MECHANICS OF A MARINE CLAY BASED ON PHYSICO-CHEMICAL INTERACTIONS WITH ORGANIC CONTAMINANTS

by

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TO MY

FATHER, ISMAIL

&

MOTHER, GUNER

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ABSTRACT

The effects of municipal (sewage) sludge and crude oil on physical and mechanical properties of laboratory prepared marine clays were investigated. Contaminants appeared to influence the development of clay microstructure and thus some of the physical and mechanical properties of sedimented marine clay.

A mixture of illite, Ca-montmorillonite, kaolinite and chlorite minerals constituted the laboratory prepared "marine clay". The samples were prepared by allowing the marine clay slurry to settle in rectangular settling columns with sampling ports. Marine clay was premixed with the predetermined amount of contaminant and transformed into a slurry using saline water. The slurries were then poured into the settling columns, mixed in place and allowed to settle in a water column of 0.6 m of height. When the sedimentation was completed, the water above the interface was drained through the sampling ports and undisturbed samples of the sediment were obtained by inserting a thin walled plastic tube into the sediment.

Among the physical and mechanical properties measured or observed are physico-chemical properties, index properties, microstructure, shear strength, stiffness, permeability and compressibility. The influence of crude oil and sludge on these physical and mechanical properties and the microstructure was evaluated based on criteria such as flocculation, dispersion and Coulombic forces between the particles and the contaminants.

CHAPTER 1

INTRODUCTION

1.1. STATEMENT OF PROBLEM

The pollution of the world oceans has become one of the most important problems for scientists to solve. The dumping of pollutants into ocean waters may adversely affect the marine environment and ocean floor. Contaminants may influence the development of clay microstructure and subsequent physical and mechanical properties of the marine sediments. Engineers and scientists, however, know little about such influences.

The rapid development of industry has resulted in the release of large quantities of industrial waste containing a variety of organic and inorganic pollutants (Geyer, 1980). Most industrial wastes contain varying amounts of total petroleum hydrocarbons (TPH), organic chemicals and heavy metals. These contaminants, in the bottom sediments of oceans, lakes and rivers, can change sediment water equilibrium and influence the depositional process. Furthermore the presence of these contaminants affect the physical and chemical processes in sediments after the deposition is completed.

Petroleum hydrocarbon contamination of ocean sediments may occur through a variety of sources such as the following: tanker accidents, discharge from coastal facilities, offshore petroleum production facilities and natural seepage (Inderbitzen,1976; Jonston,1976; Pearson and Frangipane, 1975). The environmental effects of a petroleum spill in the ocean depends not only on the chemical and physical characteristics of the sediment but also on the characteristics of the petroleum product. Petroleum is mostly composed of hydrocarbons which is immisciple with water and are chemically inactive compounds. Hydrocarbons are basically compounds of carbon and hydrogen. A component of petroleum is heavy melocular weight crude oil. When hydrocarbon such as crude oil is released into water, it spreads and floats on the surface to form an oil slick due to its low specific gravity and low solubility. Oil particles are dispersed in the water column and come into contact with suspended clay and colloidal particles. The suspended clay particles and sea water act as transfer agents of the oil to the bottom. If the quantity of suspended particles is high, so is the extent of oil transfer to the bottom sediments. Clay particles can adsorb large quantities of hydrocarbons which increases with salinity. Through this process oil wets the clay particle surfaces and also agglomerates the particles which then subsequently sink to the bottom with increased rate of sedimentation. Oil can penetrate deep into the sediment column and remain in the sediment for many years after a spill. A concentual representation of how spilled oil gets incorporated into the ocean floor sediments is shown in Figure 1.1.

One of the most heavily ocean disposed wastes is municipal or sewage sludge. Sewage sludge, a concentrated semisolid material resulting from sewage treatment, is currently disposed of in landfills and in the oceans. Disposal of sewage sludge in landfills has become more difficult in urban areas due to the scarcity of vacant land, the high cost of disposal operation and the possibility of ground water contamination. Sewage sludge outfalls can discharge large quantities of heavy metals such as zinc, copper, cadmium, lead, mercury, iron and silver in both dissolved and particulate forms into the marine environment (Alvi and Lewis, 1987). These heavy metals are deposited in the sediments and subsequently may affect not only the marine ecology but also the physical and chemical properties of these sediments. Sewage sludge is often thick in consistency, and may have fibrous solid particles in suspension. It has been shown to contain organic compounds similar in chemical structure to naturally occuring humic substances in organic soils (Rashid, 1985).

Suspended clay particles enter the marine environment by rivers, coastal erosion, aeolian transport and submarine volcanic eruptions. The physico-chemistry of these particles is important in understanding the behavior of marine sediments which cover the sea floor. Physico-chemical interactions are electrostatic in character. These interactions are responsible for repulsion forces and van der Waals' attractive forces between the clay particles in suspensions. Sediment microstructure is a function of the clay fabric (orientation and arrangement of particles) and also the physico-chemistry of the clay-water system. The geotechnical properties of the resulting deposits of clay sediments in turn are strongly influenced by their microstructure and physico-chemistry.

Contaminants may influence the physico-chemistry and the subsequent development of clay microstructure and thus their physical and mechanical properties (Tuncan, 1989; Pamukcu et al. 1990; Tuncan, 1991; Tuncan and Pamukcu, 1992a; Tuncan and Pamukcu, 1992b). Changing environmental conditions such as pH, salinity, dielectric constant, electrical conductivity, turbidity, solid concentration, and particle size distribution in the ocean water column may have significant effects on the geotechnical properties of the sedimented ocean bottom clays. The sediment behavior can be estimated with sufficient degree of consistency if the fundamental nature of these effects are understood better in any given case. Such estimations may be important in formulating procedures to prevent the following: (1) slope instability in the near or offshore areas (2) environmental damage to harbor and underwater structures, (3) damages to foundations of offshore oil drilling platforms, oil storage reservoirs.

1.2. STATEMENT OF OBJECTIVE

The main objective of this research is to investigate the influence of municipal sludge and crude oil on the physico-chemistry, microstructure and thus geotechnical properties of laboratory prepared marine sediments. Some important geotechnical properties of clays such as permeability, compressibility and strength depend on the pore fluid composition. Pore fluid influence the thickness of the diffused double layer and distance of an arbitrary defined shear plane from the clay particle surface. Changes in pore fluid composition will influence these parameters which control the clays physical and geotechnical properties.

It is proposed in this dissertation to develop empirical and qualitative relationships between the degree of crude oil and municipal sludge contamination and important geotechnical properties of marine sediments. The influence of the degree of contamination is first studied based on the physico-chemistry of clay-water-contaminant environment which reflects upon the sedimentary microstructure. The contamination influence is also studied based on certain geotechnical properties of the clay-water system which is affected by the sedimentary microstructure. Therefore, using the observations made with respect to sedimentary microstructure as qualitative confirmations, correlations between the physico-chemistry and geotechnical behavior of the clay-water systems in environments contaminated with crude oil or sewage sludge are established.

1.3. SUMMARY OF WORK

In this research, experiments were conducted on artificially prepared marine clay using a mixture consisting of illite, Ca-montmorillonite, kaolinite and chlorite. The contaminants used were crude oil and municipal sewage sludge. The test setup consisted of rectangular settling columns with sampling ports along one side. The artificial marine clay slurry was premixed with salt water and a selected amount of contaminant. The slurries were transformed into the settling columns and allowed to settle. When the sedimentation was completed, the water above the interface was drained through the sampling ports and undisturbed samples of the sediment were obtained in a thin walled tube. The influence of crude oil and sludge on physical and mechanical properties and microstructure were evaluated based on the measurements of these properties listed in Figure 1. 2.

In Chapter Two background and literature review about clay/colloid double layer theories and previously reported relations between physico-chemistry, clay microstructure and geotechnical properties are presented. Materials and methods used in this research are presented in Chapter Three. In Chapter Four, base experiments about physico-chemical properties such as specific surface area, cation exchange capacity, zeta potential, and depositional properties such as pH, dielectric constant, conductivity, rate of sedimentation etc. are presented in detail. Geotechnical properties such as consistency limits, permeability, compressibility, shear strength and shear modulus are presented in Chapter Five. Chapter Six is about analysis of the measured or observed effect of sludge or crude oil on clay microstructure. Correlations between the double layer thickness, the percentage of sludge or crude oil and geotechnical properties such as permeability and strength were presented in Chapter Seven. These correlations are confirmed with the observed microstructure and fabric features of the contaminated marine clay specimens. Finally, a summary and conclusions with recommendations for future work is presented in Chapter Eight.

