of sediments collected from the Pamlico Estuary.

5. To determine stability factors for selected Pamlico sediments.
6. To evaluate whether coagulation is a viable factor in explaining the distribution of clay minerals in the Pamlico sediments.
7. To determine the amount of adsorbed phosphorus on the Pamlico sediments.
8. To evaluate the role of the coagulation process in estuaries.

An outline of the content of this dissertation is instructive since it illustrates the general approach used in this research. Chapter II (Estuaries) serves as a foundation for this dissertation by: (1) examining the characteristics of estuaries, (2) examining factors which influence the deposition of suspended matter, and (3) discussing factors which influence the clay mineral composition of estuarine sediments. The stability of clay suspensions is examined from a theoretical basis in Chapter III. The use of the Verwey-Overbeek, Derjaguin-Landau (VODL) theory to predict α values is evaluated. The determination of stability factors (α) from coagulation rate studies is considered in Chapter IV. Sediments were collected from the Pamlico Estuary and subjected to several laboratory analyses. The results are reported in Chapter V. The significance of the coagulation process in estuaries is discussed in Chapter VI. The conclusions derived from the results of this investigation are presented in Chapter VII. It is essential for a writer to communicate with his readers. In order to meet this goal more effectively, a synopsis of this work is provided. The synopsis gives the reader an overview of this work and it has forced the writer to describe briefly the work that was done and the results that were achieved.

CHAPTER II

ESTUARIES

Estuaries are a significant natural resource providing man with numerous benefits including recreation, navigation, food production, water supply, and waste disposal. Engineers, chemists, biologists, geologists, and social scientists may be interested in estuarine circulation patterns, rates of exchange of materials with coastal and marine waters, sedimentation, pollution, and the ecology of estuarine organisms. This chapter serves as a foundation for this dissertation by (1) briefly describing the characteristics of estuaries, (2) examining the deposition of suspended matter in estuaries, (3) discussing factors which influence the clay mineral composition of estuarine sediments, and (4) summarizing the foregoing with respect to the coagulation of suspended materials in estuaries.

The first section provides the basis for sedimentation in estuaries by examining types of estuaries, circulation patterns, and suspended loads in these bodies of water. The second section is concerned with the deposition of suspended matter. The viewpoint of the engineer is used in examining estuarine sedimentation as well as the nature of the shoaling material. Special attention is also directed towards research concerned with flocculation in estuaries. The third section is devoted to those factors which influence the clay mineral composition of estuarine sediments. The viewpoint of the geologist is used to examine the role of the weathering of rocks and soils, climate, source area, and erosion. Diagenesis and differential flocculation are treated in depth since these factors are often used to explain the distribution of clays in estuarine sediments. Clay distributions in estuaries of the East Coast and Gulf of Mexico are also discussed with special attention being devoted to the estuaries of North Carolina. Finally, in the fourth section an attempt is made to summarize the foregoing sections with emphasis devoted to those parameters which this writer considers important in the coagulation of suspended materials in estuaries. The reader will find a large collection of references from many disciplines in this chapter, but the following references deserve special mention due to their extensive coverage: (1) Estuaries by G. H. Lauff, ed., (1967), (2) Clay Mineralogy by R. E. Grim, (1968), and (3) Estuary and Coastline Hydrodynamics by A. T. Ippen, ed., (1966).

Coagulation is defined in Chapter III as a two step process: (1) destabilization and (2) particle transport. According to this definition, the particle transport step is termed flocculation and the overall process, coagulation. In subsequent chapters coagulation will be used in this context; however, this is not the case in this chapter. The literature of the geologist and the hydraulic engineer is reviewed in this chapter and in this literature "flocculation" is used to describe particle aggregation due to both chemical and hydraulic conditions. Consequently, in this chapter these terms - coagulation and flocculation - are used in accordance with the discipline of the literature being reviewed.

CHARACTERISTICS

Definition

Pritchard (1967) has defined an estuary as "a semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage." Estuaries, like lakes, have relatively short-lives, geologically speaking, and rapidly fill. Areas of quiescent water become sites of deposition which in turn become the substrate for marine plants as shoaling occurs. Ultimately, marsh plants and continued sedimentation reclaim the area for the land. From a geomorphological standpoint, estuaries may be subdivided into: (1) drowned river valleys, (2) bar-built estuaries, (3) fjord-type estuaries, and (4) estuaries produced by tectonic processes. Estuaries under (1) and (2) are of particular interest in this study.

Estuaries formed when coastal areas and river valleys were drowned during the latest rise of sea level are typical of the Atlantic Coastal Plain of the United States. The Chesapeake Bay is a prime example of this type of estuary. Proceeding from the mouth of a coastal plain estuary the salinity decreases from about 35 ppt (sea water) to the upper limit of the estuary (about 0.01 ppt) where the most landward intrusion of sea-derived salt can be delineated. Above this upper limit of the estuary there is usually a stretch of fresh water which is still subject to the oscillation of the tidal currents and is called the tidal section of the river (tidal-river). The importance of the intrusion of salt water to coagulation and sedimentation will be illustrated in this chapter; consequently, the use of the term "estuary" in this research implies a salinity transition from fresh water to sea water and excludes the tidal section of the river above the estuary.

Estuaries formed when offshore barrier sand islands build above sea level and extend between headlands in a chain, broken by one or more inlets, are classified as bar-built estuaries. These estuaries approach the borderline of Pritchard's definition of an estuary with regard to free connection with the open sea. Tidal action is reduced since the inlets connecting the bar-built estuary with the ocean are usually relatively small compared to the dimensions of the sound within the barrier. These systems are usually shallow, and the wind is the important mixing mechanism. Pamlico Sound is a prime example of this type of estuary.

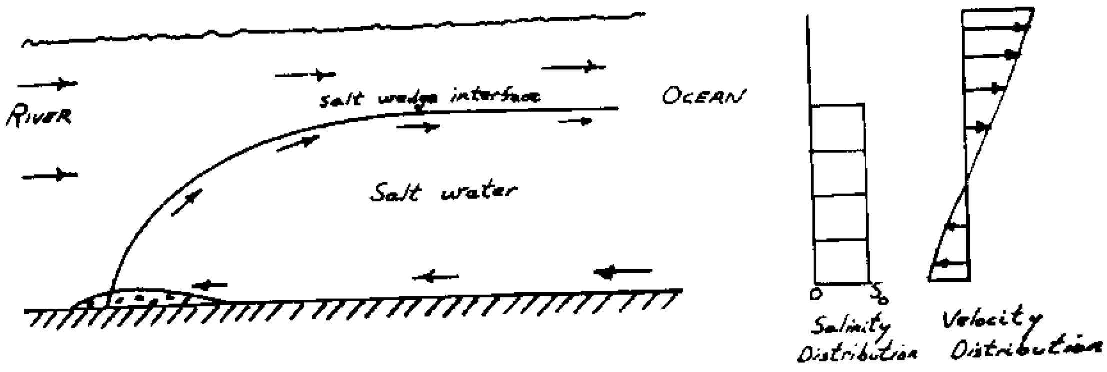
Circulation

The three basic processes which produce motion and mixing in an estuary are the wind, the tide, and the inflow of river water. The interaction between river flow and tidal currents is influenced by two other factors: the physical dimensions of the estuary and the Coriolis force. It is useful to classify estuaries according to the physical character of the circulation within these systems; consequently, the types of estuaries described below are: (1) the fully-stratified or "salt wedge", (2) the partially-stratified, and (3) the well-mixed. Ippen (1966) describes the current systems within an estuary as being dependent upon the relative strength of (1) the forcing tides at the mouth, (2) the gravitational forces due to the difference in density between fresh water and sea water, (3) the gravitational forces which produce on the average a net seaward transport of fresh water, and (4) the Coriolis and centrifugal forces. For many estuaries, the basic factor in determining the type of circulation is the role played by tidal currents relative to that of river flow. The rest of this section will be devoted to describing the circulation patterns for the three types of estuaries listed above.

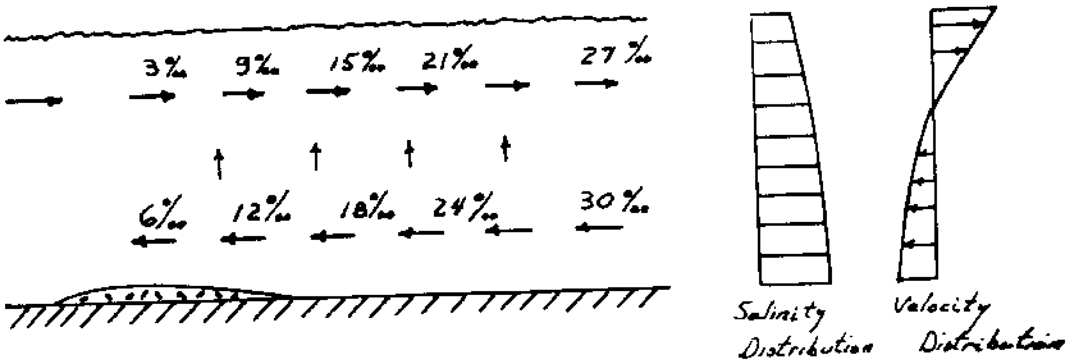
Fully-Stratified. The classic example of the fully-stratified estuary is the Mississippi River, where the river flow almost completely dominates circulation. The flow profile in this type of estuary is divided into two distinct portions as indicated in Figure 2.1A. The extent to which the salt water wedge penetrates into the estuary is a function of channel depth, river discharge, and the difference in the density between the salt and fresh water. Upstream from the limit of salt water intrusion, the direction of the current is the same at all depths, and since there is normally no reversal of flow by tidal action in a highly stratified estuary, the current direction is downstream at all times. In the region of saline intrusion, the direction of the current from the surface to the salt wedge interface is downstream; below the interface the salt water flow is still downstream and then reverses to the upstream direction as shown schematically in Figure 2.1A. In the lower zone (salt wedge) the salinity is practically the same as the ocean, while in the upper zone the fresh water flows to the ocean. The fully-stratified estuary has negligible diffusion from the lower salt water layer into the fresh water stream. Its existence is contingent upon weak tides and relatively high fresh water flow rates.

Partially-Stratified. Most estuaries along the Atlantic Coastal Plain are of the partially-stratified variety. This includes such

A. Fully-Stratified



B. Partially-Stratified



C. Model Study of Partially-Stratified

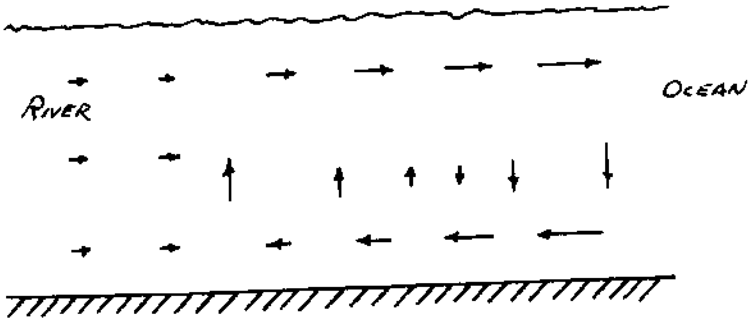


Figure 2.1. Types of Estuarine Circulation; A. Fully-Stratified or Salt Wedge, B. Partially-Stratified, C. From Model Study of Partially-Stratified by Harleman and Ippen (1967).

estuaries as the Chesapeake Bay and its tributaries in Maryland and Virginia, the Delaware River, the Savannah River in Georgia, and the harbor of Charleston, South Carolina (Meade, 1969). In these estuaries, tidal currents are sufficient to produce appreciable vertical mixing of the salt and fresh water (see Figure 2.1B). There are still two layers as far as the flow is concerned; the surface of no motion which separates the seaward-flowing upper layer from the landward-flowing lower layer usually occurs somewhat above mid-depth. There is no marked interface, but the salinity profile shows a continuous increase in salinity from surface to bottom, the maximum gradient occurring near the level of no net motion. In contrast to the fully-stratified estuary, there is a horizontal salinity gradient along the length of the estuary and the salt water advances and retreats with each rise or fall of the tides. The circulation pattern indicated in Figure 2.1B for the partially-stratified estuary was confirmed by Pritchard (1952) in a definitive series of field experiments. Pritchard measured water velocities in the James River at different depths and at frequent intervals of time over several tidal cycles and found a net seaward-flow at the surface and net landward-flow at the bottom. This concept of estuarine circulation has been supported by field measurements in other estuaries of the Atlantic Coastal Plain. Two-layer estuarine circulation has been refined by theoretical studies and by experiments with hydraulic models. Harleman and Ippen (1967) have shown from model studies that in addition to net horizontal flows seaward at the surface and landward at the bottom, there are net vertical flows upward near the landward end and downward near the seaward end as depicted in Figure 2.1C. This suggests a mechanism other than turbulent diffusion to account for the progressive landward dilution of salty bottom water observed in partially-stratified estuaries and it may help to account for the recycling of nutrients and trapping of sediments that is apparent in many estuaries.

Well-Mixed. In the well-mixed estuary tidal currents may be strong relative to the river flow so that vertical mixing becomes so intense that there is little variation in salinity from surface to bottom. Simmons (1966) describes a well-mixed estuary as one in which the bottom salinities normally exceed those at the surface by only 15 to 25 percent. There is, of course, still a horizontal gradient of salinity, increasing from the head to the mouth. Some estuaries may display a stratified character only at certain times, while at other times unusually high tides, turbulence by wave action, low fresh water flows, and wind induced currents produce a more mixed condition. An estuary is moved along the sequence from the stratified salt wedge estuary, through the partially-stratified estuary, to the vertically homogeneous estuary, with decreasing river flow and decreasing depth, and with increasing tidal current and increasing width. Wind can have an important influence on estuarine circulation and mixing, especially for wide and shallow estuaries. This is true for the Pamlico Sound which is fairly well-mixed due to its shallow depth, and wind is the dominant force producing circulation and mixing (Chu, 1970).

Sources of Estuarine Sediments

The following classification is used to describe the various sources of estuarine sediments.

1. Sediments derived from the adjacent watershed and its drainage system.
2. Sediments derived from the sea.
3. Sediments derived from the lower slopes bordering the estuaries.
4. Sediments derived from the mouths of estuaries.

The main source of sediment entering most estuaries is the adjacent watershed and its drainage system. The importance of sediment from this source varies from estuary to estuary and is dependent upon numerous hydrologic and geologic factors. An interesting contrast exists between northern and southern rivers that flow onto the Atlantic Coastal Plain. The largest rivers are concentrated in the north, for example, the Susquehanna and the Delaware. In spite of smaller water volumes, southern rivers which drain the deeply weathered piedmont area inland of the coastal plain carry more sediment than the rivers that drain the glacier-scoured and less deeply weathered areas of the north (Meade, 1969).

Estuarine sediments may be derived from the sea by the following mechanism. Off-shore bottom waters may move progressively into the mouths of estuaries and carry bottom sediments with them. There is evidence that sediments in the Dutch estuaries and the Seine estuary are of marine origin (Guilcher, 1967).

Guilcher also points out that the small rivers running to the sea around Brittany are illustrative of estuaries whose sediments come from the lower slopes bordering these waters. Generally, this source is important where fine material is derived from cliffs or banks bordering small estuaries and where the supply of suspended material from upstream is insignificant because the river is small.

Dredged material that is disposed of at the mouths of estuaries or mud flats at the mouths of estuaries may be sources of estuarine sediments. These deposits can be suspended and enter the estuary with the incoming tide and settle there at slack tide.

In conclusion, Turekian (1968) estimates the quantity of suspended material transported by the major rivers of the world to the ocean to be about 30 x 10^{15} grams/yr. Consequently, the average concentration of suspended solids in continental runoff is in the order of 500 mg/l. The traction load at the bottom of streams ("bed load") is more difficult to estimate, but according to Turekian it is probably no more than 10% of the suspended load. The suspended phase of these rivers is to a large degree colloidal and consists of inorganic materials such as oxides, silicates, carbonates, and clay minerals. It includes organic matter such as living and dead microorganisms and products of their decomposition. According to Turekian most of the clay minerals found in estuarine or ocean sediments are derived from weathering profiles on the continents and alteration products of volcanic rocks.

DEPOSITION OF SUSPENDED MATERIALS IN ESTUARIES

Characteristics of Estuarine Sediments

Sediment, both as bed material and suspended load, can be divided into two general groups: (1) cohensionless, or coarse and (2) cohesive, or fine. The first is composed predominately of sand and gravel, while the latter is essentially a mixture of silt and clay. A substantial difference exists between these two groups with respect to their interaction with the flow-induced hydrodynamic forces. Cohesionless particles - sand - remain as individual particles regardless of the flow conditions and their settling in estuaries is the net result of fluid motion and gravitational forces. On the other hand, Ippen (1966) reports that the depositional behavior of fine cohesive sediments is one of the primary factors influencing (1) shoaling in estuarial channels, (2) formation of deltas, and (3) persistence of turbidity currents, and that sand is not very important. These sediments (clays and silts) range in size from a small fraction of one micron to several microns, and normally a large proportion are colloidal; i.e., particles with large surface area per unit mass so that the effects of the surface and interparticle physico-chemical forces are at least as important as those of gravitation. These fine cohesive sediments may coagulate, i.e., form aggregates of multiples of particles in interaction with the suspending fluid.

Colloidal or semi-colloidal particles carry an electrical charge, usually negative in natural waters, which influences their behavior in suspension; of these particles, clay minerals are of primary importance. In waters of low salt content repulsive forces between the negatively charged particles dominate resulting in stable suspensions, i.e., suspensions with little tendency for particle aggregation. Some interparticle physico-chemical forces between particles are attractive - van der Waals atomic forces. These attractive forces are strong at short range, but fall inversely with the third power of separation for two spherical particles. The net effect of all interparticle forces may be either a net repulsion or attraction, depending on the dissolved contents of the solution.* In waters that are even slightly saline the net interparticle forces become attractive, and particles that collide tend to cling to each other and form agglomerations called flocs whose size and settling velocity may be of several orders of magnitude larger than those of the individual particles. Moreover, the flocs may combine into larger systems, known as floc aggregates and aggregate networks, with still larger settling velocities. This phenomenon - flocculation (hydraulic engineering literature)-is the main cause of deposition of fine suspended sediment in estuaries (Etter et al, 1968).

Flocculation involves primarily particles in the clay size range due to their electrical charge; however, particles in the silt size range also participate in flocculation, either by entrapment or because they consist of aggregates of clay minerals. It appears that suspended particles larger than about 75 microns (i.e., fine sand size) rarely participate in flocculation (Duke, 1961), probably due to their rapid settling upon entering the estuary.

Estuarine Sedimentation

General Aspects. The hydraulic and sediment characteristics of estuaries are considerably more complex than for river systems. Suspended materials consisting largely of colloidal particles are subject to two different classes of forces in an estuary: hydrodynamic forces and chemical forces. An important difference between river and estuary sediment transport is the interrupted transport of suspended sediment in estuaries. This is caused by slack currents and the floc-

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* This subject will be covered in depth in Chapter III.

culation of colloids in saline water. Some of the unique characteristics of estuaries which relate to sediment transport have been summarized by Schultz (1954) and by Klingeman and Kaufman (1965) and may be listed as follows: (1) discharge is variable; (2) velocity distributions vary horizontally and vertically in a manner independent of discharge; (3) complex flow regimens of differing characteristics are established and discarded in opposite directions during each tidal cycle; (4) successive flow cycles are not identical but may be very different; (5) in some portion of every estuary there is water of nonhomogeneous density and the difference in density which occurs is not constant; (6) instantaneous fluctuations of current velocity are appreciable; (7) suspended sediment concentrations are highly variable, both in space and time; and (8) flocculation resulting from physical and chemical forces is active in the estuary.

Mixing Characteristics. Circulation patterns in estuaries have been described in a previous section of this chapter. These circulation patterns are instrumental in the trapping of suspended matter in estuaries. Ippen (1966) has made the following general statements based on the internal flow and circulation patterns which exist in these waters.

> "Sediments settling to the bottom zone in an estuary will on the average be transported upstream and not downstream. Sediments will accumulate near the ends of the intrusion zone and form shoals. Shoals will also form where the net bottom velocity is zero due to local disturbances of the regime such as by tributary channels."

These statements are most appropriate for stratified and partially-stratified estuaries, whereas in a well-mixed system, shoaling will be more dispersed. The coagulation of particles is the result of collisions between particles (flocculation) and the cohesion of particles (sticking) when particles are brought together. The collisions of suspended particles depend upon Brownian motion of the particles, internal shear of the fluid, and differential settling velocities of the particles. Collisions induced by Brownian motion are important for particles smaller than 1 micron. Collisions induced by differential settling velocities can be considered a special case of collisions by internal shear. A qualitative presentation of the mixing characteristics of estuaries is given below as this is responsible for particle collisions (particles >1 micron) induced by internal shear of the fluid. The numerous and complex factors involved in estuarine mixing, flushing, and exchange complicate the formulation of basic rules; however, the simplified discussion which is given is useful and is based on the works of Pritchard (1969), Ippen (1966), and Klingeman and Kaufman (1965).

The basic processes that provide mixing in estuarine systems are the tides, the river inflow, and the wind. The tides provide a major portion of the turbulent energy causing estuarine mixing. The tidal range (difference in elevation between the mean values of low and high tides) is an important mixing factor. The energy required to mix salt and fresh water, largely supplied by tidal forces, appears to be proportional to the square of the tidal range.

A second source of turbulence is river inflow to the estuary. The flow ratio (river inflow/tidal prism volume) is often used to describe mixing and flushing characteristics of an estuary. This is defined as the ratio of the total fresh water discharge within a tidal cycle, which is passed to the sea, to the so-called tidal prism. The tidal prism is the volume represented by the amount of water entering an estuary between low and high tides. A large flow ratio (e.g., greater than 1.0) is indicative of a large volume of fresh water at the estuary surface and of stratified flow or a sharp vertical salinity gradient. Incoming fresh water, under these conditions, may pass through the estuary rather quickly with a minimum of mixing. A small flow ratio (e.g., less than 0.1) is indicative of a well-mixed estuary and longer residence times for incoming flows.

The size and shape of estuaries are important factors in mixing and flushing. Thus for the same fresh water runoff and tidal conditions, two estuaries of differing physical structure may possess entirely different mixing characteristics. Changes in width or depth may affect the flow ratio (river inflow/tidal prism volume) and the mixing characteristics. Decreases in depth tend to improve the effectiveness of tidal currents in promotion of vertical mixing. Increases in the depth tend to encourage stratification.

Orientation of an estuary with respect to wind direction also affects the mixing process. Mixing and fluid exchange are extensive in shallow areas exposed to a long wind-wave fetch. Winds which blow down an estuarine channel increase the transport of surface water to the sea whereas winds blowing up-channel retard the seaward movement of surface water.

Bottom currents are another factor involved in the mixing process. If flow stratification is marked, material which enters the lower layer near the mouth of an estuary may be carried into the estuary by bottom currents and remain there for a long period. Finally, an additional influence may be exerted on large estuaries due to the earth's rotation (Coriolis force).

Erosion, Transportation, and Deposition. Particles are moved by fluids when the forces exerted by the drag of the fluid overcome the gravitational and cohesive forces that hold the particles at rest. Fine-grained particles in a stream bed or on the estuary floor may remain at rest while coarser materials are being transported. This paradoxical situation arises because for cohesionless sediments the main resistance to erosion is provided by the submerged weight of the sediment - gravitational forces. For cohesive sediments (silts and clays), the main resistance to erosion is provided by net attractive physico-chemical interparticle forces (Partheniades and Paaswell, 1970). Cohesive particles are difficult to set in motion, but once in suspension they may remain so for long periods of time because of vertical turbulent current velocities that exceed the settling velocities of the clay-size particles.

A summary of relations among erosion, transportation, and deposition of particles as functions of current velocity and particle diameter is shown in Figure 2.2 (Postma (1967)). The "critical erosion velocity" is the minimum current velocity at which sediment of a particular size begins to move. Notice the minimum in the "critical erosion velocity" curve; the erosion velocity for particles greater than 0.3 mm in diameter increases with particle diameter, and for particles less than 0.3 mm the velocity increases with decreasing particle size. The material above 0.3 mm is indicative of quartz sand with a specific gravity of 2.65. For particles with a lower

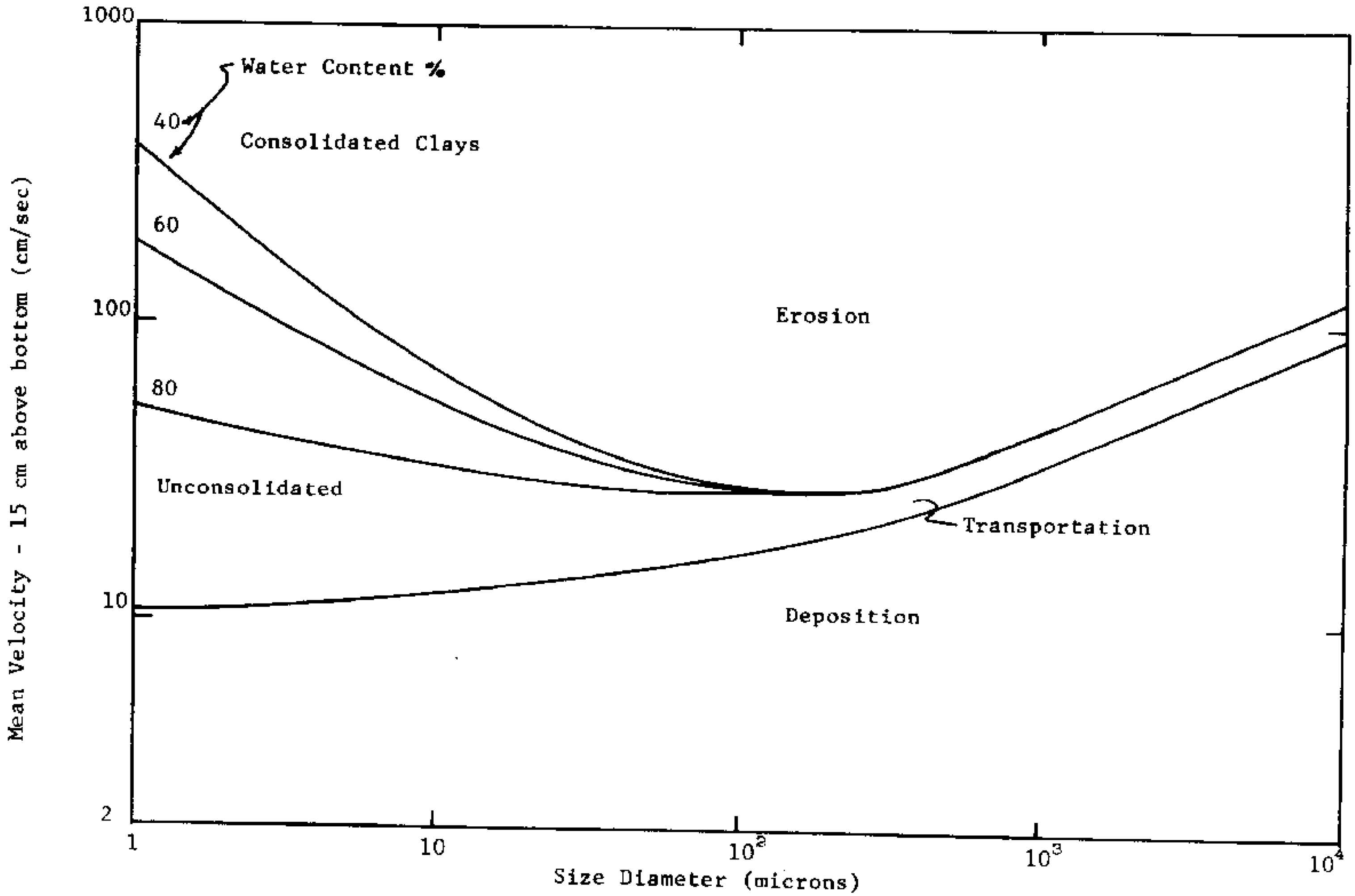


Figure 2.2 Erosion, Transportation, and Deposition Velocities for Different Particle Sizes (from Postma (1967)).

density the curves move downward; if the density is higher, the curves are located above those shown on the graph. Thus, 5 micron particles remain in suspension at current speeds greater than 10 cm/sec and bottom deposits of 5 micron particles will be eroded by current speeds greater than about 100 cm/sec depending on the stage of consolidation.

Partheniades (1965) utilized a recirculating flume to study the erosion of San Francisco Bay silty clay. Partheniades found that for each flow depth, there exists a threshold velocity above which a substantial amount of sediment is retained in suspension, and below which rapid deposition of practically all suspended sediment occurs. This threshold velocity is smaller than the minimum velocity required to erode the deposited sediment.

Partheniades and Paaswell (1970) summarized the results of laboratory investigations on the erodibility of cohesive soils and compared them with similar field results. The authors concluded that the bed shear stress strongly controls both the erosion and deposition of cohesive sediments.

Experiments by Krone (1962) on the erosion of San Francisco Bay silty clay under scour conditions showed that resuspension of deposited sediment occurred due to bed shear exerted by the flow. This occurred in one of two ways - bed failure or erosion - depending upon the bed structure. The bed structure, in turn, depended upon whether the bed was deposited from flowing or quiescent water. Flowing water gave a stronger structure due to the deposition of smaller flocs (limited in size by internal shear of the fluid) susceptible of crushing and interface contacts and having a lesser individual response to shear. In quiescent water, a less-compact bed developed with a structure changing with time, particularly immediately after deposition. Bed failure occurred within a short time after an increase in bed shear, and resulted in resuspension of material above a bed depth at which the shear strength of consolidated material allowed the remaining bed to resist the flow shear. Erosion of bed-surface particles appeared to be a relatively slow process compared with bed failure, and it was caused by a weakening of interparticle bond strength.

Flocculation

The marked physical changes which flocculation causes in the fine, cohesive suspended sediment entering an estuary are reflected by changes in the subsequent transport behavior of the suspension. The floc structure and density differ from those of individual particles. The inclusion of numerous primary particles into the flocs causes an increase in effective particle size, a reduction in the number of separate particles, and a change in the particle size distribution of suspended sediment. The larger settling velocities encourage the deposition process. This tendency is opposed by the unsteady turbulent conditions of tidal waters. According to Krone (1962), estuarine flocculation is principally affected by salinity, the suspended sediment concentration, and the internal shear of the water. Internal fluid shear places an upper limit on floc size in a suspension in addition to its role in promoting floc formation, as the larger flocs in a given flow tend to break because of their low shear strength. Concurrently, the decrease in numbers of unflocculated particles with time and the growth of flocs due to differential settling tend to narrow the particle size range from the lower end of the size distribution.

Krone (1962) performed a series of systematic experimental studies on the deposition of San Francisco Bay silty clay in an open flume. Krone's experiments with flocculent sediments under simplified saline flow conditions demonstrated that an interchange occurred between suspended and deposited sediment during the suspension transport. It was found that the deposition rate was sensitive to the factors which affect the flocculation rate - increasing with suspension concentration, particle size, and size distribution of the flocs. Deposition occurred below some critical value of flow shear at the bed and the deposition rate increased with decreasing bed shear. Krone also studied experimentally the shear strength of flocs, and derived an empirical relationship which showed that the floc strength depends on the floc size and the suspension shearing rate.

Deposition studies conducted by Partheniades (1965), using a recirculating flume, showed that the concentration of suspended sediment initially decreases rapidly (due to flocculation), and approaches asymptotically a more or less constant value called the equilibrium concentration. Etter et al (1968) investigated the depositional characteristics of kaolinite in turbulent flow. A comparison of the size distribution of the parent material with the material retained in suspension when equilibrium was achieved indicated that greatest deposition occurs among the clay-size fractions, suggesting that the deposition was controlled predominantly by flocculation.

Krone (1962) concluded that shoaling in San Francisco Bay was the result of flocculation in regions where sea water mixed with river water followed by deposition. Laboratory studies indicated that attractive forces dominate the repulsive forces at salinities above 1 gm/l, so that under the most common conditions in the Bay the particles have a tendency to form bonds with one another. Meade (1969) has presented data showing the evidence of flocculation in the Savannah River estuary. Neiheisel and Weaver (1967) found the shoals in Charleston Harbor to be comprised predominantly of fines which had flocculated. Allersma et al (1966) investigated the transport patterns of sediment in the Chao Phya estuary (Thailand). The authors stated that stable clay (or silt) suspensions exist in the fresh river water. Rapid flocculation starts when the suspended sediments enter saline water causing great quantities of silt to settle where it enters the inward density flow which carries it back towards the tip of the salt wedge.

Duke (1961) examined shoaling in the lower Hudson River. From model studies at Vicksburg, it was concluded that the extensive shoaling in the lower Hudson stems from three main sources: (1) the constriction in the cross-sectional area of the river at the George Washington Bridge, (2) an environment that is extremely favorable to flocculation, and (3) the differential in depth between the artificial channel on the New Jersey shore and the natural deep-water channel on the New York shore. The principal source of sediment was attributed to the upper watershed with contributions from the eroding banks, the adjacent ocean area, industrial wastes, and sewage waste. Sheldon (1968) examined sedimentation in the estuary of the River Crouch, Essex, England. Sheldon found that the material in suspension was flocculated and mainly inorganic. Particle diameters of the flocculi ranged from 1μ to about 80μ with a mean at about 10-15μ. Fleming (1970) made a sediment balance on the Clyde estuary (Scotland). Results indicated that all sediment which enters the Clyde estuary undergoes flocculation and deposition in the upper reaches of the estuary with little transport of sediment to the sea. Particle size analyses (Coulter Counter) indicated a predominantly fine suspended sediment supply. The main sources of sediment that enter the estuary were attributed to the rivers, sewage discharges, and spillage from harbors and docks. Little sediment was found to enter the estuary from the sea.

CLAY MINERAL COMPOSITION OF SEDIMENTS

Factors Influencing Clay Formation and Distribution

The formation of clay minerals is highly dependent upon the weathering process and factors controlling this process. The distribution of clays in recent sediments depends upon factors which affect the formation of clays as well as the environment of deposition. A brief discussion of the weathering process is presented below and was obtained primarily from Grim (1968) and Keller (1970). The section concerned with the environment of deposition was obtained from several sources; these are cited accordingly.

Weathering Process. Rocks exposed at the earth's surface are subjected to continuous alteration by chemical, biological, and physical processes. The most important of these is chemical, whereby chemical reactions between rock minerals and soil waters produce dissolved constituents and solid residues. The major elements in the earth's crust and rocks are O, Si, Al, Fe, Mg, Ca, Na, and K; consequently, this is reflected in the composition of clay minerals and the composition of natural waters. Several parameters are important in controlling the weathering process and include parent rock, climate, topography, vegetation, and time.

The composition of the parent rock, specifically, the amount of alkalies and alkaline earths is important in determining the composition of weathered products. Different clay minerals may be formed from the same parent rock under different conditions of climate, topography, and time. Igneous rocks, shales, slates, and schists yield a variety of clays, at least in the initial stages of weathering, due to their alkali and alkaline earth content in addition to alumina and silica.

Temperature and rainfall are climatic parameters which affect weathering. Decomposition of the parent rock occurs most rapidly in warm, humid climates where the components of the parent material are removed from the site by leaching. The rate of erosion and removal of weathered products are influenced by climate and topography. The topography is important in determining whether or not there is movement of water through the weathering material. In poorly drained areas or low, flat areas with relatively little leaching, the components of weathering are not removed from the zone of decay.

The decomposition products of vegetation also enter into the alteration processes. Elements such as silicon, aluminum, calcium, magnesium, and iron are accumulated by some plants and these elements are released when the plants decay. Since weathering is a relatively slow process, time is significant in the development of alteration products. If the parent material contains alkalies and alkaline earths, time and climate are significant, leading to a variety of products; initially, the parent rock may yield certain products, but after a long time interval all of the alkalies may be removed by leaching and different products will form. The rate of alteration under different weathering conditions obviously varies widely, depending on factors of climate, parent rock, and topography.

Kaolinite is indicative of an environment of strong leaching and removal of Ca, Mg, Na, K, and Fe, possibly SiO_2, and the addition of H^+. Calcium has a tendency to block the formation of kaolinite. The presence of K and Mg in the environment of alteration and the length of time they remain in the environment are important, since K leads to the formation of illite and Mg leads to the formation of montmorillonite. Montmorillonite is indicative of an environment where Mg, Ca, Fe, and Na are retained either by ineffective leaching or in a semi-arid climate. Illite requires a high concentration of K relative to the other cations.

Diagenesis. An area of disagreement in clay petrology concerns the origin of clay minerals in the sediments. Are the clays in the sediments derived from weathering profiles on the continents or are they formed in their depositional environment; or stated formally, are the clays detrital, diagenetic, or a combination of both? Diagenesis includes all modifications that sediments undergo when transported from one environment to another - for example, fresh water environ to marine. In a more restricted sense, diagenesis is defined as the chemical rearrangements and replacements that occur while the sediment is still on the marine floor (Weaver, 1958). The allied question to be examined is, how do clays respond when transported from the land into the marine environment; e.g., will montmorillonite be transformed in the marine environment to illite?

Whitehouse and McCarter (1958) exposed clays to sea water for periods of 6 months to 5 years. They concluded that chloritic and illitic clay types may develop from montmorillonite in the marine environment. The extent of modification of the montmorillonite clay was more dependent upon the Mg/K ratio than the total salt concentration. Powers (1957) reported that chloritic clays form from the diagenesis of weathered illite in the Atlantic Coastal Environment, in which the chlorite-like clay probably passes through a vermiculite stage. According to Powers, montmorillonite and to a lesser extent illite, are altered to a chloritic material in the Gulf of Mexico. Grim and Johns (1955) reported the gradual loss of montmorillonite with the ultimate formation of poorly crystalline illitic and chloritic phases in the Rockport, Texas area (Guadalupe River and Delta). The dioctahedral character of the chlorite and illite indicated that the change from montmorillonite to these components involved only the exchange and/or addition of components in interlayer positions. The exchange reactions involved the acceptance of K^+ and Mg^{++} from the salt water by the clay for Ca^{++}. There was no indication of a breakdown to constituent oxides and hydroxides prior to regrouping. Johns and Grim (1958) found montmorillonite to be the dominant clay mineral being deposited in the Mississippi River Delta. A small amount of the montmorillonite changes to illite and chlorite; the authors suggest that this material was degraded micaceous material (identified by X-ray diffraction analysis as montmorillonite) which undergoes regradation in a marine environment.

Keller (1970) concludes that degraded illite resembles montmorillonite (expanding, mica-derived) and can adsorb potassium from sea water and contract to 10 Å. This is in accordance with the results of Johns and Grim (1958) where degraded illite which was identified as montmorillonite underwent regradation in a marine environment. Keller states that insufficient potassium is taken up by true montmorillonite (not degraded illite) from salt water to convert to illite. Keller (1970) notes that chlorite is prevalent in soils in higher latitudes where chemical weathering is not intense, but chlorite or a chlorite-like mineral may form from montmorillonite in the ocean where there is a high concentration of Mg^{++}. Weaver (1958) examined the X-ray patterns of thousands of sediments and concluded that the majority of clays in sediments are detrital in origin and that clays are only slightly modified in their depositional environment. Powers' work (1957) was cited in which it was reported that chlorite may form in the marine environment; Weaver (1958) points out that even here the basic lattice is detrital and that only the interlayer material is authigenic. Weaver claims that much of the controversy concerning the origin of clays - detrital vs. diagenetic - is due in part to semantics. The term diagenesis is very broad in meaning and has been used to describe very minor changes such as base exchange. Weaver states that it is common for investigators to speak of the diagenesis of montmorillonite to illite under marine conditions, while there is no evidence to suggest that true montmorillonite as defined by the structure and chemical character of the lattice adsorbs K^+ and becomes illite. Weaver agrees that degraded illite, which has had K removed to the extent that water is adsorbed between the layers and thus superficially resembles montmorillonite, can adsorb K in salt water and contract to 10 Å (illite). The author considers this an adsorption phenomenon and not diagenesis where a more fundamental modification or alteration of a mineral is implied. The reader should note that this section on diagenesis has excluded alteration of clay minerals due to metamorphic processes, i.e., changes in sediments subjected to deep burial.

It is the opinion of this writer that most of the clay minerals found in sediments are derived from weathering profiles on the continents and alteration products of volcanic rocks. Clays may be modified to some degree by interactions with sea water but this involves, for the most part, adsorption of K or Mg and thus regradation of the original clay mineral (e.g., degraded illite resembling montmorillonite to illite). It is interesting to examine the results of a series of papers by Hurley and associates (1958, 1961, 1963) on the potassium-argon age determinations of the mica components of sediments. This group concluded that illite in the Mississippi River Delta sediments was detrital with an age in excess of 200 million years. They also found the illite in the sediments of the Rappahannock River had an age of 300 million years and pelagic sediments from several locations in the North Atlantic showed K-Ar age values in the range 200-400 million years.

Differential Flocculation. The work of Whitehouse, Jeffrey, and Debbrecht (1960) on the differential settling velocities of clay minerals has had a significant impact on the diagenesis vs. detritus schools. Many investigators have explained the distribution of clays in sediments by differential flocculation citing the results of Whitehouse's group. In this section the methods employed by Whitehouse and his associates and the results achieved will be developed in some detail since their work is frequently cited and since it is pertinent to Chapter V of this dissertation.

The following is a summary of the experimental techniques used by Whitehouse to determine the settling velocities of several clays in waters at various salinities. Clay minerals were pretreated with a dispersing agent prior to fractionation using a centrifuge to obtain clay fractions $< 2\mu$. A pipette analysis method (other methods were also employed) was used to determine the settling rates of the clays in quiescent saline waters. Velocities measured by this method are interpreted in terms of "equivalent diameters". The pipette analysis method determines the weight of solid material that accumulates at a given depth in the suspension using selected time intervals. Clay suspensions ($< 2\mu$ fraction) were dispersed initially in a Hamilton Beach dispersion apparatus at 14000 rpm for periods of 5-10 minutes for kaolinite and illite and 20 minutes for montmorillonite. The pipette method was based upon the settling of clay suspensions of 3.6 gm/l or less in columns of 32.2 cm in height and 6.3 cm in diameter. A pipette extraction of 20 ml was made after a time t at a depth h. The weight of clay in this 20 ml volume was determined and the total amount of clay having a settling velocity less than h/t was calculated. The suspension was agitated again and a longer period of time was allowed to elapse before the second sample was extracted. This procedure of repeated agitation and settling was used to determine the settling velocities of the clays. Whitehouse reported that the settling values obtained apply to thoroughly agitated and flocculated clays with no time dependence for flocculation involved.

Table 2.1 shows the relationship between salinity and settling velocity for various clays in synthetic sea water.

Table 2.1

REPRESENTATIVE SETTLING VELOCITIES* (cm/min)

	Salinity	(ppt)				
Clay Mineral	0.9	1.8	3.6	10.9	18.1	32.5
Illite	0.89	0.90	1.05	1.10	1.10	1.10
Kaolinite	0.80	0.81	0.81	0.81	0.81	0.81
Montmorillonite	0.0023	0.0036	0.0078	0.041	0.076	0.088

* (Whitehouse et al (1960), Pipette method, 26°C, pH = 8.2)

The settling velocities for kaolinite and illite exhibited little dependence upon salinity above 3.6 ppt. Settling velocities for montmorillonite were found to be a function of salinity over the entire range. In addition, the results of Whitehouse and associates indicated that settling velocities were relatively the same over the entire clay concentration range of 0.01 - 3.6 gm/l. Finally, it was concluded that clays do not settle as single solid grains but the settling unit is an assembly of solid grains in association with occluded water and water of hydration. This assembly is termed a coacervate.

Interpretation and extrapolation of Whitehouse's results to natural waters such as estuaries is difficult, especially since terms like flocculation can have several meanings depending on one's field. The following will be developed in detail in Chapters III and IV but is outlined at this point to insure a common ground for all disciplines before this writer discusses the results of Whitehouse. Clay suspensions are destabilized in waters of high ionic strength; i.e., repulsion between the electrical double layers surrounding the particles is reduced by double layer compression. Thus in saline waters destabilization is accomplished to varying degrees dependent upon the clay type and salinity; if particle transport is provided, particles can be brought into contact with each other to form aggregates. This latter process is often termed flocculation (particle transport) and the aggregates of particles frequently form a loose network of particles containing water within this network. For colloidal particles less than about 1 micron in diameter, particle transport is achieved by Brownian diffusion of the colloids. For particles larger than 1 micron, Brownian diffusion becomes negligible and mixing of the suspension must be provided in order to induce particle contacts. The opportunity for particle contacts is greater with increasing clay concentration since the probability of collisions between particles is enhanced by the greater number of particles. Finally, the rate of particle aggregation depends upon the degree of destabilization (a function of salinity and clay type) and particle transport (a function of clay size and clay concentration).

In the paper of Whitehouse et al. (1960), the clay suspensions were sized and the clay fraction less than 2 microns used at clay concentrations of 0.01 to 3.6 gm/l. The suspensions were dispersed by intense agitation throughout the settling experiments indicating that settling velocities of clays, destabilized to varying degrees, were computed. Clay concentrations of 0.01 to 3.6 gm/l had no effect on the settling velocities. This was probably due to the repeated and intense agitation employed after each sample withdrawal used in the pipette method. It is the opinion of this writer that the work of Whitehouse et al showed that montmorillonite was much smaller than kaolinite and illite. Their results should be interpreted for the most part as settling velocities of clays in sea waters of varying salinity. Under the experimental conditions employed by this group, their results should not be construed as flocculation rates or the ability of clays to flocculate. In estuaries it is the rate of particle aggregation that is important in determining the distribution of clays in sediments. The clays which aggregate rapidly will tend to form flocs of such a size that they can settle from the suspension.

Clays in Sediments

Oceans. Rateev (1969) has published a paper which summarizes the distribution of clay minerals in the sediments of the oceans and relates the distribution to the geographical latitude or climate. Rateev found that kaolinite, gibbsite, and montmorillonite have an "equatorial" type of distribution. The maximum amounts of kaolinite are found near the equator with a gradual decrease in content toward the poles. The distribution of montmorillonite coincides in general with kaolinite, but the presence of montmorillonite in some regions of the oceans is associated with volcanism. Furthermore, Rateev reported that the distribution of chlorite and illite is "bipolar" and not "equatorial". The maximum amounts of chlorite are located far from the equator mainly in the northern and southern zones. The northern zone coincides with the region adjacent to continents with soils rich in chlorite; the southern zone is related to the Antarctic continent. High concentrations (60-80% of the clay fraction) of illite are found in the northern part of the Atlantic Ocean near the eastern shores of Canada and the western shores of Europe. The amounts of illite in the sediments gradually decrease to the south of this zone; however, an equatorial zone of minimal content of illite is missing from the Atlantic basin.

Biscaye (1965) concluded that the bulk of clays in recent sediments of the Atlantic Ocean are of continental origin and that the formation of minerals _in situ_ on the ocean bottom is of minor importance. According to Grim (1968) all types of clays are present in recent sediments, but in general the clay composition reflects climatic conditions of the source area. Grim indicates that chlorite and illite are abundant components of marine sediments, with kaolinite commonly abundant near-shore in localized areas. Grim concludes that the distribution of montmorillonite is irregular, but its distribution is associated with volcanism.

Gulf of Mexico. Grim and Johns (1955) investigated the clay mineral composition of the Guadalupe River and Delta which empties into the Gulf of Mexico along the central part of the Texas coast. The authors found montmorillonite to be the dominant clay in the Guadalupe River and Delta, but the percentage of montmorillonite in the sediments decreased towards the Gulf of Mexico. Illite and chlorite made up a small fraction of the sediments in the River and Delta but increased towards the Gulf. Grim and Johns concluded that poorly crystalline illitic and chloritic phases are being formed from montmorillonite via exchange and/or addition of components in interlayer positions. The Guadalupe Delta was found to be the area of greatest sedimentation due to the sediment load being transported and deposited by the Guadalupe River. It was noticed in the fractionation procedures that a few samples exhibited differential flocculation. In such cases, the bulk of the material would flocculate, but an appreciable amount would remain in suspension. It was found that the material which exhibited this initial flocculation was composed mostly of montmorillonite. Apparently, the rate of particle aggregation for montmorillonite is rapid. Frequently, researchers cite the study of Whitehouse, Jeffrey, and Debbrecht (1960) and conclude that montmorillonite should be deposited downstream of illite and kaolinite due to its low settling velocity. However, it was indicated in a previous section that the deposition of clays is highly dependent upon the rate of particle aggregation (flocculation).

Johns and Grim (1958) also investigated the clay mineral composition of sediments from the Mississippi River Delta. Johns and Grim found that montmorillonite is the dominant clay being deposited in the Delta region. It was suggested that a small amount of this montmorillonite represents degraded micaceous materials from the Ohio River drainage system. This degraded micaceous fraction undergoes regradation in saline water yielding reconstituted illitic and chloritic phases. The bulk of the montmorillonite is bentonite in character, undergoes no apparent change, and represents the contribution of the Missouri River drainage system.

Griffin (1962) examined the clay mineral distribution in the sediments of the Northeastern Gulf of Mexico. Griffin found that the Mississippi River contributes primarily montmorillonite with some illite and kaolinite, the Apalachicola River contributes primarily kaolinite with some montmorillonite, and the Mobile River contributes kaolinite and montmorillonite clay minerals. It was concluded that the type of clay supplied to the Gulf is a direct function of the clay minerals in the soils of the river basins and is controlled by parent rock and weathering.

Jacobs and Ewing (1969) investigated the source and transport of minerals in the Gulf of Mexico and Caribbean Sea. The authors reported that the montmorillonite-rich sediments of the Mississippi River appear to be flocculated and deposited near the front of the delta. Slumping and turbidity flows transport these sediments along the bottom to the central area of the basin leaving very little montmorillonite in suspension. Jacobs and Ewing found that the waters flowing into the Caribbean are rich with micaceous material; the influence of discharge from the Amazon River extends into the Caribbean with a suspended load in which 10 Å minerals (illite) are most abundant. Suspended clays in the Gulf of Mexico and Caribbean Sea were predominantly mica-like (illite). It was concluded that circulation in the upper layers of water flowing from the Caribbean and carrying a micaceous-rich mineral assemblage affects mineral transport into the Gulf of Mexico. This is different from the montmorillonite-rich load delivered by the Mississippi River.

<u>Atlantic Coast</u>. Powers (1957) found well-crystallized and weathered illite as the predominant clay minerals in sediments from

the Chesapeake Bay area. Minor amounts of kaolinite and traces of weathered chlorite were also found. Powers reported that in the estuaries a chlorite-like clay is being formed from weathered illite. Powers stated that there is a elongated lens of mud deposits in estuaries due to flocculation, and that downstream water is depleted of its suspended load by flocculation. The mud lens begins near fresh water, then has a maximum, and then decreases.

Nelson (1960) examined the clay mineralogy of the bottom sediments of the Rappahannock River and Estuary. There were differences in the mineralogical composition of the sediments. Chlorite and feldspar occurred exclusively in the estuary while kaolinite, illite, dioctahedral vermiculite, and montmorillonite occurred in both the fresh water and estuarine sediments. Nelson observed that the amount of kaolinite in the sediments decreased between the upper Rappahannock River and the lower Rappahannock Estuary. In the estuary, there was an increase of well-crystallized illite and a decrease in unorganized illite.

Neiheisel and Weaver (1967) investigated the relationship between source area and clay minerals in rivers and estuaries of South Carolina and Georgia including Charleston Harbor, Port Royal Sound, and Brunswick Harbor. The authors noted that kaolinite is the dominant clay in the Piedmont Province and montmorillonite is the major clay mineral in the Coastal Plain. Neiheisel and Weaver stated that the shoals in Charleston Harbor are comprised predominantly of fines which have flocculated. Kaolinite and montmorillonite were found in the sediments of Brunswick and Charleston Harbors. The authors concluded that the ratio of kaolinite to montmorillonite serves to identify the relative proportion of clay sized sediment derived from the two source areas. In addition, illite can be used to determine the off-shore contribution to the estuaries. Biscaye (1965) found that the clays in the surficial Continental Shelf sediments along the southern Atlantic Coast are predominantly illite. This illite is derived from the central and northern Appalachians and carried southward by long-shore currents.

North Carolina. Brown and Ingram (1954) examined the clay minerals of the Neuse River and found kaolinite as the dominant clay decreasing downstream. Illite occurred sporadically throughout the length of the river while a chlorite-like clay became dominant in the lower part of the stream and in the estuary. Brown and Ingram concluded that the great predominance of kaolinite in the Neuse River sediments is due to kaolinite in the soils of the drainage basin being eroded into the river.

Griffin and Ingram (1955) studied the clay mineral composition of the Neuse River estuary and found kaolinite as the dominant clay being introduced into the estuary. Chlorite increased downstream becoming the dominant mineral at the lower end of the estuary while illite increased rapidly near the end of the estuary.

Park (1971) studied the clay mineralogy of recent sediments from North Carolina sounds and estuaries. The most abundant clays found in the study area were kaolinite and illite with minor amounts of chlorite-like intergrade clay, chlorite, and montmorillonite. Kaolinite was found to be most abundant in the western parts of Albemarle Sound, Pamlico River estuary, and Neuse River estuary. Illite was found to be most abundant in the eastern parts of Albemarle

Sound, Pamlico Sound, Core Sound, Bogue Sound, North River estuary, and Newport River estuary. It was observed that kaolinite and chlorite-like intergrade clay, in general, decrease in a seaward direction while illite, chlorite, and montmorillonite increase seaward.

Murray and Sayyab (1955) investigated the clay mineral composition of sediments off the North Carolina coast. Samples were collected from the Continental Shelf, the Continental Slope, and the floor of the northwestern basin, north of Bermuda. Illite and chlorite were the dominant clays found in the samples with minor amounts of kaolinite and montmorillonite.

Pamlico River Estuary and Pamlico Sound. Allen (1964) examined the clay composition of the Tar-Pamlico River and found kaolinite to be dominant in the river and upper estuary but decreased rapidly along the lower estuary. Illite and chlorite-like intergrade clay were found in varying amounts along the entire length but increased substantially through the lower estuary. Montmorillonite was present in minor amounts but showed a slight increase in the lower estuary.

Park (1971) found the following seaward trends for clay minerals in the sediments of the Pamlico River estuary and across Pamlico Sound towards the Outer Banks. Kaolinite was the dominant clay in the upper end of the estuary but decreased along the estuary and the Pamlico Sound. Illite occurred in small amounts in the upper end of the estuary but increased rapidly along the estuary becoming the dominant clay in Pamlico Sound. Chlorite and montmorillonite were found in small amounts along the length of the system while intergrade clay increased along the estuary but decreased in Pamlico Sound.

Dobbins, Ragland, and Johnson (1970) examined the clay mineralogy of the Pamlico River estuary and Pamlico Sound. Kaolinite was found to be the dominant clay in the upper part of the Pamlico estuary but decreased along the estuary and in Pamlico Sound. Illite showed an inverse trend as it increased along the estuary becoming the dominant clay mineral in Pamlico Sound. Chlorite and chlorite-like intergrade clay were found along the entire length of the system while montmorillonite was present in minor amounts.

SUMMARY

The purpose of this chapter is to examine parameters which affect the coagulation and deposition of suspended materials in estuaries. Estuarine sediment, both as bed material and suspended load, can be divided into two general groups: (1) cohesionless or coarse and (2) cohesive or fine. The first is composed predominately of sand while the latter is essentially a mixture of silt and clay. Cohesionless particles remain as individual particles regardless of the flow conditions and their settling in estuaries is the net result of fluid motion and gravitational forces. Cohesive particles range in size from a small fraction of one micron to several microns, and normally a large proportion are colloidal; i.e., particles with large surface area per unit mass, so that the effects of the surface and interparticle physico-chemical forces are at least as important as those of gravitation. These fine cohesive sediments may coagulate i.e., form aggregates of multiples of particles in interaction with the suspending fluid.

The basic processes that provide mixing in estuarine systems are the tides, the river inflow, and the wind. An estuary is moved along the sequence from the stratified salt wedge estuary, through the partially-stratified estuary, to the vertically homogeneous estuary, with decreasing river flow and decreasing depth, and with increasing tidal current and increasing width. Wind can have an important influence on estuarine circulation and mixing, especially for wide and shallow estuaries. The circulation patterns in estuaries are instrumental in the trapping of suspended material and the recycling of nutrients in these systems.

Cohesive sediments (clays and silts) are responsible for the shoaling of estuarine channels, the formation of deltas, and the persistence of turbidity currents in estuaries. Clays carry an electrical charge, usually negative in natural waters, which influences their behavior in suspension. In waters of low salt content repulsive forces between the negatively charged particles dominate, resulting in stable suspensions; i.e., suspensions with little tendency for particle aggregation. Some interparticle physico-chemical forces between particles are attractive - van der Waals forces. In waters that are even slightly saline the net interparticle forces become attractive, and particles that collide tend to cling to each other and form agglomerations called flocs, whose size and settling velocity may be several orders of magnitude larger than those of the individual particles. This phenomenon - coagulation - is the main cause of deposition of fine suspended materials in estuaries.

An area of disagreement concerns the origin of clay minerals in estuarine sediments. It is the opinion of this writer that most of the clay minerals found in sediments are derived from weathering profiles on the continents and alteration products of volcanic rocks. Clays may be modified to some degree by interactions with salt water but this involves, for the most part, adsorption of K or Mg and thus regradation of the original clay mineral. The clay mineral composition of the Pamlico Estuary indicates that kaolinite is the dominant clay in the upper estuary but decreases along the estuary. Illite occurs in small amounts in the upper end of the estuary but increases rapidly along the estuary becoming the dominant clay in Pamlico Sound. Chlorite and chlorite-like intergrade clay are present in the Pamlico sediments while montmorillonite is present in minor amounts.

CHAPTER III

STABILITY OF CLAY SUSPENSIONS

COAGULATION: TWO-STEP PROCESS

The coagulation process has been described by O'Melia (1969) as a two-step process: (1) destabilization and (2) particle transport. The destabilization step is concerned with eliminating or nullifying the repulsive energy barrier that exists between two colloidal particles in an aqueous system. The second step of particle transport is concerned with inducing interparticle contacts by: (1) Brownian motion, (2) fluid motion, or (3) differences in the settling velocities of the particles. Particle transport is treated in depth in Chapter IV. This chapter discusses mechanisms of particle destabilization, the structure of the electrical double layer, and the stability of clay suspensions. Special emphasis is devoted to the destabilization and stability of clays relative to estuarine systems.

MECHANISMS OF DESTABILIZATION

Particle destabilization can be accomplished by four distinct mechanisms: (1) adsorption to produce charge neutralization, (2) adsorption to permit interparticle bridging, (3) enmeshment in a precipitate of a metal hydroxide, and (4) double layer compression.

Adsorption and Charge Neutralization

Hydrolyzed metal species, organic polyelectrolytes, and/or surface active materials may be adsorbed onto colloidal surfaces causing charge neutralization. Specific chemical interaction between the adsorbing species and the surface active site on the colloid may overshadow the coulombic effect in bringing about particle destabilization. Stumm and O'Melia (1968) have pointed out that the energy involved in forming a chemical bond (up to 100 kcal/mole) can be much greater than the energy involved in a simple electrostatic interaction (about 2 kcal/mole). Thus one can envision that a coagulant having a positive charge can be chemically adsorbed onto the surfaces of negatively charged particles. At a certain dosage, sufficient adsorption occurs so as to eliminate the repulsive energy barrier that existed between particles and particle destabilization is achieved. Higher dosages of the same coagulant increase the amount of surface adsorption and can reverse the charge on the particles. This can cause particle restabilization.

Hahn and Stumm (1968) have used this mechanism - adsorption and charge neutralization - to explain the destabilization of negatively charged colloidal silica with hydrolyzed species of aluminum. This model predicts a stoichiometric relationship between the optimum coagulant dose and the colloid concentration; a high colloid concentration requires a high coagulant dosage for optimum surface coverage by adsorption.

Adsorption and Bridging

Anionic or nonionic organic polymers can destabilize negatively charged particles. This has been explained by an interparticle bridging model (Ruehrwein and Ward (1952) and LaMer and Healy (1963)). This model requires that the polymer molecules attach to one or more adsorption sites and that part of the polymer chain extends into the bulk of the solution. These extended chain segments, if of adequate size, can make contact with other colloid particles and bridges can be formed. The repulsive energy barrier is not eliminated in this case, but its effects are nullified so that particle aggregation can occur.

The extent to which aggregation occurs depends on the number of sites on the particle surface that are occupied. If too few sites are occupied by polymers, interparticle bridging may be weakened and interparticle bridges broken by shear arising from fluid motion. Thus, no net aggregation occurs at low particle surface coverage. Conversely, as more sites are covered, the free sites available for formation of bridges become limited and again particle aggregation is hindered. Therefore, an optimum surface coverage and an optimum coagulant dosage must exist. In summary, an optimum coagulant dosage, colloidal restabilization at dosages higher than the optimum, and a stoichiometry between the optimum coagulant dosage and the colloid concentration are characteristics of this mechanism - interparticle bridging - of particle destabilization.

Enmeshment in a Precipitate of a Metal Hydroxide

When a salt of a hydrolyzing metal (e.g., $Al_2(SO_4)_3$) is added to a solution in sufficient quantity to exceed the solubility of the metal hydroxide, an amorphous precipitate is formed. If chemical conditions (pH and degree of oversaturation) are proper for rapid precipitation of the metal hydroxide, colloidal particles present in the solution may be removed by being enmeshed within the precipitate of the metal hydroxide.

Double Layer Compression

Particle destabilization by compression of the electrical double layer is postulated as the primary mechanism for destabilization of colloidal particles in estuarine systems. The repulsive energy barrier that exists between clays in fresh waters (low ionic strength) is reduced as these clays are transported into waters of increasing ionic strength (estuaries). The increase in the ionic strength of the system compresses the electrical double layer and permits van der Waals attractive forces to become effective at short range interparticle distances. This mechanism of particle destabilization - double layer compression - is a naturally occurring process that is active when clay suspensions are transported into estuaries. Therefore, this mechanism is treated in depth in subsequent sections of this chapter. It is noted that the other mechanisms of particle destabilization are commonly used in the treatment of water and wastewater.

STABILITY

Definition

A stable clay suspension is one in which the discrete particles show little or no tendency to agglomerate. The stability of clay suspensions is due to the repulsion between similarly charged double layers and to the surface hydration of the clay particle which physically hinders contact between particle surfaces. The degree of hydration is important for extremely short range particle interactions because the adsorbed layer of water is only a few molecules thick. In this chapter a theoretical model for particle stability is developed. The effect of surface hydration on particle stability is neglected in this treatment, but the reader should be aware that this effect does exist. The theoretical development will be based on the interaction of double layers between particles. The electrical double layer surrounding clay particles in an aqueous system is a result of the net negative charge on the clay surfaces.

The structure of the electrical double layer (Gouy-Chapman) and the interaction of double layers according to Verwey-Overbeek and Derjaguin-Landau (VODL model) are developed and presented in this chapter. The assumptions of these models and the equations are presented but the derivation of the equations is not explored. The derivation of these equations is presented in the following references: Verwey and Overbeek (1948), Kruyt (1952), and van Olphen (1963).

Origin of Primary Charge

The primary electrical charge on a colloidal particle may be due to three principal mechanisms.

First, the substitution of one atom for another in a crystal lattice (isomorphic replacement) due to lattice imperfections creates a surface charge which is independent of the characteristics of the aqueous phase. For clays such as illite and montmorillonite, it is common to have Fe^{+2} or Mg^{+2} substituted for Al^{+3} in the octahedral sheet or Al^{+3} substituted for Si^{+4} in the tetrahedral sheet.

The second mechanism is the ionization of chemical groups present at the surface of the particle. For clays (e.g. kaolinite) this particular charge mechanism is highly dependent on the aqueous phase and in particular, the pH. The exposed alumina and silica groups on the edges of the clay particles behave as weak acids whose degree of ionization is favored by a reduction of the hydrogen ion concentration. Michaels and Bolger (1964) have estimated the isoelectric point of the edge alumina to be 7.8 and have envisioned the deprotonation to proceed in the following manner:

$$-AlOH_2^+ + H_2O = -AlOH + H_3O^+$$

$$-AlOH + H_2O = -AlO^- + H_3O^+$$

Similarly, the isoelectric point for the edge silica is in the range 1.8 to 2.4 (Parks (1967)):

$$-SiOH + H_2O = -SiO^- + H_3O^+$$

For natural waters, the pH is such that the silica groups are always negatively charged whereas the alumina groups may be positively or negatively charged.

Finally, the third mechanism in which colloidal particles become charged is the preferential adsorption of certain ions from solution. Specific ions may be adsorbed on the surface via hydrogen bonding, covalent bonding, or by van der Waals attractive forces. This charge mechanism depends on the characteristics of the aqueous phase. Ions which are preferentially adsorbed from solution or which cause the ionization of chemical groups on the colloid are called "potential determining ions". H^+ and OH^- are "potential determining ions" for -AlOH and -SiOH.

Diffuse Double Layer after Gouy and Chapman

The theory of the electric double layer deals with the distribution of counter-ions and co-ions in the locality of a charged surface, and with the magnitude of the electric potentials which occur in this region. A treatment of the double layer is a necessary first step towards the understanding of colloid stability.

Clay particles carry a net negative charge; however, in water a charge balance must be established in the vicinity of the particle-water interface to fulfill the requirement of electroneutrality. Counter-ions in the solution are attracted toward the particle surface giving rise to a concentration gradient of ions. Thermal diffusion causes some of the counter-ions to diffuse to the bulk of the solution where the concentration is lower. The opposing forces of diffusion and electrostatic attraction lead to a density gradient of charges in which the concentration is highest adjacent to the particle surface and which decreases exponentially with distance from the particle-water interface. This phenomenon is illustrated in Figure 3.1.

The electric double layer can be regarded generally as consisting of two regions: an inner region which includes the charged surface of the particle (may include adsorbed ions-Stern Model), and a diffuse region in which ions are distributed according to the influ-

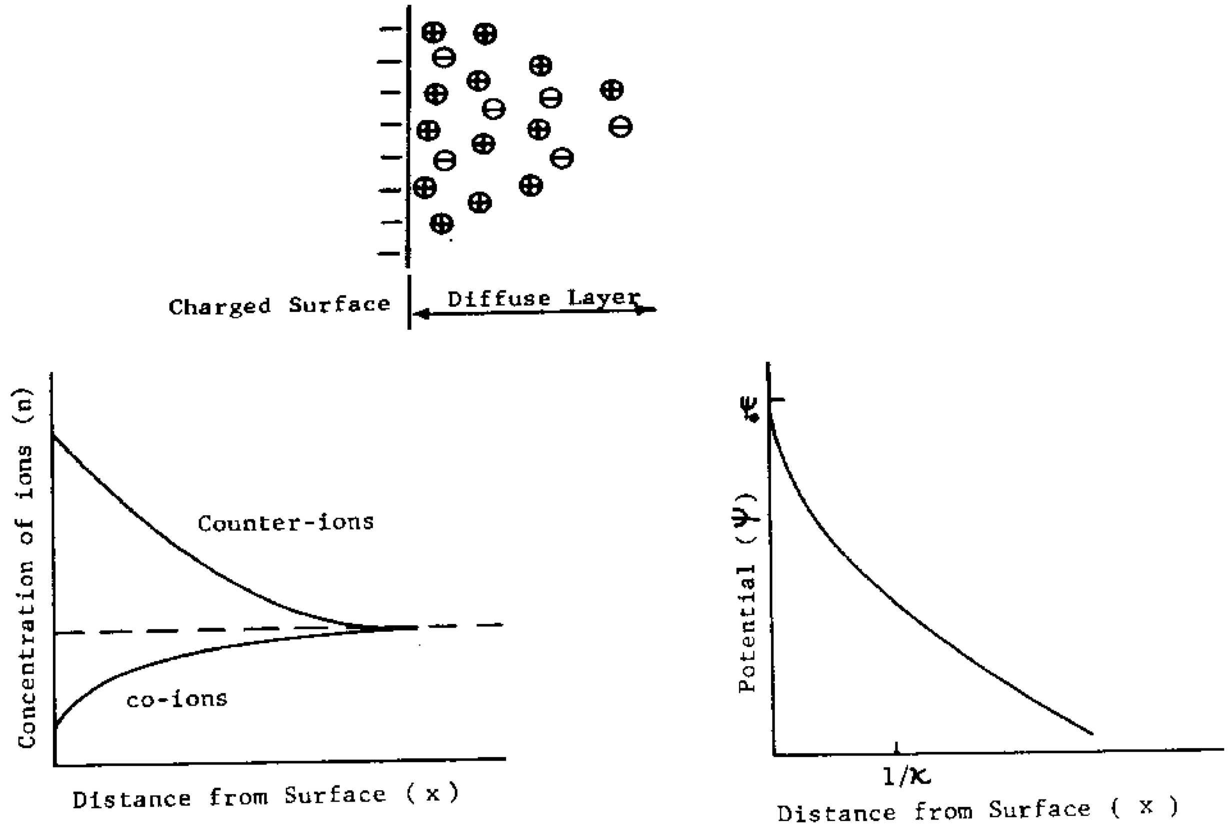


Figure 3.1 Schematic Representation of the Diffuse Electric Double Layer and the Electric Potential of a Colloidal Particle.

ence of electrical forces and random thermal motion. The simplest quantitative treatment of the diffuse electric double layer is the Gouy-Chapman model. The Gouy-Chapman model is based on the following considerations and assumptions.

1. The surface is assumed to be flat, of infinite extent and uniformly charged.
2. The ions in the diffuse part of the double layer are assumed to be point charges distributed according to the Boltzmann distribution.
3. The solvent (water) is assumed to influence the double layer only through its dielectric constant, which is assumed to have the same value throughout the diffuse part.
4. A single symmetrical electrolyte of valence z is assumed. This assumption facilitates the derivation while losing little owing to the relative unimportance of co-ion valency.

The surface potential (ψ_0) can be related to the surface charge density (σ) by equating the surface charge with the net space charge in the diffuse part of the double layer and applying the Poisson-Boltzmann distribution. The resulting expression is

$$\sigma = \left(\frac{2n\varepsilon kT}{\pi}\right)^{1/2} \sinh\left(\frac{ze\psi_0}{2kT}\right) \qquad [3\text{-}1]$$

where n is the concentration of ions/cm^3, ε is the dielectric constant, k is Boltzmann's constant, T is the absolute temperature, z is the valence of the counter-ions, and e is the elementary charge.

It is customary to refer to $1/\kappa$ (the distance over which the potential decreases by an exponential factor at low surface potentials) as the "thickness" of the diffuse double layer or the double layer thickness. For low surface potentials ($\psi_0 < 25/z$ mvolts) the potential decreases exponentially with distance (x) from the charged surface.

$$\psi = \psi_0 \exp(-\kappa x) \qquad [3\text{-}2]$$

The reciprocal of the double layer thickness can be computed by the relationship

$$\kappa = \left(\frac{8 \pi z^2 e^2 n}{\varepsilon kT} \right)^{\frac{1}{2}} \qquad [3\text{-}3]$$

The double layer thickness is defined as the distance at which the potential is equal to the surface potential divided by e (base of natural logarithms). Equation [3-3] holds for all surface potentials whereas Equation [3-2] is applicable for low surface potentials as described above.

The computation of the ion distribution in the diffuse double layer as a function of the electrolyte content of the bulk solution shows that the diffuse counter-ion atmosphere is compressed towards the surface when the bulk electrolyte concentration is increased. If the surface charge of the particle is determined by interior lattice imperfections (isomorphic substitution), the surface charge does not change with increasing electrolyte concentration. The diffuse double layer is compressed and the surface potential decreases with increasing electrolyte concentration. The degree of compression of the double layer thickness is governed by the concentration and valence of the ions of opposite sign from that of the surface charge (See Figure 3.2). The surface potential, for particles with a constant surface charge, is also governed by the ion concentration and valence of the counter-ions as indicated in Figures 3.3 and 3.4. Figures 3.2, 3.3, and 3.4 were constructed for water at 25°C.

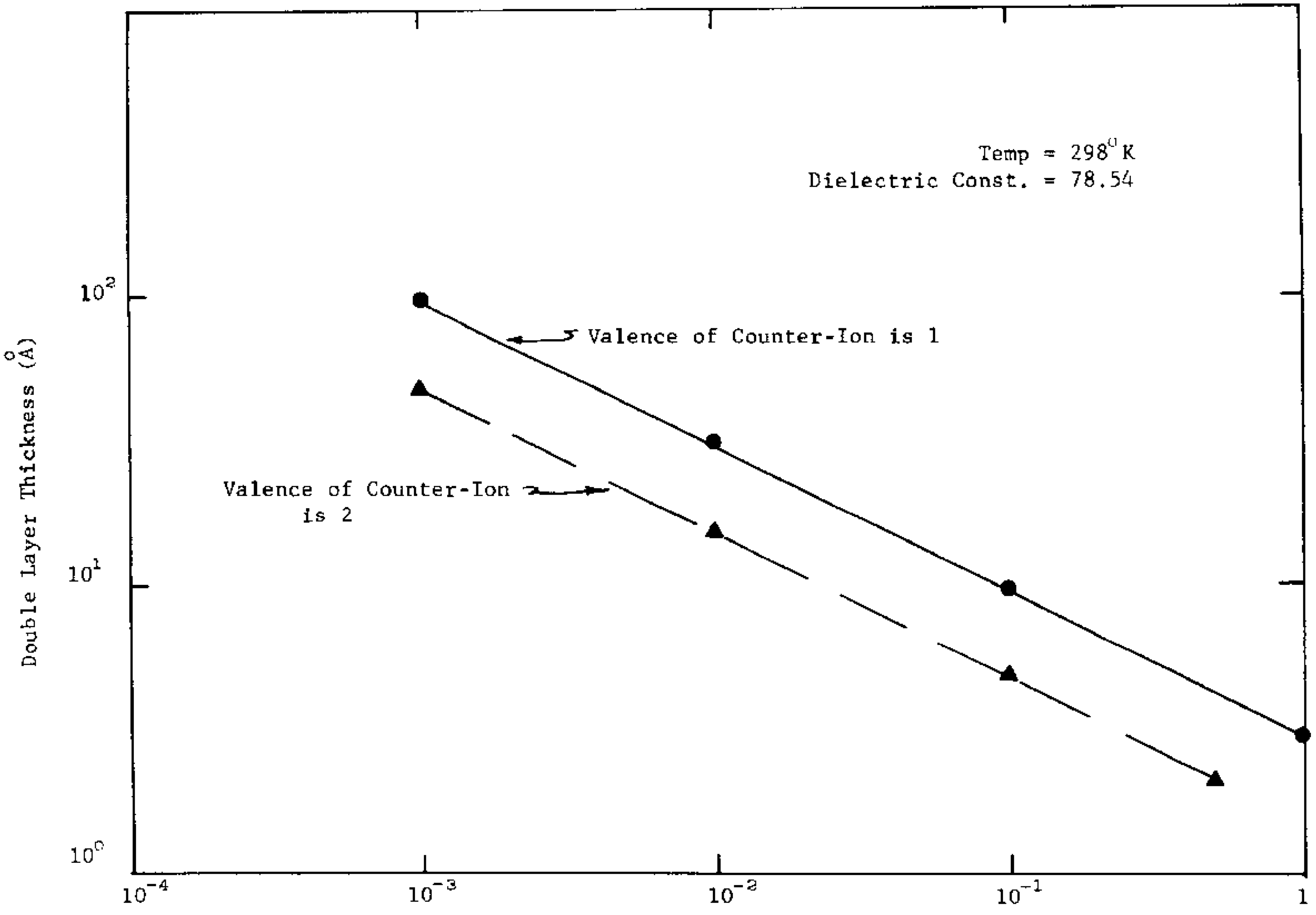


Figure 3.2 Double Layer Thickness as a Function of Ionic Strength

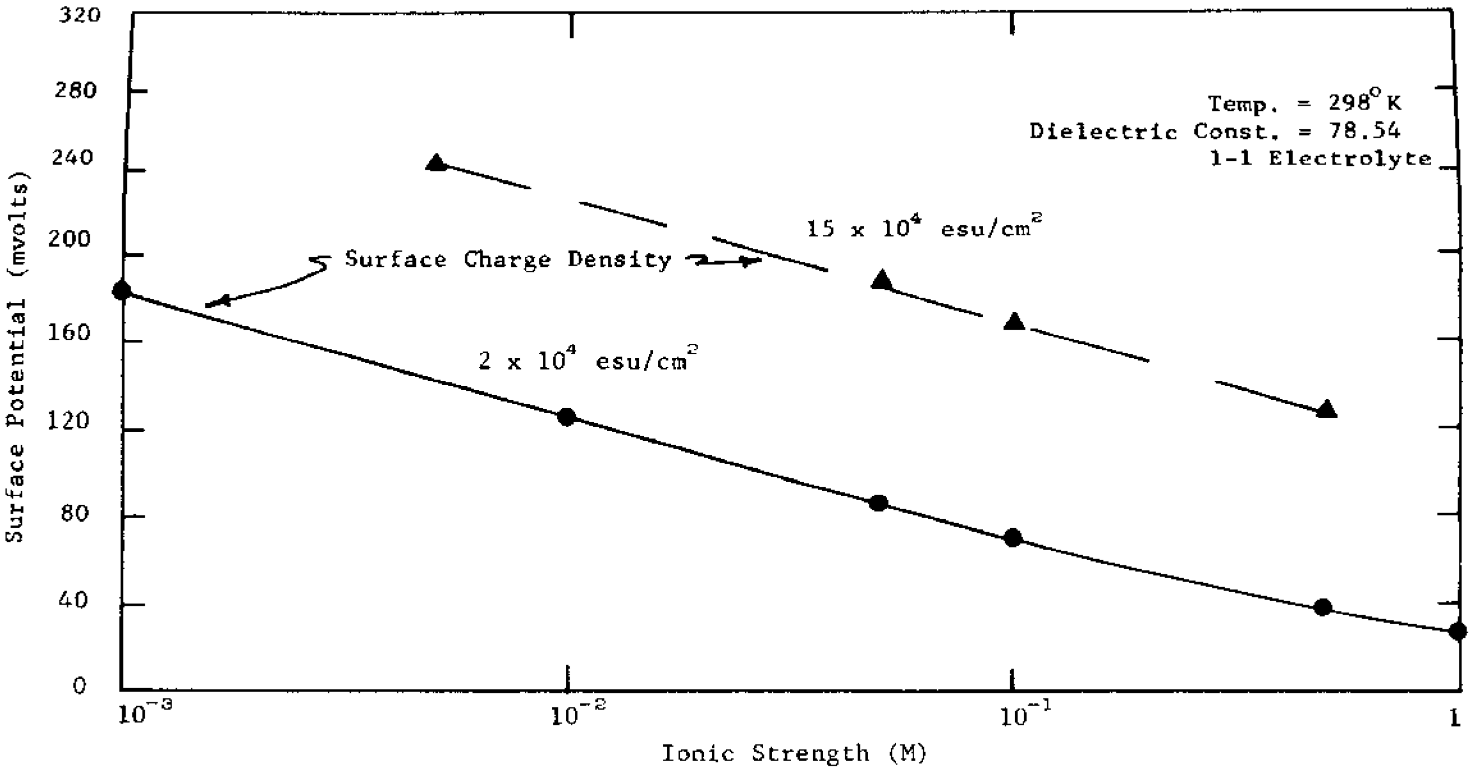


Figure 3.3 Surface Potential as a Function of Ionic Strength According to the Gouy Chapman Theory, (Particles With a Constant Surface Charge and 1-1 Electrolyte).