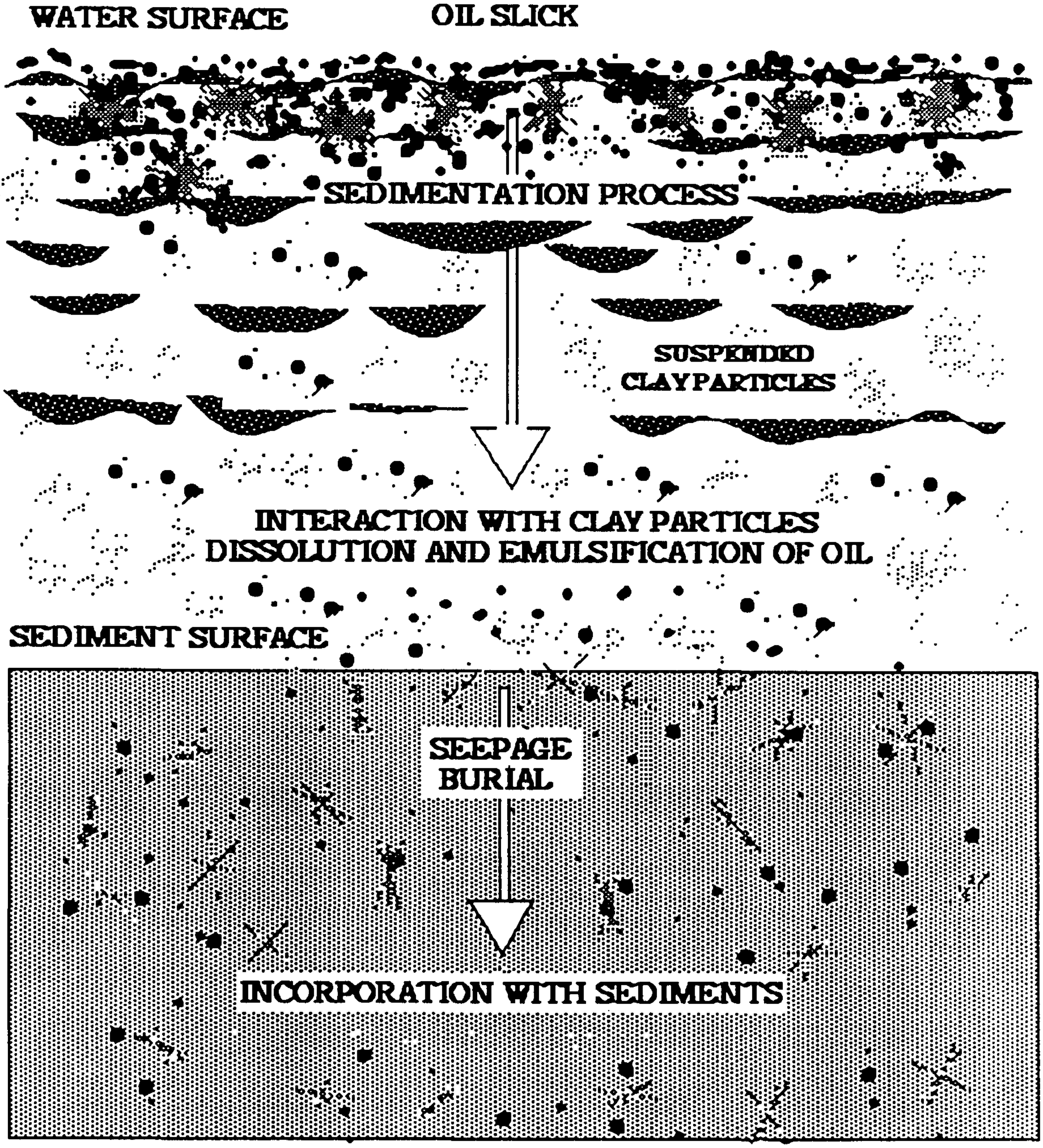
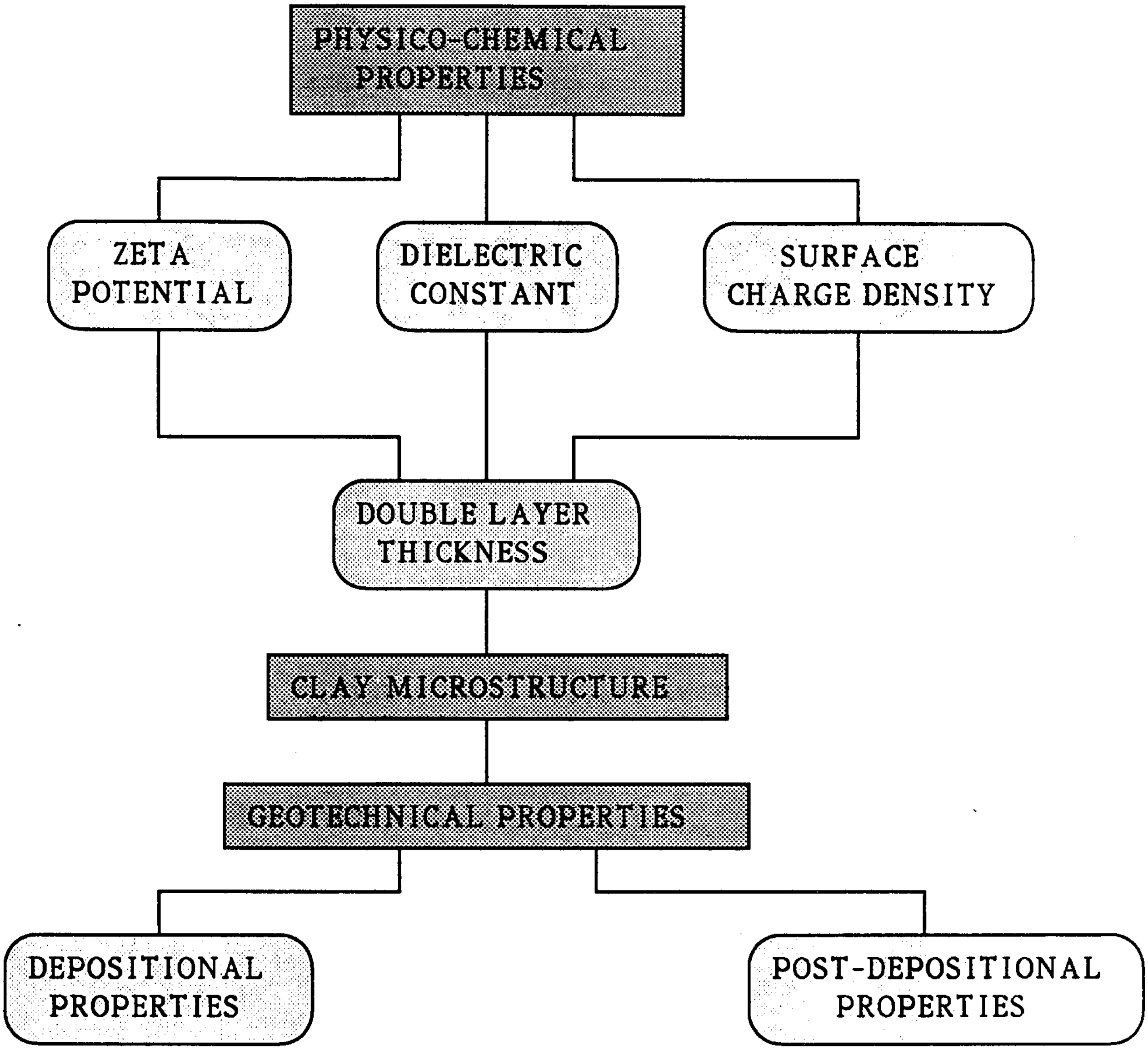


Figure 1.1 Schematic Diagram of Oil Spill in the Sea



Rate of sedimentation
pH variation in the Water Column
Dielectric constant of the suspension
Conductivity of the Suspension
Turbidity of the suspension
Particle Size Dist.in Water Column
Total Diss. Solids in Water Column
Total Solids Conc. in Water Column

1. PhysicalProperties:
   - a. Water Content
   - b. Bulk Unit Weight
   - c. Atterberg Limits
   - d. Porosity
2. MechanicalProperties:
   - a. Permeability
   - b. Shear strength
   - c. Compressibility
   - d. Max. Shear Modulus.