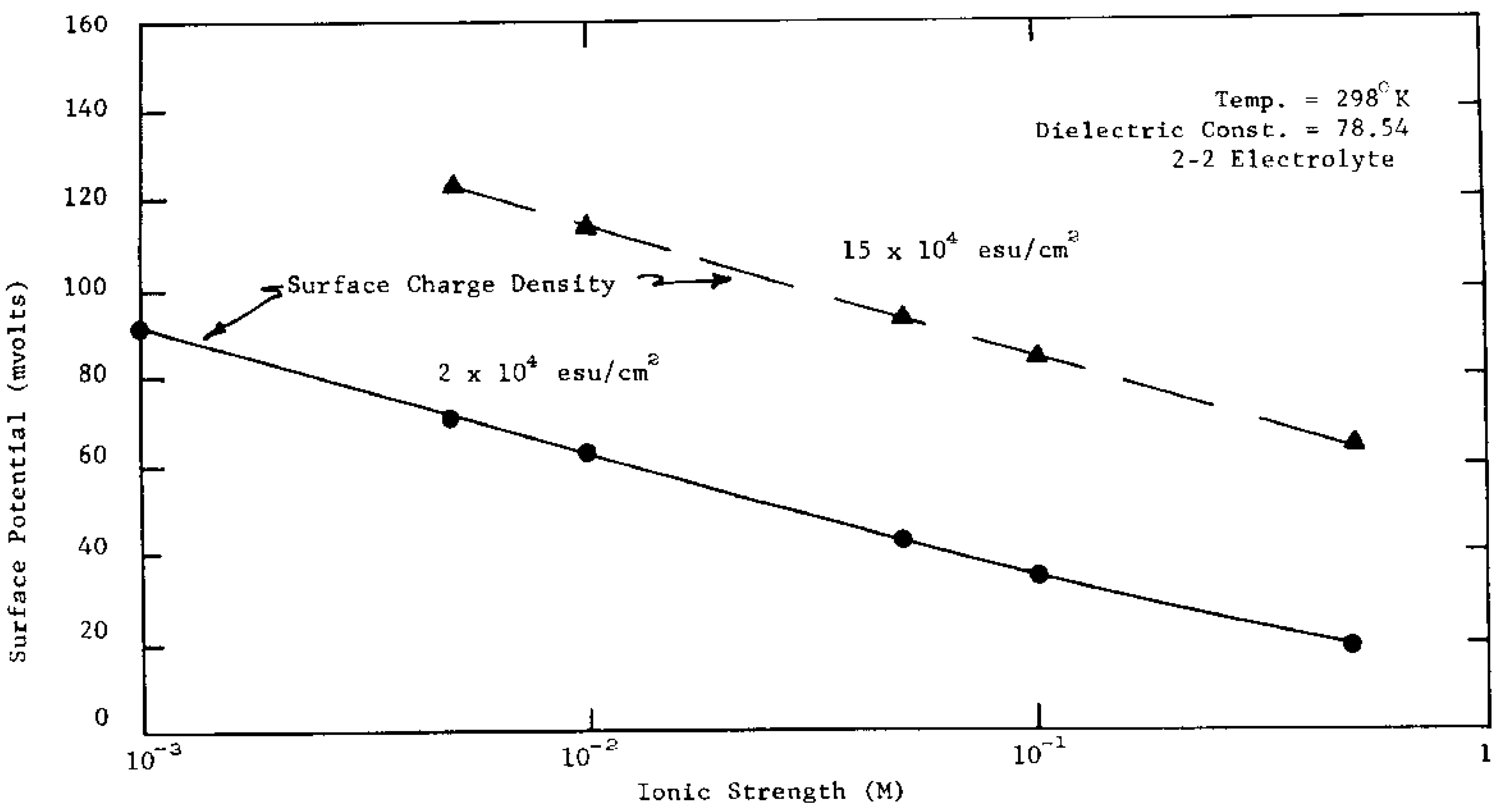


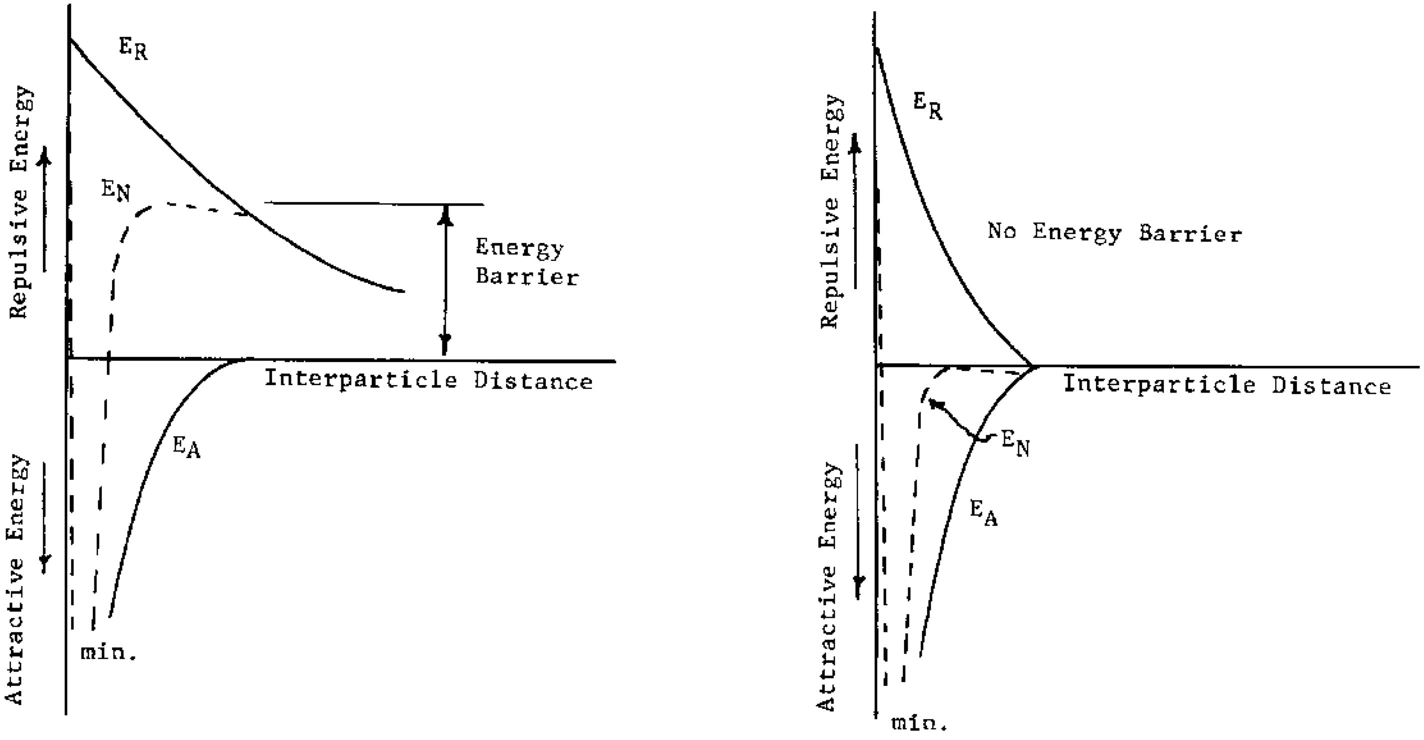
Figure 3.4 Surface Potential as a Function of Ionic Strength According to the Gouy Chapman Theory, (Particles With a Constant Surface Charge and 2-2 Electrolyte).

Interaction of Double Layers (VODL Theory)

Verwey-Overbeek and Derjaguin-Landau (Verwey and Overbeek (1948)) have independently developed a quantitative theory in which the stability of lyophobic colloids is treated in terms of the energy changes which take place when particles approach one another. The theory involves estimations of the energy of attraction (London-van der Waals forces) and the energy of repulsion (overlapping of electric double layers) in terms of interparticle distance.

When two colloidal particles having the same charge approach each other, their diffuse counter-ion atmospheres begin to interfere. This interference leads to changes in the distribution of the ions in the double layer of both particles, which involves an increase in the free energy of the system. Work must therefore be performed to bring about these changes; in other words, there is repulsion between the particles. The amount of work required to bring the particles from infinite separation to a given distance between them can be calculated. The amount of work is the repulsive energy at the given distance and is shown as a function of distance in Figure 3.5. The repulsive energy decreases roughly exponentially with increasing particle separation.

If the double layer is "flat", then the energy of repulsion (E_R) between two spheres having surface potential (ψ_o) can easily be calculated. When the surface potential is small ($\psi_o <$ 25/z mvolts) and the double layer is "flat" - $\chi a > 3$ (Morgan (1971)) - then the energy of repulsion can be computed from the relationship



A. Low Ionic Strength

B. High Ionic Strength

Figure 3.5 Net Interaction Energy as a Function of Interparticle Distance.

$$E_R = \epsilon a \psi_0^2 \; \tfrac{1}{2}\ln (1 + \exp(-\chi H)) \qquad [3\text{-}4]$$

where H is the separating distance.

When the surface potential is large ($\psi_0 > 25/z$ mvolts) and the double layer is "flat", the energy of repulsion can be calculated by the relationship

$$E_R = \frac{8 a \epsilon (kT)^2 \gamma^2}{e^2 z^2} \exp(-\kappa H) \qquad [3\text{-}5]$$

where $\gamma = \dfrac{\exp(ze\psi_0/2kT) - 1}{\exp(ze\psi_0/2kT) + 1}$

The van der Waals attractive forces are also operative when two colloidal particles approach each other. The van der Waals attraction between atom pairs is additive; hence, the total attraction between particles containing a very large number of atoms is equal to the sum of all the attractive forces between every atom of one particle and every atom of the other particle. For two spherical particles, the attractive energy due to van der Waals forces is inversely proportional to the second power of the distance between surfaces. In the lower part of Figure 3.5, the attractive energy (E_A) is plotted as a function of the distance separating two particles.

In the VODL theory the attraction between particles is entirely due to the London-van der Waals forces. The attractive energy for the case of two equal spheres of radius, a, can be calculated by the relationship

$$E_A = \frac{-A}{6}\left[\frac{2}{s^2-4} + \frac{2}{s^2} + \ln\left(\frac{s^2-4}{s^2}\right)\right] \qquad [3\text{-}6]$$

where A is the Hamaker constant (generally between 10^{-13} and 10^{-12} erg) and $s = (H + 2a)/a$.

The summation of repulsive and attractive energy is carried out as follows: the net energy curve (E_N) of particle interaction is constructed simply by adding the attractive and repulsive energy at each particle distance, considering the attractive energy as negative and the repulsive energy as positive. The total net interaction energy between two charged spheres is:

$$E_N = E_R + E_A \qquad [3\text{-}7]$$

Figure 3.5 shows the net interaction energy curves for low ionic strength and high ionic strength solutions. There is an energy barrier at low ionic strength due to the magnitude and range of the double layer repulsive energy (Figure 3.5A). The stability of clay suspensions can be represented qualitatively by the height of this energy barrier. Clay suspensions are stable at low ionic strength due to this energy barrier. An increase in ionic strength causes a compression of the double layer and therefore a reduction of the range of repulsion and a reduction of the energy barrier. Figure 3.5B illustrates the case where the energy barrier has been eliminated by an increase in ionic strength.

The effect of an increase in ionic strength on the stability of clay suspensions is pertinent to this study. It is postulated that clay suspensions are destabilized by double layer compression as these suspensions are transported from fresh waters into estuaries.

Schulze-Hardy Rule

Numerous coagulation experiments have led to the formulation of certain empirical rules, the most important of which is the Schulze-Hardy rule formulated in 1900 (Kruyt (1952)). The rule states that the destabilizing power of indifferent electrolytes (electrolytes which do not specifically react with the colloidal particles) is primarily determined by the valence of the counter-ions. Specifically, the rule states that divalent counter-ions are 50-60 times more effective than monovalent, and trivalent counter-ions are 700-1000 times more effective than monovalent in the destabilization of colloidal suspensions.

An attribute of the VODL theory of colloid stability is that the Schulze-Hardy rule may be derived from the theory. The derivation is obtained by considering the case as depicted in Figure 3.5B - the net energy barrier having been reduced to zero. For such a case, the condition $E_N = 0$ and $dE_N/dH = 0$ hold for the same value of H. Applying these conditions to Equations [3-5], [3-6], and [3-7], it can be shown that the destabilizing concentrations of indifferent electrolytes are given by the following relationship

$$c = \frac{K}{z^6} \qquad [3\text{-}8]$$

where c is the destabilizing concentration, K is a constant, and z is the valence of the counter-ions. Therefore, trivalent counter-ions are 729 times more effective than monovalent and divalent counter-ions are 64 times more effective than monovalent.

VODL CALCULATIONS

As indicated earlier, the stability of colloidal suspensions is proportional to the magnitude of the net interaction energy barrier depicted in Figure 3.5. Equations [3-1] through [3-7] were used to compute the net interaction energy as a function of distance. Net interaction energy curves were generated using an IBM 360/75 computer system. These curves were generated for various particle sizes, surface charge densities and ionic strengths. The values used to produce these curves are representative of the clay minerals.

The effect of ionic strength on net interaction energies for various size particles and for two surface charge density values is shown in Tables 3.1 and 3.2. In Table 3.1 a 1-1 electrolyte (e.g. NaCl) is the destabilizing agent while in Table 3.2 a 2-2 electrolyte (e.g. $MgSO_4$) is indicated. These results predict substantial energy barriers for large particles and the magnitude of the energy barrier is quite sensitive to the ionic strength. The interparticle distances at which the energy barriers exist are 15 Å or less for all conditions. It was decided to disqualify any calculations which predicted energy barriers at interparticle distances of less than 4 Å. It is reasonable to assume that adsorbed water on two clay particles would cover distances of this order (4 Å); thus energy barriers due to double layer repulsion at these distances ($<$ 4 Å) were considered illegitimate. The VODL theory predicts this quite frequently when a 2-2 electrolyte is used as the destabilizing agent. Consequently, very few legitimate predictions were obtained for the 2-2 electrolyte as idicated in Table 3.2.

A theoretical model that can predict the stability of clay suspensions would be a valuable tool. A stability factor (α) for colloidal particles has been related to the interaction energy (Verwey and Overbeek (1948)) by

Table 3.1

INTERACTION ENERGY RESULTS: 1-1 ELECTROLYTE

$\sigma = 2 \times 10^4$ esu/cm^2 $A = 10^{-12}$ ergs

$T = 298^\circ K$ 1-1 electrolyte

I. S. M	*Energy Barrier (ergs)		
	Particle Radius		
	1 μ	0.1 μ	0.01 μ
10^{-3}	2.98×10^{-10} @ 15 Å	3.04×10^{-11} @ 15 Å	$\kappa a < 3$
10^{-2}	1.52×10^{-10} @ 10 Å	1.57×10^{-11} @ 10 Å	- -
5×10^{-2}	2.03×10^{-11} @ 10 Å	2.60×10^{-12} @ 10 Å	5.34×10^{-13} @ 9 Å
6×10^{-2}	- -	- -	3.99×10^{-13} @ 10 Å
6.5×10^{-2}	1.31×10^{-12} @ 10 Å	7.29×10^{-13} @ 10 Å	- -
7×10^{-2}	- -	- -	2.92×10^{-13} @ 10 Å
8.5×10^{-2}	0	0	- -
5×10^{-1}			0

* Magnitude of energy barrier in ergs, distance at which this barrier occurs is also given.

$\sigma = 15 \times 10^4$ esu/cm^2 $A = 10^{-12}$ ergs

$T = 298^\circ K$ 1 - 1 electrolyte

I. S. M	Energy Barrier (ergs)	
	Particle Radius	
	1 μ	0.01 μ
5×10^{-3}	2.71×10^{-10} @ 10 Å	$\kappa a < 3$
5×10^{-2}	1.30×10^{-10} @ 7 Å	1.70×10^{-12} @ 6 Å
7.5×10^{-2}	9.84×10^{-11} @ 6 Å	1.39×10^{-12} @ 6 Å
10^{-1}	- -	1.16×10^{-12} @ 6 Å
2.5×10^{-1}	0	- -
5×10^{-1}		0

Table 3.2

INTERACTION ENERGY RESULTS: 2-2 ELECTROLYTE

$\sigma = 2 \times 10^4$ esu/cm^2 A = 10^{-12} ergs

T = 298° K 2-2 Electrolyte

* Energy Barrier (ergs)

I.S. M	Particle Radius		
	1 μ	0.1 μ	0.01 μ
10^{-3}	---	---	---
5×10^{-3}	---	9.9×10^{-11} @ 4 Å	**
10^{-2}	7.9×10^{-10} @ 4 Å	**	---
5×10^{-2}	**		**

* Magnitude of energy barrier in ergs, distance at which this barrier occurs is also given.

** Energy barrier occurred at an interparticle distance of less than 4 Å.

$\sigma = 15 \times 10^4$ esu/cm^2 A = 10^{-12} ergs

T = 298° K 2-2 electrolyte

Energy Barrier (ergs)

I.S. M	Particle Radius	
	1 μ	0.01 μ
5×10^{-3}	---	1.32×10^{-11} @ 4 Å
10^{-2}	**	---
5×10^{-2}		**

$$\alpha = 2\, a \kappa \, \exp(E_{max}/kT)^{-1} \qquad [3\text{-}9]$$

where κ is the reciprocal of the double layer thickness, a is the particle radius, k is Boltzmann's constant, T is the absolute temperature, and E_{max} is the maximum in the net interaction energy curve (energy barrier). Hahn and Stumm (1970) have used this relationship to calculate α values for various clay minerals. However, this relationship only yields reasonable α values for particles smaller than 1μ since it was developed for the interaction between particles during a Brownian encounter. Even for small particles ($<$ 1μ) there are several problems associated with the VODL theory. Some of these problems are summarized below:

1. The Gouy-Chapman treatment of the double layer is based on an assumption of point charges in the electrolyte medium. The finite size of the ions will, however, limit the inner boundary of the diffuse part of the double layer, since the center of an ion can only approach the surface to within its hydrated radius. Stern's theory of the double layer should be considered in any refined models. The Stern model divides the double layer into two parts separated by a plane (the Stern plane) located at about a hydrated ion radius from the surface. Stern also considered the possibility of specific ion adsorption.
2. The VODL theory predicts large energy barriers especially for particles of about 1μ. This is due to the high surface potentials (ψ_0) predicted by the Gouy-Chapman model. The use of the Stern potential (ψ_s) would improve these

calculations since the charge of the diffuse double layer is decreased by using ψ_δ .

3. Theoretical calculations based on the VODL theory - or even with a refined model using the Stern double layer - require assumptions. There are uncertainties concerning the size and shape of colloids, the charge on the surface of the colloids, and the magnitude of Hamaker's constant.

In summary, the interaction of double layers according to the theory of Verwey-Overbeek and Derjaguin-Landau (VODL) was used to calculate interaction energy curves. The VODL theory is based on the interaction of double layers using the Gouy-Chapman model for the double layer. The Stern model of the double layer could improve calculations of the interaction energies. A relationship between the stability factor (α) and the energy is needed. This relationship should be based on particle encounters due to fluid motion and thus applicable to particles larger than 1μ . Finally, in view of the limitations of present theoretical models describing the stability of colloids, it seemed expedient to determine values of stability (α) experimentally. This approach was then used in this research to evaluate α for various clays.

CHAPTER IV

COAGULATION IN ESTUARIES: KINETIC APPROACH

Agglomeration of suspended colloids occurs when sufficiently destabilized particles collide with each other. These collisions result from either (1) Brownian motion of the particles, (2) effects of velocity gradients within the suspending liquid, or (3) differential settling velocities of suspended particles. In this chapter the equations describing perikinetic flocculation - collisions due to Brownian motion - and orthokinetic flocculation - collisions due to fluid motion - are presented. In addition the use of these equations is explored with particular emphasis devoted to orthokinetic flocculation in the sanitary engineering literature. Finally, the experimental results used in this research are presented and discussed. A kinetic approach was used in which rates of particle aggregation were used to determine stability factors for various clay minerals.

FLOCCULATION KINETICS

Perikinetic Flocculation

Smoluchowski (1917) published a mathematical theory for the coagulation kinetics of colloidal suspensions in which kinetic equations were presented to describe the rate of change in total particle concentration after the repulsive forces between similarly charged double layers surrounding the particles were reduced sufficiently so that interparticle collisions were not hindered. Smoluchowski developed two kinetic equations. The first described the kinetic process when interparticle collisions occurred through Brownian diffusion of the individual colloidal particles - perikinetic flocculation. The second described interparticle collisions resulting from fluid motion - orthokinetic flocculation.

For perikinetic flocculation the frequency of collisions is obtained by calculating the diffusional flux of particles towards a single stationary particle. The calculation requires solution of the continuity equation from which a concentration gradient around the stationary particle is obtained. Smoluchowski showed that the collision frequency (I_{ij}) between particles of radius r_i and r_j present at concentrations n_i and n_j is given by the relation

$$I_{ij} = \frac{2kT}{3\mu} (r_i + r_j) \left(\frac{1}{r_i} + \frac{1}{r_j}\right) n_i n_j \qquad [4\text{-}1]$$

where k is Boltzmann's constant, T the absolute temperature, and μ the fluid viscosity. In deriving this expression it is assumed that the diffusion coefficients of the individual particles are given by the Stokes-Einstein relation:

$$D = \frac{kT}{6\pi\mu r} \qquad [4\text{-}2]$$

To simplify the mathematics, Smoluchowski made the assumption that

$$(r_i + r_j) \left(\frac{1}{r_i} + \frac{1}{r_j}\right) = 4 \qquad [4\text{-}3]$$

This is exact when the coagulating particles are all the same size (monodispersed suspension), but it is a good approximation even when r_i/r_j is equal to 2 (Equation [4-3] is then equal to 4.5). Using this simplification and expressing Equation [4-1] as the rate of change in the total concentration of particles with time Smoluchowski obtained

$$\frac{dn}{dt} = \frac{-4\ kTn^2}{3\mu} \qquad [4\text{-}4]$$

where n is the total concentration of particles at time t. This expression is Smoluchowski's equation for perikinetic flocculation and is based on complete discharge of the double layer; i.e., no electrical repulsion between particles. This case is called rapid coagulation since there is no energy barrier preventing particle agglomeration. A stability factor (α) has subsequently been introduced by Fuchs (Verwey and Overbeek (1948)) to account for incomplete discharge of the double layer (slow coagulation); i.e., repulsive energy barriers between particles. The following equation is then used to describe perikinetic flocculation:

$$\frac{dn}{dt} = \frac{-4\alpha\ kTn^2}{3\mu} \qquad [4\text{-}5]$$

where α (alpha) is the stability factor. It should be noted that α takes on values between 0 and 1. A completely destabilized suspension has a stability factor of 1 (rapid coagulation), whereas stable suspensions are characterized by $\alpha \ll 1$.

Orthokinetic Flocculation

Smoluchowski also derived an expression for the collision frequency among particles in a laminar shear field. He showed that:

$$J_{ij} = \frac{4}{3} \frac{dU}{dZ} (r_i + r_j)^3 n_i n_j \qquad [4\text{-}6]$$

where n_i, n_j, r_i, and r_j carry the same connotation as in Equation [4-1], dU/dZ is the laminar velocity gradient, and J_{ij} is the collision frequency due to laminar fluid motion. For a system of particles of uniform size, the rate of change in the total concentration of particles with time due to orthokinetic flocculation may be described by the following equation:

$$\frac{dn}{dt} = \frac{-2}{3} \alpha\, d^3 n^2 \frac{dU}{dZ} \qquad [4\text{-}7]$$

where d is the diameter of the particles. The stability factor has been included in this equation thus describing the general case of rapid or slow coagulation.

Camp and Stein (1943) provided the next major contribution to the theory of orthokinetic flocculation. They observed that in most practical cases, flocculation was achieved under turbulent flow conditions and generalized Smoluchowski's equation to include these conditions. For the case of turbulent flow, even at steady state, the fluid velocity fluctuates around a temporal mean value, creating local microscopic velocity gradients superimposed on the macroscopic gradients of the mean velocity. To overcome this difficulty Camp and Stein adopted a procedure by which they substituted a measurable parameter, G, for dU/dZ. They defined an "absolute velocity gradient" at a point (G_p) as:

$$G_p = \left[\left(\frac{dU}{dy} + \frac{dV}{dx}\right)^2 + \left(\frac{dU}{dZ} + \frac{dW}{dx}\right)^2 + \left(\frac{dV}{dZ} + \frac{dW}{dy}\right)^2\right]^{\frac{1}{2}} \qquad [4\text{-}8]$$

where U, V, and W are the three velocity components in the x, y, and z directions, respectively. It was shown that this velocity gradient equals the square root of the energy dissipation at a point divided by the fluid viscosity. Camp and Stein related the total energy input into the fluid to what they called a root-mean-square velocity gradient (G):

$$G = \left(\frac{\phi_m}{\mu}\right)^{\frac{1}{2}} = \left(\frac{\varepsilon}{\nu}\right)^{\frac{1}{2}} \qquad [4\text{-}9]$$

where ϕ_m is the total work input per unit of time divided by the volume of the fluid body, ε is the total energy dissipated per unit time and unit fluid mass, ν is the kinematic viscosity, and μ is the fluid viscosity. Substituting the root-mean-square velocity gradient (G) for dU/dZ, Equation [4-7] becomes

$$\frac{dn}{dt} = \frac{-2}{3}\ \alpha\ d^3 n^2\ G \qquad [4\text{-}10]$$

It is instructive to consider the relative effectiveness of orthokinetic flocculation and perikinetic flocculation by dividing Equation [4-10] by Equation [4-5], as follows:

$$\frac{dn/dt\ \text{(ortho)}}{dn/dt\ \text{(peri)}} = \frac{\dfrac{-2\ \alpha\ Gd^3 n^2}{3}}{\dfrac{-4\ \alpha\ kT\ n^2}{3\ \mu}}$$

so that

$$\frac{\text{ortho}}{\text{peri}} = \frac{\mu\ \alpha\ Gd^3}{\alpha\ 2\ kT} \qquad [4\text{-}11]$$

In water at 25°C containing particles with a diameter of 1μ, the relative effectiveness is one (ratio) when the velocity gradient is 10 sec^{-1} (assuming α is constant). As the flocs grow larger, however, the relative effectiveness increases very rapidly. In other words for particles larger than 1 μ, perikinetic flocculation is not very important. Accordingly for particles with a diameter of 4 μ, the relative effectiveness is approximately 340 when the velocity gradient is 50 $\sec^{-1}$; this is typical of the experimental conditions used in this research. It illustrates the insignificance of particle aggregation (in this study) due to perikinetic flocculation. Flocculation - in particular orthokinetic flocculation - is an important factor in estuarine transport of suspended materials because of the changes it causes in the settling character of suspended particles. Perikinetic flocculation (particles less than 1 μ) causes particles to aggregate to a size where fluid motion becomes effective in inducing collisions but the particles undergoing perikinetic flocculation are too small to undergo rapid settling. As the flocs continue to grow, the relative effectiveness of orthokinetic flocculation increases very rapidly.

The floc volume fraction of suspended particles (ϕ, the volume of suspended particles per unit volume of suspension) may be expressed as follows:

$$\phi = \frac{\pi \, d_o^3 \, n_o}{6} \qquad [4\text{-}12]$$

where d_o is the diameter of the particles at time = 0. Substitution of Equation [4-12] into Equation [4-10] yields the following:

$$\frac{dn}{dt} = \frac{-4 \, \alpha \, \phi \, G \, n}{\pi} \qquad [4\text{-}13]$$

Equation [4-13] is the relationship used in subsequent parts of this thesis to evaluate stability factors for clay particles from coagulation kinetic data.

REVIEW OF THE LITERATURE

Perikinetic Flocculation

Higuchi et al. (1963, 1965) confirmed the applicability of Equation [4-1] by experimental rate studies in the laboratory using polystyrene latex and polyvinyltoluene particles. The maximum rates of particle aggregation approached one-half the rate for rapid coagulation. This indicates that the stability factors (α) for these particles approached a value of $\frac{1}{2}$.

Gillespie (1960) proposed a simple kinetic picture to explain particle flocculation and breakup in Brownian motion experiments by considering the flocculation step as second order and the deflocculation step as first order with respect to total particle concentration. Experiments were conducted using latex and methyl cellulose particles. The results were in agreement with the flocculation and deflocculation model. Hiemenz and Vold (1965) performed similar experiments with dispersions of carbon black in various hydrocarbon solvents and interpreted their results in terms of the model of Gillespie. Mockros et al. (1967) modified Smoluchowski's equation by including a feed term. The particle size distribution of an aerosol continually reinforced by the introduction of particles (feed) and undergoing Brownian motion was calculated by numerical methods.

Hidy (1965) reviewed the theory for the coagulation of particles for the case of particle transport by Brownian motion. The effects of heterogeneity in particle size, and of particle motion in a rarefied medium were examined using numerical solutions of the coagulation equation. Swift and Friedlander (1964) conducted Brownian motion coagulation experiments with two heterogeneous hydrosols showing that the size distributions were "self-preserving". This principle of a "self-preserving" size distribution has been described by Snodgrass (1971) as follows: "...while there are particles moving through a given size distribution spectrum (smaller particles entering, growing by aggregation, and larger particles settling out), the shape of the curve describing the distribution remains unchanged over time." Hidy and Lilly (1965) compared the classical solution of Smoluchowski's equation (Brownian motion) to the "similarity or self-preserving" solution. In spite of the theoretical limitations, the authors showed mathematically that the classical solution for Smoluchowski's relation gives satisfactory results for the following conditions: (1) for coagulation times up to twice as long as the half-time, and (2) for particle size distributions in which the ratio of the maximum to minimum particle radius is less than 5. Similar results were reported by Matthews and Rhodes (1970a). Gillespie (1963) has shown mathematically that polydispersity increases the rate of particle collisions due to Brownian motion and decreases the collision rate for the case of transport by fluid motion.

Orthokinetic Flocculation

TeKippe and Ham (1971) discussed the effects of different velocity-gradient paths on the removal of turbidity. The vigor of mixing and the duration of mixing - or in quantitative terms the product of Gt - was evaluated. This product (Gt) is commonly used in the design of flocculation tanks for water treatment. Ham and Christman (1969) examined agglomerate size changes in coagulation studies. From these studies, information was obtained on the rate and extent of coagulation, as well as on the strength and settling characteristics of the floc. Hannah et al. (1967) reviewed some of the factors that affect floc strength and described a method for measuring the relative strength of floc formed under various conditions. Floc strength was estimated by applying a known shear to a flocculated system and measuring the change in the particle size distribution. Floc strength depended upon the initial size distribution, velocity gradient, and duration of mixing. In addition, for the alum-coagulated kaolin suspensions the following affected floc strength: pH, coagulant dosage, coagulant aids, and polyphosphates. Krone (1962) showed that the floc strength depends on the floc size and the suspension shearing rate.

Argaman and Kaufman (1968, 1970) developed a rational model for the collision mechanism between suspended particles in a turbulent fluid. A rate equation describing the change in concentration of primary particles was developed by considering their simultaneous removal by aggregation and reformation by breakup. A simplified breakup model was proposed, implying that the only mode by which primary particles are formed is through erosion from the surface of preformed flocs. The authors verified their model via laboratory experiments. Argaman and Kaufman also concluded that: (1) the physical parameters directly affecting the performance of a flocculation reactor are the residence time and its distribution, the total power input, and the energy spectrum of the turbulence field, and (2) chemical conditions prevailing in a flocculation system that affect the kinetics of the process are floc strength and particle stability. Argaman (1971) conducted pilot plant studies that showed the general validity of the aforementioned model.

Fair and Gemmell (1964) developed a mathematical model for floc growth by imposing various upper particle size limits and floc breakup modes on Smoluchowski's equation for flocculation in a laminar shear field. The particle growth pattern became oscillatory, however, as the velocity gradient-particle number product was increased, presumably because of the increased rate of particle aggregate breakup and reformation when the gross particle contact frequency was increased. Based on the results of Fair and Gemmell it can be concluded that Equation [4-13] - which was derived for monodispersed systems - is an adequate description of the initial stages of coagulation, and holds for coagulation times up to twice as long as the half-time.

Manley and Mason (1955) found that Equation [4-6] was valid for 100μ diameter glass spheres. Harris, Kaufman, and Krone (1966) measured the rate of orthokinetic coagulation of polydispersed kaolinite suspensions. The investigators demonstrated a linear relationship between the coagulation rate and the velocity gradient, G. Furthermore, the experimental results indicated that there are optimal values of G and the reaction time (detention time) t for efficient particle agglomeration. Parker, Kaufman, and Jenkins (1971, 1972) proposed a floc breakup term for the rate equation describing the aggregation of activated sludge floc. The investigators concluded that floc conditioning in most activated sludge plants is not optimum for secondary clarification because of excessive floc breakup.

It was suggested that the addition of a flocculation step (mildly stirred) between the aeration basin and clarifier would provide a better environment for aggregation.

Swift and Friedlander (1964) conducted coagulation experiments in a simple laminar shear field using a homogeneous polystyrene latex dispersion. The results indicated a linear relationship between the coagulation rate and G (values ranging from 1-80 sec^{-1}). Swift and Friedlander also demonstrated that the stability factor (α) is independent of G. Their results were in agreement with Equation [4-13]. In addition, the latex suspensions were destabilized the same way in both perikinetic and orthokinetic experiments. The α values were approximately the same - $\alpha = 0.375$ (perikinetic) and $\alpha = 0.364$ (orthokinetic) - indicating that the stability factor is not affected by the mode of particle transport.

Hahn and Stumm (1968) examined the kinetics of agglomeration of silica dispersions coagulated with hydrolyzed Al(III). Perikinetic and orthokinetic flocculation were studied using 15 mμ and 1.1 μ particles, respectively. The results of this study indicated that particle transport was the rate limiting step for the two step coagulation process (destabilization plus particle transport). Hahn and Stumm concluded that the collision rate is a function of predominantly physical factors, while the stability factor is dependent upon chemical parameters.

Birkner and Morgan (1968) investigated the effects of mixing intensity, mixing time, and cationic polymer dosage on the orthokinetic coagulation of polystyrene latex suspensions. The investigators found the particle transport step to be rate controlling and their results at the optimum polymer dosage are in accordance with Equation [4-13].

PRELIMINARY EXPERIMENTS

Jar Tests

Procedures. Kaolinite, illite, and montmorillonite clay minerals were obtained from Ward's Natural Science Establishment. These clays were subjected to X-ray diffraction analysis using a Phillips-Norelco diffractometer to verify clay type and purity. A discussion of the equipment and techniques employed is presented in Chapter V. The results of the X-ray diffraction analyses of the Ward's clays and other pertinent data concerning these clays are presented in Appendix A.

Stock clay suspensions were prepared and used for X-ray analysis, jar tests, cation exchange capacity measurements, and electrophoretic mobility determinations. The following procedure was used in the preparation of these stock clay suspensions:

1. Approximately twenty-five grams of clay were crushed and added to an Erlenmeyer flask containing 100 ml of distilled water. Grinding of the clay during crushing was carefully avoided since this may alter the characteristics of the clay surfaces.
2. The clay suspension was stirred rapidly for about 5 minutes using a magnetic stirrer. The purpose of this stirring was to disperse the clay suspension and to break up any large clay particles.

3. The $< 2\,\mu$ clay fraction was obtained by centrifuging at 590 rpm for 5 minutes using an International Centrifuge.
4. The $< 2\mu$ clay fraction was stored in polyethylene bottles and the clay concentration was determined by gravimetric analysis.

Standard jar tests were employed to determine the effect of ionic strength on the coagulation of the three clays. These jar tests were performed using two different aqueous systems. The first aqueous system - buffered NaCl solutions - was prepared with $NaHCO_3$ and/or NaCl yielding solutions with monovalent sodium ions as the only cations. The ionic strength varied from 10^{-4}M to 1 M (10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, and 1 M solutions) with the 10^{-4}M and 10^{-3}M solutions prepared with the appropriate concentration of $NaHCO_3$. The higher ionic strength solutions were prepared with 10^{-3}M $NaHCO_3$ - as a buffer - with the remaining fraction of the ionic strength being due to NaCl. The second aqueous system was a synthetic sea water which was prepared according to the formula of Lyman and Fleming (1940). Dilutions of this synthetic sea water were used to obtain the desired ionic strengths - 0.0017 M to 0.684 M - but a $NaHCO_3$ concentration of at least 10^{-3}M was maintained at all ionic strengths. The pH of all suspensions was between 7.8 and 8.2 except for clay suspensions using 10^{-4}M $NaHCO_3$ which had a pH of about 6.6.

Table 4.1

*SYNTHETIC SEA WATER

Species	gms/1
NaCl	23.477
$MgCl_2$	4.981
Na_2SO_4	3.917
$CaCl_2$	1.102
KCl	0.664
$NaHCO_3$	0.192
KBr	0.096
H_3BO_3	0.026
$SrCl_2$	0.024
NaF	0.003

* Lyman and Fleming (1940)

The following procedure was employed for the jar test experiments:

1. A series of beakers containing different ionic strength solutions with a constant clay concentration were prepared. These suspensions were stirred rapidly by means of a magnetic stirrer for two minutes.
2. After this initial rapid mixing period, the speed of the stirrer was reduced and the suspensions were stirred slowly for twenty minutes.
3. The magnetic stirrer was then turned off and 50 ml of each suspension was transferred to separate 50 ml graduated cylinders for a thirty minute settling period.