Figure 1.2. Flow Chart of the Research

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1. PERTINENT THEORIES AND CONCEPTS USED IN THIS WORK

Introduction

Clay minerals are composed of small plate-like particles. The crystal lattice of clay particles consists of unit layers. Each unit layer consists of tetrahedrally coordinated silica sheet which shares oxygen atoms with an octahedrally coordinated alumina or magnesia sheet. Clay particles carry a net negative charge because of the following: (1) isomorphous substitution: isomorphous substitution is the substitution of one cation in the lattice by another of similar size (e.g., Si^{4+} by Al^{3+} in the silica sheet and Al^{3+} by Mg^{2+} in the alumina sheet) (van Olphen, 1963), (2) the acidic nature of clay particles: hydrogen atoms of the hydroxyl groups come out in the presence of water and therefore give the clay particles net negative charge, (3) the dissociation of hydroxyl groups, (4) broken bounds at the edges of the particles.

The negative charge is balanced by exchangeable cations. The concentration of these ions is highest close to particle surface. When a clay particle is placed in water, the cations and some anions swarm around the particles. The swarm of counterions is called the "double layer". The tendency of the cations and anions to be attracted and repelled by the clay surface and diffuse away from or toward the surface gives rise to the term "diffuse double layer". Double layer surrounding clay particles are responsible for the stability of clay suspensions because of the repulsion between similarly charged double layers.

If the cation density in the suspension is decreased, the density of the cations near the clay surface will decrease, and a thicker layer of cations will be needed to screen the negative charge on the clay particle and the double layer will be thicker. Conversely, if the cation density in the suspension is increased, the density of the cations near the clay surface will increase, and a thinner layer of cations will be needed to screen or to neutralize the negative charge on the clay particle and the double layer will be thinner. Water movement is influenced by the thickness of this double layer. The thicker the double layer the higher is the potential at the arbitrary slipping or shear plane in front of clay surface and less rapidly water will move through a soil column.

Physico-chemistry of particles and the chemical environment is important in the development of clay fabric (Bennett and Hulbert, 1986). The chemical nature of the fluid medium during sedimentation is important with respect to electrostatic interactions among clay particles. If the response of the slipping plane potential of clay-water micelle to chemical changes in the pore fluid is understood, the interactions between sediment particles and various results can be predicted better. Analogous to the statement above, if the double layer thickness is known, some engineering properties and behavior can be predicted and better understood.

2.1.1. Definition of Zeta (ζ) Potential

ζ- potential is an important factor controlling the stability of clay solutions. ζ-potential is the electrical potential in the double layer at an arbitrary interface between a particle and the surrounding liquid. The thickness of the double layer affects the magnitude of the ζ-potential. ζ-potential is influenced by the type and concentration of the electrolytes added to suspension.

H^+ and OH^- ions are the potential determining ions. Therefore a small increase of OH^- ions increase the negative ζ-potential whereas H^+ ions decrease this potential.

Adding hydrogen ions increases the concentration of the trivalent aluminum ion in the solution. Because hydrogen ion is an exchangable ion which takes up the sites on clay minerals and releases cations such as aluminum into the solution. Hence the negative ζ-potential decreases with the addition of H^+ ion because of a shift of counter-ions toward the clay particle surface compressing the diffuse double layer.

At high concentrations of electrolyte or cation concentration, the negative ζ-potential decreases because of the increased cations. The negatively charged surface is diminished. The thickness of the double layer is reduced and therefore reduce the surface charge. Riddick (1968) gave the following relations between stability of clays and ζ- potential.

Zeta (ζ) Potential (mV)	Stability Characteristics
-81to -100	Maximum dispersion
-61 to -80	Exellent dispersion
-51 to -60	Very dood dispersion
-41 to -50	good dispersion
-31 to -40	Moderate dispersion
-21 to -30	Plateau of silight dispersion
-11 to -20	Threshold of agglomeration and flocculation
-5 to -10	Fair agglomeration and Flocculation
-1 to -4	Excellent agglomeration and Flocculation
+3 to 0	Maximum Agglomeration and Flocculation

2.1.2. Stability of Colloidal Systems

Colloidal stability was independently studied by B.V. Derjaguin and L. Landau in the USSR and E.J.W. Verwey and J.Th. Overbeek in the Netherlands and is called "DLVO" theory (Verwey and Overbeek, 1948). The basic idea of the theory is that the stability of a solution is determined by the sum of attractive and repulsive forces between individual particles. The mutual attraction of particles is because of the van der Waals forces. The mutual repulsion of the particles is because of the interactions of the electrical double layers surrounding each particle.

In DLVO theory, the stability of colloids is treated in terms of the energy changes which takes place when colloidal particles approach each other. According to DLVO theory, the thickness of the electrical double layer is because of the electrolyte concentration and the valence of the ions of opposite sign from the particle surface. The double layer thickness is compressed with increasing electrolyte concentration and the valence of the counterions which allow particles to approach each other.

"STABILITY" of a colloidal system refers to its state and the particle associations. Stable clay suspensions exist low salt content conditions. The stability of clays can be attributed to repulsive forces between the particles. When a colloidal solution is dispersed or deflocculated the system is called "STABLE" and it is called "UNSTABLE" when the particles are flocculated or coagulated. Stable systems settle to very dense sediments because the particles can roll over each other until the closest packing is reached. If the system is unstable, the sediment volume is large and it may even fill the whole suspension formation of a gel.

Flocculation or coagulation can be accomplished by compression of the electrical double layer surrounding the clay particles. The flocculation of suspensions is a result of attractive forces holding particles together when they colloide. The forces between dispersed particles can be changed by the addition of electrolytes. Because electrolytes eliminates the repulsive interactions and cause the suspension to flocculate rapidly.

Jenny and Reitemeier (1935) studied the significance of exchange reactions on the stability of colloidal clay systems. They showed that there was a close relationship between the stability of colloidal system and the zeta potential. The flocculation values which were obtained by adding KCl to clays saturated with the various cations were plotted as a function of the zeta potential. The stability of a clay suspensions increased rapidly with a small rise in the zeta potential.

van Olphen (1964) analyzed the flocculation behavior of hydrous clay suspensions. He found that clay particles can associate in the flocculation process in two different ways: (1) face-to-face, leading to thicker plates, and (2) edge-to-face or edge-to-edge, resulting in flocs and gels. He observed the effect of salt on the behavior of clay particles. Addition of salt made the double layers on both edge and face surfaces were compressed. The counter ions partially shifted to the Stern layer and the effective charge which determines the electrostatic attraction between edges and faces was reduced.

Friend and Hunter (1970) reviewed the well known and generally accepted theory for the stability of hydrophobic colloids of DLVO. They concluded that the theory considered particle interactions for two geometrically-simple systems: (1) the interaction between infinite flat plates and (2) the interaction between finite spheres. In practice, particles in most real systems are neither flat plates nor perfect spheres. Depending on the size, shape and ionic environment of specific particles, one of the above two conditions is assumed to apply. Alumino-silicate clay minerals have uniform flat plate shapes. The equilibrium separation between the primary sheets of these materials varies as a function of solution ionic strength.

2.1.3. Double Layer Theories

The Structure of the double layer is important to understand the colloidal behavior of the suspensions and sediments. Mathematical expressions of double layer theories were proposed by Helmholtz (1879), Gouy (1910), Chapman (1913), Debye and Hunkel (1923), and by Stern (1924). The double layer theory have been discussed in great detail in Verwey and Overbeek (1948), Kruyt (1952), Bolt(1955), and van Olphen (1963). In here, a short summary is presented. The double layer theories pertinent to the work presented here are discussed briefly below:

2.1.3.1. Helmholtz Theory

Clay particles are charged and surrounded by a water layer when they are suspended in water. Water molecules within this layer are rigidly held by the particle and have different character and properties from those in the dispersion medium. The water layer contains cations and anions which play an important role in determining the clay behavior. The surface of clay particles is negatively charged when suspended in a water column. Therefore it attracts cations, and as a result clay particles are swarmed by positively charged ions in order to maintain electrical neutrality.