4. After this settling period, a small volume of supernatant was withdrawn from each sample and the residual turbidity was determined. A Beckman DB spectrophotometer was used to determine residual turbidities using a 1 cm cell at a wavelength of 400 mμ. This wavelength was selected after examining the absorbance of clay suspensions over a range of wavelengths - 375 to 650 mμ. Curves indicating absorbance as a function of clay concentration for each clay mineral at a wavelength of 400 mμ are presented in Appendix A.

Results and Discussion. The results of the jar tests are summarized in Figures 4.1 and 4.2. Figure 4.1 shows the results of the coagulation of clay suspensions where Na^+ was the destabilizing cation. The ionic strength was varied from 10^{-4}M to 1 M with sodium ions as the only counter-ion in these aqueous suspensions. The jar test results using synthetic sea water diluted to obtain various ionic strengths ranging from 0.0017 to 0.684 M are illustrated in Figure 4.2.

The results indicate that the coagulation of kaolinite and montmorillonite is improved with increasing ionic strength in either the NaCl or synthetic sea water systems. The coagulation of kaolinite and montmorillonite is better in synthetic sea water solutions - as compared to buffered NaCl solutions - as indicated by the residual turbidities in Figures 4.1 and 4.2. This is in agreement with the Verwey-Overbeek, Derjaguin-Landau (VODL) theory of destabilization by compression of the electrical double layer in which divalent counter-ions are more effective in destabilization than monovalent counter-ions. The synthetic sea water contained divalent as well as monovalent cations while the buffered NaCl solutions contained only

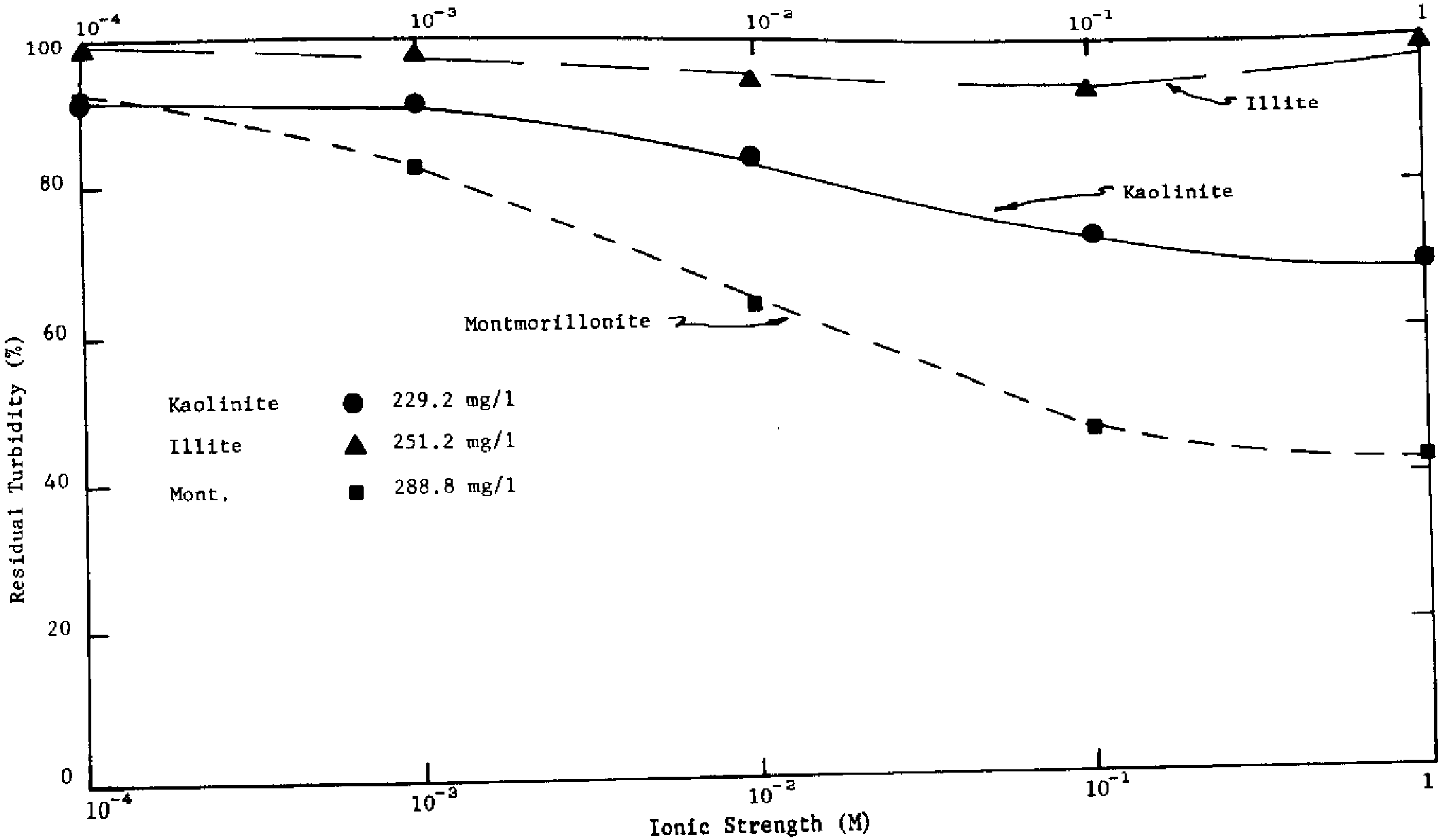


Figure 4.1 Jar Tests for Clays in Buffered NaCl Solutions.

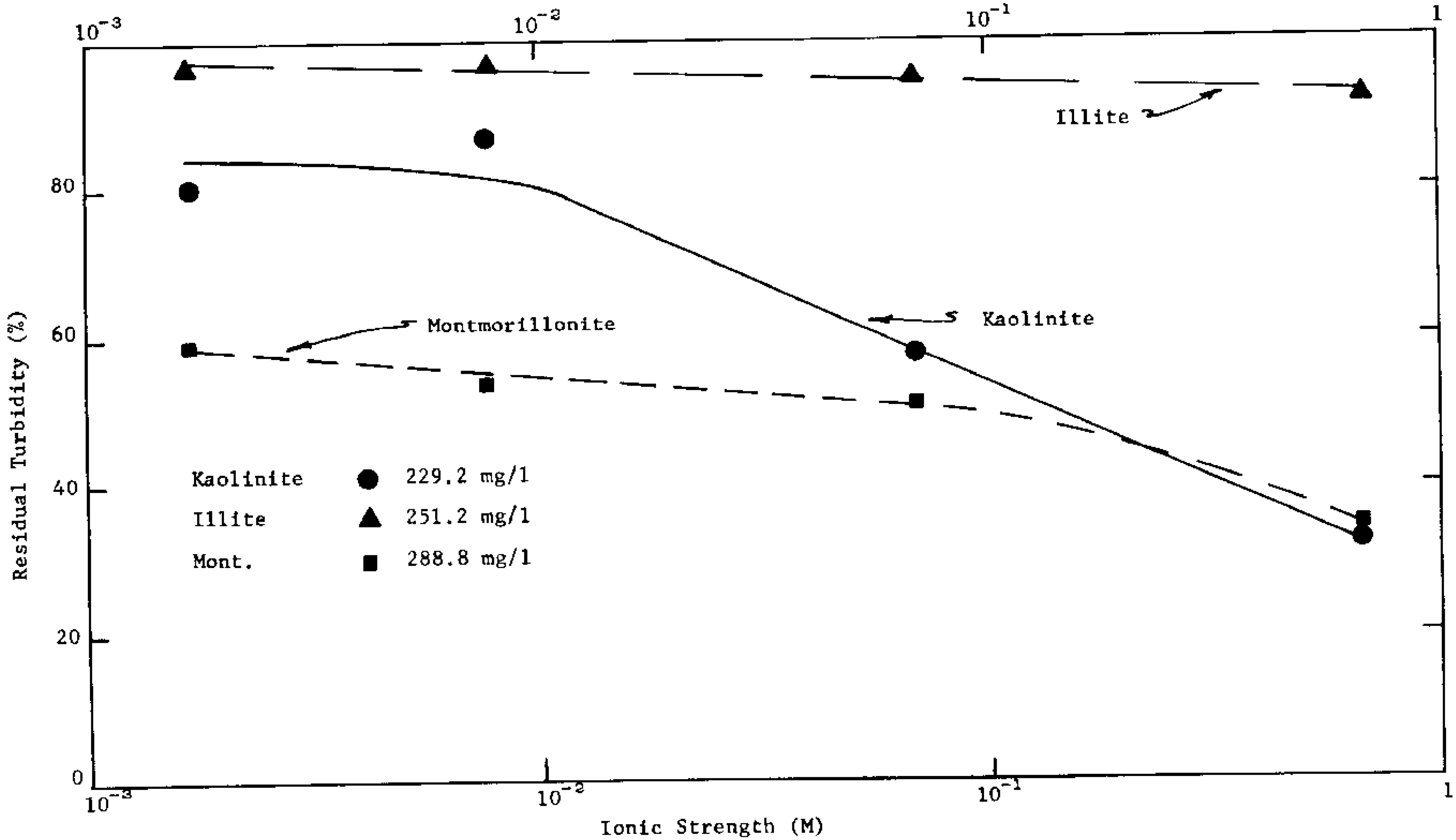


Figure 4.2 Jar Tests for Clays in Synthetic Sea Water Solutions

monovalent cations. These results also indicate that illite is a fairly stable clay with little improvement in coagulation with increasing ionic strength. It can be concluded on a qualitative basis that montmorillonite and kaolinite are unstable relative to illite.

Electrophoretic Mobility Determinations

Procedures. A glass Briggs cell mounted on an American Optical Series 10 microscope was utilized for the measurement of the electrophoretic mobilities of the clay particles. A variable-voltage power supply manufactured by the Kensington Scientific Corporation provided the required voltage; the output current was determined by using a Simpson Model 262 Volt-Ohm Ammeter.

The procedures developed by Black and Smith (1962, 1965) were followed for the measurement of particle mobilities. Briefly, clay suspensions of approximately 50 mg/1 were prepared and subjected to a two minute rapid stirring period to insure complete mixing. Electrophoretic mobility determinations were made for the three clays at various ionic strengths in both the buffered NaCl and synthetic sea water solutions. Twenty individual particle mobilities, ten in either direction, were used to obtain an average particle mobility for each sample. The pH of each sample was recorded and the specific resistance of the sample was determined with a Serfass Model BCM 15 conductivity bridge and a calibrated conductivity cell.

Results and Discussion. The results of the electrophoretic mobility determinations are presented in Figure 4.3. Figure 4.3A shows that montmorillonite has lower mobility values than kaolinite and illite in buffered NaCl solutions. Figure 4.3B indicates that

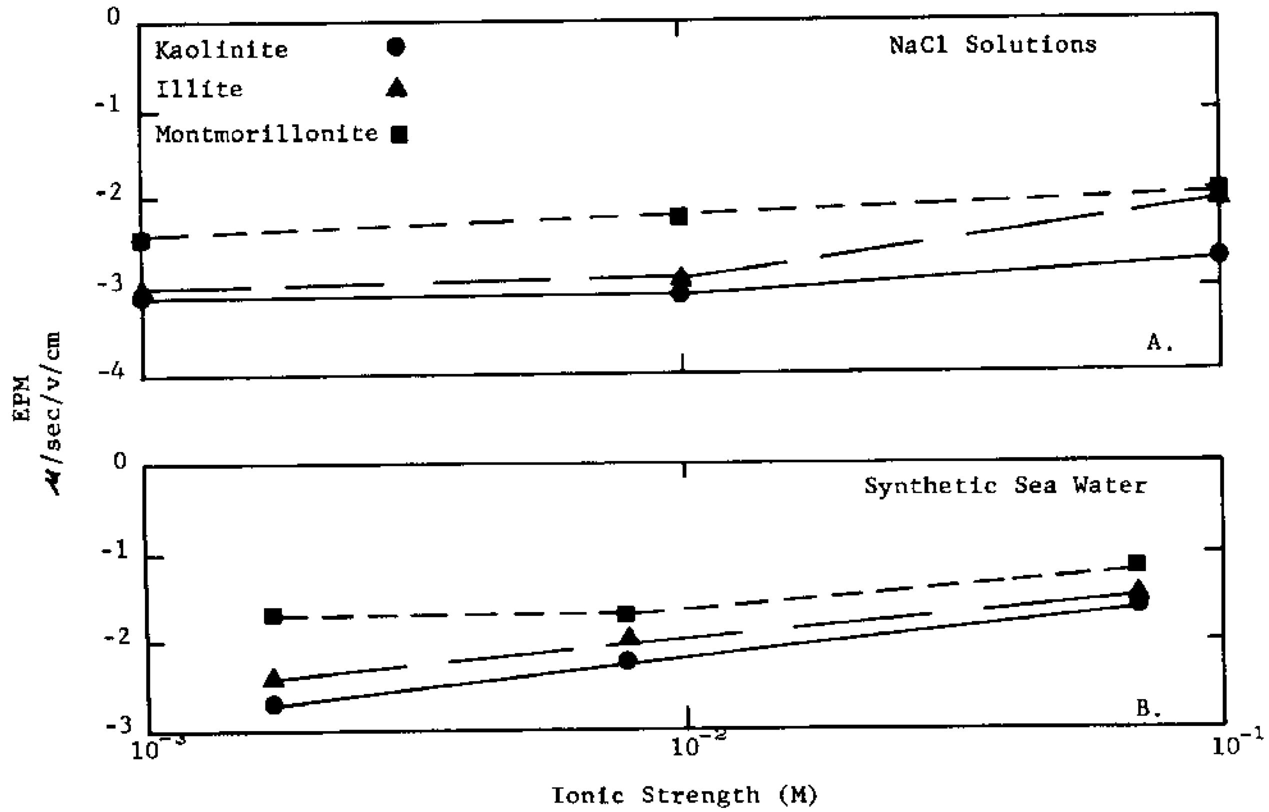


Figure 4.3 Electrophoretic Mobilities; A. Clays in Buffered-NaCl Solutions, B. Clays in Synthetic Sea Water Solutions

all these clays have lower mobilities (smaller negative values) in synthetic sea water solutions as compared to the buffered NaCl solutions. These results indicate that the clays do not undergo charge reversal when exposed to synthetic sea water solutions of increasing ionic strength. This is in qualitative accord with destabilization being accomplished by compression of the electrical double layer (VODL); if charge reversal had occurred, this mechanism of destabilization could not be applicable. Further discussion concerning charge reversal is given in Chapter V within the section examining the electrophoretic mobilities of the Pamlico sediments. The mobility determinations are inconclusive with respect to the stability of the clays.

Cation Exchange Capacity

Method. The cation exchange capacities of the Ward's clays used in this investigation are reported in the literature. A method for measuring cation exchange capacities was developed and tested using these clays. This procedure was subsequently used to measure the cation exchange capacities of sediments collected from the Pamlico Estuary (Chapter V). This is a useful measurement since for the same size particles, the cation exchange capacity and the surface charge density are directly proportional.

A review of cation exchange capacity methods for soils and clays is treated by Chapman (1965). The method used in this research is based on the method of Mortland and Mellor (1954). It is based on saturation of the clay with Ba^{+2} and then determining the cation exchange capacity by conductometric titration with a standard magnesium sulfate solution.

$$\text{Ba-Clay} + Mg^{+2} + SO_4^{-2} = BaSO_{4\,(s)} + \text{Mg-Clay}$$

Before the equivalence point, the conductance remains comparatively constant as the magnesium sulfate reacts to form insoluble barium sulfate and magnesium clay. When all of the barium saturated clay has been titrated, the conductance of the suspension increases sharply as increments of the magnesium sulfate solution are added.

Procedure. The following procedure was developed by Upchurch (1971) in the early phases of this investigation and was used to determine the cation exchange capacities of the Ward's clays as well as the Pamlico sediments.

1. A 100 ml of a stock clay suspension (see Jar Tests, Procedures) was added to a beaker containing 150 ml of $BaCl_2$-triethanolamine solution. The $BaCl_2$-triethanolamine solution was prepared according to the description provided by Mehlich (1948).
2. After 2 hours of stirring, this suspension was filtered using a 0.45μ Millipore filter.
3. The clay was transferred to a beaker by washing the Millipore filter with distilled water.
4. One hundred ml of 1 N $BaCl_2$ solution was added to the beaker and the suspension was stirred for 2 more hours.
5. This suspension was filtered as before and the clay was washed free of chloride with distilled water as indicated by the $AgNO_3$ test.

6. The clay was transferred to the titrating beaker with 100 ml of distilled water and 50 ml of ethanol.
7. The suspension was titrated with standard $MgSO_4$ and the conductance (equipment described in previous section) was measured with each added increment of the titrating solution.
8. The endpoint of the reaction was obtained by plotting the data graphically, drawing in the two linear portions of the curve, and taking the point of intersection as the equivalence point.

Results. The cation exchange capacities determined by the method described above is presented in Table 4.2.

Table 4.2

CATION EXCHANGE CAPACITIES

Determination	Kaolinite *meq/100 gm	Illite meq/100 gm	Montmorillonite meq/100 gm
1	9.15	31.7	101.0
2	9.30	24.9	99.0
3	9.11	32.4	89.3
4	8.61	24.5	89.3
5	8.64	22.6	92.7
6		27.1	
7		24.1	
8		22.5	
9		24.3	

* milliequivalents per 100 grams

The standard statistical procedure based on the t-distribution was used to compute the 95% confidence interval for the average cation exchange capacity of each clay (Dixon and Massey, (1969)). The results of this statistical analysis are summarized in Table 4.3. The limits of the 95% confidence intervals of the true mean values of the cation exchange capacities are indicated in the last column of the table.

Table 4.3

STATISTICAL ANALYSIS: CATION EXCHANGE CAPACITIES

Clay	Observed Mean meq/100 gm	Observed Standard Deviation meq/100 gm	95% Confidence Interval for true mean CEC meq/100 gm
Kaolinite	8.96	0.316	8.96 ± 0.39
Illite	26.0	3.68	26.0 ± 2.83
Montmorillonite	94.3	5.47	94.3 ± 6.8

These values for the cation exchange capacities are in agreement with those reported in the literature for the three clays (Grim, (1968), American Petroleum Institute, (1949), and Whitehouse, (1960)).

Iron and Manganese Extractions

Methods. Iron and iron oxides are commonly associated with soils and clays; consequently, it was decided to employ various extraction techniques to determine the amounts of extractable Fe and Mn associated with the Ward's clays.

1. *Oxalate Extraction* - an oxalate solution (0.2 M ammonium oxalate and 0.1 M oxalic acid) was used to extract iron ac-

cording to the procedure of Saunders (1965). The extracted iron was measured with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer.

2. Acid Extraction - an acid mixture at pH 1.1 (HCl-H_2SO_4) was used to extract iron as well as manganese from the clays. The extracted iron and manganese were measured by atomic absorption. In addition, the Ferrozine method of Stookey (1970) was used to measure total-Fe as well as Fe^{2+}. The procedures involved with these various extraction methods are not presented here, but can be found in Upchurch (1972).

Results and Discussion. Very little Mn was extracted from the clays as illustrated in Table 4.4. Table 4.5 presents the results of the Fe extractions for: (1) oxalate extraction, total-Fe (Fe_T), (2) acid extraction, total-Fe (Fe_T), and (3) acid extraction, Fe(II).

Table 4.4

Mn EXTRACTIONS

Clay	Acid Method Mn_T (mg/gm)
Kaolinite	None detectable
Illite	0.07
Montmorillonite	Trace

Table 4.5

Fe EXTRACTIONS

Clay	Oxalate Fe_T (mg/gm)	Acid Fe_T (mg/gm)	Acid Fe(II) (mg/gm)
Kaolinite	0.06	0.03	0.006
Illite	1.54	1.57	0.75
Montmorillonite	0.48	0.17	0.06

These results demonstrate that the largest amount of extractable Fe was obtained from illite - approximately half of the Fe was Fe(II) - while an intermediate amount was extracted from montmorillonite and very little was extracted from kaolinite. Similar results were obtained by Anderson and Jenne (1970) for these Ward's clays. According to Anderson and Jenne, iron oxides are believed to be present on the clays as surface oxide coatings and as discrete oxide particles.

COAGULATION RATE STUDIES

Smoluchowski's model for orthokinetic flocculation which has been described and subsequently derived for monodispersed systems (Equation [4-13]), was used in this investigation to determine stability factors for the clays. This model has been shown to be quite adequate in describing the initial stages of coagulation for: (1) reaction times up to twice the half-time and (2) ratio of particle diameters up to 5.

Experimental Materials and Equipment

Preparation of Clay Suspensions. The procedure described here was used throughout this research to obtain clay suspensions with a narrow particle size distribution.

1. Approximately 3 grams of crushed clay were added to a 125 ml Erlenmeyer flask containing 50 ml of distilled water. The resulting clay suspension was mixed violently for 1 hour using a mechanical shaker in order to disperse the clay.
2. The clay suspension was transferred to two centrifuge tubes (divided equally) and centrifuged for 30 sec at 500 rpm (International Centrifuge). The supernatant was retained while the material that was spun to the bottom was discarded. Theoretically (calculations based on the centrifuge system used) all particles with an equivalent spherical diameter of 9 μ (assuming gravity of clays is 2.60) or greater were discarded.
3. The supernatant from step 2 was then centrifuged for 1 minute at 700 rpm. Afterwards, this supernatant was discarded and the clay on the bottom of the tube was resuspended using distilled water. This was repeated several times until the supernatant was quite clear.
4. The clay on the bottom of the tubes was resuspended using a small volume of filtered (0.45μ Millipore) deionized water.
5. This clay suspension was transferred to a plastic bottle and the clay concentration determined gravimetrically. These clay suspensions were used in the rate studies within 36 hours after preparation.

This centrifugation procedure should yield - according to calculations - clay suspensions with a 4-9 μ (equivalent spherical diameter) size range. A microscopic check of the size distribution of several clay suspensions indicated 80% of the clay particles had an equivalent diameter between 1.5 and 6 μ with a mean of 4.2 μ. The centrifugation procedure yielded particles with a smaller size range than expected but one that was entirely satisfactory.

Preparation of NaCl and Sea Water Solutions. Buffered-NaCl solutions and synthetic sea water solutions were prepared and used as the destabilizing agents in the coagulation rate studies. Coagulation experiments using the NaCl solutions dictated that only monovalent cations (Na^+) were involved in destabilization. The contents of the buffered-NaCl solutions are presented in Table 4.6. These solutions were buffered with 2 x 10^{-3}M $NaHCO_3$ yielding solutions with a pH of 7.9-8.2.

Table 4.6

BUFFERED NaCl SOLUTIONS

Species	Conc. (M)	Conc. (M)	Conc. (M)
$NaHCO_3$	0.002	0.002	0.002
NaCl	0.298	0.088	0.048
Ionic Strength	0.300	0.090	0.050

The formula for sea water proposed by Lyman and Fleming (1940) and presented in Table 4.1 was used as a basis in the preparation of synthetic sea water solutions. These sea water solutions were prepared by appropriate dilutions of Lyman and Fleming's sea water. The

$NaHCO_3$ concentration was maintained at 2×10^{-3}M for all solutions. The pH of all sea water solutions was within the range of 7.8 to 8.2. The ionic strength of these solutions was calculated using the following equation.

$$I.S. = \tfrac{1}{2} \Sigma m_i z_i^2 \qquad [4\text{-}14]$$

where I.S. is the ionic strength

m_i is the molar concentration

z_i is the valance

The compositon of these sea water solutions are summarized in Table 4.7.

Table 4.7

COMPOSITION OF SYNTHETIC SEA WATER SOLUTIONS

Species	Ion Conc. moles/l	Ion Conc. moles/l	Ion Conc. moles/l
Na^+	0.231	0.0577	0.0231
Mg^{+2}	0.026	0.0065	0.0026
Ca^{+2}	0.005	1.25×10^{-3}	5×10^{-4}
K^+	0.005	1.25×10^{-3}	5×10^{-4}
Sr^{+2}	7.5×10^{-5}	1.87×10^{-5}	7.5×10^{-6}
H_3O^+	10^{-8}	10^{-8}	10^{-8}
Cl^-	0.268	0.067	0.0268
$SO_4^=$	0.014	0.0035	0.0014
HCO_3^-	0.002	0.002	0.002
Br^-	5×10^{-4}	1.25×10^{-4}	5×10^{-5}
F^-	3.6×10^{-5}	9×10^{-6}	3.6×10^{-6}
OH^-	10^{-6}	10^{-6}	10^{-6}

Table 4.7 (con't.)

Species	Ion Conc. moles/l	Ion Conc. moles/l	Ion Conc. moles/l
Ionic Strength	0.343	0.087	0.036
Salinity (ppt)	17.5	4.4	1.8

The ionic strengths given in this table are based on total ion concentrations. Corrections for ion-pair associations were not considered in these calculations. Ion-pair association would be important for sea water (salinity 35 ppt); however, as the sea water is diluted the error associated with this becomes quite small. The salinity of 97 per cent of the sea water in the world lies between 33 ppt and 37 ppt (Cox, (1965)). The salinities of the sea water solutions (diluted sea water) used in this research are indicated in Table 4.7. The sea water solutions provided a destabilizing mechanism involving divalent cations. The effects of synthetic sea water solutions on the coagulation rates of clay suspensions were compared with the buffered-NaCl solutions.

Stirred Reactor Assembly. The coagulation rate studies were conducted in the stirred-tank-type reactor illustrated in Figure 4.4. A torquemeter* was coupled between the dc stirring motor and the stirring shaft so that the stirring power input to the reactor could be determined by direct measurement of the torque on the paddle shaft. The power transmitted by the shaft is composed of the power transferred to the water and the power lost in the bearings due to friction.

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* A product of Power Instruments Inc., Skokie, Ill.

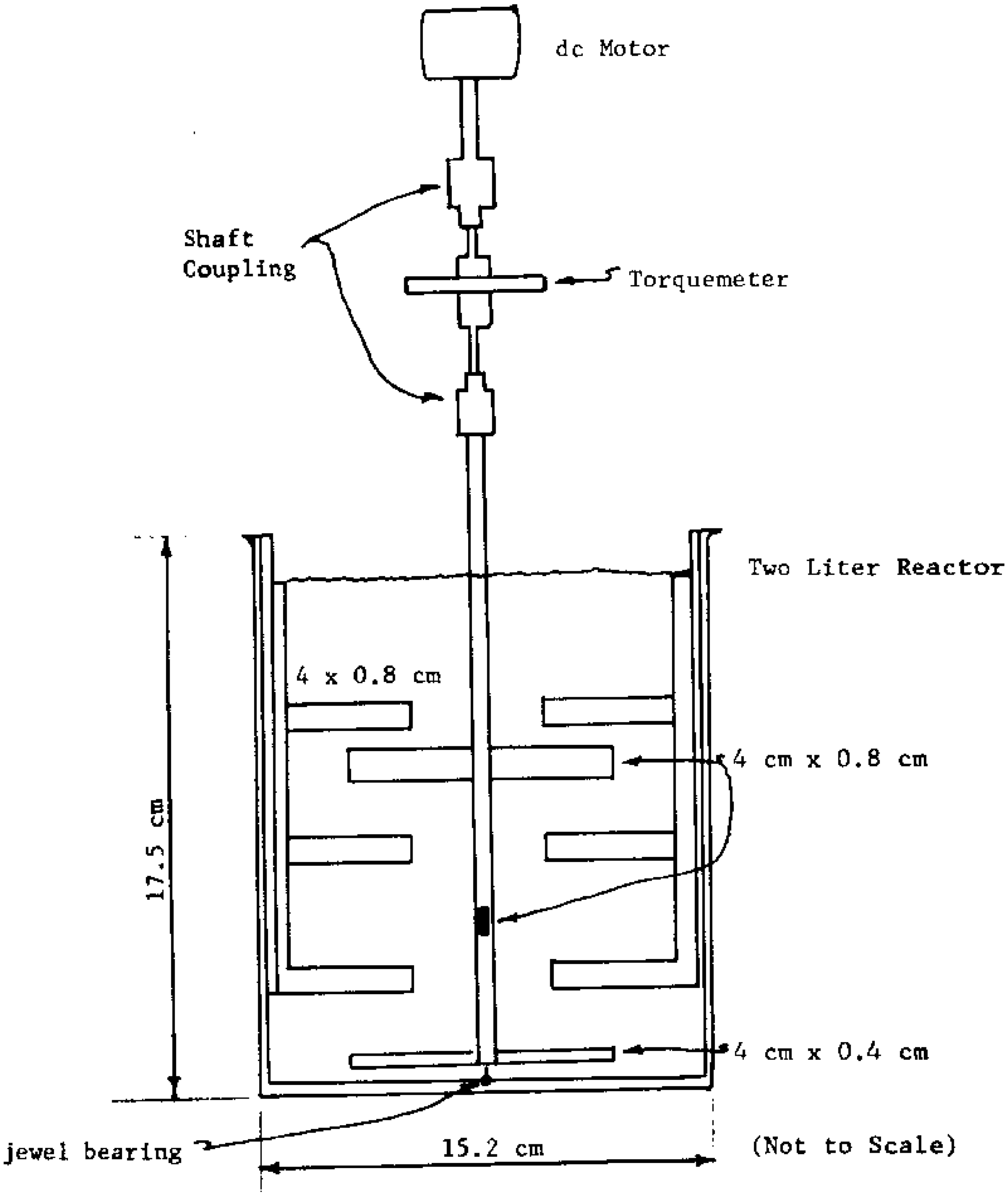

Figure 4.4 Stirrer Reactor Assembly

Torque measurements were carried out with water at normal operation level and with the reactor empty. The net power transferred to the fluid was calculated by subtracting the latter from the former. The relation between power, torque, and rotation speed in general is given by

$$P = \tau \omega \qquad [4\text{-}15]$$

where P is the power input (dyne-cm/sec), τ is the torque (dyne-cm), and ω is the angular velocity of the rotating paddle. The power input per unit mass of fluid was calculated by

$$\varepsilon = \frac{P_n - P_e}{\rho V} \qquad [4\text{-}16]$$

where ε is the power input per unit mass of fluid, P_n and P_e are the power transmitted to the paddle shaft with water at normal operating level and with the empty reactor, respectively, ρ is the water density and V is the reactor volume. The root-mean-square velocity gradient, G, was calculated by the equation of Camp and Stein (1943),

$$G = (\varepsilon/\nu)^{\frac{1}{2}} \qquad [4\text{-}17]$$

where G is the root-mean-square velocity gradient (sec^{-1}) and ν is the kinematic viscosity. A sample calculation of G is presented in Appendix B.

Particle Counting Methods

Two particle counting methods were used in this research. A Model B Coulter Counter was used to determine the floc volume fraction

(ϕ) for the montmorillonite clay suspensions. An American Optical Series 10 Microscope was used during the kinetic experiments in conjunction with a hemacytometer to determine the clay particle number concentration (particles per volume).

Coulter Counter. The operation and theoretical principles of the Coulter Counter have been discussed in detail by Kubitschek (1960). The use of this instrument in coagulation studies has been evaluated by Matthews and Rhodes (1970b). Numerous investigators have applied this method to coagulation kinetic studies including Birkner and Morgan (1968), Swift and Friedlander (1964), Matthews and Rhodes (1970a), Hannah et al. (1967), and Higuchi et al. (1963, 1965). A brief description of the principle of operation is as follows:

> The sample suspension is diluted with a suitable electrolyte solution which is devoid of any particulate matter. A known volume of this diluted suspension is drawn through an orifice - small aperture of 30μ or 100μ - which has an immersed electrode on either side. A particle passing through the aperture changes the resistance between the electrodes and produces a voltage pulse of short duration having a magnitude proportional to the particle volume. The series of pulses is then electronically scaled and counted. Kubitschek (1960) has shown that the pulse amplitude depends also upon the shape of the particle. The nearly linear relationship between the amplitude of the voltage pulse and the particle volume holds only for particle diameters between

2% and 40% of the aperture size. Thus a 100 μ orifice can count particles with diameters between 2 and 40 μ .

The calibration of the Coulter Counter has been discussed in detail by Morgan and Birkner (1966), Matthews and Rhodes (1970 b), and Sheldon and Parsons (1967). In this study, a 30 μ orifice was used to determine the floc volume fraction of the montmorillonite suspensions. It was calibrated using polystyrene latex particles which were known to have a diameter of 3.49μ .

Microscopic Counting. In the kinetic studies, the rate of particle aggregation was determined by observing the change in the clay particle number concentration (particles per ml) over time. Phase contrast microscopy was used for particle counting at a magnification of 450x. An American Optical Spencer hemacytometer was used as a particle counting chamber. The hemacytometer is commonly used for blood counting in hospitals. Its use permits one to obtain particle counts per unit volume.

A comparison of particle counting methods - Coulter Counter and microscopic - was made using 7.6μ latex particles and kaolinite clay particles. Table 4.8 summarizes particle counts using a latex suspension. The agreement between the 30μ aperture (Coulter Counter) and the hemacytometer is excellent.

Table 4.8

PARTICLE COUNTS: 7.6μ LATEX SUSPENSION

Method	Particle Counts particles/ml
Microscope	
Hemacytometer	5.15×10^8
Coulter Counter	
100μ Aperture	5.0×10^8
30μ Aperture	5.16×10^8

The low count for the 100μ aperture (Coulter Counter) is an indication that the smallest particles were not being counted. Table 4.9 summarizes particle counts using a kaolinite clay suspension. The results clearly demonstrate that there is good correlation between the two counting methods, especially with the 30μ orifice. The 100μ orifice should count particles larger than about 2μ. It was

Table 4.9

PARTICLE COUNTS: KAOLINITE CLAY SUSPENSION

Method	Particle Counts particles/ml
Microscope	
Hemacytometer	1.44×10^8
Coulter Counter	
100 μ	1.0×10^8
30 μ	1.45×10^8

cited earlier that the normal particle size range for the clay suspensions was 1.5 to 6μ . Some of the clay particles were smaller than 2μ and thus the 100μ orifice gave a low particle count (Table 4.9). The microscopic method of particle counting was selected for the kinetic studies. It was not feasible to use the 30μ orifice to determine the rate of particle aggregation due to operational difficulties - the 30μ orifice clogs easily and operates slowly. Obviously, the 100μ orifice could not be used since it does not count particles at the lower end of the size distribution. The Coulter Counter (30μ orifice) was used in this investigation to determine the floc volume fraction of the montmorillonite suspensions.

Determination of the Floc Volume Fraction

The floc volume fraction, ϕ, was introduced in Equation [4-12] and is defined as the volume of total solid mass suspended per volume of fluid.

Kaolinite and Illite. For non-expanding clays such as kaolinite and illite, ϕ can be determined by

$$\phi = \frac{c}{\rho'} \qquad [4\text{-}18]$$

where c is the clay concentration (grams of clay/cm^3 of fluid) and ρ' is the density of the clay (grams of clay/cm^3 of clay). The densities of kaolinite and illite were determined by the pycnometer method. The densities of kaolinite and illite were found to be 2.61 gm/cm^3 and 2.72 gm/cm^3, respectively. These values are in agreement with those reported by Whitehouse et al. (1960) for the same clays (Ward's: Kaolinite #3 and Illite #35).

Montmorillonite. Montmorillonite is an expanding three-layered clay which contains water in the interlayer position. Due to this interlayer water, densities based on its dry weight do not reflect the volume of solid mass in an aqueous suspension. An alternative method of evaluating the floc volume fraction is

$$\phi = \Sigma n_i V_i \qquad [4\text{-}19]$$

where n_i is the number of i particles per cm^3 of fluid, with particle volume V_i (cm^3). The floc volume fraction was calculated by determining the particle size distribution of the montmorillonite suspensions. The Coulter Counter (30μ orifice) was employed for this task.

Results and Discussion

Rates of coagulation were determined in the laboratory by observing the change in the clay particle number over time. Samples of the flocculating clay suspensions were withdrawn from the reactor with a Pasteur pipet and the particle number concentration (particles per ml) was obtained using the microscopic counting technique described earlier. Stability values (α) were evaluated from the kinetic coagulation data using Smoluchowski's equation (Equation [4-13]) for orthokinetic flocculation.

Buffered-NaCl Solutions. A series of experiments were conducted in which the coagulation rates of clay suspensions were observed using three different ionic strength NaCl solutions. Figures 4.5, 4.6, and 4.7 illustrate the effect of increasing ionic strength on the coagulation rates of various clay suspensions. Stability values were evaluated from the slopes of the least squares regression lines.

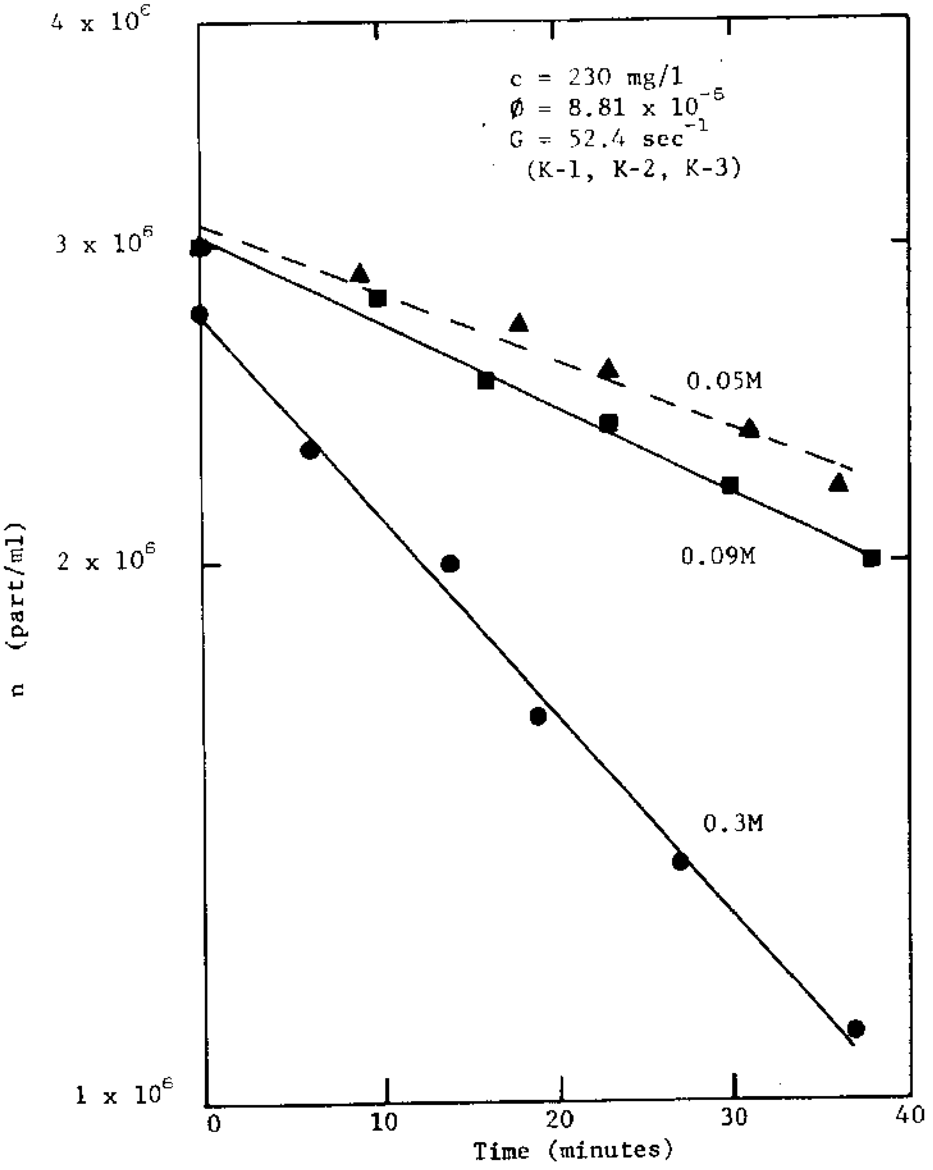

Figure 4.5 Rates of Coagulation for Kaolinite in Buffered NaCl Solutions.