Originally the structure of this double layer was proposed by Helmholtz (1879). Helmholtz was the first one who recognized this important principle. He claimed that a rigid double layer was formed in close proximity to the clay surface. According to Helmholtz (1879), negatively charged particles are surrounded by positively charged particles at a fixed distance. This fixed distance is a monomolecular distance. For two unit planes of clay particles, each particle carrying a charge, σ_0, in a medium of dielectric constant, D, is separated by a distance, δ. For flat surfaces the following formula derived by Muller and Abramson (Abramson, 1934) is used to calculate the double layer thickness according to Helmholtz theory.

$$\delta = \frac{\zeta \varepsilon_0 D}{\sigma_0} \qquad [1]$$

where,

δ= Double layer thickness, m

ζ= Zeta potential, mV

ε_0= permittivity of vacuum = 8.854×10^{-12} Coulomb/Vm

D = Dielectric constant of the medium

σ_0= Surface charge density, Coulomb/m^2

σ_0 is given by the following expression (Mitchell, 1976):

$$\sigma_o = \Gamma \bullet F$$

$$\Gamma = \frac{\text{Cation Exchange Capacity}}{\text{Specific Surface Area}}, \text{ meq} / \text{m}^2$$

$$F = \text{ Faraday Constant} = 96.5 \text{ Coulomb} / \text{meq}$$

The general form of this equation is still in use with the following assumptions:

1) Particle surface is rigid and nonconducting.
2) The thickness of the double layer is a molecular diameter.
3) The layer of water molecules in contact with the particle surface is not movable.
4) Only a laminar flow of liquid can occur. That is the lines of flow must be parallel to the axis of the tube or flow channel.
5) The surface is an insulator and contained liquid has the property of electrolytic conductance.
6) Dielectric constant, D, and the coefficient of viscosity have the same values within the electric double layer as in the liquid in the bulk solution.
7) The charge distribution in the double layer is unaffected by the impressed electrical field or by the relative motion of the particle and the suspension medium.

Application of the Helmholtz model to clay particles allows the zeta potential to be used in the quantitative description of some properties of clay suspensions and clay sediments saturated with water. Consider clay particles suspended in water, if two like particles are brought close enough together, they will tend to adhere to each other because of the short-range forces that holds the particles together internally. As more and more particles agglomerate, they settle from the suspension and form a sediment in which all the interparticle spaces are filled with water. If the Helmholtz description is appropriate, then presence of the counter-ions becomes important in prediction of the behavior.

The thickness of the double layer is affected by the magnitude of the ζ-potential pH and dielectric constant of the medium. Decrease in double layer thickness allows the particles to approach each other closely, therefore, they adhere each other. When the double layer is compressed, counter-ions shift to clay surface. In Helmholtz theory double layer thickness represents the fictitious thickness of the firmly attached ionic layer. That's why the calculated double layer thickness values are small close to monomolecular thickness.

2.1.3.2. Gouy-Chapman Theory

Gouy (1910) and Chapman (1913) independently developed a theory to describe the electrical potential and ionic distribution in the double layer for electricaly charged clay particles. While Helmholtz proposed that the double layer was a monomolecular layer thickness, the Gouy-Chapman suggested that diffuse layer extends away from the surface. This theory shows how the double layer varies with the characteristics of the suspending medium. The theory also includes same influences of the physico-chemical environment on stability of the suspended clay particles.

Gouy and Chapman proposed that the counter-ions are not held rigidly at a fixed distance from the particle surface, as Helmholtz had suggested. However, their concentration falls off exponentially with increasing distance from the surface. In this theory, the size of the ions is not taken into account, and they are considered as point charges. Particle surface is uniformly charged and the ionic solution is an ideal solution. Dielectric constant is considered constant and equal to that of the bulk solution. Using Gouy-Chapman approach the following formula was derived which can be used to calculate double layer thickness (Mitchell, 1976):

$$\delta = \left(\varepsilon_0 \frac{DkT}{2n_0 e^2 z^2} \right)^{1/2} \qquad [2]$$

Where,

δ = Double layer thickness

D = Dielectric constant

ε_0 = Permittivity of vacuum=8.85×10^{-12} farad/m

e = Unit electric charge, 16×10^{-20} Coulombs

Z = Charge of counter ions

k = Boltzman constant, 1.38×10^{-16} erg/^{o}KT

T = Absolute temperature in ^{o}K.

n_o= Electrolyte concentration

The Gouy-Chapman Model predicts an increase in the tendency toward flocculation with an increase in the concentration of the electrolyte in the pore fluid, valence of the ions in the pore fluid, temperature, or by a decrease in the dielectric constant of the pore fluid. Factors such as size of the hydrated ions, pH, and anion adsorption also influence the clay behavior. These factors are not accounted for in the Gouy-Chapman theory. However observations have shown that a decrease in these factors increases the tendency toward flocculation.

2.1.3.3. Stern Theory

Stern (1924) combined the Helmholtz and Gouy-Chapman models. Stern suggested that some counter-ions are held firmly at a fixed distance close to the surface, and others are held more loosely at a distance from the surface determined by the balance between electrostatic forces which is called Gouy-Chapman layer. The firmly fixed ions constitute the "Stern layer" or the "Helmholtz layer", while the loosely held ions constitute the "Gouy-Chapman". Therefore, Stern's double layer is composed of two layers, an inner, immobile and an outer, mobile layer. Stern layer thickness is about the diameter of the adsorbed cation. Beyond the Stern layer the normal Gouy-Chapman or diffuse layer extends into the bulk solution. The thickness of the diffuse layer depends on the concentration and the type of ion in the suspension. Increasing the concentration of electrolyte in the solution compresses the double layer, decreases the repulsion forces and therefore tends to decrease Stern potential.

The ζ-potential is usually close to the Stern potential (ψ_d). Therefore, the shear plane is assumed to be located at or near the interface of the Stern layer and the diffuse double layer where ζ- potential is approximately equal to the ψ_d. It may be noted here that the ζ-potential is the potential between the mobile and immobile layers. The total charge density of the clay surface is given by:

$$\sigma_0 = \sigma_1 + \sigma_2 \qquad [3]$$

σ_1 is the Stern layer charge density which is given by the following equation (van olphen, 1963):

$$\sigma_1 = \frac{N_1 e}{1 + (N_A / M_w n_0) \exp\left[-(2e \Psi_d / kT)\right]} \qquad [4]$$

where,

$\mathbf{N_1}$ = Number of available exchange sites

$\mathbf{N_A}$ = Avagadro's number = 6.02×10^{23}

$\mathbf{M_w}$ = Molecular weight of water

$\mathbf{n_o}$ = Number of ions/cm^3 of the solution

$\mathbf{e}$ = Charge of electron = 6.02×10^{-19} Coulombs

$\mathbf{k}$ = Boltzman constant = 1.38×10^{-23} J/K

$\mathbf{T}$ = Temperature in degrees kelvin

ψ_d= Stern potential or ζ-potential

σ_2 is the diffused double layer charge which is related to the Stern layer potential given by the following equation (van Olphen, 1963):

$$\sigma_2 = (n_o \varepsilon_o D\, e/2)^{1/2} \,\mathrm{Sinh}\, (z\, e\, \psi_d / 2kT) \qquad [5]$$