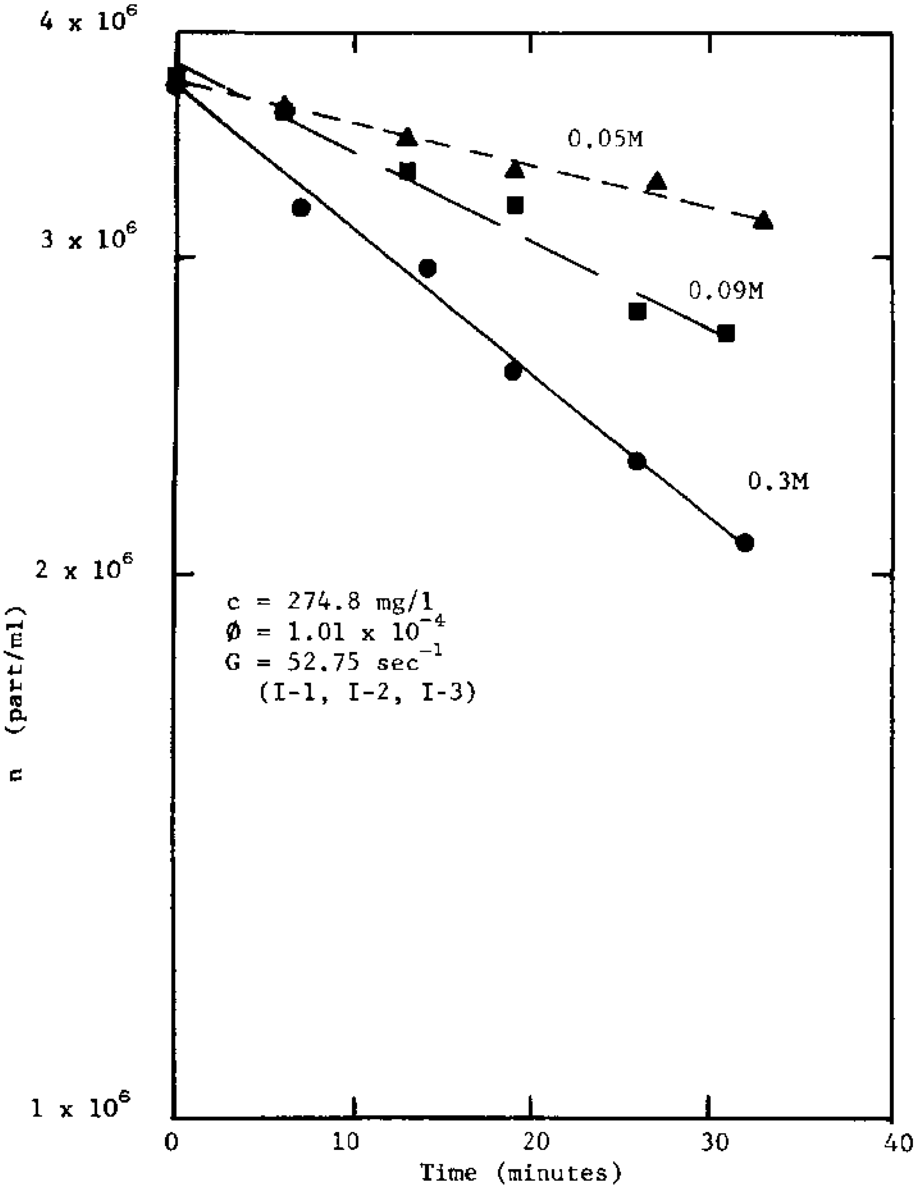

Figure 4.6 Rates of Coagulation for Illite in Buffered NaCl Solutions.

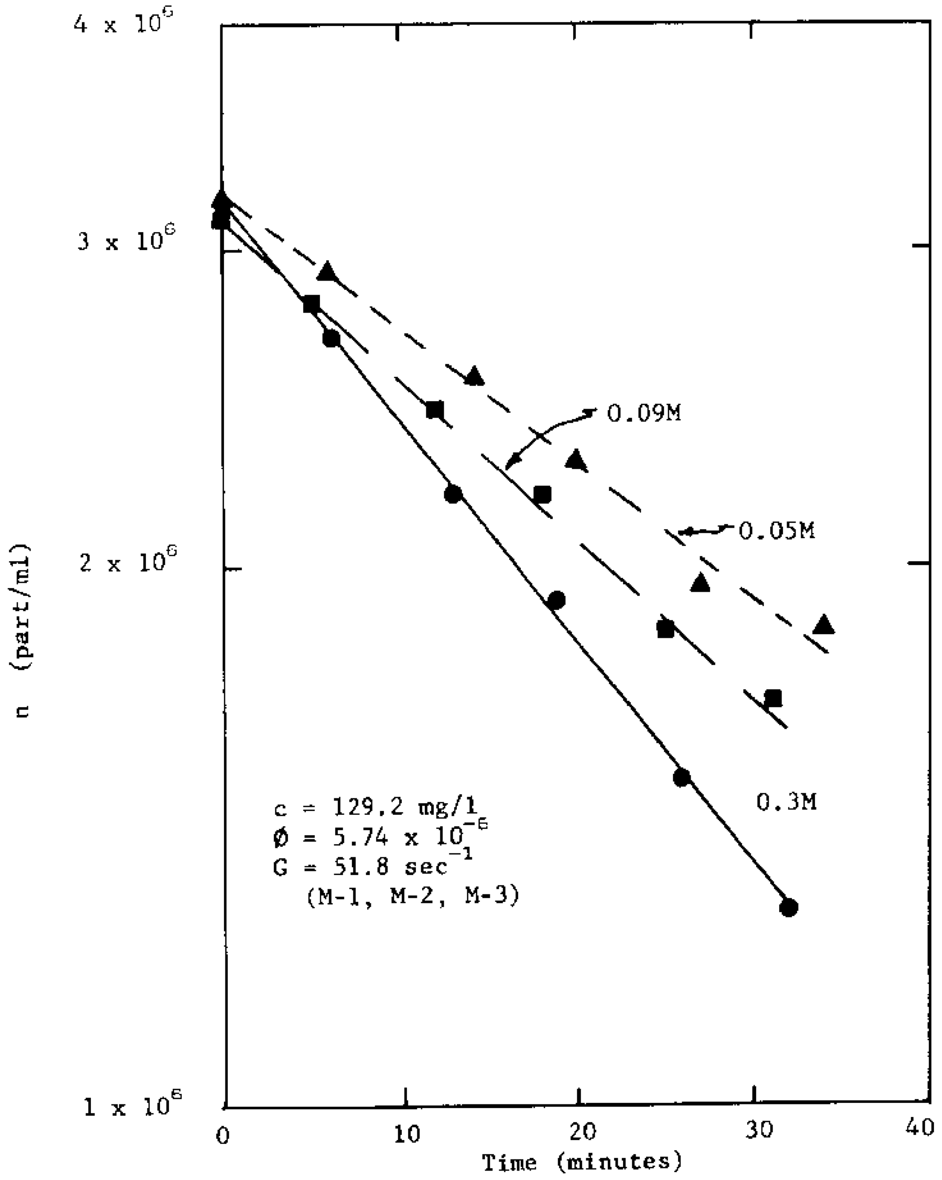

Figure 4.7 Rates of Coagulation for Montmorillonite in Buffered NaCl Solutions.

The stability factor (α) depends on the degree of destabilization (ionic strength of the solution); consequently, for constant ionic strength, changes in ϕ and G should not affect α . Additional experiments* were conducted for kaolinite and illite at lower clay concentrations (lower ϕ values). These experiments yielded two independent determinations of α for kaolinite and illite suspensions at each ionic strength.

Stability values obtained from the experiments using the buffered NaCl solutions are summarized in Table 4.10. Statistical techniques used in this phase of the investigation are summarized in Appendix D and include least squares regression, 95% confidence intervals for α, and the test of the hypothesis $\alpha_1 = \alpha_2$. The latter statistical test compares the slopes of two regression lines obtained from two independent experiments. It compares α values determined from experiments at two different clay concentrations (ϕ values); for example, is the α value from experiment K-3 ($\alpha = 0.0724$) significantly different from experiment K-6 ($\alpha = 0.0738$)? The statistical analyses indicate that all duplicate alpha values do not differ significantly at the 5% level of significance. The clay concentration was not varied for montmorillonite due to cumbersome experimental procedures required in the rate studies for this clay.

Synthetic Sea Water Solutions. Figures 4.8, 4.9, and 4.10 illustrate the effect of increasing ionic strength - synthetic sea water solutions - on the coagulation rates of various clay suspensions. Table 4.11 summarizes the alpha values (α) obtained from experiments using synthetic sea water solutions. Statistical analyses indicate

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* Figures showing the results of these experiments are presented in Appendix C.

Table 4.10

STABILITY VALUES: NaCl SOLUTIONS

Kaolinite

I. S. M.	Exper.	G sec^{-1}	ϕ	α*	Exper.	G sec^{-1}	ϕ	α
0.05	K-1	52.4	8.81×10^{-5}	0.0245 ± 0.007	K-4	52.3	5.20×10^{-5}	0.0279 ± 0.0048
0.09	K-2	52.4	8.81×10^{-5}	0.0308 ± 0.004	K-5	52.3	5.20×10^{-5}	0.0326 ± 0.014
0.3	K-3	52.4	8.81×10^{-5}	0.0724 + 0.007	K-6	52.3	5.20×10^{-5}	0.0738 ± 0.012

Illite

I. S. M.	Exper.	G sec^{-1}	ϕ	α	Exper.	G sec^{-1}	ϕ	α
0.05	I-1	52.75	1.01×10^{-4}	0.0128 ± 0.003	I-4	53.0	7.1×10^{-5}	0.0119 ± 0.002
0.09	I-2	52.75	1.01×10^{-4}	0.0275 ± 0.005	I-5	53.0	7.1×10^{-5}	0.0262 ± 0.01
0.3	I-3	52.75	1.01×10^{-4}	0.0455 ± 0.005	I-6	53.0	7.1×10^{-5}	0.0467 ± 0.005

Montmorillonite

I. S. M.	Exper.	G sec^{-1}	ϕ	α
0.05	M-1	51.8	5.74×10^{-5}	0.075 ± 0.009
0.09	M-2	51.8	5.74×10^{-5}	0.089 ± 0.006
0.3	M-3	51.8	5.74×10^{-5}	0.125 ± 0.005

* The 95% Confidence Interval for α is indicated.

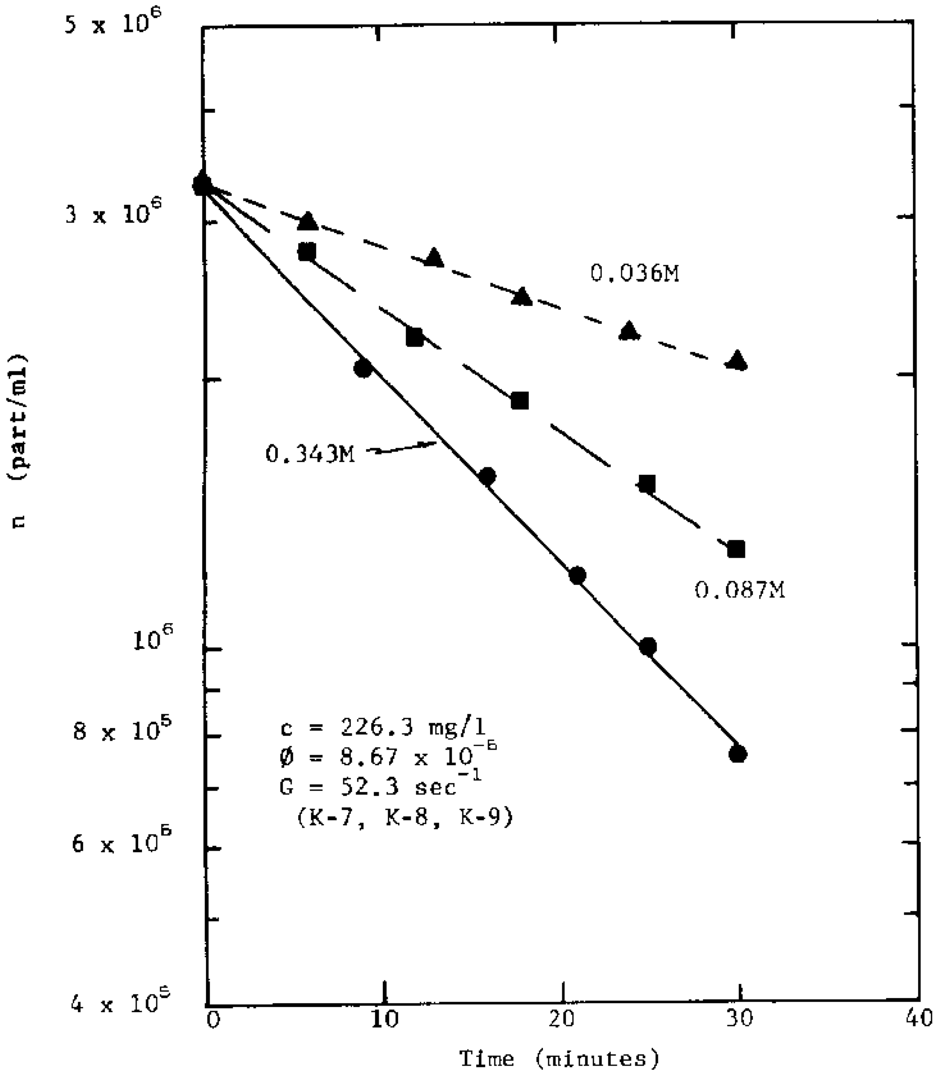

Figure 4.8 Rates of Coagulation for Kaolinite in Synthetic Sea Water Solutions.

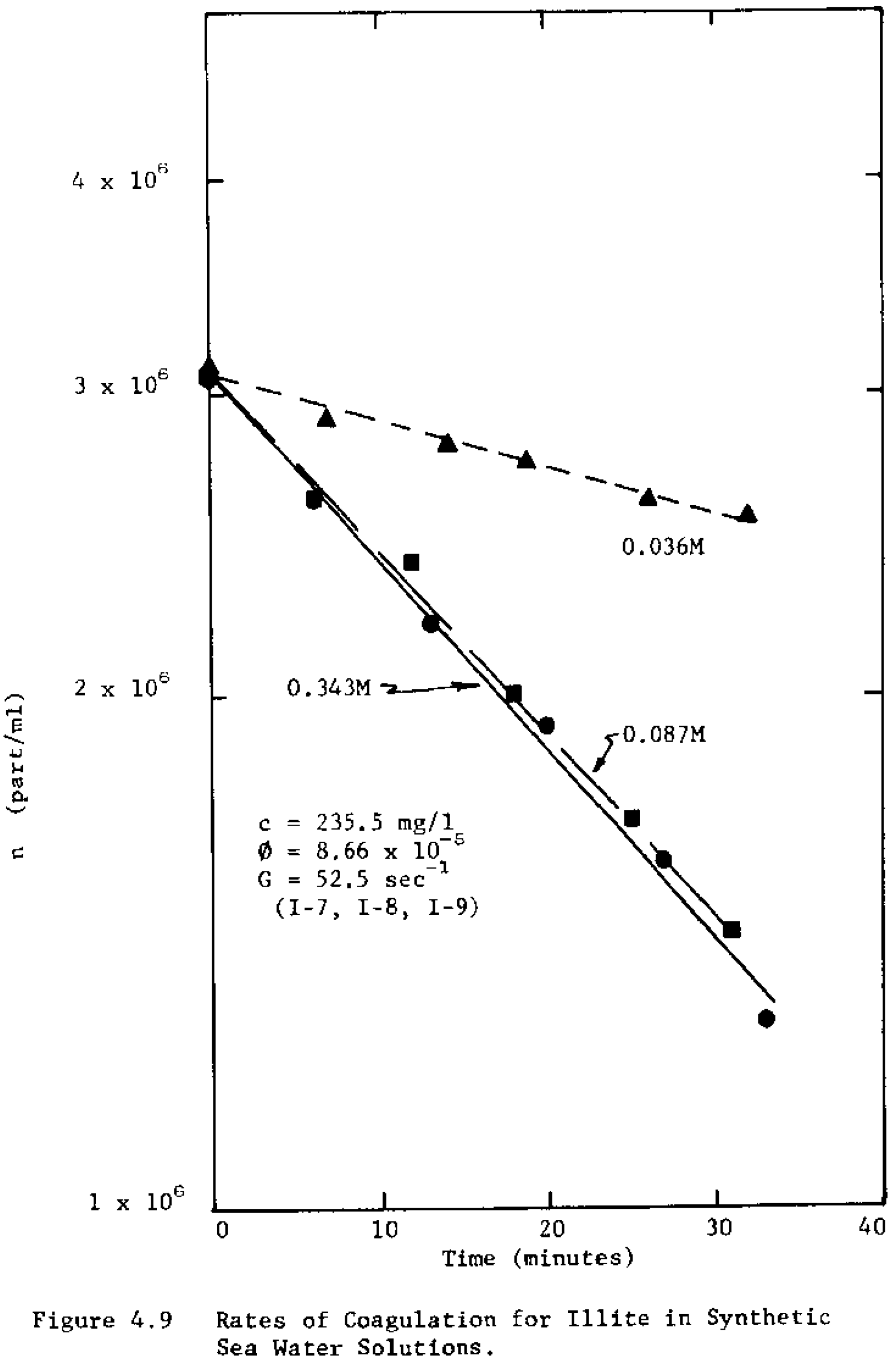

Figure 4.9 Rates of Coagulation for Illite in Synthetic Sea Water Solutions.

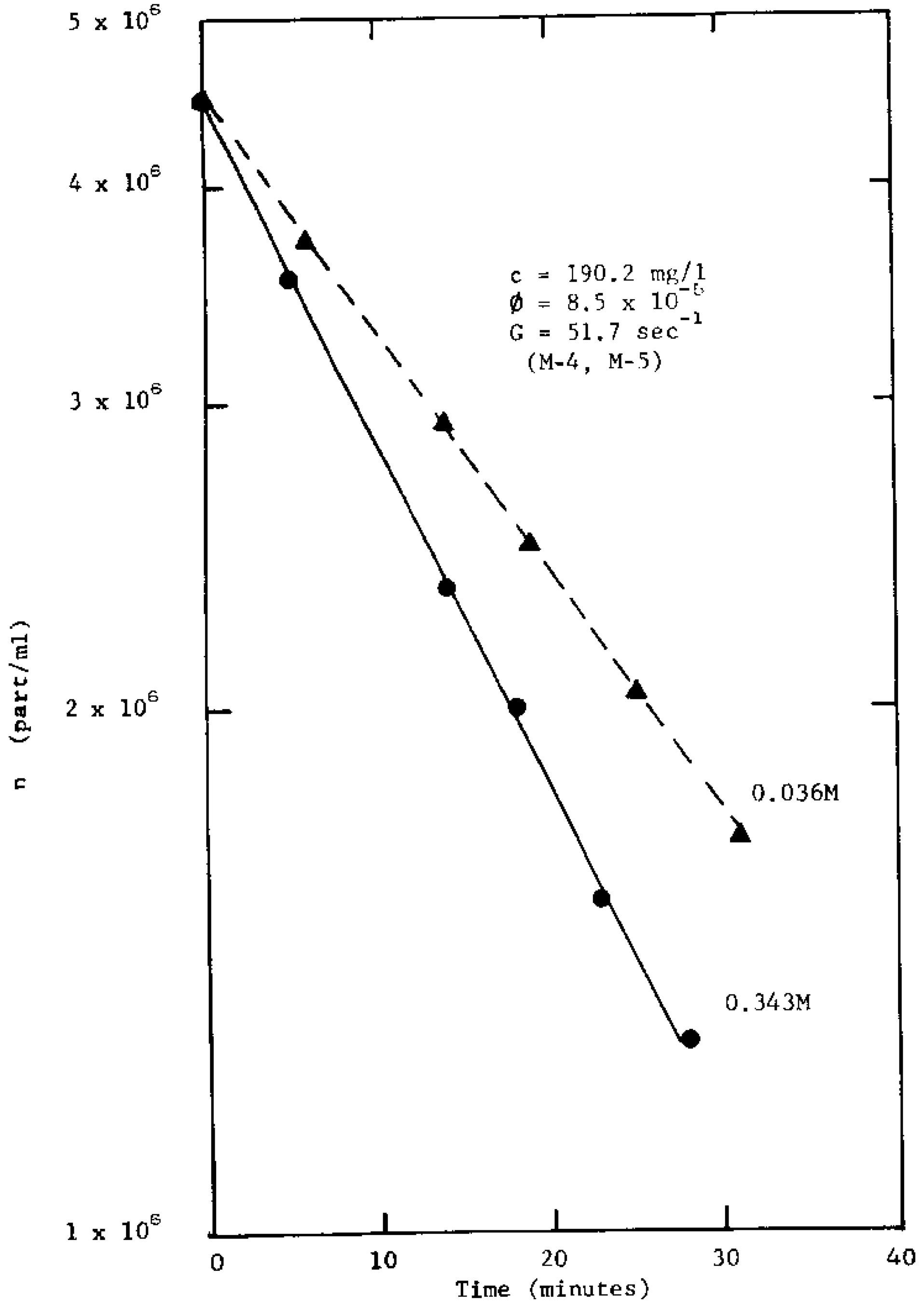

Figure 4.10 **Rates of Coagulation for Montmorillonite in Synthetic Sea Water Solutions.**

Table 4.11

STABILITY VALUES: SYNTHETIC SEA WATER SOLUTIONS

Kaolinite

I. S. M.	Exper.	G sec^{-1}	ϕ	α *	Exper.	G sec^{-1}	ϕ	α
0.036	K-7	52.3	8.67×10^{-5}	0.0445 ± 0.002	K-10	53.0	5.63×10^{-5}	0.0400 ± 0.006
0.087	K-8	52.3	8.67×10^{-5}	0.0915 ± 0.006	K-11	53.0	5.63×10^{-5}	0.0899 ± 0.006
0.343	K-9	52.3	8.67×10^{-5}	0.138 ± 0.009	K-12	53.0	5.63×10^{-5}	0.141 ± 0.015

Illite

I. S. M.	Exper.	G sec^{-1}	ϕ	α	Exper.	G sec^{-1}	ϕ	α
0.036	I-7	52.5	8.66×10^{-5}	0.0180 ± 0.003	I-10	53.0	5.09×10^{-5}	0.0190 ± 0.006
0.087	I-8	52.5	8.66×10^{-5}	0.0701 ± 0.007	I-11	53.0	5.09×10^{-5}	0.0708 ± 0.032
0.343	I-9	52.5	8.66×10^{-5}	0.0740 ± 0.009	I-12	53.0	5.09×10^{-5}	0.0724 ± 0.015

Montmorillonite

I. S. M.	Exper.	G sec^{-1}	ϕ	α	Exper.	G sec^{-1}	ϕ	α
0.036	M-4	51.7	8.5×10^{-5}	0.0943 ± 0.003	- -	- -	- -	- -
0.087	- -	- -	- -	- - - -	M-6	51.8	5.74×10^{-5}	0.113 ± 0.019
0.343	M-5	51.7	8.5×10^{-5}	0.134 ± 0.006	M-7	51.8	5.74×10^{-5}	0.148 ± 0.006

* The 95% Confidence Interval for α is indicated.

that the duplicate* alpha values are not significantly different at the 5% level of significance.

Aging Experiments. A set of experiments was conducted for the purpose of evaluating the long term effects of exposing clay particles to various solutions. Clay suspensions were prepared using deionized water, 0.3 M NaCl, and 0.343 M synthetic sea water. These suspensions were allowed to sit for two months. Periodic agitation was employed to resuspend the clays and expose their surfaces to the solution being used for aging. At the end of two months, rate studies were conducted as described previously and alpha values were obtained. Table 4.12 summarizes the results of these aging experiments. Statistical analyses indicate that: (1) the α (0.0465) obtained from Experiment K-13 (aged in deionized water and coagulated in 0.3 M NaCl solution) is significantly different from the α (0.0738) from Experiment K-6 (no aging and coagulated in 0.3 M NaCl solution) and (2) the α (0.195) obtained from Experiment K-16 (aged in 0.343 M sea water solution and coagulated in same) is significantly different from the α (0.141) from Experiment K-12 (no aging and coagulated in 0.343 M sea water solution). There is no significant difference between (1) the α (0.0775) obtained from Experiment K-15 (aged in 0.3 M NaCl solution and coagulated in same) and the α (0.0738) obtained from Experiment K-6 (no aging and coagulated in 0.3 M NaCl solution) or (2) the α (0.127) obtained from Experiment K-14 (aged in deionized water and coagulated in 0.343 M sea water solution) and the α (0.141) obtained from Experiment K-12 (no aging and coagulated in 0.343 M sea water solution).

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*Additional experimental data are presented in Appendix C.

Table 4.12

STABILITY VALUES: AGING EXPERIMENTS

Kaolinite

*Aging Conditions	**Ionic Strength M	Exper. #	G sec^{-1}	ϕ	α ***
Deionized Water	0.3 (NaCl)	K-13	52.5	5.63×10^{-5}	0.0465 ± 0.016
Deionized Water	0.343 (Sea)	K-14	52.5	5.63×10^{-5}	0.127 ± 0.027
0.3M NaCl	0.3 (NaCl)	K-15	52.5	5.63×10^{-5}	0.0775 ± 0.018
0.343M Sea	0.343 (Sea)	K-16	52.5	5.63×10^{-5}	0.195 ± 0.029
No aging	0.3 (NaCl)	K-6	52.3	5.20×10^{-5}	0.0738 ± 0.012
No aging	0.343 (Sea)	K-12	53.0	5.63×10^{-5}	0.141 ± 0.015

* Kaolinite was aged in the designated solution for two months.

** Rate Experiment was conducted in this solution.

** The 95% Confidence Interval for α is indicated.

The results indicate that kaolinite clay suspensions which are aged in deionized water are more stable than unaged suspensions when NaCl solutions are involved in coagulation. The exposure of clay particle surfaces to deionized water over a long time period may result in a greater degree of surface hydration which physically hinders contact between particles. The degree of hydration is important for extremely short range particle interactions and could cause an increase in particle stability. On the other hand, clay suspensions aged in sea water are unstable relative to unaged suspensions. This may be the result of the surface adsorption of divalent cations (for aged suspensions) which reduces the surface charge densities of the clays by the mechanism of charge neutralization. This set of experiments was rather limited in scope and the conclusions derived from the experimental results should be taken accordingly. The results do indicate, however, that the aging of clay suspensions does affect the stability of these suspensions.

Discussion of the Stability Factor. The results of these kinetic experiments demonstrate that the stability factor depends upon chemical parameters and that different clays have different α values. Tables 4.10 and 4.11 demonstrate the effects of increasing ionic strength on particle destabilization - α increases. A comparison of α values between NaCl solutions and sea water solutions shows lower α values for clay suspensions destabilized with NaCl. This is to be expected since the sea water contains divalent cations which are more effective in accomplishing particle destabilization. These results - effects of ionic strength and valency of cations - are in qualitative accord with the theory of particle destabilization by double layer compression.

The stability factor was not affected by physical parameters such as ϕ and G. It was concluded from the statistical analysis that there was no significant difference between α values determined at two different clay concentrations. This is in agreement with the results of Hahn (1968) who concluded that the stability factor is dependent upon chemical solution parameters. Table 4.13 compares the stability factors obtained from this research with values obtained by other investigators. The stability factors for the clays vary over a range typical of values reported for other colloids. The results of the kinetic studies (See Tables 4.10 and 4.11) indicate that the stability of the clays is as follows: Illite $>$ Kaolinite $>$ Montmorillonite. This is in agreement with the results of the jar tests where it was concluded that montmorillonite and kaolinite are unstable relative to illite.

Table 4.13

EXPERIMENTAL DETERMINATION OF α

Investigators	Coagulant	Colloid	Type of Flocculation	α
Hahn (1968)	Al(III)	Silica	perikinetic	*.01 to .1
Hahn (1968)	Al(III)	Silica	orthokinetic	*.01 to .1
Swift and Friedlander (1964)	NaCl (1 M.)	Polystyrene latex	perikinetic	0.375
Swift and Friedlander (1964)	NaCl (1 M.)	Polystyrene latex	orthokinetic	0.364
Birkner and Morgan (1968)	NaCl (1 M.)	Polystyrene latex	orthokinetic	0.344, 0.448
Present study	NaCl Solutions	Clay minerals	orthokinetic	**0.012-0.12
Present study	Sea Water Solutions	Clay minerals	orthokinetic	0.02-0.15

* Values in the order of .01 to 0.1 depending upon coagulant dosage and solution pH.

** Values of this order depending upon ionic strength.

CHAPTER V

PAMLICO ESTUARY

DESCRIPTION AND SEDIMENT COLLECTION

The Pamlico Estuary runs in an approximate northwest-southeast direction from Washington, North Carolina to the vicinity of Pamlico Point where it enters Pamlico Sound (Figure 5.1). The Tar River is the principal tributary of the Pamlico Estuary. The Tar River and Pamlico Estuary drain approximately 4000 square miles of the Piedmont and Coastal Plain of North Carolina. The average daily suspended load in the Tar River at Tarboro is 243 tons/day (based on a 5 year period) and consists mainly of silt and clay (N.C. Dept. of Water and Air Resources (1965-1969)).

The Pamlico Estuary is a shallow well-mixed estuary with a maximum width of about 8 miles and an average depth of about 10.5 feet (Horton (1967) and Hobbie (1970)). The outer banks of North Carolina have a damping effect on the lunar tides; consequently, the lunar tide is only about 6 inches and is greatly overshadowed by wind tides of up to 3 feet. The average variation of surface and bottom salinity (June '68-Dec. '70) is shown in Figure 5.2. The salinity data is based on the average of approximately 50 observations at each station and was obtained from Hobbie and Copeland (1971). The salinity varies from about 0 ppt near Washington to around 16 ppt at the mouth. The water is well stirred because of the shallowness so that stratification

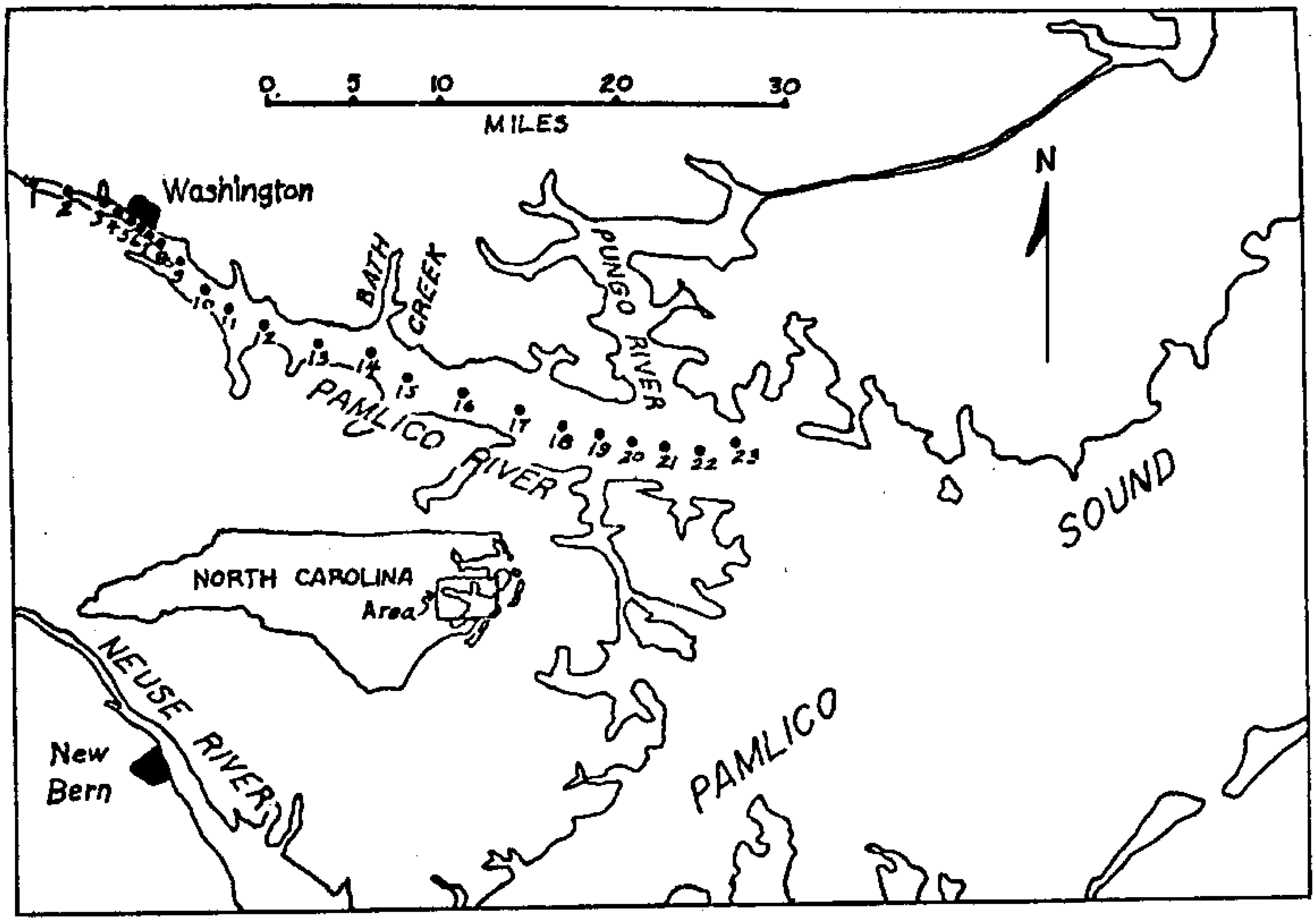


Figure 5.1 Map of the Pamlico Estuary. Numbered points represent sediment sample numbers and approximate locations.

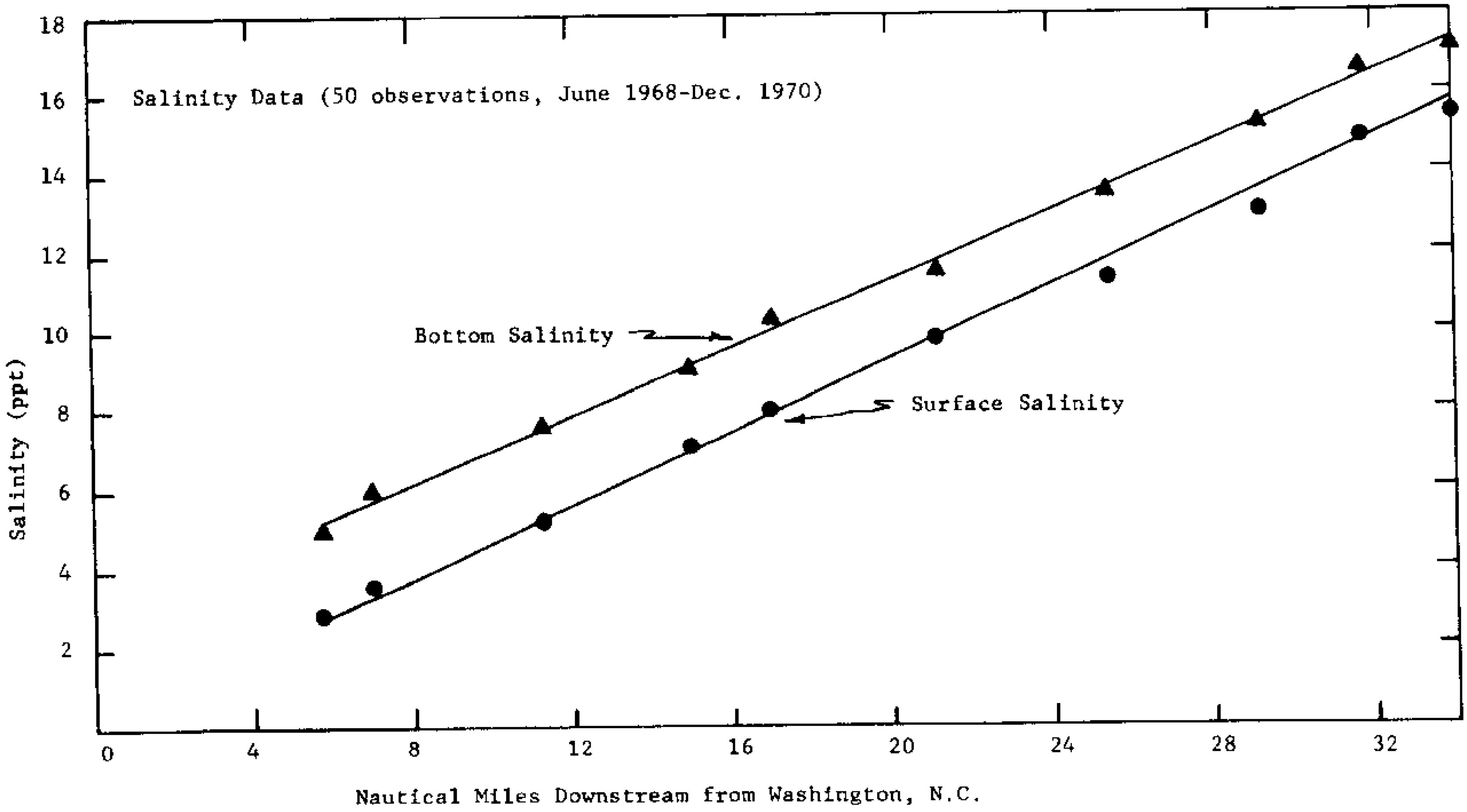


Figure 5.2 Salinity Distribution for the Pamlico Estuary (Hobbie and Copeland (1971)).

is irregular with no permanent salt wedge (Hobbie (1970)). Hobbie reported that the water temperature ranges from 3°C in the winter to 34°C during the summer. The dissolved oxygen concentration may drop to 1 mg/l on the bottom during the summer but this condition is easily destroyed by wind.

An Ekman dredge was used to collect bottom sediments from the middle of the Pamlico Estuary. The sample stations are indicated in Figure 5.1 and their locations relative to the railroad bridge at Washington, North Carolina are indicated in Table 5.1. Formaldehyde was used during collection to retard biological activity and the samples were frozen in the field with dry ice. In the laboratory, the amount of adsorbed phosphorus was determined for all sediment samples. Several representative samples were selected and subjected to the following analyses: X-ray diffraction, jar tests, and coagulation rate studies. In addition, the cation exchange capacities and electrophoretic mobilities of these pre-selected sediments were determined.

LABORATORY ANALYSES AND PROCEDURES

X-ray Diffraction

It is not the purpose of this study to determine, per se, the clay mineral composition of the Pamlico sediments. The clay mineralogy of sediments collected from the Pamlico has been determined by Park (1971), Dobbins et al. (1970), and Allen (1964). However, the clay mineral composition was obtained, because of its relevance to the coagulation rate studies and the adsorbed phosphorus analyses. The following sediment samples were chosen for X-ray diffraction: #7, #12, #15, #18, and #22 (Figure 5.1).

Table 5.1

PAMLICO SEDIMENTS DATA

Sample	*Nautical Miles	Cation Exchange Cap. (meq/100 gm)	Adsorbed Phosphorus** (mg P/gm Sediment)
1	-2.8		1.23
1A	-2.8		0.43
2	-2.3		0.98
3	-1.9		1.60
4	-1.4		0.53
5	-0.3		0.56
6	0.2		0.51
7	0.6	5.0	0.71
8	1.5		1.08
9	3.1		1.61
10	4.0		0.45
11	5.3		0.59
12	7.2	17.2	0.67
13	10.1		0.58
14	12.3		0.82
15	14.2	21.7	0.69
16	16.3		0.86
17	19.2		0.51
18	21.4	22.6	0.45
19	22.7		0.07
20	25.3		0.45
21	27.1		0.35
22	29.3	20.6	0.33
23	30.8		0.02

*Nautical miles downstream of railroad bridge at Washington, N.C.

**From Upchurch, 1972.

Procedure. The clay size fraction ($< 2\mu$) of the sediment samples was isolated by centrifugation and used in the X-ray analyses. The clay mineral composition was determined by X-ray diffraction using a Phillips-Norelco diffractometer. An iron tube was used at 35 kV and 8 ma and monochormatic K-alpha radiation was obtained via a manganese filter. The rate meter setting was varied according to the diffraction intensity while the scanning speed was normally set at $1^{\circ}2\theta$ per minute. The following X-ray diffraction patterns, of oriented aggregate on glass or ceramic slides, were obtained for each sample: Mg-saturated, Mg-ethylene glycolated, K-saturated, and 550°C heated. Approximately, 50 mg of clay were used on each slide to obtain uniform and maximum peak heights.

Identification. Quartz, kaolinite, illite, montmorillonite, chlorite, and chlorite-like intergrade clay were found in the sediments. These clays were identified by X-ray diffraction analysis using the various chemical and physical treatments mentioned above. Quartz is identified by the strong peak at 3.33-3.34 Å. Kaolinite has strong diffraction peaks at 7.2 Å and 3.58 Å and is identified by heat treatment above 500°C at which temperature the kaolinite structure collapses. Illite has basal reflections at 10, 5, and 3.3 Å which do not shift with cation saturation or heat treatment. Montmorillonite has a 15.5 Å peak for Mg-saturated samples that shifts to 17-21 Å for Mg-ethylene glycolated samples. True chlorite is distinguished from the intergrade clay and other 14 Å clays by the fact that its 14 Å and 7 Å peaks remain after one hour heating at 550°C. The chlorite-like intergrade clay has been discussed by Griffin and Ingram (1955) and by Weed and Nelson (1962). Chlorite-like intergrade clay is distinguished from vermiculite by the K-saturated treatment. The 14 Å peak for vermiculite shifts to 10-11 Å with this treatment whereas the chlorite-like intergrade clay does not. Heat-treatment at 550°C distinguishes chlorite-like intergrade from true chlorite: the 14 Å peak for the chlorite-like intergrade clay shifts to 10-12 Å.

Semi-Quantitative Analysis. The difficulty in the determination in the relative amounts, as percentages or parts in ten, of clay minerals in sediments is well known. Pierce and Siegel (1969) have discussed the variables which affect attempts at quantification in clay mineral studies. The variables are many and include sample treatment, slide preparation, structural and chemical variations between mineral groups and within the mineral species, equipment conditions, and the method used to calculate the relative amounts of the different minerals in the sample. The results of such quantitative techniques should be termed "semi-quantitative", at best. However, the results can be used to indicate trends in the clay mineral composition of sediments.

In this investigation, calculations of the relative amounts of clay minerals in each sample were based upon ratios of basal peak areas. The basal peak areas were weighted and the calculations performed in accordance with the procedures outlined by Park (1971).

Cation Exchange Capacities and Electrophoretic Mobilities

The cation exchange capacities and electrophoretic mobilities of sediments #7, #12, #15, #18, and #22 were determined in accordance with the procedures outlined previously for these methods (Chapter IV).

Jar Tests

Jar tests were performed using sediments #3 (fresh water sediment), #12 (sediment midway down estuary), and #18 (near mouth of estuary) in synthetic sea water solutions. The jar test procedure has been described in Chapter IV.

Coagulation Rate Studies

Sediments #3, #12, and #18 were also used in coagulation rate studies. The preparation of sediment suspensions used in these rate studies was performed as follows:

(1) Samples were removed from the freezer and allowed to thaw overnight. The sediments had been frozen in polyethylene bags.

(2) The sediment samples were mixed thoroughly within the plastic bags. Portions of the sediments were removed and placed in Erlenmeyer flasks.

(3) The sizing procedure described in Chapter IV was then employed to obtain sediment suspensions with narrow particle size distributions.

Drying of the sediments was not involved in this procedure, since it was felt that it could change the characteristics of the sediments.

The coagulation rate studies were conducted using the synthetic sea water solutions described in Table 4.7. The floc volume fraction was determined using Equation [4-18] and the particle densities were determined by the pycnometer method. The densities are 2.66, 2.72, and 2.76 grams/cm^3 for sediments #3, #12, and #18, respectively.

Adsorbed Phosphorus

A modification of the procedure proposed by Wentz and Lee (1969) was used to extract the available phosphorus from the sediments. Available phosphorus refers to a fraction of the total phosphorus and is an indication of the amount of phosphorus that is biologically usable. It has been related to the ability of sediments to support algal growth (Porcella et al. (1970)). This modified acid extraction (HCl-H_2SO_4, pH 1.1) procedure was developed by Upchurch (1972). The amount of orthophosphate extracted by this method was measured by the vanadomolybdophosphoric acid colorimetric procedure of Kitson and Mellon (1944). A Beckman DB Spectrophotometer was used to measure the absorbance of the solutions at a wavelength of 420 mμ. Wentz and Lee (1969) used this wavelength to avoid interference with Fe(III).

DISCUSSION AND RESULTS

Clay Mineral Composition

The relative percentages of the clays in the Pamlico sediment samples are summarized in Table 5.2. The composition of the clay fraction, as a function of sediment sample location (distance downstream from railroad bridge at Washington, North Carolina) is plotted in Figure 5.3. Kaolinite is the dominant clay in the upper end of the estuary where salinity is lowest and decreases towards the mouth where salinity is greatest. Illite occurs in minor amounts in the upper end and increases towards the mouth, while montmorillonite is present in minor amounts along the entire length of the estuary. Chlorite and chlorite-like intergrade clay comprise the remainder of the clay fraction. The trends for kaolinite and illite are most interesting

Table 5.2

RELATIVE PERCENTAGE OF CLAYS

Percentage

Sediment	Kaolinite	Illite	Chlorite	Chlorite-like Intergrade	Montmorillonite
7	60	5	10	25	Trace
12	50	10	10	30	Trace
15	45	10	10	30	5
18	35	20	10	30	5
22	30	30	10	25	5

and similar trends have been reported by Park (1971), Dobbins et al. (1970), and Allen (1964).

Park (1971) explained the seaward decrease of kaolinite by the flocculation of this clay in salt water whereas the seaward increase of illite was explained by the landward transport of illite from the Atlantic Ocean. Dobbins et al. (1970) used the results of Whitehouse et al. (1960) on the settling rates of clay minerals in salt waters to explain the distribution of the clays in the Pamlico sediments. The distribution of kaolinite was attributed to the fact that it flocculates easily. The authors were puzzled by the distribution of illite, since according to Whitehouse, it should flocculate early (upper reach of estuary). Allen (1964) explained the distribution of kaolinite on the grounds of flocculation and speculated that illite flocculates more slowly. Allen stated that a small portion of the increase in illite is probably the result of diagenesis.

The methods employed by Whitehouse and the results achieved were developed in detail in Chapter II. Whitehouse et al. (1960) reported

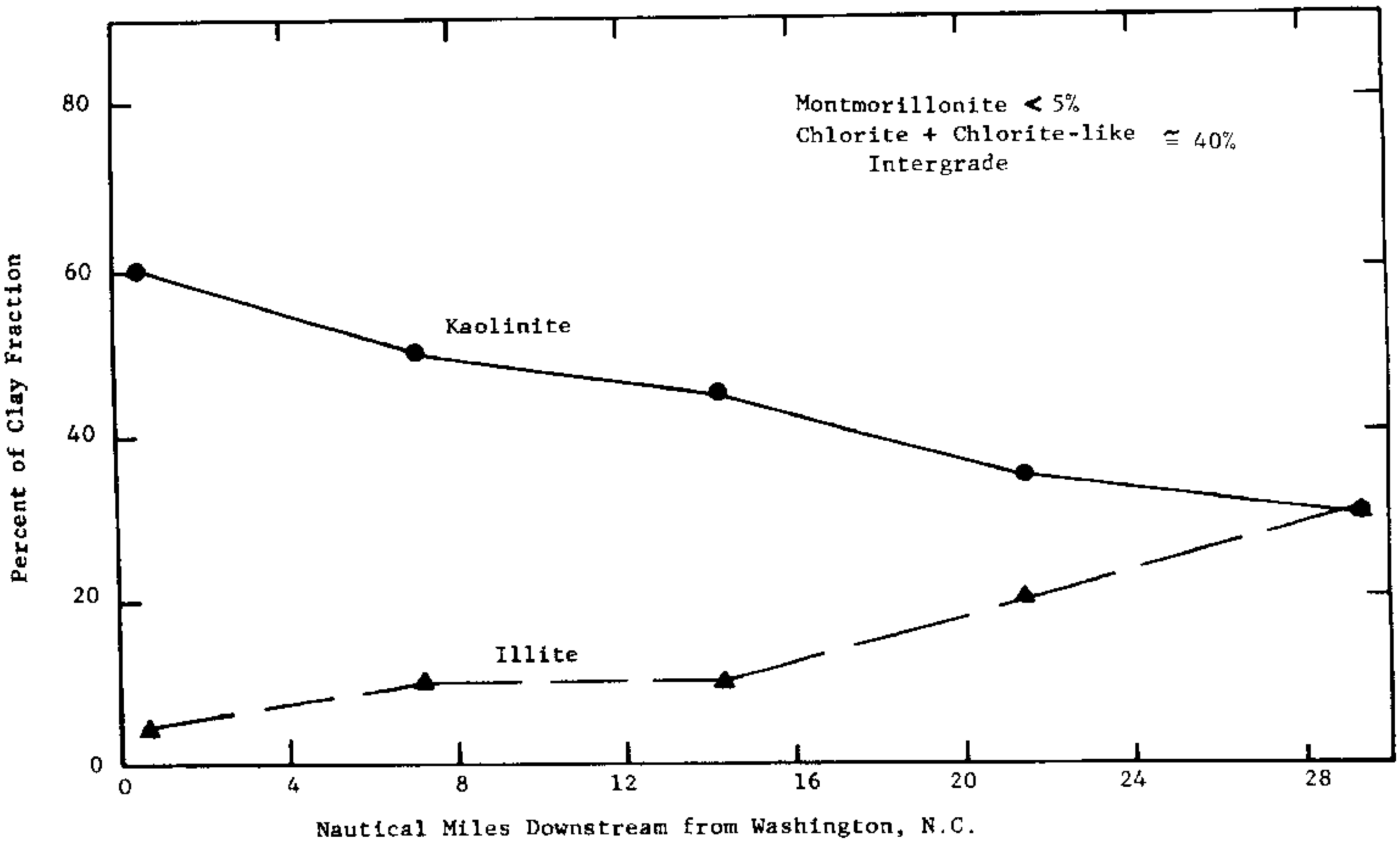


Figure 5.3 Clay Mineral Composition of the Pamlico Sediments

the settling velocities of clay minerals in sea waters of varying salinity. Under the experimental conditions employed by this group, their results should not be construed as flocculation rates or the ability of clays to flocculate. In estuaries it is the rate of particle aggregation that is important in explaining the distribution of clays in sediments. The clays which aggregate rapidly will tend to form flocs of such a size that they can settle from suspension. These clays will be concentrated upstream of the clays that aggregate slowly.

The distribution of kaolinite and illite in the sediments can be explained by coagulation. In the kinetics phase of this research (Chapter IV) it was observed that kaolinite is unstable relative to illite. The coagulation rate studies showed that under similar conditions, kaolinite aggregates much more rapidly than illite.

Coagulation Results. It is shown qualitatively in Figure 5.4 that the upstream sediments coagulate better than the downstream sediments. Rates of coagulation were determined for sediments #3, #12, and #18 in various synthetic sea water solutions. Figures 5.5, 5.6, and 5.7 illustrate the effect of increasing salinity (ionic strength) on the coagulation rates of these sediments. Stability factors were evaluated from the slopes of the least squares regression lines as described in Chapter IV. The stability factors are summarized in Table 5.3 and Figure 5.8. It can be concluded from these results that the upstream sediments are unstable (higher α values) relative to the downstream sediments.

The cation exchange capacities provide additional evidence that the upstream sediments are relatively unstable. Table 5.1 shows a seaward increase in the cation exchange capacity of the sediments.

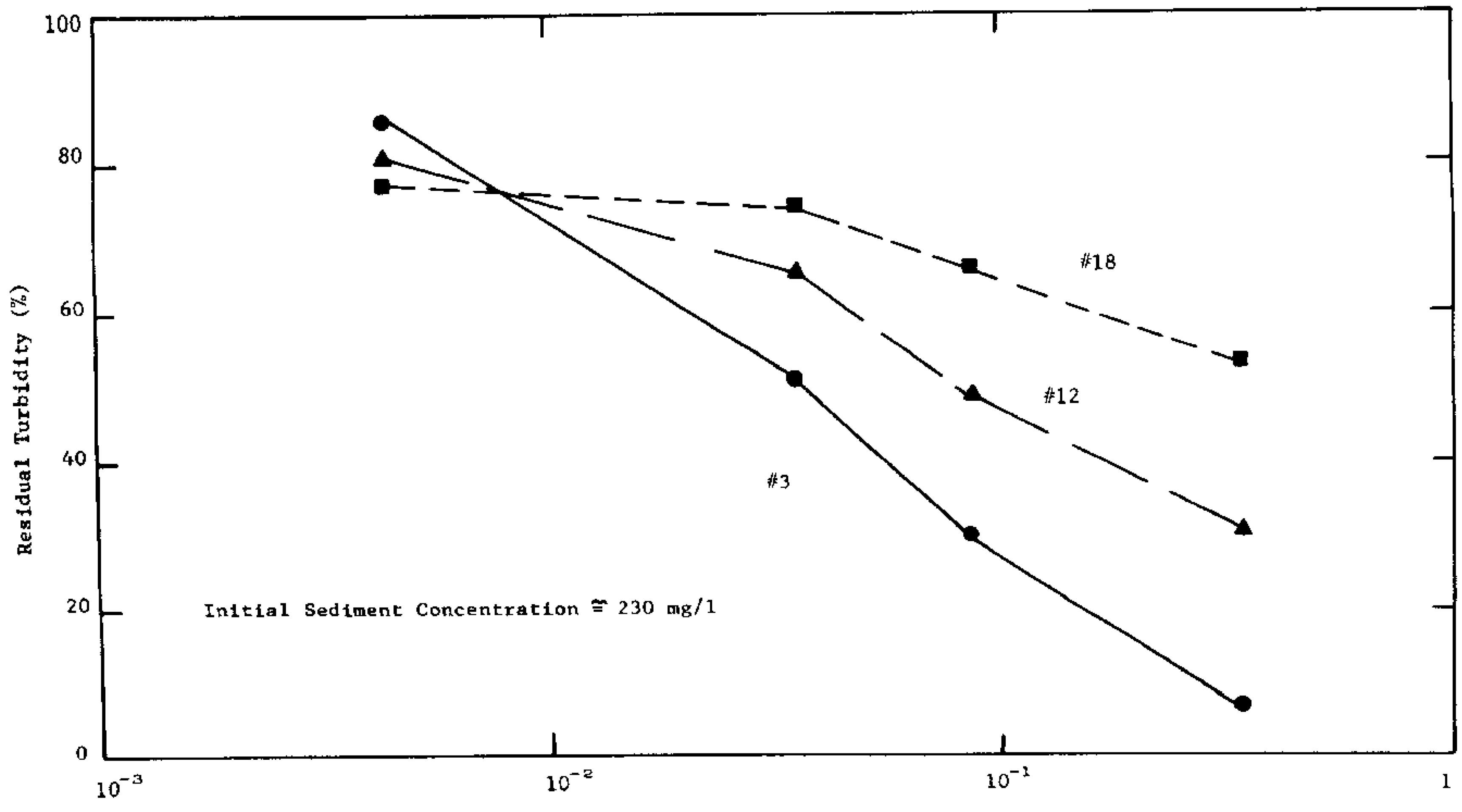


Figure 5.4 Jar Tests for Pamlico Sediments in Synthetic Sea Water Solutions.

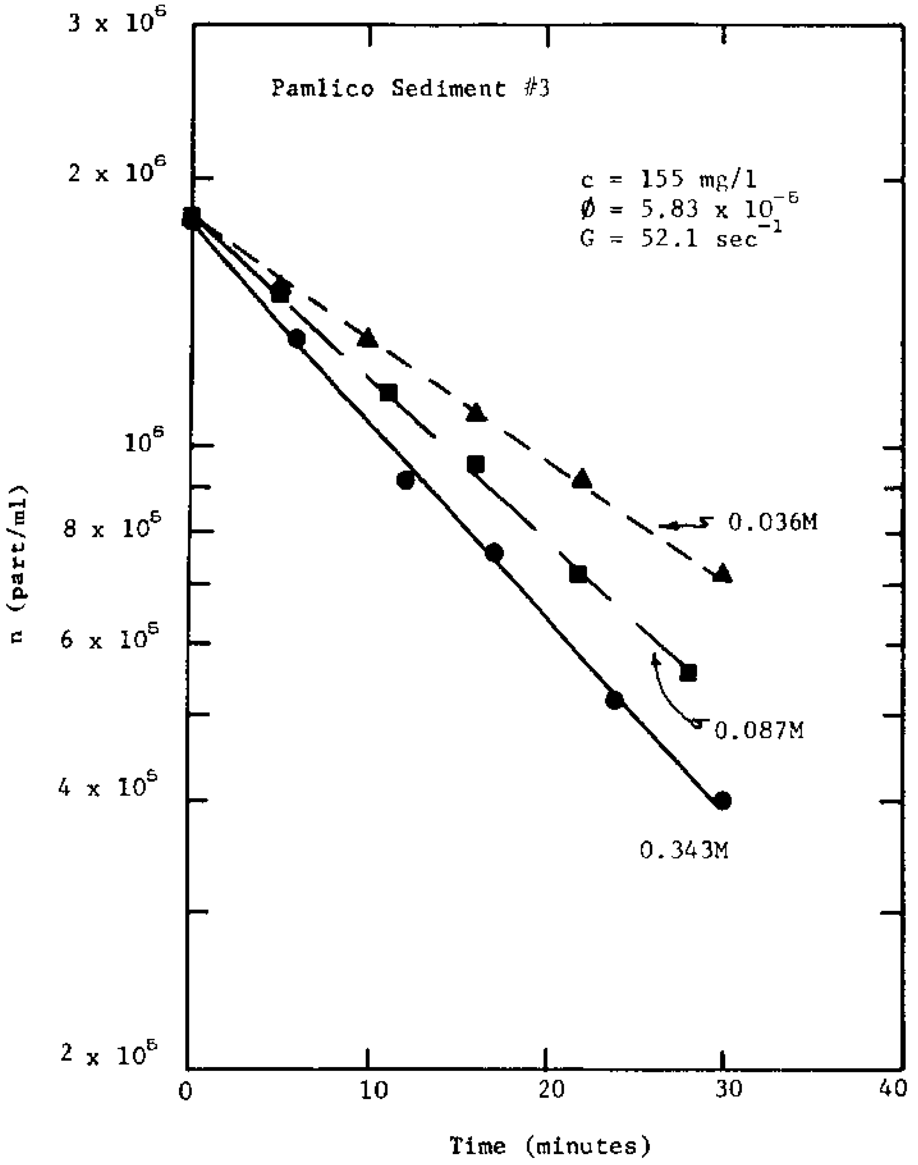


Figure 5.5 Rates of Coagulation for Pamlico Sediment #3 in Synthetic Sea Water Solutions

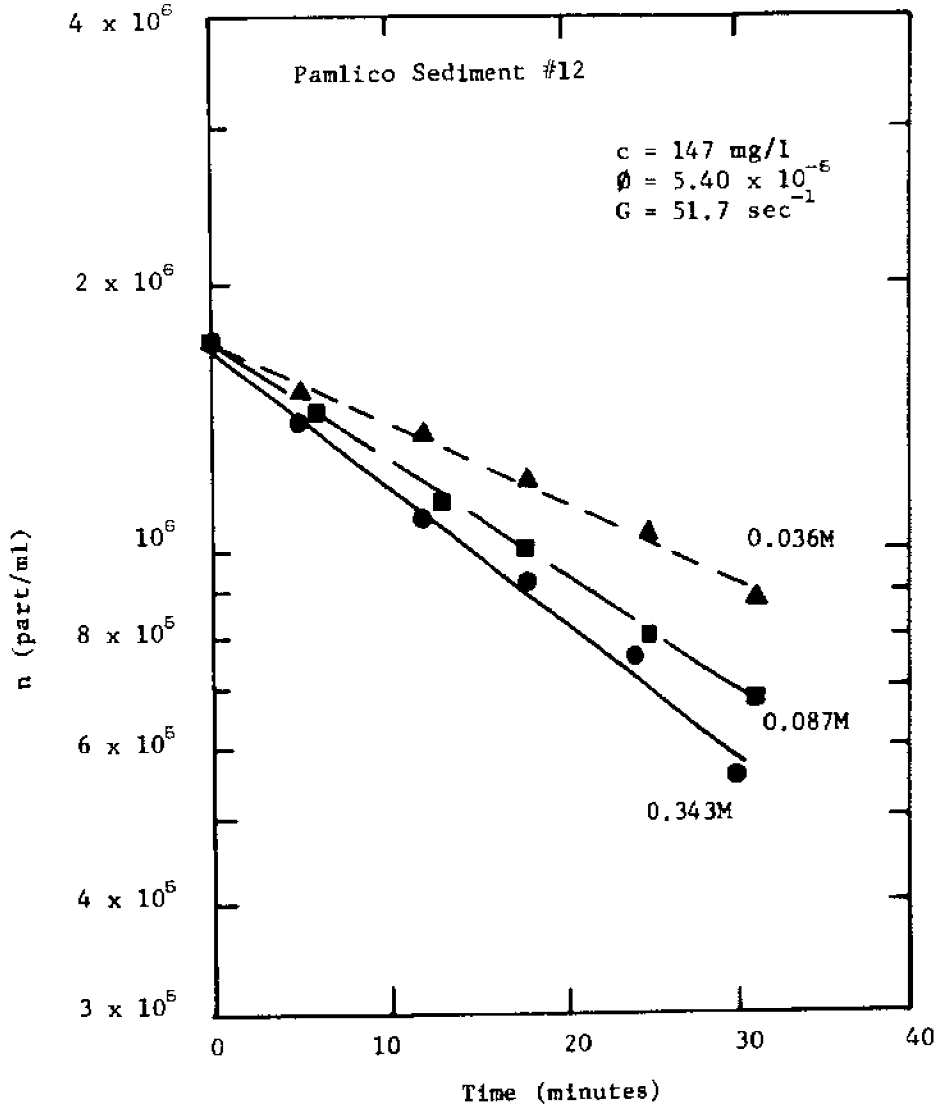


Figure 5.6 **Rates of Coagulation for Pamlico Sediment #12 in Synthetic Sea Water Solutions**

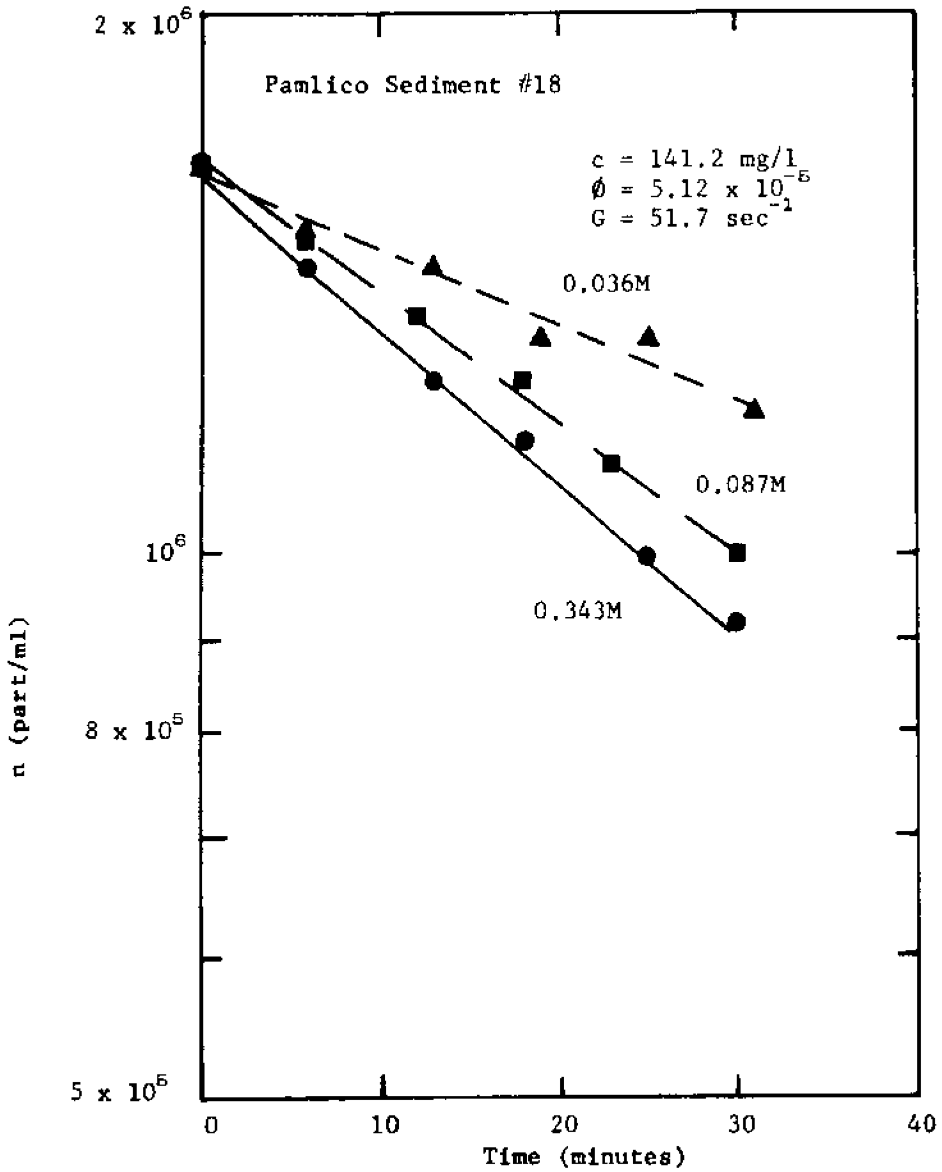


Figure 5.7 **Rates of Coagulation for Pamlico Sediment #18 in Synthetic Sea Water Solutions**

Table 5.3

STABILITY FACTORS FOR PAMLICO SEDIMENTS

Sediment #3

Salinity ppt	*Ionic Strength M	G sec^{-1}	ϕ	α **
1.8	0.036	52.1	5.83×10^{-5}	0.131 ± 0.005
4.4	0.087	52.1	5.83×10^{-5}	0.180 ± 0.008
17.5	0.343	52.1	5.83×10^{-5}	0.217 ± 0.015

Sediment #12

Salinity ppt	Ionic Strength M	G sec^{-1}	ϕ	α
1.8	0.036	51.7	5.40×10^{-5}	0.098 ± 0.01
4.4	0.087	51.7	5.40×10^{-5}	0.139 ± 0.003
17.5	0.343	51.7	5.40×10^{-5}	0.167 ± 0.02

Sediment #18

Salinity ppt	Ionic Strength M	G sec^{-1}	ϕ	α
1.8	0.036	51.7	5.12×10^{-5}	0.047 ± 0.01
4.4	0.087	51.7	5.12×10^{-5}	0.0814 ± 0.005
17.5	0.343	51.7	5.12×10^{-5}	0.0954 ± 0.009

* Synthetic Sea Water Solutions

** The 95% Confidence Interval for α is indicated

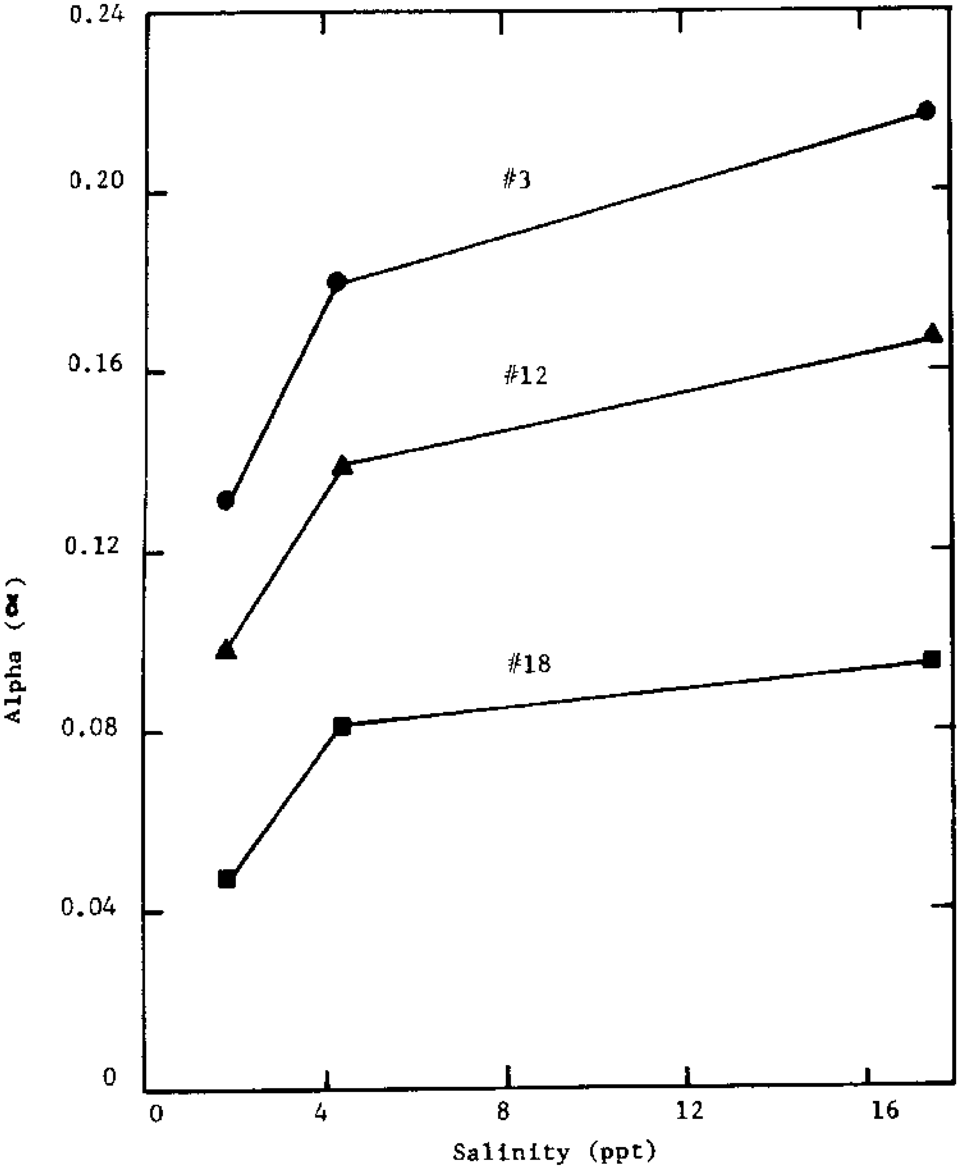


Figure 5.8 Stability of Pamlico Sediments as a Function of Salinity

For the same size clays, the cation exchange capacity and the surface charge density are directly proportional. Thus the sediments in the lower end of the Pamlico are representative of clays with higher surface charge densities and stabilities.

The electrophoretic mobilities of the Pamlico sediments were determined in NaCl solutions, synthetic sea water solutions, and Pamlico Estuary water. The ionic strengths of these solutions varied from 10^{-4}M to approximately 0.2M. Electrophoretic mobilities could not be measured for solutions with salinities above 9 ppt due to the high currents produced by these highly conductive solutions. All mobility values were negative indicating that charge reversal of the sediments does not occur for suspended sediments as they are transported from fresh waters into estuaries. The mechanism of double layer compression has been proposed as the mode of destabilization of suspended solids in estuaries. If charge reversal had occurred, other mechanisms of destabilization would be applicable.

Pravdic (1970) examined the surface charge characterization of sea sediments collected from both the Mediterranean and North Seas. Pravdic used the technique of streaming current to determine the charge of the sediments in sea water of varying salinity. Charge reversal occurred between 2 and 6 ppt salinity. Pravdic's results are in disagreement with those reported here. This discrepancy may be due to differences in techniques (electrophoresis versus streaming current), or the nature of the sediments and sea water solutions.

Adsorbed Phosphorus

The amounts of available P extracted from the sediments of the Pamlico Estuary are summarized in Table 5.1. Figure 5.9 is a plot of the phosphorus content of the sediments as a function of sediment location. This figure includes only those samples in which the silt and clay fraction was greater than 90 per cent. Samples 1A, 4, 5, 6, 7, 19, and 23 contained a mixture of sand and mud (Upchurch (1972)); consequently, these points have been excluded from Figure 5.9. Less phosphorus was extracted from the sediments containing a substantial amount of quartz as compared to the sediments composed primarily of clay and silt. This is in agreement with the work of Stumm and Leckie (1970) in which silica was shown to adsorb very little phosphorus.

The amount of available P extracted from the sediments is shown to decrease from 1.6 mg P/gm sediment in fresh water to 0.3 mg/gm sediment in water with a salinity of about 16 ppt (Figure 5.9). Upchurch (1972) has found a high degree of correlation between oxalate-extractable iron and available phosphorus in the upper reach of the Pamlico Estuary (salinity less than 1 ppt) whereas in the lower part of the estuary the Fe-P correlation decreased. Upchurch concluded that the decrease in the available P and in the Fe-P correlation along the length of the estuary are indications that the P is held to suspended sediments by some type of Fe-inorganic P complex of limited strength. It is possible that with increasing salinity, phosphorus that is adsorbed or complexed may be released or displaced by competing ions such as sulfate or chloride.

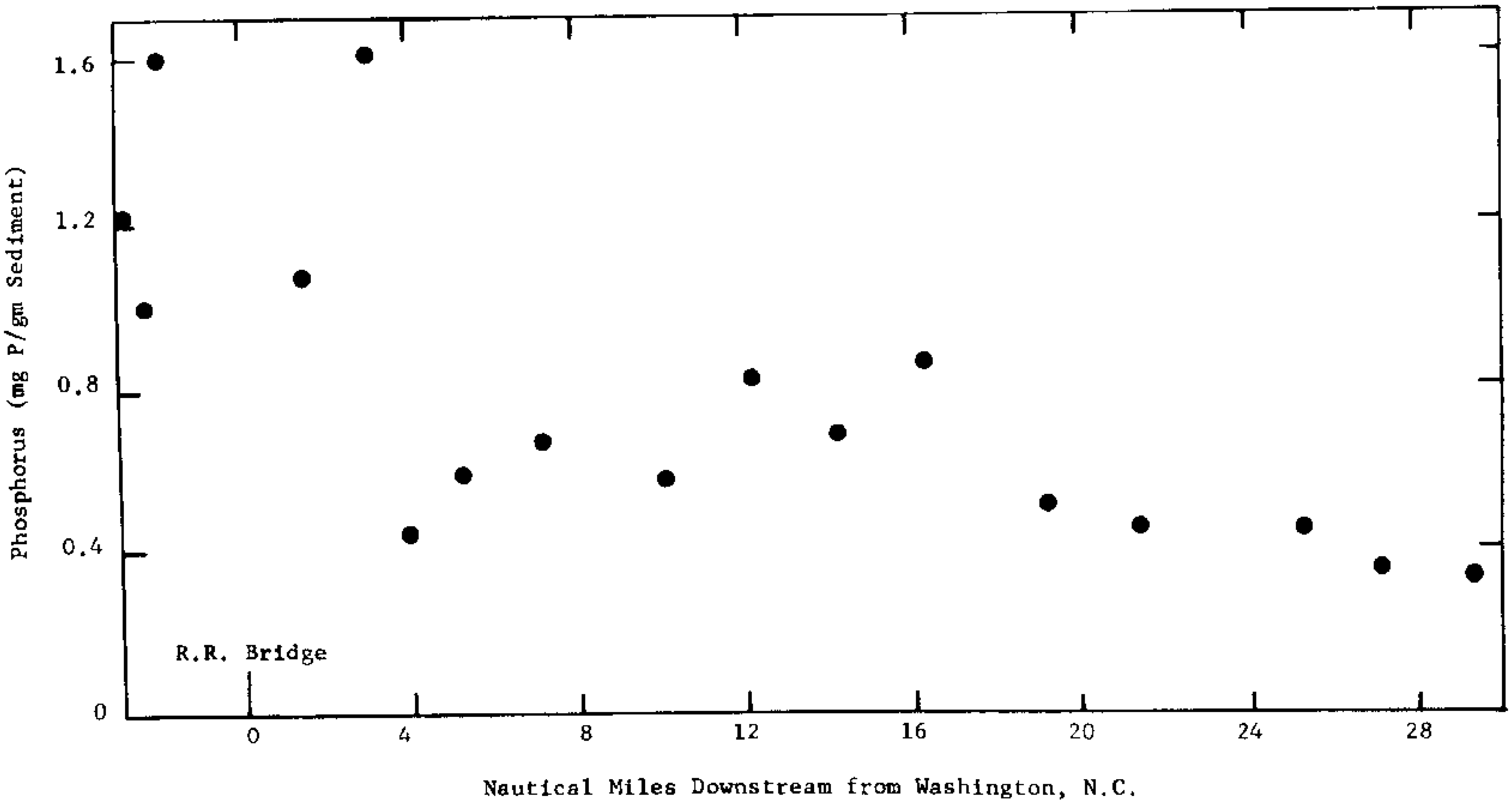


Figure 5.9 Available Phosphorus on the Pamlico Sediments (Upchurch (1972)).