where, D = Dielectric constant of the suspending medium

z = charge of counterions

ε_0=permittivity of vacuum=$8.854\mathrm{x}10^{-12}$ Coulomb/m^2

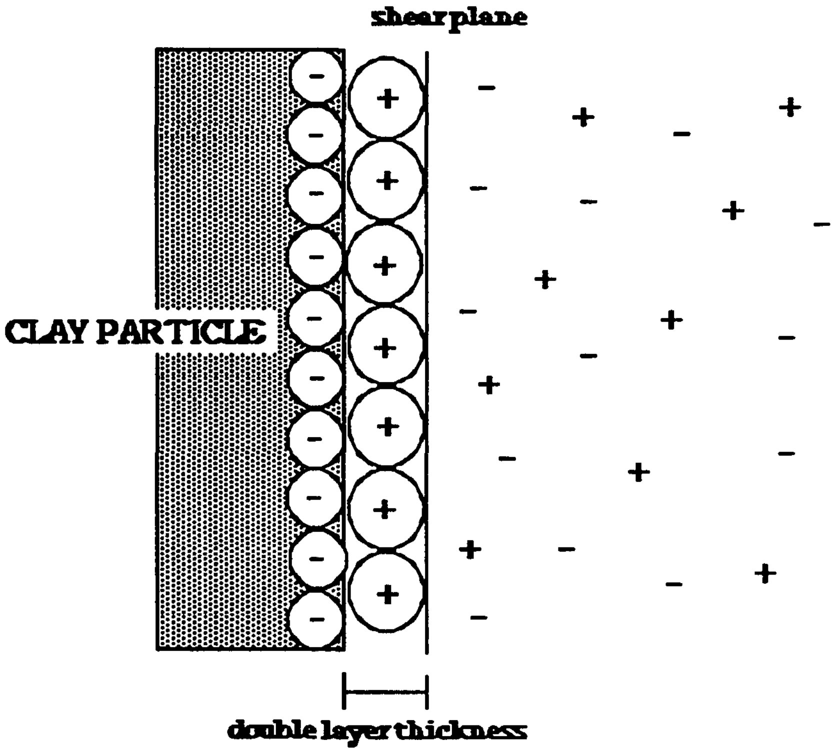


Figure 2.1 Helmholtz Model of a Charged Clay Particle in Suspension.

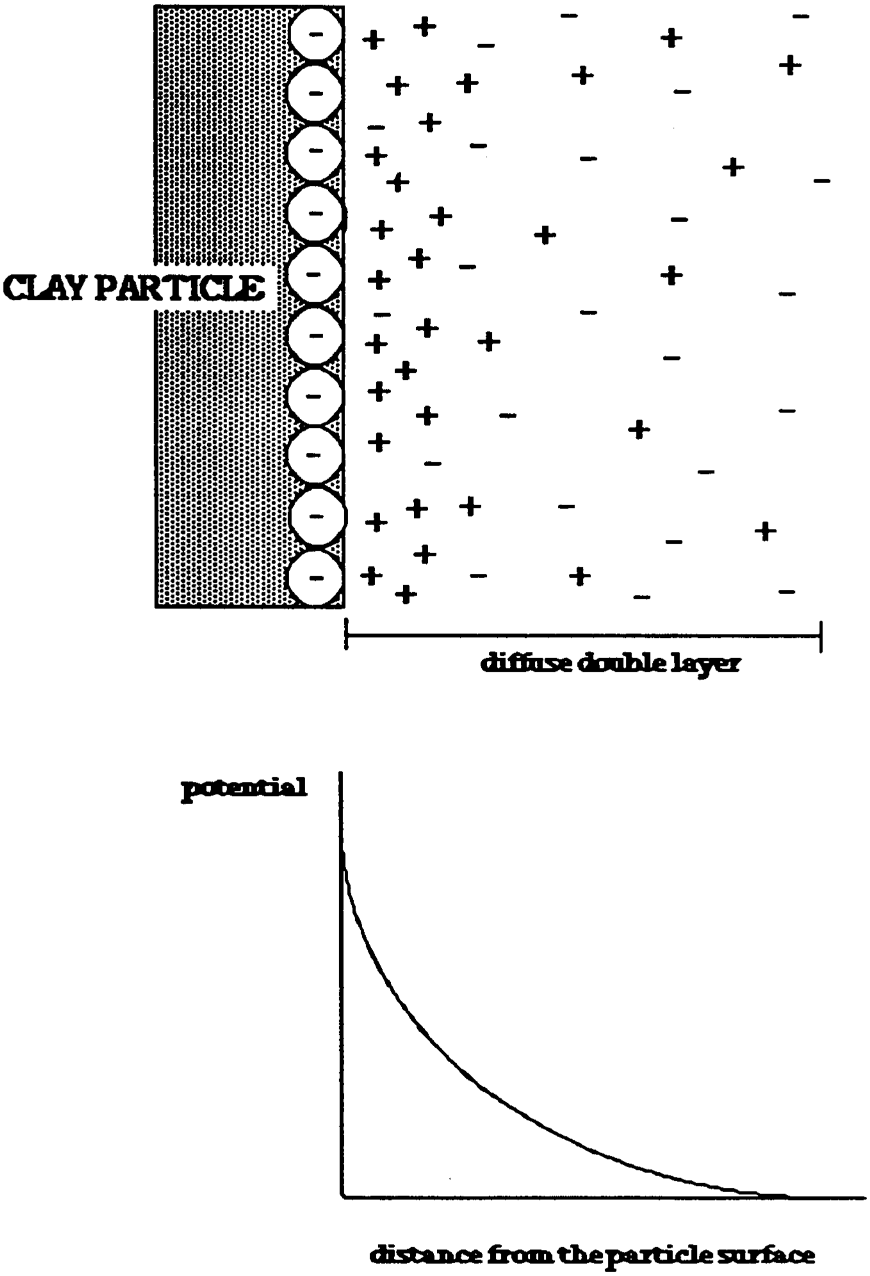


Figure 2.2 Gouy-Chapman Model of a Charged Clay Particle in Suspension.

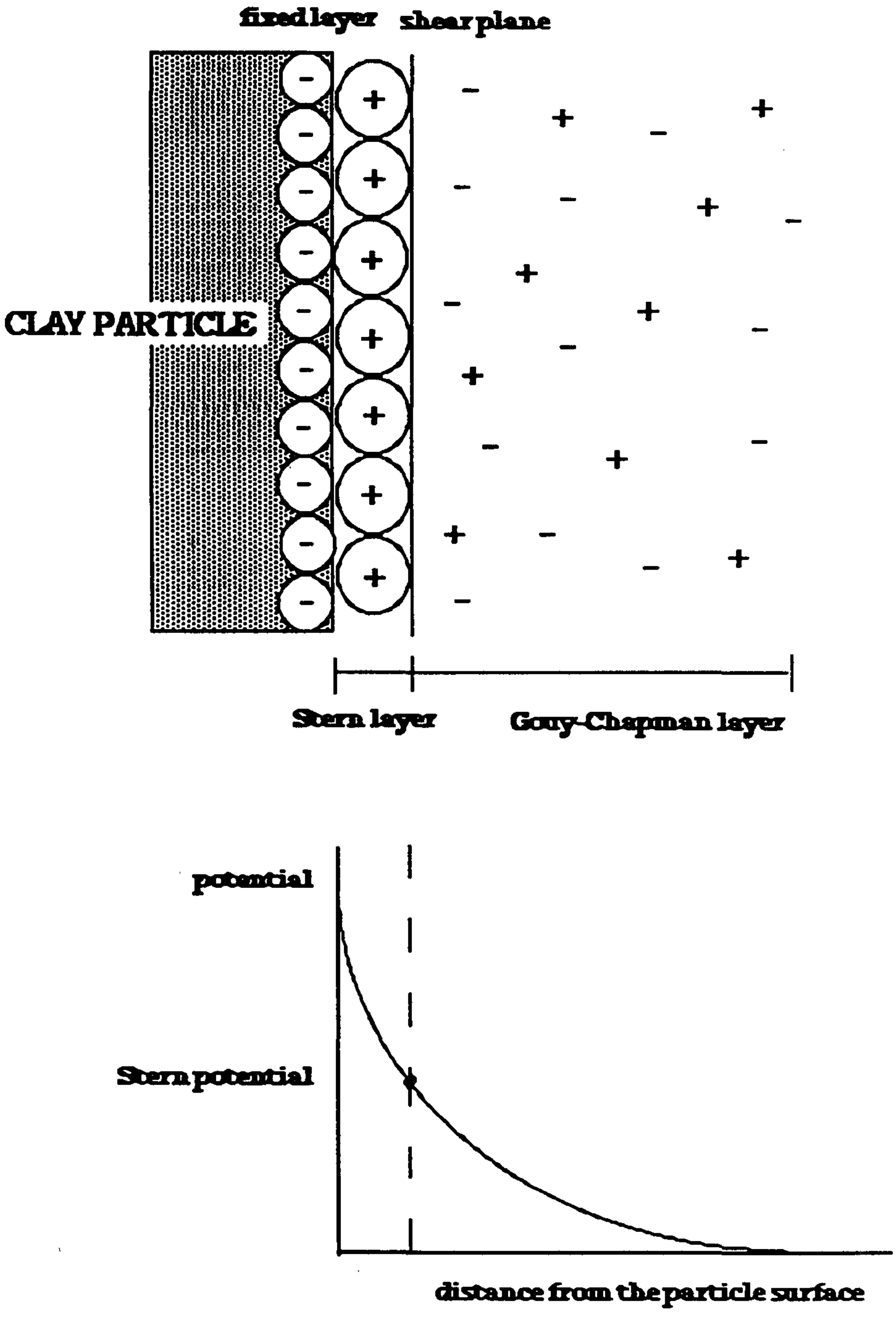


Figure 2.3 Stern Model of a Charged Clay Particle in Suspension.

Grahame (1947) discussed the theory of electrical double layer. He thought that the electrical double layer consisted of a layer of electrons, a layer of adsorbed ions, and a diffuse double layer. He showed the effect of dielectric saturation on the structure of the double layer of mercury-water systems. The effect was small when the surface charge density was about 1 to 2 x 10^{-7} meq/cm^2.

van Olphen (1957) studied the electrical double layer of Ca-montmorillonite. He found that double layer of Ca-montmorillonite was more condensed than Na-montmorillonite. He made some qualitative observations: a divalent cation compresses the electrical double layer more than a monovalent cation, a lower electrophoretic mobility was observed for Ca-montmorillonite, the higher degree of layer association in the case of Ca-montmorillonite indicated less double layer repulsion, which was in agreement with a more compressed double layer.

Shainberg and Kemper (1966) suggested that in the theory of the diffuse double layer, the ions can be considered as point charges without dimensions. as long as they are far from the particle surfaces and at low concentration. In such case, ion shape and size would have little influence on the diffuse double layer. However, in the vicinity of the particle surface where the concentration of cations is high, the distance of closest approach to the surface is important and size of the ions and the energy of hydration must be considered to give an accurate description of the cations adsorbed on clay particles.

Kjellander et al, (1988) examined the mechanism of swelling of calcium clays in water and in aqueous salt solution. The crystals of Na-montmorillonite expanded at low electrolyte concentration because of the development of diffuse double layer between the silicate layers of montmorillonite. They also showed that Ca-montmorillonite crystals did not swell to the same extent and have a high permeability even in distilled water.

2.1.4. Sedimentation Theories

The soil particles suspended in water settle under their own weight and form a layer of soil sediment. This sediment will further be consolidated by the weight of the overlaying sediment. Therefore, the sedimentation has three different phenomena : (1) settling, (2) sediment formation and (3) consolidation. During sedimentation there is no effective stress and the slurry behaves like a fluid. When soil particles settle a mass of sediment is formed and soil particles interact with each other and form an aggregate by particle-to-particle contacts.

Kynch (1952) developed a theory for hindered settling. According to his theory, the free settling of particles is interrupted by their mutual collosions and the particles settle in the aggregate form. He assumed that the aggregate of settled particles never consolidates and he introduced a mechanism for hindered settling. Uniformly dispersed particles settle in the aggregate form and create an interface between the dispersion and clear water. Therefore, new sediment is formed at the boundary between the dispersion and sediment.The uniform settling of particles and the lack of consolidation in the sediment makes it a straight line.

Kranck (1980) reported the results of a series of experiments studying the settling behavior of flocculated suspensions. He found measurable difference in settling rate of fine grained sediment when settling as part of flocs and when settling as single grains, the former being faster than the latter. He also studied the factors controlling floc formation and settling.

Imai (1981) examined the sedimentation mechanism and sediment formation characteristics using dilute clay-water mixtures. He used sedimentation tubes of 25 cm in height and 5 cm inside diameter. He observed four different modes of settling of a clay-water mixture. When both the solid concentration and the salt concentration were low, dispersed free settling was observed in which dispersed soil particles settle freely. When solid concentration was low but salt concentration was high, flocculated free settling took place. When solid concentration was higher than in the case of flocculated free setling, zone settling occured. Flocs settled in the aggregate form creating a sharp interface. This type of settling is the same as hindered settling. Finally, consolidation settling was observed under high solid concentration, independent of salt concentration.

Tan et al. (1990) studied the validity of Kynch theory to describe the sedimentation of a clayey slurry. They paid particular attention to the hindered sedimentation. They investigated the validity of Kynch's theory that the settling velocity is a function of the concentration alone and found that it is also a function of the initial conditions. They reformulated the theory and they concluded that the permeability versus void ratio relationship of the slurry can be determined from its surface settlement versus time curve.

2.2. PHYSICO-CHEMICAL PROPERTIES

The terms, physical and chemical, are applied to describe the interaction of clay particles. The term, physical, is used to describe the interactions which are controlled by factors such as the size, shape, settling rate, solid concentration, and friction between particles. The term, chemical, is applied to interactions which are controlled by factors such as, diffuse double layer, mineralogy and van der Waals forces. Physico-chemical interactions are expression of the forces between the clay particles. Physico-chemical properties of clay particles are dependent on particle surface characteristics, such as particle surface area, cation exchange capacity, surface charge density, zeta potential, dielectric constant, and electrical conductivity.

2.2.1. Specific Surface Area

Surface area of clay particles is an important property influencing the particles' behavior (Fang, 1989 and Fang, 1991). There are two reasons for this. Firstly, flocculation, dispersion and ion exchange depend on surface phenomena. Secondly, specific surface area is related to the particle size and shape of a clay minerals. Double layer thickness is directly related to the surface area of the clay particles, such that double layer thickness increases with increasing surface area.

The specific surface area of a soil is a fundamental property which has been found to correlate with important phenomena such as CEC, retention and release of various chemicals including certain pollutants in the environment, retention of water, physical and mechanical properties such as strength, permeability and plasticity. Kelley and Jenny (1936) observed that physical grinding increased the CEC of clays because of the exposure of more exchange sites on their particle surfaces.

Hammel et al., (1983) investigated the relationship between Atterberg limits and surface area to estimate the latter from the former. The results showed that there was a very strong relationship which allows surface area to be estimated rapidly and cheaply.

Sawhney and Gent (1990) demostrated that non-polar hydrophobic compounds in vapor phase were rapidly adsorbed on dry clay mineral surfaces and diffused into the micropores. The molecules in the micropores condensed on mineral surfaces and were slowly desorbed.

2.2.2. Cation Exchange Capacity (CEC)

Cation exchange phenomena is important for the fundamental understanding of the differences in the nature and development of electric charges between the clay particles which affect the flocculation and dispersion processes in clay systems.

Cations are attracted and hold onto the surfaces and edges to preserve electrical neutrality. These cations are exchangeable cations because they can be replaced by cations of another type. CEC is a measure of the degree of the isomorphous substitution. This substitution gives a net negative charge to clay particles (van Olphen, 1963). Grim (1968) indicated that the magnitude of the CEC is also affected by factors such as particle size and lattice distortion. CEC can be considered a material constant for a given clay. However, soil humus plays an important role in cation exchange. A considerable part of the CEC of soils is because of the organic substances (Kelley, 1948).

Holdridge (1966) studied the sorption of heavy metal cations by a Dorset Ball clay. Normal cation exchange reactions accounted for a limited proportion of the sorption, particularly with Mn^{+2}, but that preferential adsorbtion on the surface was responsible for the removal of cations from solution in excess of CEC of the clay.

The organic matter of most mineral soils accounts for about 30-65% of the total CEC (Allison, 1973). In sandy and organic soils more than 50% of the CEC is because of the organic component of the soil. The more humified the organic matter the higher is its CEC. Allison reported that the CEC of humus was between 150-300 meq/100g.