CONCLUSIONS

The distribution of kaolinite and illite as indicated in Figure 5.3 can be explained by coagulation. It was concluded from the coagulation rate studies of Chapter IV that kaolinite is unstable relative to illite; consequently, it should coagulate prior to illite and be deposited upstream of illite. Further verification that the upstream sediments are relatively unstable is illustrated in Figure 5.8. The transport of colloidal suspensions from fresh waters into estuaries is accompanied by a reduction in particle stability resulting in coagulation. The stability of the colloidal suspensions is reduced by an increase in ionic strength (salinity). These colloidal suspensions may contain a variety of materials (clays, organic colloids, inorganic colloids), but the rate of particle aggregation is affected by the stability of these suspensions (chemical parameter) and by physical parameters. These physical parameters include the degree of mixing as well as the concentration of suspended particles. Under constant physical conditions, the least stable (higher α) fractions of the suspended load will coagulate and be deposited upstream of the stable fractions.

It is concluded from the adsorbed phosphorus data that sediments (containing adsorbed P) entering the estuary in the fresh water inflow would lose phosphorus as they are transported through waters of increasing salinity to the mouth of the estuary.

CHAPTER VI

THE EFFECTS OF COAGULATION ON WATER QUALITY IN ESTUARIES

The purpose of this chapter is to discuss the significance of the coagulation process in estuaries. Suspended materials not only rank, in a physical sense, as a major pollutant but they also serve as the transporting agent for soluble adsorbable pollutants. The silt and clay fractions of suspended sediments have the ability to sorb soluble pollutants. The environmental changes to which fresh waters are subjected upon reaching estuarine zones can have a marked effect upon the transport of these soluble pollutants. On arriving in waters of increasing salinity (estuaries), the fine sediment fraction undergoes coagulation and sedimentation which may eventually result in a concentration of certain pollutants (sorbed) in those bottom areas of estuaries subject to shoaling. However, the high concentration of cations and anions in sea water may in some cases have the opposite effect, causing the desorption of pollutants, releasing them to the overlying waters.

This chapter examines direct and indirect effects of coagulation on water quality. Organic colloids which are deposited in estuaries can have a direct effect on water quality by exerting an oxygen demand. Inorganic colloids such as clays contribute to shoaling of these waterways. Under indirect effects, the role of the coagulation process in affecting the fate of soluble adsorbable pollutants such as radionuclides, trace metals, pesticides, and phosphorus is examined. Finally, the incorporation of results generated from this research into water quality models for estuaries is discussed.

DIRECT EFFECTS ON WATER QUALITY

The transport of colloidal suspensions from fresh waters into estuaries is accompanied by a reduction in particle stability resulting in coagulation. Inorganic colloids such as clay minerals subjected to coagulation and deposition in estuaries contribute to shoaling of these waterways.

A substantial portion of the BOD in the effluent from conventional secondary waste treatment plants is colloidal (Bishop et al. (1967)). These organic colloids, like the inorganic clay minerals, will coagulate in estuaries. The resulting deposits can have several adverse effects including: oxygen demand, release of bacteria and viruses, and shoaling of the waterway. Gross et al. (1971) report that about 40% of New York Harbor is covered by fine-grained wastes with sewage solids being a major constituent.

INDIRECT EFFECTS ON WATER QUALITY

A task committee (Task Committee, American Society of Civil Engineers, (1971)) on sedimentation has recognized the various effects that sediments (suspended and bottom) may have on water quality. This task committee cited the following research needs with respect to the effects of sediments on water quality: (1) the adsorption and desorption of radionuclides, pesticides, and trace elements, (2) waste assimilation, storage, and release by bed sediments, (3) effects of bottom and suspended sediments on aquatic life, (4) the role of sediments in eutrophication, and (5) the effect of sediments on dissolved oxygen.

Lee (1970) has reviewed the factors affecting the transfer of materials between water and sediments. The sediments of an estuary and other natural waters potentially represent a buffer system for many elements which could control the concentrations in the overlying waters because of the large concentrations of some elements present in the sediments. The effect of this buffer system could be to keep the concentrations in the overlying waters relatively constant even though the concentrations of the element in the inflowing waters vary widely. Lee points out that sorption reactions are probably the most important type of reaction with respect to controlling the exchange of materials between sediments and water.

The fate of soluble sorbable pollutants is affected by the transport of suspended materials from fresh waters into estuaries. Suspended solids which are deposited in estuaries may serve as a sink or source of soluble sorbed pollutants. Some soluble pollutants may be strongly adsorbed to the sediments (sink) while others are released (source) in the estuarine environment. The purpose of this section is to examine qualitatively the fate of several soluble adsorbable pollutants in estuaries.

Radionuclides

Klingeman and Kaufman (1965) have published a comprehensive study concerned with the transport of radionuclides with suspended sediment in estuarine systems. This study included field work in the lower Sacramento River and in the northern San Francisco Bay system as well as laboratory studies. The field studies indicated that sediment-sorbed radionuclides (Zr^{95}-Nb^{95}) constituted the bulk of fission debris transported through rivers tributary to the San Francisco Bay system. The authors concluded that because of the sorptive characteristics of many fallout radioisotopies, suspended sediment is important to the river-estuary transport of these radionuclides. It was pointed out that the clay fraction of suspended sediments determines the extent of radionuclide transport. Laboratory experiments with Zr^{95}-Nb^{95} and sediment suspensions indicated that ion exchange was of much less importance than other forms of sorption. Klingeman and Kaufman concluded that the ultimate distribution of Zr^{95}-Nb^{95} in river-estuary systems is almost completely describable by the distribution of the radionuclide-sorbed sediments, due to the nearly complete and relatively irreversible sorption of Zr^{95}-Nb^{95} to suspended sediments.

Johnson (1967) examined the behavior of Zn^{65} sorbed on Columbia River sediments when exposed to sea water. Most of the Zn^{65} remained bound to the particles indicating that most of the Zn^{65} was held by "specific sorption" and ion exchange was a relatively minor mechanism. Klingeman and Kaufman (1965) reported on work conducted by Reynolds and Gloyna on the transport of Cs^{137} by sediments. They reported that Cs^{137} was released from the sediments when exposed to solutions of increasing salinity. Table 6.1 provides a summary of the role that suspended sediments have on the transport of sorbed pollutants into estuaries. From the literature cited, radionuclides are not released from sediments in waters of increasing salinity (estuaries) with the exception of Cs^{137}. Estuaries may be a sink for those radionuclides which are strongly adsorbed to the sediments as indicated in Table 6.1.

Table 6.1

ROLE OF TRANSPORT AND DEPOSITION OF SUSPENDED SEDIMENTS IN ESTUARIES

Sorbed Pollutant	Role
Radionuclides	
Zr^{95} - Nb^{95}	Sink
Zn^{65}	Sink
Cs^{137}	Source
Trace Metals	
Pb, Cr, Cu	Sink
Hg	?
Pesticides	?
Phosphorus	Source

Trace Metals

In the coastal water around New York City, the levels of chromium, copper, and lead in the sediments were found to be as much as an order of magnitude higher for the Inner Harbor deposits as compared to Continental Shelf sediments (Gross et al. (1971)). A small fraction of the total concentration of these metals (Cr, Cu, Pb) was acid extractable indicating that it is unlikely that these metals would enter the overlying waters via release from the sediments.

Jernelöv (1970) conducted laboratory experiments in which he examined the release of mercury from sediments. The author found that in a system without macroorganisms - in particular, Anodonta - formation and release of methyl mercury occurs almost entirely in the upper three centimeters of the sediments. Klein and Goldberg (1970) examined sediments off the southern California coast. Mercury concentrations in the sediments in the environs of the Hyperion sewer outfall, Los Angeles, were as much as fifty times higher than the mercury concentrations in sediments collected offshore. Cranston and Buckley (1972) have reported high levels of mercury on suspended particulate matter in the LaHave River and Estuary. They observed that the sediments, which were flocculated and deposited in the estuary, contained smaller amounts of mercury than the fine-grained suspended matter. Feich et al. (1972) studied (in the laboratory) the release of mercury from fresh water sediments exposed to solutions of varying salinity. The authors found that Hg^{+2} was released from sediments when exposed to 0.6 M NaCl or 0.67 M $CaCl_2$ solutions. This release was explained by the complexing of mercury by chloride ions and by the competition of Na^+ and Ca^{++} with Hg^{+2} for exchange sites on the sediment. It is the opinion of this writer that the extrapolation of these latter results to estuaries is clouded since the pH was not controlled for these experiments. The pH was as low as 3.6 for some of the experiments.

It is difficult to make conclusions concerning whether sediments in estuaries can be a sink or source of mercury (Table 6.1). There are several reasons for this: first, very little research in this area has been reported in the literature; second, some reported laboratory results are not representative of conditions in estuaries; and third, the uncertainty of the analytical methods used for the determination of mercury.

Pesticides

This writer did not find any published information on the adsorption and release of pesticides from sediments exposed to conditions representative of estuaries. There is an obvious need for research in this area; however, the reader can gain an appreciation of the pesticide-sediment problem by the literature which is cited.

Bailey and Hannum (1967) reported that the temporal distribution of pesticides in California surface waters is related to agricultural drainage patterns and to rainfall runoff. The sediments contained much higher pesticide concentrations than the surface waters of California - approximately 200 times as much. There was a positive relationship between the surface area of the sediments and the amount of sorbed pesticide. Huang and Liao (1970) studied the adsorption of pesticides by clay minerals. The authors concluded that the adsorption of DDT and heptachlor to clays occurs by H-bonding while the adsorption of dieldrin occurs by chemical bonding between the dieldrin epoxide ring and oxygen on the clays.

Rowe et al. (1970) conducted laboratory studies on the interaction of dieldrin and endrin with bottom sediments. They found that the sorption of both endrin and dieldrin is time dependent and pH sensitive and that endrin sorption is salinity dependent but dieldrin sorption is not. Veith and Lee (1971) studied the role of lake sediments in the detoxification of lakes which were treated with toxaphene. This was evaluated under field and laboratory conditions. Toxaphene was not detected below the 20-cm level of the bottom sediments. In addition, toxaphene which was sorbed onto the sediments in the lake could not be leached from the sediments by lake water under laboratory conditions.

Based on the information available, the fate of sorbed pesticides on clays is not known when these clays are transported from fresh waters into estuaries (Table 6.1). Depending upon the strength of the pesticide-clay interaction, coagulated materials could serve as a source or a sink for pesticides in estuarine waters.

Phosphorus

Lee (1970) points out in a review of the literature that phosphate tends to be sorbed readily by lake sediments. Ferric iron in lake sediments influences and often controls the exchange of phosphates from the sediments to the overlying waters. Lee concluded that the actual species present in the sediments is not ferric phosphate but some complex or hydrous oxide of ferric iron which tends to sorb the phosphorus from the water. Shukla et al. (1971) and Williams et al. (1971) have investigated the sorption of inorganic phosphate by lake sediments. They concluded that the best single criterion explaining P sorption in the noncalcareous and calcareous sediments investigated was the amount of oxalate-extractable Fe, presumed to be derived from amorphous Fe oxides.

Carritt and Goodgal (1954) examined the sorption of phosphorus on bentonite and Fullers Earth as well as sediments from the Chesapeake Bay and Roanoke River. Maximum uptake of phosphorus by the solids occurred in the pH range in which the singly charged $H_2PO_4^-$ is the predominant species. The magnitude of the heats of reaction suggested that the phosphorus-solids complex is of limited strength. Their sorption studies also indicated a competition between sulfate and phosphate. The authors concluded that the environmental characteristics of estuaries and the measured sorption properties suggest a mechanism by which dissolved substances (such as dissolved inorganic phosphorus) can be removed by sorption processes from turbid fresh waters, transported to and then released in estuarine regions where fresh and salt water mix. Pomeroy et al. (1965) investigated the exchange of phosphate between water and sediments of Doboy Sound, Georgia. This study was conducted in the laboratory with core samples and suspensions of surface sediment, using P^{32} as a tracer. The authors found that the sediments maintain the phosphate concentration in the water between 0.7 and 0.9 μ moles/l. The daily exchange across a submerged and undisturbed surface of sediment was estimated to be in the order of 1 μmole PO_4/m^2. Burns and Ross (1971) investigated the nutrient relationships in the Central Basin of Lake Erie. The authors found that anoxic conditions in the Central Basin caused an internal loading of phosphorus from the sediments at least equal to the external loading during the same period. The results of this study demonstrate the significance of the sediments as a nutrient source in natural waters.

The role of the sediments in affecting the soluble phosphorus concentrations in the Pamlico Estuary has been evaluated in Chapter V. The amount of available P extracted from the sediments was observed to decrease from 1.6 mg P/gm sediment in fresh water to 0.3 mg/gm sediment in water with a salinity of about 16 ppt (Figure 5.9). It was concluded that the decrease in the available P and in the Fe-P correlation along the length of the estuary suggests that the P is held to suspended sediments by some type of Fe-inorganic P complex of limited strength. The Fe-P correlation is in agreement with the results of Shukla et al. (1971) and Williams et al. (1971). From these results, it is concluded that sediments (containing sorbed P) entering an estuary in the fresh water inflow can lose phosphorus as the sediments are transported through waters of increasing salinity to the mouth of the estuary; i.e., sediments in estuaries can be a source of P (Table 6.1).

ESTUARINE MODELING

Coagulation of clay minerals is an important factor in the estuarine transport of sorbed pollutants because of the changes in the character of the suspension which it causes. The transport of clays from fresh waters into estuaries is accompanied by a reduction in particle stability resulting in particle aggregation (coagulation). As a result of particle aggregation, clay aggregates can readily settle and be deposited in the estuary. The role of coagulation is one of hindering longitudinal particle transport by increasing the settling velocity of suspended particles. Mathematical models which are used to predict the fate of soluble pollutants in aqueous systems are based on the continuity equation. The one dimensional case of this equation is

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} - E \frac{\partial^2 c}{\partial x^2} = \pm \Sigma S \qquad [6\text{-}1]$$

where c is the concentration at some point in time (t), v is the local velocity of the water, E is the eddy diffusivity coefficient, and S represents sources and sinks of variable c. The equation might be viewed as consisting of hydrodynamic terms on the left hand side and reaction rate terms (sources and sinks) on the right.

The application of coagulation kinetics to estuarine modeling involves the incorporation of rate terms into the right-hand side of Equation [6-1]. This research is not concerned with the development of mathematical models for specific water quality parameters; however, the results of this research may be beneficial to those who are concerned with reaction rate terms in Equation [6-1]. The Environmental Protection Agency (1971) has recommended laboratory and field research directed towards the source and sink processes active in estuaries. EPA points out that this work may not necessarily be of a modeling nature, but the results of these studies can be incorporated into estuarine models. The rest of this chapter will sketch the use of the coagulation-deposition process in estuarine modeling.

Particulate Matter Model

The deposition of clays and silts in estuaries is responsible for shoaling in estuarine channels as well as the formation of deltas. In a recent report published by the Environmental Protection Agency (1971), the modeling of particulate matter in estuaries is recommended. In the past coagulation has only been recognized qualitatively as a process in estuaries. Gaps in our knowledge concerning this process in these systems have prevented quantitative applications to the deposition of particulate matter. The loss of particulate matter due to coagulation and settling would be described by the incorporation of terms into the right-hand side of Equation [6-1].

Coagulation and sedimentation occur simultaneously in natural waters. The following is based on the work of Hahn and Stumm (1970). Two simplified particulate matter models are described conceptually for the following two cases: (1) low ionic strength (salinity) waters and (2) high ionic strength waters. For the first case, it is assumed that the particle stability ($\alpha<<1$) is high and coagulation occurs slowly. Thus it is assumed that coagulation is the rate limiting step. In other words, a rate term describing coagulation kinetics would be used in the model and settling would be neglected. The term describing coagulation kinetics requires values for the stability factor (α). This could be determined in the laboratory (as described in this research) or estimates of α based on the results of this research might be used. For the second case - high ionic strength waters - it could be assumed that coagulation occurs (particles aggregate to some maximum equivalent size) within a period of time that is short compared to the time of settling. In other words the rate of sedimentation is the rate limiting step. Thus a rate term describing settling would be used in the model and coagulation would be neglected.

Soluble Pollutants

The role of coagulation in the transport of soluble pollutants which are sorbed by clays or other suspended matter has been discussed earlier in this chapter. It was illustrated that suspended sediments may serve as a source or a sink for soluble pollutants in estuaries. Incorporation of reactions whether they be adsorption of a soluble pollutant that ultimately becomes associated with the sediments (sink) or terms describing release of pollutants from suspended sediments (source) may be essential for the estuarine modeling of some water quality parameters.

CHAPTER VII

CONCLUSIONS

In summary, the transport of colloidal suspensions from fresh waters into estuaries is accompanied by a reduction in particle stability resulting in coagulation. The role of coagulation is one of hindering longitudinal particle transport by increasing the settling velocity of suspended particles. Conclusions are classified according to general areas covered in this investigation.

VERWEY-OVERBEEK AND DERJAGUIN-LANDAU CALCULATIONS

Some conclusions which were reached concerning the interaction of electrical double layers according to the VODL theory are:

1. The VODL theory predicts large interaction energy barriers for particles of about 1 μ in diameter.
2. The VODL theory quite frequently predicts interparticle distances of 4 Å or less for the location of energy barriers when a 2-2 electrolyte is used as the destabilizing agent.
3. Physically, predictions 1. and 2. are not reasonable. Hence the stability factor (α) in estuaries can not be predicted from the interaction energy calculations of the VODL theory.

COAGULATION STUDIES: KAOLINITE, ILLITE, AND MONTMORILLONITE

Some conclusions based on coagulation studies (in the laboratory) of kaolinite, illite, and montmorillonite clays in solutions at various ionic strengths are:

4. Jar tests indicated that the coagulation of kaolinite and montmorillonite is improved in synthetic sea water solutions as compared to buffered NaCl solutions.
5. Jar tests indicated that montmorillonite and kaolinite are unstable relative to illite.
6. The coagulation kinetic studies showed that the stability factor (α) depends upon chemical parameters and that different clays have different α values. Destabilization of clay suspensions was improved (increase in α values) with an increase in ionic strength and with solutions containing divalent cations.
7. These results - effects of ionic strength and valency of cations - are in qualitative accord with the theory of particle destabilization by double layer compression.
8. The coagulation rate studies indicated that the stability of the clays is as follows: Illite > Kaolinite > Montmorillonite. This is in agreement with the results of the jar tests.

PAMLICO STUDIES

Some conclusions based on studies of sediments collected from the Pamlico Estuary of North Carolina are:

9. The clay mineral composition based on X-ray diffraction of the Pamlico sediments showed that: kaolinite is the dominant clay in the upper end of the estuary where salinity is lowest, and decreases towards the mouth where salinity is greatest; illite occurs in minor amounts in the upper end and decreases towards the mouth, while montmorillonite is present in minor amounts along the entire length of the estuary, and chlorite and a chlorite-like intergrade clay comprise the remainder of the clay fraction.
10. The distribution of kaolinite and illite can be explained by coagulation. The coagulation rate studies indicated that kaolinite is unstable relative to illite; consequently, it should coagulate prior to illite and be deposited upstream from illite.
11. The results of coagulation rate studies using Pamlico sediments indicated that the upstream sediments are relatively unstable (higher α values) compared to downstream sediments. This is in agreement with the distribution of kaolinite and illite.
12. It is concluded from the adsorbed phosphorus data that sediments (containing adsorbed P) entering the estuary in the fresh water inflow would lose phosphorus

as they are transported through waters of increasing salinity to the mouth of the estuary.

THE EFFECTS OF COAGULATION ON WATER QUALITY IN ESTUARIES

Some conclusions concerning the significance of the coagulation process in estuaries are:

13. Inorganic and organic colloids subjected to coagulation and deposition in estuaries contribute to shoaling of these waters. The organic colloids can have a direct effect on water quality by exerting an oxygen demand.
14. Coagulation and deposition of clays in estuaries can affect water quality via adsorption and release of soluble pollutants.
15. Dissolved substances such as phosphorus, radionuclides, trace metals, and pesticides may be removed by sorption processes from turbid fresh waters, transported to and then released in estuarine regions. Depending upon the strength of the solid-solute interaction, coagulated materials could serve as a source or a sink for a soluble substance in estuarine waters.

SUGGESTIONS FOR FURTHER RESEARCH

The following suggestions are offered for continued research in these areas: coagulation of suspended materials in estuaries and the role of estuarine sediments on water quality.

1. A theoretical model that can predict stability factors (α) for colloidal particles in various ionic strength waters would be a valuable tool. It is recommended that the Stern model of the double layer be considered in any refined models for the interaction of double layers. A relationship between the stability factor (α) and the energy barrier is needed. This relationship should be based on particle encounters due to fluid motion and thus applicable to particles larger than 1μ.
2. A mathematical model describing the deposition of suspended sediments in estuaries is needed. An investigation which considers the incorporation of rate terms describing the coagulation process is recommended.
3. This investigation demonstrated the role of coagulation in the transport of soluble pollutants which are sorbed by clays or other suspended matter. Emphasis in future research should be placed upon the source and sink processes of specific water quality parameters. Specific research that is recommended:
    a) A mass balance of phosphorus in the Pamlico Estuary is needed. This would be useful in illustrating the sources and sinks of P in the system as well as helpful to those who are responsible for assessing the impact of future development of the Pamlico.

b) Additional research is needed to elucidate the interactions of phosphorus and sediments in estuaries. The effects of ionic strength, competing ions, and organic matter on phosphate sorbed to clay minerals, iron coated clays, and ferric oxides should be investigated.

c) Research concerned with the adsorption and release of mercury and pesticides associated with suspended sediments transported into estuaries is needed.

SYNOPSIS

INTRODUCTION AND SCOPE

The broad purposes of this research were (1) to determine (in the laboratory) the coagulation rates of three clay minerals in solutions at various ionic strengths (salinities), (2) to determine (in the laboratory) the coagulation rates of sediments collected from the Pamlico Estuary of North Carolina, and (3) to evaluate the role of the coagulation process in affecting the fate of soluble adsorbable pollutants such as phosphorus, radionuclides, trace metals, and pesticides.

Suspended materials consisting largely of colloids are subject to two different classes of forces in an estuary, viz., hydrodynamic and chemical. Colloidal suspensions are quite stable (i.e., they have little tendency for particle aggregation) in fresh waters due to the repulsion that exists between the electrical double layers surrounding the negatively charged particles. In accordance with the theory of colloid stability developed by Verwey-Overbeek and Derjaguin-Landau (VODL theory), the stability of colloidal suspensions is reduced (particle aggregation is enhanced) by an increase in ionic strength. Conditions in an estuary are conducive for coagulation; the colloidal suspensions are destabilized by the salt water and mixing is provided by the interaction of the river inflow, tides and winds.

A large fraction of the colloids in natural waters are clay minerals which have relatively large surface areas and exchange capacities. These clay minerals have the ability to concentrate appreciable quantities of soluble species on their surfaces. Soluble pollutants may be removed by sorption processes from turbid fresh waters, and then transported to estuaries where fresh and salt water mix. In estuaries the sorbed pollutants may be released by the sediments (source) or they may be retained and be incorporated into the bottom sediments (sink). Consequently, the coagulation and deposition of suspended sediments in estuaries can affect the fate of soluble adsorbable pollutants.

COAGULATION RATE STUDIES

Procedures

Initially, standard jar test procedures were used to evaluate the effect of ionic strength on the coagulation of clay suspensions. Rates of coagulation were then determined in the laboratory by observing the change in clay particle number over time using microscopic counting and Coulter Counter techniques. Stability values (α) were evaluated from the kinetic coagulation data using Smoluchowski's equation for orthokinetic flocculation.

$$\frac{dn}{dt} = \frac{-4\alpha\phi G n}{\pi} \qquad [S-1]$$

Here n is the concentration of particles at time t, particles/cm^3, α is the stability factor, ϕ is the volume of colloidal particles per unit volume of suspension, and G is the root-mean-square velocity gradient, sec^{-1}. A completely destabilized suspension has a stability factor of 1; stable suspensions are characterized by $\alpha << 1$.

Kaolinite, Illite, and Montmorillonite

The results of the rate studies using kaolinite, illite, and montmorillonite clays are reported in Chapter IV and summarized below. Table S.1 summarizes stability values obtained from coagulation experiments using clays with synthetic sea water solutions. These results demonstrate the effect of increasing ionic strength on particle destabilization. Rate studies conducted in buffered NaCl solutions (pH 8 with $NaHCO_3$) yielded lower α values (Table S.2). This is to be expected since the sea water solutions contain divalent cations which are more effective in accomplishing particle destabilization. These results - effects of ionic strength and valency of cations - are in qualitative accord with the theory of double layer compression and indicate that the stability of clays is as follows: Illite $>$ Kaolinite $>$ Montmorillonite. This is in agreement with the results of the jar tests.

Pamlico Sediments

The results of laboratory analyses and experiments using sediments collected from the Pamlico Estuary are reported in Chapter V. The composition of the clay fraction of sediments collected from the Pamlico Estuary as determined by X-ray diffraction is presented in Figure S.1. Kaolinite is the dominant clay in the upper end of the estuary where salinity is lowest, and decreases towards the mouth of the estuary where salinity is greatest. Illite occurs in minor amounts in the upper end and increases towards the mouth, while montmorillonite is present in minor amounts along the entire length of the estuary. Chlorite and a chlorite-like intergrade clay comprise the remainder of the clay fraction. The distribution of kaolinite and illite can be explained by

Table S.1

STABILITY VALUES: SYNTHETIC SEA WATER SOLUTIONS

		α *		
I. S.	Salinity	Mont.	Kaolinite	Illite
0.036 M	1.8 ppt	0.0943 ± 0.003	0.0445 ± 0.002	0.0180 ± 0.003
0.087 M	4.4 ppt	0.113 ± 0.019	0.0915 ± 0.006	0.0701 ± 0.007
0.343 M	17.5 ppt	0.148 ± 0.006	0.138 ± 0.009	0.0740 ± 0.009

Table S.2

STABILITY VALUES: BUFFERED NaCl SOLUTIONS

	α *		
I. S.	Mont.	Kaolinite	Illite
0.05 M	0.075 ± 0.009	0.0245 ± 0.007	0.0128 ± 0.003
0.09 M	0.089 ± 0.006	0.0308 ± 0.004	0.0275 ± 0.005
0.3 M	0.125 ± 0.005	0.0724 ± 0.007	0.0455 ± 0.005

* The 95% Confidence Interval for α is indicated.

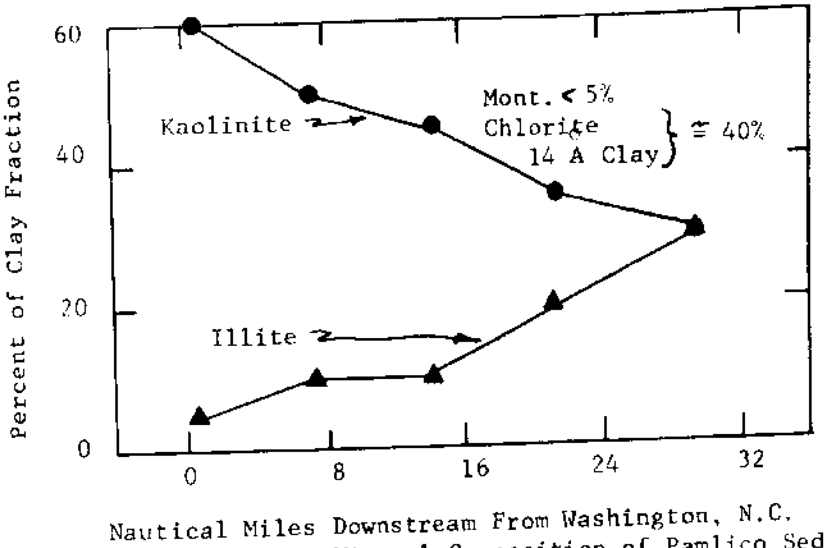


Figure S.1. Clay Mineral Composition of Pamlico Sediments

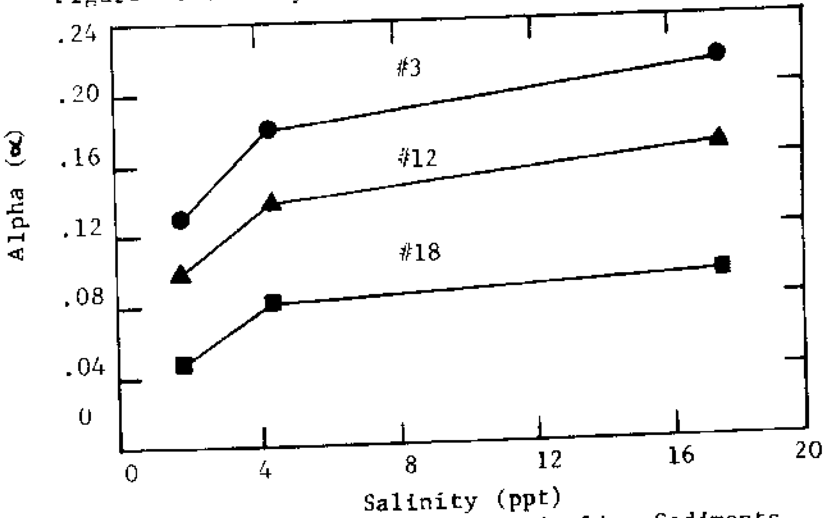


Figure S.2. Stability of Pamlico Sediments

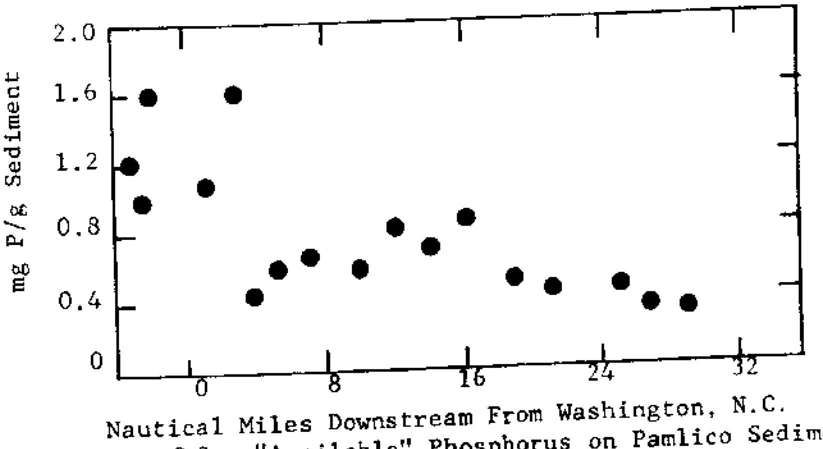


Figure S.3. "Available" Phosphorus on Pamlico Sediments (Upchurch, 1972) coagulation. In the rate studies reported above, kaolinite is observed to be unstable relative to illite; consequently, it should coagulate prior to illite and be deposited upstream from illite. Further verification that the upstream sediments are more unstable than those in the lower end of the estuary is illustrated in Figure S.2. Pamlico sediments #3 (fresh water), #12 (midway down the estuary), and #18 (near mouth of estuary) were subjected to coagulation rate studies and the results indicate that the upstream sediments are relatively unstable (higher α values) compared to downstream sediments.

THE EFFECTS OF COAGULATION ON WATER QUALITY IN ESTUARIES

The significance of the coagulation process in estuaries is evaluated in Chapter VI. Inorganic and organic colloids subjected to coagulation and deposition in estuaries contribute to shoaling of these waters. The organic colloids can have a direct effect on water quality by exerting an oxygen demand. The role of the coagulation process in affecting the fate of soluble adsorbable pollutants has been classified under indirect effects on water quality.

The role of the sediments in affecting the soluble phosphorus concentrations in the Pamlico Estuary is reported in Chapter V and is based to a large extent on the work of Upchurch (1972). The amount of "available" P extracted from the sediments of the Pamlico Estuary was observed to decrease from 1.6 mg P/gm sediment in fresh water to 0.3 mg P/gm sediment in water with a salinity of 16 ppt (Figure S.3). A high degree of correlation between oxalate-extractable Fe and "available" P was observed in the upper reach of the estuary. However, a reduction in the

Fe-P correlation and the decrease in "available" P along the length of the estuary are consistent with the suggestion that P is held to suspended clays and sediments by some type of Fe-inorganic P complex of limited strength. Clays entering the estuary in the fresh water inflow would then lose P as they are transported through waters of increasing salinity.

A review of the literature (Chapter VI) indicated that the following trace metals and radionuclides are not released from sediments in waters of increasing salinity: Cr, Cu, Pb, Zn^{65}, Nb^{95} and Zr^{95}. The fate of sorbed pesticides and mercury on clays is not known when these clays are transported from fresh waters into estuaries.

CONCLUSIONS

The transport of colloidal suspensions from fresh waters into estuaries is accompanied by a reduction in particle stability resulting in coagulation. The role of coagulation is one of hindering longitudinal particle transport by increasing the settling velocity of suspended particles.

The coagulation kinetic studies showed that the stability factor (α) depends upon chemical solution parameters and that different clays have different α values. Destabilization of clay suspensions was improved (increase in α values) with an increase in ionic strength and with solutions containing divalent cations. The stability of the clays is as follows: Illite > Kaolinite > Montmorillonite. In addition it was found that α could not be calculated from interaction energy calculations of the VODL theory (Chapter III); however, the laboratory results are in qualitative accord with the theory of particle destabilization by double layer compression. The results of coagulation rate studies using Pamlico sediments indicated that the upstream sediments are relatively unstable (higher α values). This is in agreement with the clay mineral distribution of kaolinite and illite in the sediments.

The coagulation and deposition of clays in estuaries can affect water quality via adsorption and release of soluble pollutants. The strength of adsorption of P on clays is apparently low, so that the suspended clays or sediments in estuaries may be a source of P. Estuaries may be a sink for pollutants which can be strongly adsorbed, such as some trace metals and radionuclides. The strength of the adsorption of mercury and pesticides on inorganic colloids when transported from fresh waters into estuaries is not known. Depending upon the strength of the solid-solute interaction, coagulated materials could serve as a source or sink for a soluble substance in estuarine waters.

APPENDIX A

Basic Data Pertaining to Ward's Clays

A. Clay Types and Locations (Obtained from Ward's Natural Science Establishment)

Kaolinite #3, Macon, Georgia

Illite #35, Fithian, Illinois

Montmorillonite #21, Polkville, Mississippi

B. Basic Structures

Schematics of the basic structures from which these clay minerals are derived are presented in Figure A.1.

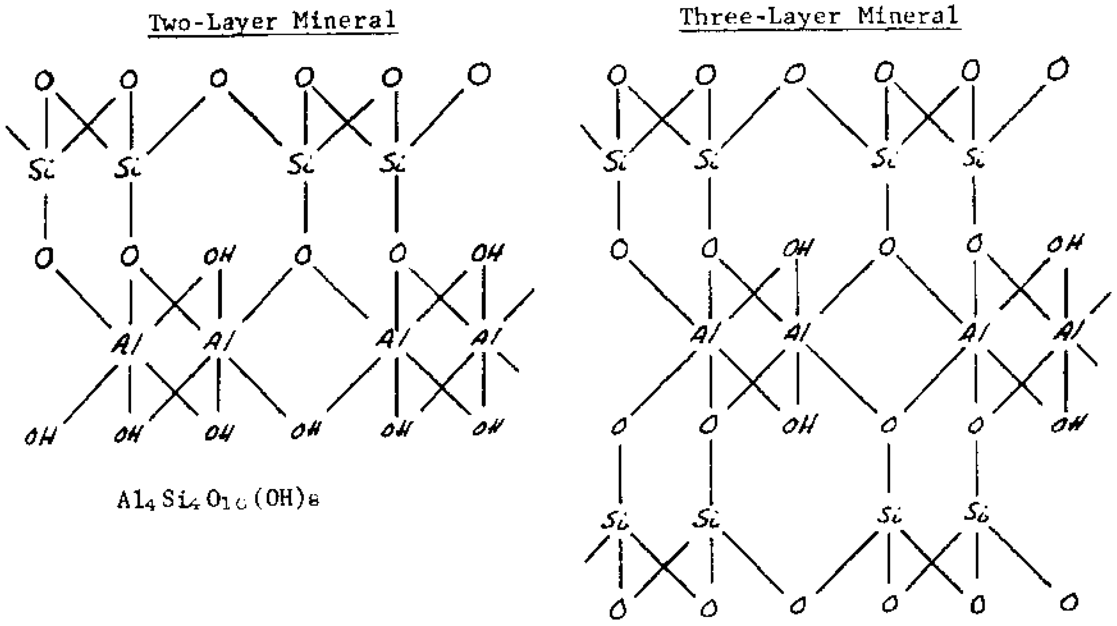
C. Properties (Determined in this Research)

1. Cation Exchange Capacities

	95% Confidence Interval meq/100 gm
Kaolinite #3	8.96 ± 0.39
Illite #35	26.0 ± 2.83
Montmorillonite #21	94.3 ± 6.8

2. Particle Densities

Kaolinite #3	2.61 gm/cm^3
Illite #35	2.72 gm/cm^3



$Al_4Si_4O_{10}(OH)_8$

Pyrophyllite: $Al_4Si_8O_{20}(OH)_4$

Two-Layer Clay: Kaolinite

Three-Layer Clays: Illite
Montmorillonite

Figure A.1 Schematics of the Basic Structures of Two-Layer and Three-Layer Clay Minerals.

D. Chemical Structure (from API #49)

Kaolinite #3	Structure not given, generally: $Al_4Si_4O_{10}(OH)_8$ with some substitution.
Illite #35	$(Al_{2.44}\,Fe^{3+}_{0.90}\,Fe^{2+}_{0.40}\,Mg_{0.30}\,Ti_{0.08})$ $(Si_{6.66}\,Al_{1.34})\ O_{20}(OH)_4\ (K_{1.14}Na_{0.10}Ca_{0.14})$
Montmorillonite #21	$(Al_{2.98}\,Fe_{0.18}\,Mg_{1.06})\ (Si_{7.8}\,Al_{0.2})$ $O_{20}\ (OH)_4\ (Na_{0.04}\,Ca_{0.35})$

E. Standard Curves Used for Jar Tests

Standard Curves indicating the response of absorbance to clay concentration for each clay mineral at a wavelength of 400 mμ are presented in Figure A.2.

F. Identification of Ward's Clays

The results of the X-ray diffraction analyses are presented in Tables A.1, A.2, and A.3.