2.2.3. pH

pH variations influence the behavior of marine sediments. Low pH promotes flocculation and loose sediments while high pH promotes dispersion and dense sediments. The simplest model assumes edge-to-face flocculation at low pH, while high pH bring about repulsion between negative faces and negative edges and therefore dispersion. pH influences the double layer thickness and electrochemical forces. Low pH reduces the double layer thickness and allows the van der Waals forces to become dominant. At high pH values particles are seperated, therefore double layer thickness increases and repulsion forces become dominant.

Nicol and Hunter (1970) studied the rheological behavior of kaolinite solutions as a function of pH and in the presence of adsorbates. Adsorption of long-chain quaternary ammonium compounds on the clay surface at high pH was able to change the particle interaction energy to over a wide.

Buchanan and Oppenheim (1972) leached aqueous suspensions of kaolinite from Mt Egerton, Victoria, at pH 2.25 and 6.0. More aluminium ions were detected in the leachate than predicted from the published cation exchange capacity.

Rand and Melton (1977) also concluded that at low pH values, the edge of the kaolinite particles were positively charged and therefore electrostatic attraction was promoted between the edges and the negatively charged faces, resulting a card-house structure.

Bruckert and Rouiller (1982) found that the pH of natural soils can vary from 2 to 10. Between these two extremes, the pH of the majority of the soils ranged between 4 and 8. The pH of weakly acid soils depended mainly on the system water-CO_2, however, in a more acid media the pH was regulated by interactions between the solution and organo-mineral constituents of soil. The buffering ability of organic matter was very high whatever the pH was. However, the chemical affinity of humic compounds for the metals Fe and Al modified the potential acidity and buffer power to some extent particularly between pH 4 and 5 where the neutralization of carboxyles occured.

Rashid (1985) showed that pH affected the adsorption characteristics of humic compounds and clay minerals. Acidity promotes greater adsorption than alkaline conditions. This is because of the development of positive charges at the edges of the clay particles in acid conditions. Low pH conditions also affected the electro-chemical properties of colloidal particles. Lowering the pH reduced the surface potential of clay minerals and humic compounds by neutralizing the negative charges.

Lagaly (1989) showed that increasing pH reduced the viscosity and the yield strength of kaolinite. Increasing pH breaks down the card-house structure formed in acidic conditions previously.

2.2.4. Organic Matter Content

Organic compounds influence the sediments behavior. Their reactions with clay materials result in formation of organo-clay complexes. These reactions modify porosity, permeability, water holding capacity, surface area, adsorption characteristics, cation exchange reactions, and a number of other physico-chemical characteristics of sediments. Organo-clay interactions affect the flocculation characteristics of colloidal compounds and rates of sedimentation.

Hedges (1977) investigated the interactions of simple organic molecules with clay minerals settling through the water column. He found that clay minerals adsorbed organic material through the settling water column. Dissolved organic substances transported to the underlying sediments through clay minerals.

Rashid (1985) explained the adsorption characteristics of organic matter on different clay minerals in the presence of different electrolytes. The quantities of humic acid adsorbed on clay minerals was small in the absence of any electrolytes because of the increased double layer thickness of the clay particles and high level of their zeta potential. Addition of electrolytes reduced the repulsive forces between the clay particles and organic material so that they could approach each other. When the molecules come closer, the van der Waals forces become dominant. Because these forces are attractive, physical adsorption occurs between the organic molecules and clay particles. Physical adsorption increases chemical reactions between humic compounds and clay minerals.

Lagaly (1987) investigated the adsorption of organic molecules by hydrophobic and hydrophilic clay minerals. He showed that organic molecules exerted much influence on clay rheological properties. This influence was illustrated by the effect of cationic and anionic surfactants on the viscosity of kaolinite dispersion and of polyvinyl alcohol on dispersions of sodium montmorillonite.

Brown (1988) showed that organic liquids caused clay-rich soils to shrink and crack. Most common organic liquids have dielectric constants considerably lower than water which probably caused clay-rich soil to shrink.

Krumgalz (1989) determined the interaction of trace metals with sediments. One of the most significant parameters influencing trace metal content in the sediment was sediment particle size. High concentration of trace metals and organic matter content in the sediment fractions were explained by the formation of large agglomerates. Agglomerates formed from smaller sediment fraction particles mixed with various contaminants kept on their large specific area by adsorption forces. The formed agglomerates consist of small particles cemented either by dissolved organic matter or by sea salts present in the marine sediment.

Stockmeyer (1991) studied the adsorption behavior of organophilic bentonites in contact with aqueous solutions of organic compounds. Phenol, aniline, maleic acid, nitroethane, and acetic acid were used as test substances. He concluded that the adsorption of organic compounds on organophilic clays of aqueous solutions depended on several factors. The adsorption behavior could be controlled by the adsorbent, the kind of the interlayer cation, and the degree of organophilic exchange.

2.2.5. Electrical Conductivity

The electrical conductance of a colloidal solution can be considered to be built up from contributions of the charged colloidal particles and the ions present in the solution. The electrical conductivity can be spilt up into a contribution of the soil particles and their counter ions (micellar conductivity) and a contribution of the rest of the liquid (intermicellar conductivity).

Daskhinamurti (1960) investigated the ionic diffusion and electrical conductivity in sands and clays. The rigidity of the gel solution was lowered with decreasing electrolyte concentration. Below a critical concentration, the clay suspension was deflocculated and the conductivity of the electrolyte solution in which the clay was suspended increased.

2.2.6. Dielectric Constant

Colloidal particles are electrically charged by fixed or adsorbed ions and are surrounded by counterions, forming an electric double layer. A shift of ions within this layer by an external electrical field would result in a dielectric dispersion. Counterions on the surface of the highly charged colloidal particle are strongly bound by the electrostatic attraction. They have to overcome a high potential barrier in order to diffuse away from the surface into the bulk solution. However, they can move along the surface easily. Therefore they will be moved by an external field, polarizing the ion atmosphere and producing an electric dipole moment of the particle.

Dielectric constant is frequency dependent phenomena. At very high frequencies electrons polarize. At intermediate frequencies, ions and polar molecules polarize. At low frequencies, interfacial polarization may be important. If there is a considerable difference in dielectric constant between the dispersion and the dispersing medium, interfacial polarization causes dielectric loss and also frequency dependence of the dielectric constant in the low frequencies. In aquaeous colloidal solutions, the presence of electrolyte, even in small amounts in the water should commonly cause sufficient conductivity difference. This causes interfacial polarization. At the high frequencies, where the effects of conductivity and interfacial polarization are unimportant, orientation of the colloidal particles is commonly prevented by their long relaxation times.

The electrolyte would be expected to influence the dielectric properties in two ways. (1) its ions may associate and produce ion pairs. (2) the ions or their aggregates in the medium could influence the solvent's molecular interactions. Solvent molecules may be firmly bonded to the ions and therefore new of molecules of solvation appear. The first attempt to develop a theory of the dielectric constant of polar liquids at high field strengths was made by Debye (1929). He pointed out that in electrolytes, having sall size ions, very intense fields would be set up in their neighborhood.

Schwarz (1962) observed that the colloidal particles suspended in electrolyte had low dielectric constant. This was because of the polarization of the counterion atmosphere around the particles by an electrical field. The displacement of counterions in the double layer was shown to be equivalent to the existence of a surface capacitance displaying a diffusion controlled relaxation. This effect could be explained by an additional apparent dielectric constant of the suspended particles, exceeding their actual dielectric constant at low frequencies by many orders of magnitude. He concluded that suspensions of colloidal particles in aqueous electrolyte solutions showed usually high dielectric constants at low frequencies.

Thorpe (1962) studied the dielectric properties of benzene vapors adsorbed on the surface of silica. Its dielectric constant was reduced. Consequently reduction in the dielectric constant of the suspension of silica in benzene was expected with increase in the specific surface of the silica.

Sachs and Spiegler(1964) made measurements of the dielectric constants and electrical conductivities of the soils immersed in distilled water and in $CaCl_2$ solutions of different concentrations. They found that wet soils and rocks had dielectric constants larger than 1000 while the dielectric constants of most dry soils and water were lower than 10 and 80, respectively.