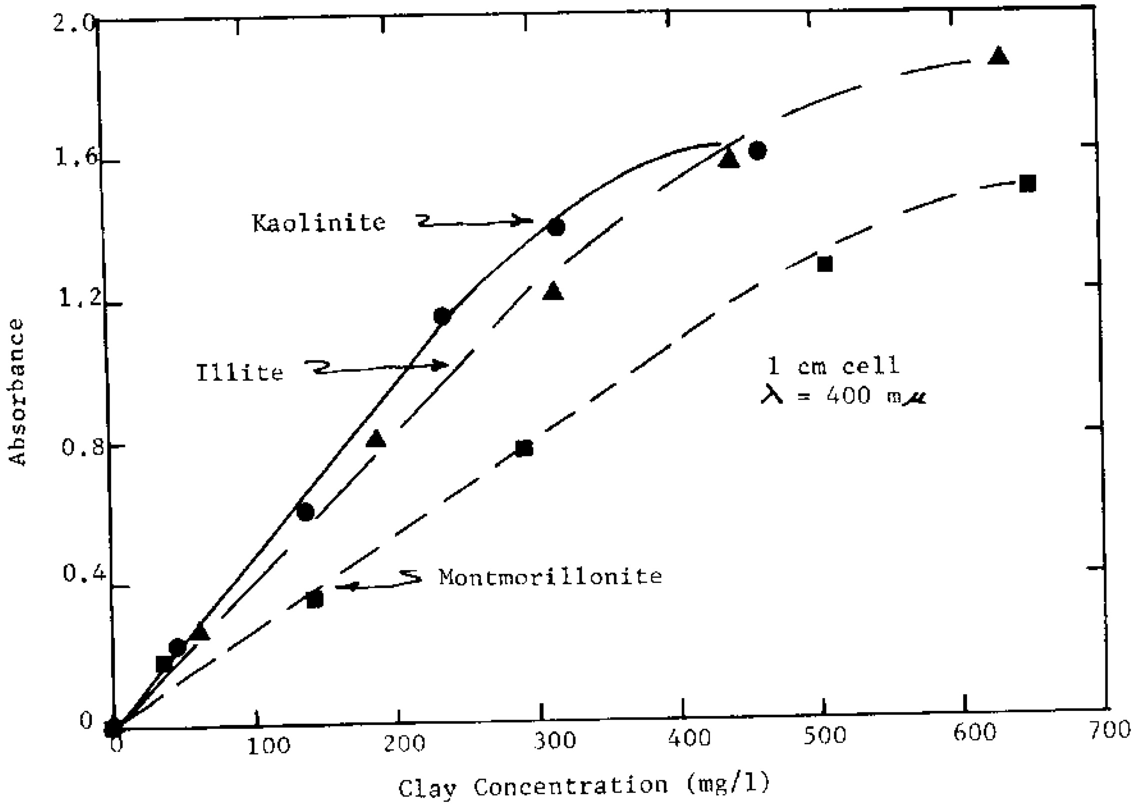


Figure A.2 Standard Curves for Jar Tests

Table A.1

Table of d-spacings vs. intensities Kaolinite #3

Sample Preparation	Reference Data	
Mg, random	Kaolinite Well-xl	Kaolinite disordered
7.16 - 10	7.16 - 10	7.16 - 10
4.45 4.34 4.16 3.89 3.83	4.46 - 4 4.36 - 5 4.18 - 5 4.13 - 3 3.84 - 3	4.46 - 10 Band
3.57 - 10	3.57 - 10	3.58 - 10
2.56 2.53 Triplet 2.49	2.56 - 6 2.53 - 4 2.49 - 8	2.56 - 8 2.50 - 8
2.37 2.34 2.28	2.38 - 6 2.34 - 9 2.29 - 8	2.39 - 8 2.34
		2.21 -1B
1.99	1.99 - 6	1.99 -4B
1.78		
1.68 1.66 1.62	1.66 - 7	1.67 -5B
	1.54 -5B	
1.49	1.49 - 8	1.49 - 10

Remarks: Kaolinite #3 was verified to be a fairly well crystallized Kaolinite. No impurities were found.

Table A.2

Table of d-spacings vs. intensities　　　　Illite #35

Sample Preparation	Reference Data		
Mg, random	Muscovite, 2M	Disordered Illite Muscovite, 1 Md	Well-xl Illite Muscovite, 1M
10.1 -5B	10.01 - 10B	10.07 - 10	10.07 - 10
7.11 - 1			
5.0 - 2	5.02 - 5	5.04 - 4	5.04 - 4
4.46 - 7 4.25 - 2	4.48 - 5	4.49 - 9	4.49 - 9
3.88 - 1 3.83 - 1	3.89 - 4		
3.74 - 1 3.68 - 1	3.74 - 3	3.66 - 10	3.66 - 6
3.34 - 10	3.35 - 10		3.36 - 10
2.81 - 1 2.57 - 7	3.21 - 5 3.00 - 5 2.87 - 4	2.56 - 5 2.55 - 2 Band	3.07 - 5 2.69 - 1 2.56 - 5 2.57 - 9
2.44 - 2 2.43 - 2 2.41 - 2 2.39 - 2	2.59 - 5 2.55 - 4 2.56 - 9		
2.25 - 1 2.13 - 1			
2.01 - 2 1.96 - 2	2.01 - 7	2.01 - 3	
1.81 - 1 1.50 - 3	1.50 - 4	1.50 - 3	1.50 - 3

Remarks: Illite #35 was verified to be a muscovite. No impurities were found.

Table A.3

Table of d-spacings vs. intensities Montmorillonite

Sample Preparation		Reference Data	
Mg, O.A.	Mg-glycol, O.A.	Mg, Mont.	Mg-glycol, Mont.
	16.6 - 10		16.9 - 10
15 - 10		14-15 - 10	
	6.5 7.9 } -1B		6.45
7.52 - 3		7.5 -	
	5.55 -2B		5.64
4.4 - 2		5.0 -	
		3.75 -	
2.51 -1B		2.50 -	

Remarks: Montmorillonite #21 was verified to be montmorillonite.

No impurities were found.

APPENDIX B

Root-Mean-Square Velocity Gradient

The root-mean-square velocity gradient was evaluated by expressing Equation [4-17] in the following form:

$$(1) \qquad G = \left(\frac{\tau \omega}{\mu V} \right)^{\frac{1}{2}}$$

where G is the root-mean-square velocity gradient (sec^{-1}), τ is the net torque (dyne-cm), ω is the angular velocity of the rotating paddle (rpm), μ is the fluid viscosity (gm per cm-sec), and V is the fluid volume (cm^3).

<u>Sample</u> <u>Calculation</u>:

The following sample calculation is based on data collected for Experiment K-3.

Torque (reactor full):	9.75 dyne-cm
Torque (reactor empty):	0.1 dyne-cm
Fluid Volume:	2 liters
Fluid Temperature:	24.5° C
Fluid Viscosity:	0.9039×10^{-2} gm/cm -sec
Paddle speed:	50 rpm

(2) $$G = \left(\frac{(9.65)\ (50)\ (2\pi)\ (980)}{(.9039)\ (10^{-2})\ (2000)\ (60)} \right)^{\frac{1}{2}}$$

$$G = 52.3\ \text{sec}^{-1}$$

APPENDIX C

Data: Coagulation Rate Studies

The following figures contain data from the coagulation rate studies and are not presented in the text.

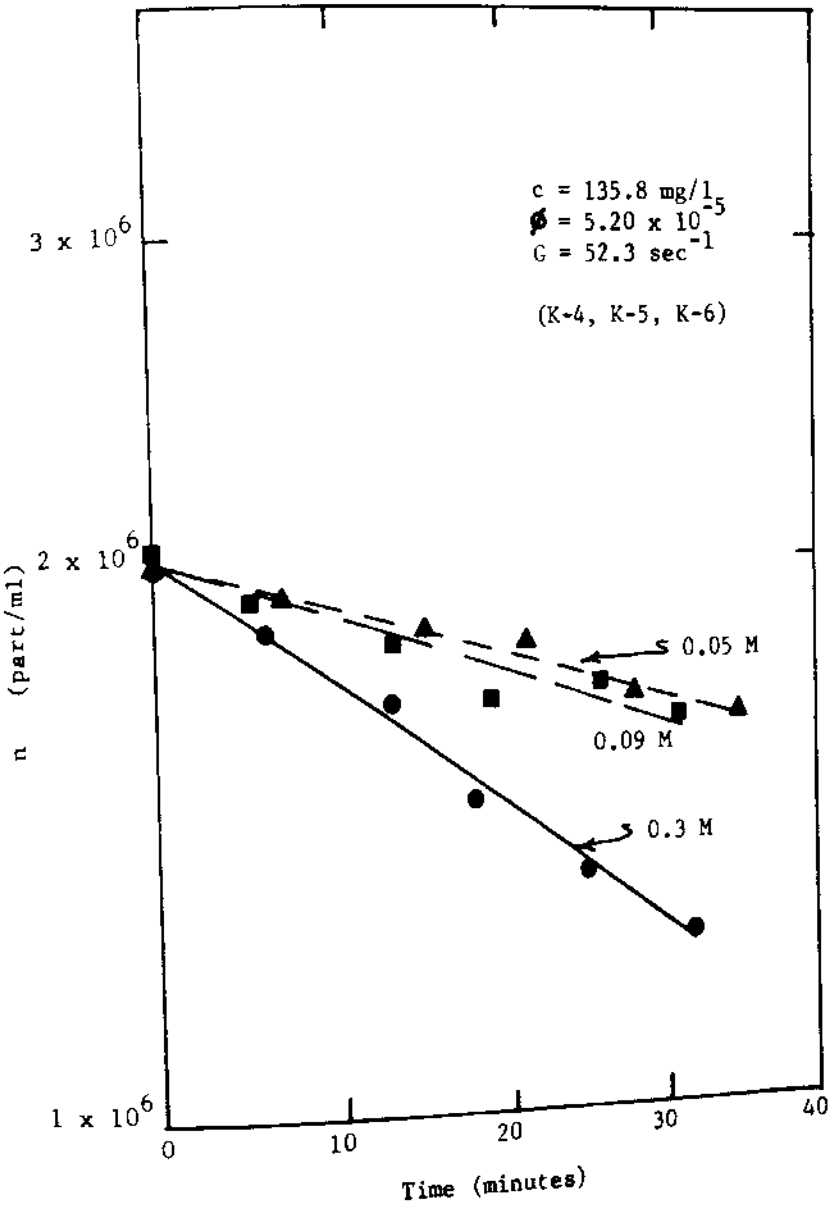


Figure C.1 Rates of Coagulation for Kaolinite in Buffered NaCl Solutions

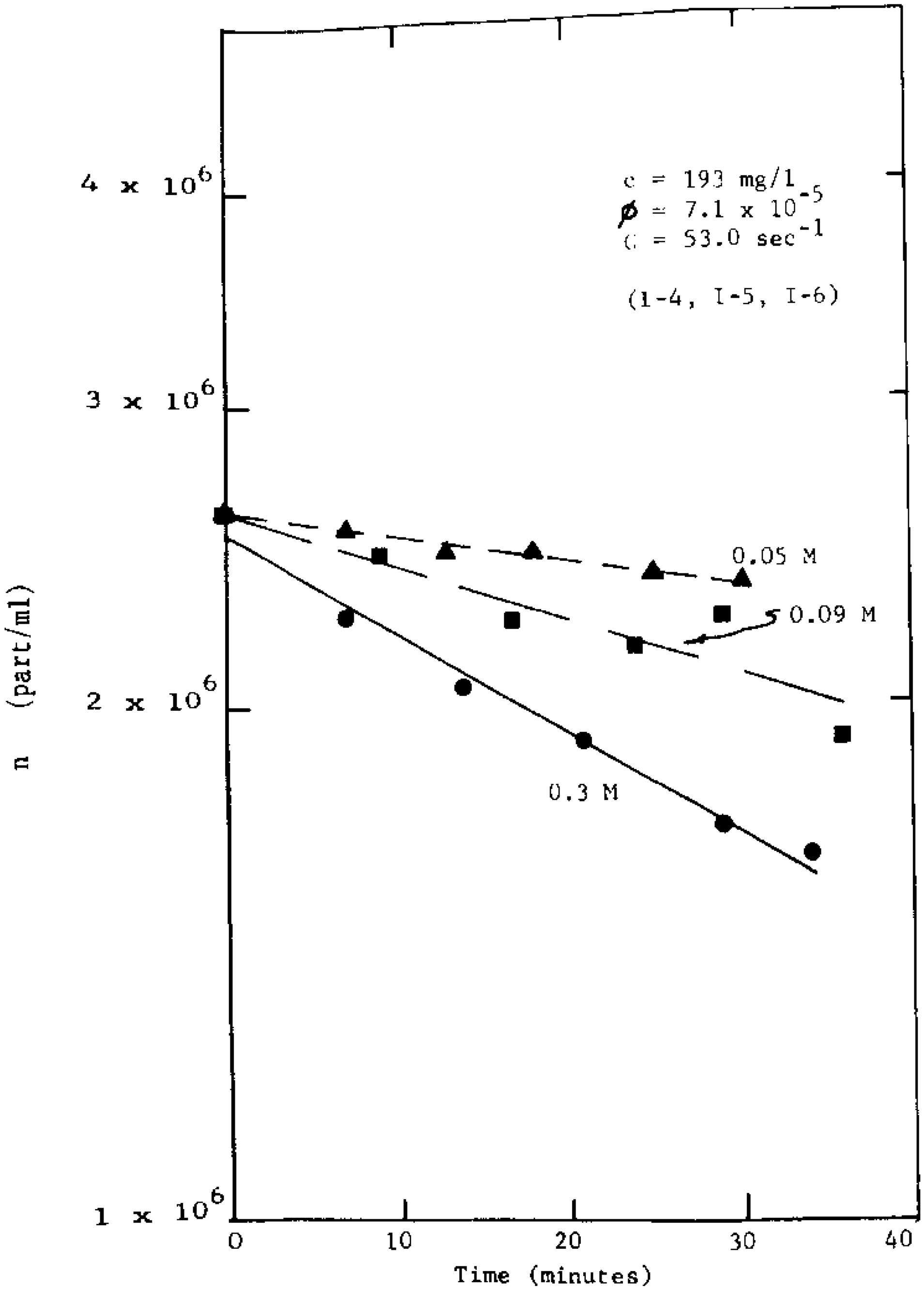


Figure C.2 Rates of Coagulation for Illite in Buffered NaCl Solutions

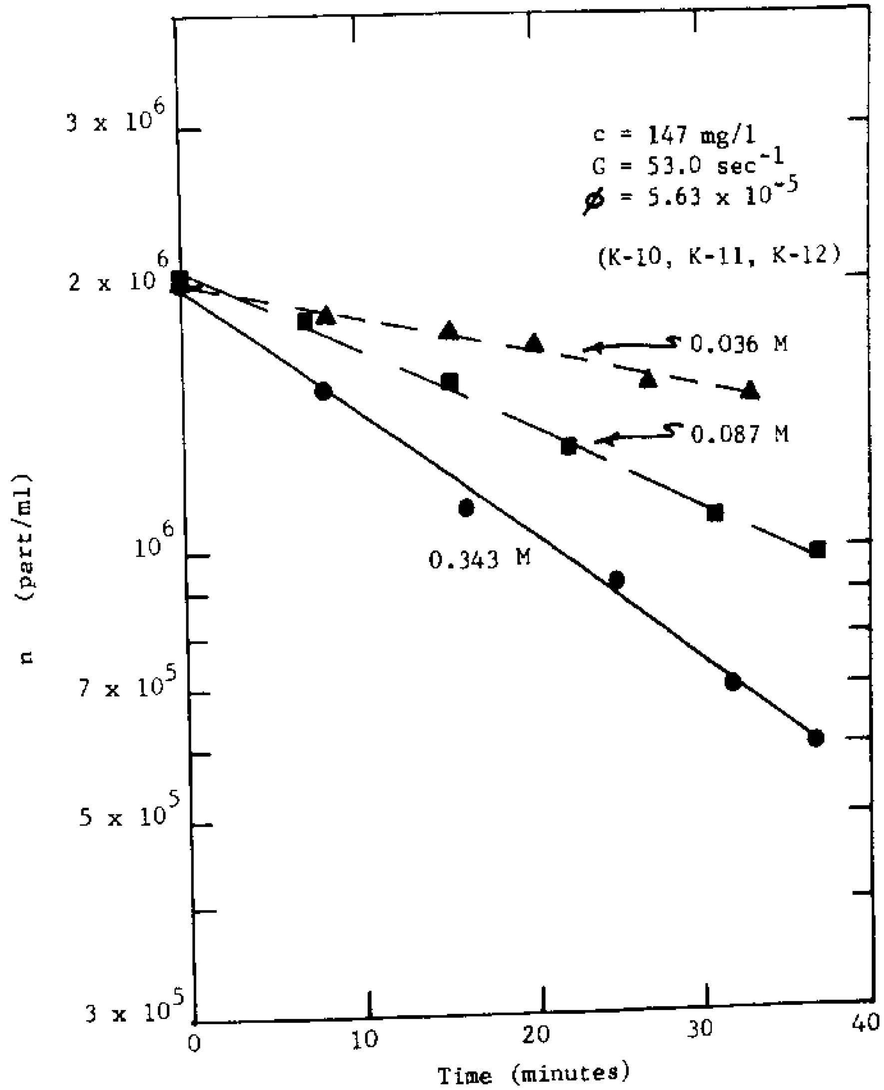


Figure C.3 Rates of Coagulation for Kaolinite in Synthetic Sea Water Solutions

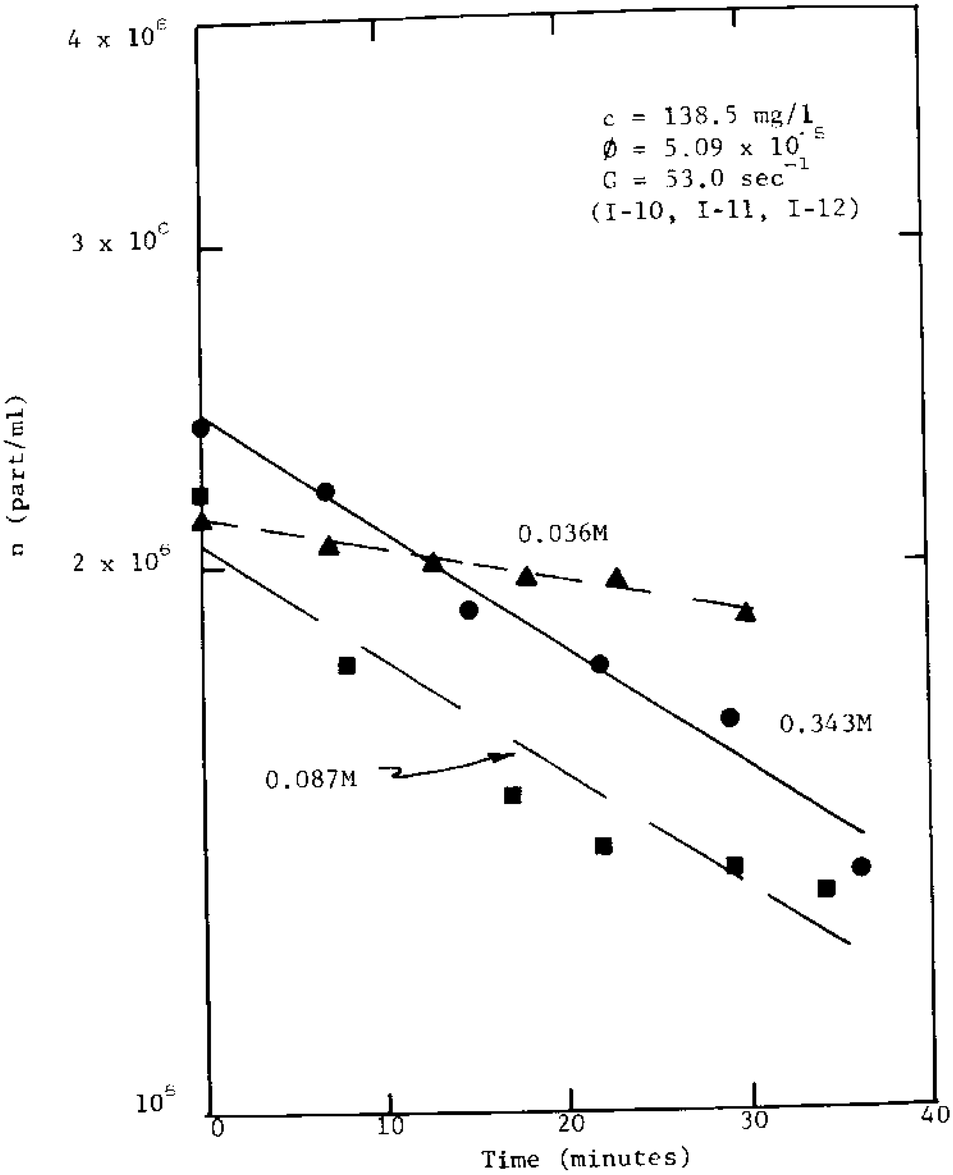


Figure C.4 Rates of Coagulation for Illite in Synthetic Sea Water Solutions

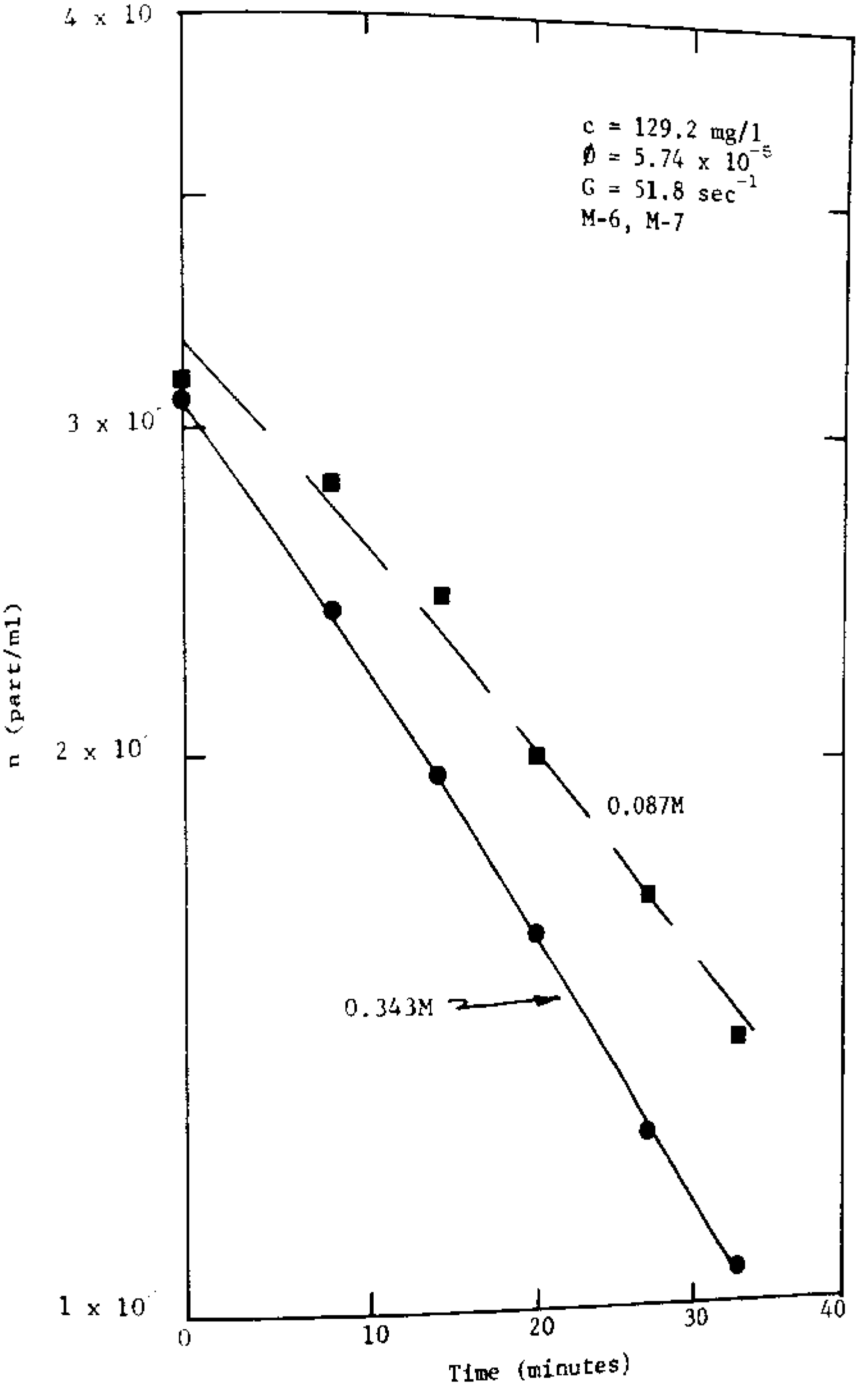


Figure C.5 Rates of Coagulation for Montmorillonite in Synthetic Sea Water Solutions

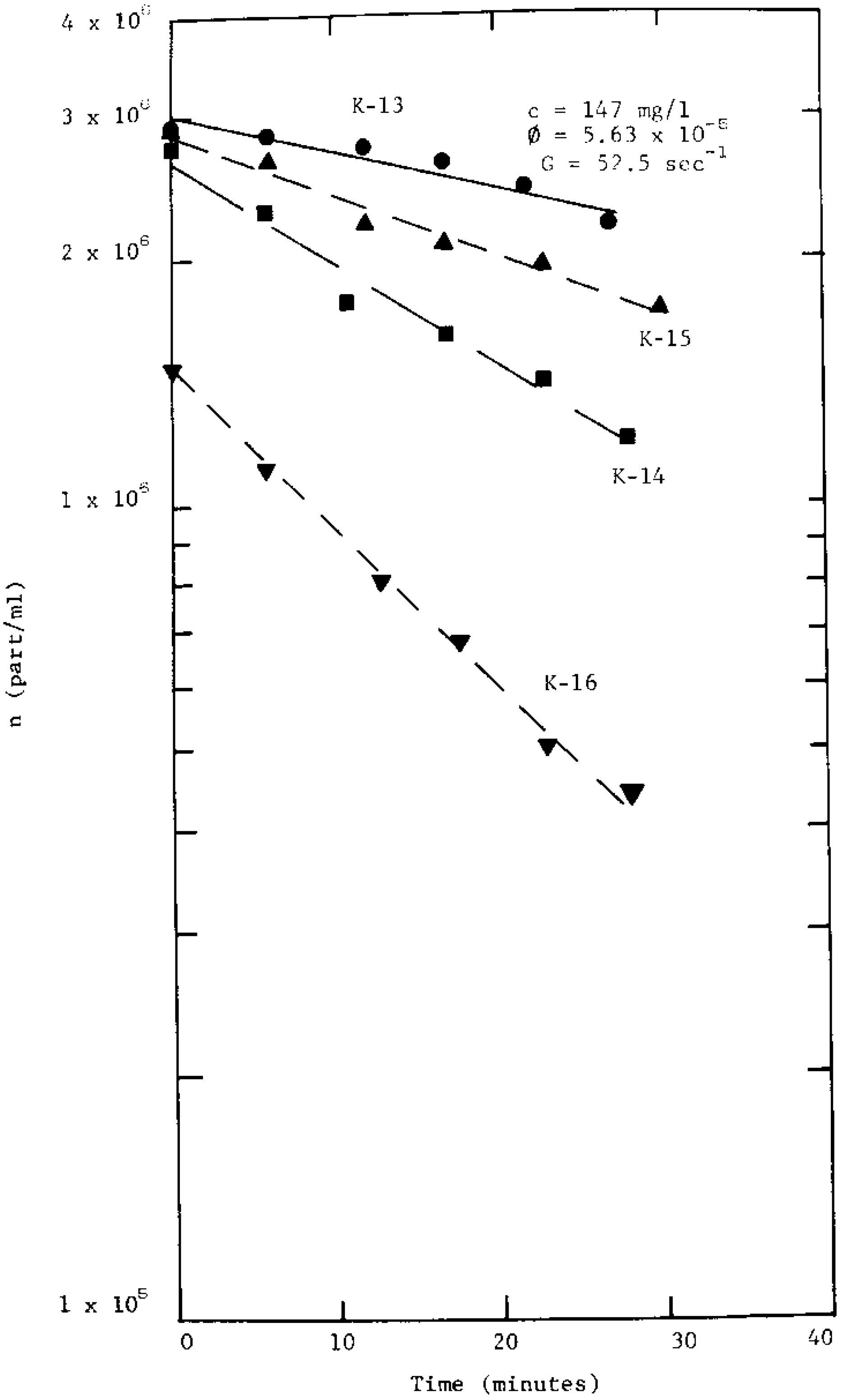


Figure C.6 Rates of Coagulation for Aged Kaolinite Suspensions

APPENDIX D

Statistical Analyses: Coagulation Rate Studies

A. Description

A mathematical model describing the aggregation of particles where collisions are due to fluid motion was developed by Smoluchowski:

$$(1) \quad \frac{dn}{dt} = \frac{-4\alpha G\phi n}{\pi}$$

where: ϕ is the volume of solids per volume of fluid,

G is the root-mean-square velocity gradient, time^{-1},

n is the number of particles per fluid volume,

α is the stability factor,

and t is the time.

An experimental investigation was performed in which the decrease in particle number over time was measured. In this investigation ϕ and G were kept constant and if it is assumed that α is constant during the experiment:

$$\int_{n_0}^{n} \frac{dn}{n} = \frac{-4\alpha G\phi}{\pi} \int_{t_0}^{t} dt$$

$$(2) \quad \ln n/n_0 = \frac{-4\phi G\alpha t}{\pi}$$

$$\text{or} \quad \ln n = \ln n_0 - \frac{4\phi G}{\pi} t\,\alpha$$

The objective of this phase of the research is to obtain stability values (α) for the clays. The stability factor (α) depends on the degree of destabilization (ionic strength of the system); consequently, for a constant ionic strength, ϕ and G do not (theoretically) affect the α value for that clay. Equation (2) was rearranged in order to compare α values obtained from two independent experiments for the same clay at constant ionic strength but at different values of ϕ and G.

$$(3) \quad \left(\frac{(2.303)\,\pi}{4\ \phi\ G}\right) \log n = \left(\frac{(2.303)\ (\pi)}{4\ \phi\ G}\right) \log n_0 - \alpha t$$

The data was plotted on semi-log paper and a least squares regression* was used to obtain the line of best fit. The slope of this line is the stability factor (α).

B. Least Squares Regression

Sample Calculations: Experiment K-3

Kaolinite

$c = 230$ mg/l

$\phi = 8.81 \times 10^{-5}$

$G = 52.4\ \text{sec}^{-1}$

Ionic Strength: 0.3 M (NaCl Solution)

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* See Dixon, W.J. and Massey, Jr., F.J., Introduction to Statistical Analysis, Chapter 11, McGraw-Hill, N.Y., (1969).

(4a) Let $y = \dfrac{\eta(2.303)\ \log n}{4\ \phi\ G}$

Linear Regression of $\dfrac{\eta(2.303)\ \log n}{4\ \phi\ G}$ vs t

(4b) $\dfrac{\eta(2.303)}{4\ \phi\ G} = \dfrac{\eta(2.303)\ \text{min}}{4\ (8.81)\ 10^{-6}(52.4)\ \text{sec}^{-1}(60)\ \text{sec}} = 6.530$

n part/ml	log n	y	time (x) minutes	x^2	y^2	xy
2.76×10^6	6.441	42.060	0	0	1769.044	0
2.32×10^6	6.365	41.563	6	36	1727.483	249.378
2.0×10^6	6.301	41.146	14	196	1692.993	576.044
1.64×10^6	6.215	40.584	19	361	1647.061	771.096
1.36×10^6	6.134	40.055	27	729	1604.403	1081.485
1.08×10^6	6.033	39.395	37	1369	1551.966	1457.615
	Σ	244.803	103	2691	9992.950	4135.618

(5) $\bar{y} = \dfrac{\Sigma y}{n} = \dfrac{244.803}{6} = 40.801$

(6) $S_{xx} = \Sigma x^2 - \dfrac{(\Sigma x)^2}{n}$

$= 2691 - \dfrac{(103)^2}{6} = 922.833$

(7) $S_{yy} = \Sigma y^2 - \dfrac{(\Sigma y)^2}{n}$

$= 9992.950 - \dfrac{(244.803)^2}{6} = 4.865$

(8) $S_{xy} = \Sigma(x)(y) - \dfrac{(\Sigma x)(\Sigma y)}{n}$

$= 4135.618 - \dfrac{(103)(244.803)}{6} = -66.834$

(9) $r = \dfrac{S_{xy}}{\sqrt{S_{xx}\ S_{yy}}} = -0.997$

(10) $r^2 = 0.995$

(11) $\hat{\alpha} = \frac{S_{xy}}{S_{xx}} = -0.07242$ ($\hat{\alpha}$ is the sample estimate of α)

(12) $s^2_{y \cdot x} = \frac{S_{yy} - \hat{\alpha} S_{xy}}{n-2} = 0.00622$

(13) $s_{y \cdot x} = 0.078870$

Linear Regression Equation

(14) $\bar{y}_x = \bar{y} + \hat{\alpha}(x - \bar{x})$

$= 40.801 - .07242 (x - 17.167)$

$= 40.801 - .07242x + 1.243$

$\bar{y}_x = 42.044 - .07242x$

C. 95% Confidence Interval for the Slope α

(15) $\hat{\alpha} \pm \frac{t_{0.975} s_{y \cdot x}}{\sqrt{S_{xx}}}$; with (n-2) degrees of freedom (Dixon and Massey, p. 198).

$-0.07242 \pm \frac{2.776 (.07887)}{\sqrt{922.833}}$

thus 0.0724 ± 0.007 are boundaries of a 95% confidence interval for α.

Sample Calculations: Experiment K-6

Kaolinite

$c = 135.8$ mg/l

$\phi = 5.20 \times 10^{-6}$

$G = 52.3 \text{ sec}^{-1}$

Ionic Strength: 0.3 M (NaCl Solution)

n part/ml	log n	y	time (x) minutes	x^2	y^2	xy
2.0×10^6	6.301	69.805	0	0	4872.738	0
1.84×10^6	6.265	69.406	6	36	4817.193	416.436
1.68×10^6	6.225	68.963	13	169	4755.895	896.519
1.48×10^6	6.170	68.354	18	324	4672.269	1230.372
1.36×10^6	6.134	67.955	25	625	4617.882	1698.875
1.24×10^6	6.093	67.501	32	1024	4556.385	2160.160
	Σ	411.984	94	2178	28292.363	6402.362

(16) $\bar{y} = \frac{\Sigma y}{n} = \frac{411.984}{6} = 68.664$

(17) $S_{xx} = 2178 - \frac{(94)^2}{6} = 705.333$

(18) $S_{yy} = 28292.363 - \frac{(411.984)^2}{6} = 3.894$

(19) $S_{xy} = 6402.362 - \frac{(94)\ (411.984)}{6} = -52.054$

(20) $r = -0.993$

(21) $r^2 = 0.987$

(22) $\hat{\alpha} = \frac{S_{xy}}{S_{xx}} = -.0738$

(23) $s^2_{y \cdot x} = 0.013104$

(24) $s_{y \cdot x} = 0.11447$

<u>Linear</u> <u>Regression</u> <u>Equation</u>

(25) $\bar{y}_x = \bar{y} + \hat{\alpha}(x - \bar{x})$

$= 68.664 - .0738\ (x - 15.667)$

$\bar{y}_x = 69.820 - .0738x$

95% Confidence Interval for the Slope α

$$(26)\quad \hat{\alpha} \pm \frac{t_{0.975}\, s_{y\cdot x}}{\sqrt{S_{xx}}}$$

$$-0.0738 \pm \frac{2.776\ (0.11447)}{\sqrt{705.33}}$$

thus 0.0738 ± 0.012 are boundaries of a 95% confidence interval for α.

D. Comparison of Slopes (Alpha Values): (Dixon and Massey, pp. 206-209)

Sample Calculation: Compare α_1, (Experiment K-3) vs α_2 (Experiment K-6)

I. Ho: $\alpha_1 - \alpha_2 = 0$, level of significance = 0.05, $(n_1 + n_2 - 4)$ d.f. where $\hat{\alpha}_1$ and $\hat{\alpha}_2$ are the estimated slopes.

II. Reject Ho if $|t| \geq 2.306$

III. From the data

Pooled variance is

$$(27)\quad s^2_{y\cdot x\cdot p} = \frac{(n_1 - 2)\, s^2_{y_1\cdot x} + (n_2 - 2)\, s^2_{y_2\cdot x}}{n_1 + n_2 - 4}$$

$$= \frac{4(.00622) + 4(.013104)}{8} = .009662$$

$$(28)\quad t = \frac{\hat{\alpha}_1 - \hat{\alpha}_2}{s_{y\cdot x\cdot p}\sqrt{\frac{1}{S_{xx_1}} + \frac{1}{S_{xx_2}}}}$$

$$= \frac{-.0724 - (-.0738)}{(.098295)\sqrt{\frac{1}{922.833} + \frac{1}{705.333}}}$$

$|t| = 0.281$

IV. Accept H_0. The observed slopes ($\hat{\alpha}_1$ and $\hat{\alpha}_2$) do not differ significantly at the 5% level of significance.

LIST OF SYMBOLS

Symbol	Description
A	Hamaker constant
Å	Angstrom
a	Particle radius
c	Concentration (weight)
D	Einstein diffusion coefficient
d	Particle diameter
dU/dZ	Laminar velocity gradient
E	Eddy diffusivity coefficient
E_A	van der Waals attractive energy between two spheres
E_N	Net interaction energy
E_R	Energy of repulsion between two spheres
e	Elementary charge
G	Root-mean-square velocity gradient
G_p	Absolute velocity gradient
H	Distance between two spheres
I_{ij}	Collision frequency between particles (perikinetic flocculation)
I.S.	Ionic Strength
J_{ij}	Collision frequency between particles (orthokinetic flocculation)
k	Boltzmann constant
m_i	Molar concentration of species i
n	Particle concentration
n	Concentration of ions

Symbol	Description
P	Power input
r	Radius of particle
S	Sources or sinks
T	Absolute temperature
t	Time
U	Velocity component, x-direction
V	Fluid volume
V	Velocity component, y-direction
V_i	Volume of particle i
v	Fluid velocity
W	Velocity component, z-direction
x	Distance
z	Valence
α	Stability factor
ε	Total energy dissipated per unit time and unit fluid mass
ϵ	Dielectric constant
χ	Reciprocal of the double layer thickness
μ	Micron
μ	Fluid viscosity
ν	Kinematic viscosity
π	3.1416
ρ	Fluid density
ρ'	Particle density
σ	Surface charge density

Symbol	Description
τ	Torque
ϕ_m	Total work input per unit of time divided by the fluid volume
ϕ	Floc volume fraction
ψ	Electrical potential
ψ_0	Surface potential
ψ_δ	Stern potential
ω	Angular velocity

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