Frommer and Ish-Shalom (1966) measured the static dielectric constants of suspensions of pyrogenic silica in organic liquids. It was found that the dielectric of silica increased with increasing specific surface and decreased with temperature. This increase was because of the orientational polarization of the OH groups on the surface of the silica. Surface polarization was because of the interaction between the external surface of the silica and the dispersing liquid.

Dukhin and Shilov (1974) reported that low frequency dielectric constant of suspensions are strongly dependent on the zeta potential of the particles, which points to the predominant role of the double layer. Low frequency dielectric dispersion is due to the relaxation of double layer polarization.

Chaussidon (1984) found high values of dielectric constants of clay suspensions at low frequencies. This was attributed to the heterogeneity of the medium.

Chew (1984) gave a method to calculate the response of charged clay particles which was immersed in electrolytic solutions in the presence of an externally applied electric field. The large value of dielectric constant of 1000 for the colloidal solutions contaning clay particles were remarkable, since the dielectric constant of water was about 80 and that of dry clay was between 2 and 10. He presented a rigorous analysis of this problem using the technique of matched asymptotic expansions commonly used in boundary layer theory. The solution was valid for large value of the zeta potentials.

Raythatha and Sen (1986) measured the dielectric response of Na-montmorillonite and kaolinite suspensions in the range of 0.5 MHz to 1.3 GHz. A swelling clay, Na-montmorillonite, showed large values of dielectric constants (200 at 0.5 MHz for 1.5% by weight suspension). The dielectric constant showed a monotonic increase with particle concentration, however the conductivity did not decrease monotonically. The dielectric constant of Na-montmorillonite first decreased and then increased with salinity. This was because of the decrease in double layer thickness. When the salinity of the suspension was increased, the dielectric constant agreed well with the geometrical model. A dilute suspension of kaolinite, a non-swelling clay, showed no dielectric enhancement, which was expected from its low cation exchange capacity. However, at high concentration, electrochemical effects were observed. Therefore, both size and the charge effects became important in this frequency range of measurement.

Myers and Saville (1989) measured the conductivity and dielectric constant of the suspensions consisted of 0.191-μm amphoteric latex particles in 10^{-4} M HCl. Zeta potential of these particles in 10^{-4} M HCl was roughly 80 mV. They found that there was a tremendous change in the dielectric constant due to the addition of relatively small amounts of colloidal material. Dielectric constants around 800 (10 times that of water were measured) the values decreased as the frequency was increased. At 50kHz, the dielectric constant of the suspension was very close to that of pure water.

2.2.7. Zeta (ζ) Potential

Zeta potential is a measure of the magnitude of the forces arising from the electrical charges on the particle. Clays contain counter ions in the colloidal micelle that controls the colloidal behavior such as flocculation or dispersion. At high concentrations of electrolyte or cation concentration, the zeta potential decreases. If the number of cations is increased excessively, they compress the diffuse double layer. The thickness of the double layer is reduced and cations invade the surface layer and so reduce the surface charge. The reduction in zeta potential causes coagulation.

Bull and Gortner (1931) showed that the zeta potential decreased with increasing concentration of electrolytes in the aqueous phase. This decrease in the zeta potential was because of an increase in the charge on the particle and a decrease in the double layer thickness. The thickness of the double layer was decreased with increasing salt concentration. Salt did not reduce the electric charge on the particle to zero. However, there was a decrease in the thickness of the double layer which allowed the particles to approach each other close enough so that they adhered to each other.

Jenny and Reitemeier (1934) demonstrated a close relation between the electrokinetic potential (zeta potential) of colloidal particles and the amount of electrolyte necessary to flocculate the systems. They attempted to clarify the relation among ionic exchange, zeta potential, and flocculation value for colloidal clay systems and to set up quantitative correlations among these three magnitudes.

Coughanour and Utter (1944) observed the effect of particle size, kaolinite concentration, and electrolyte concentration on migration velocity of the particles. Calculations of zeta potential, charge density and total charge were made for the various systems. Zeta potential decreased with increasing clay concentration. They concluded that the zeta potential increased with decreasing particle size having to do with the increased surface area on the broken edges. The zeta potential increased with an increase in concentration of NaOH to a point where the unsaturated bonds are completely satisfied. In this work, they showed that the zeta potential increased in magnitude with a decrease in particle diameter.

Fuerstenau (1956) measured the zeta potential of quartz as a function of the concentration of various ammonium acetates by streaming potential technique. He showed that monovalent inorganic counterions can not change the sign of the zeta potential. However, it causes it to approach to zero at high concentrations. The total double layer potential ψ_0 at the quartz surface depended on the pH of the solution since hydrogen and hydroxyl ions are the potential determining ions for quartz. If the pH is increased, the surface will become more negatively charged and the adsorption of counterions increases. As the solution pH is increased, experiments indicated that the bulk concentration at which semi-micelles form is lowered. He found that the zeta potential appeared to increase with increasing concentration of electrolyte, although zeta potential might actually be decreasing. The zeta potential of quartz measured to be -70 mV in water. It increased with the concentration of an indifferent electrolyte such as NaCl, to a maximum value of about -100 mV in

6×10^{-5} molar solutions before decreasing to zero at high concentrations. Electrolytes reduce the value of zeta potential by compressing the double layer. The zeta potential can change sign by the addition an electrolyte. If the counterions are attracted to the surface by the electrostatic forces, they can reverse the sign of the zeta potential. Hydrogen and hydroxyl ions are the potential determining ions for quartz and are responsible for the existance of the electrical double layer around quartz surface. Fuerstenau (1956) showed that as the pH of a quartz solution was lowered below 7 with hydrochloric acid, zeta potential decreased because of the reduction in the total double layer potential, ψ_0. As the pH was increased above 7 with NaOH, zeta potential increased because of increasing ψ_0.

Street (1957) found that when the electrolyte concentration increased, the zeta potential decreased. This decrease in zeta potential caused a decrease in surface conductance which was reflected in a decrease in suspension conductance.

Ho and Handy (1963) measured the zeta potentials of Na- and Ca-bentonites treated with varying amounts of $Ca(OH)_2$. Addition of small amounts of $Ca(OH)_2$ to the Ca-bentonite suspension increased negative surface charge and zeta potential through the dissociation of acidic groups. If more lime was added , Ca^{2+} adsorption reduced zeta potential.

Hunter and Alexander (1963a) studied the elctrophoretic mobility of kaolinite solutions as a function of electrolyte concentration in $NaHCO_3$-$NaCO_3$ buffer at pH 10.4. The positive charges at the edges of the kaolinite particles in acid solution were no longer present at this pH and the particles were negatively charged. Exchangeable cations were attached to the particles in a Stern layer. He calculated the zeta potential which gave a measure of potential at the outher edge of the Stern layer (diffuse double layer potential ψ_δ). This potential is used to calculate the potential energy of repulsion between the particles as a function of distance. At pH 10.4 the positive charges on the crystal edges are completely neutralized by the adsorption of OH ions. They found that double layer ions were adsorbed as a Stern layer on the particle surface so that the diffuse double layer potential (ψ_δ) was quite low.

Hunter and Alexander (1963b) calculated the zeta potential and surface charge density of kaolinite at pH 7.4 in mixtures of NaCl. Chloride ion was also adsorbed at pH 7.4, possibly by a physical process. It was assumed that the zeta potential was a direct measure of the Stern potential. They concluded that the adsorption of anions in acid solution was generally attributed to the existence of positive sites because of broken bonds on the edges of the crystal. Zeta potential increased with increasing NaCl concentration in the kaolinite solution. They assumed that the changes in zeta potential represent changes in the double layer potential (that is $\zeta=\psi_\delta$). They implied that the shear or slipping plane was in the double layer at some small distance from the particle surface. Chlorite ions were adsorbed onto the clay surface. Because the positive charges on the crystal edges existed in acid solution and also chemisorption occured in acid solution.

Cremers (1968) examined the electrical conductivity of clay water systems in terms of a formation factor and surface conductivity. Surface conductivity values were obtained for montmorillonite, kaolinite, and illite. He used the double layer theory and surface conductivity values to estimate the potential at the slipping plane. The zeta potentials obtained from surface conductivity were consistent with a slipping plane at 4-7 Angstrom from the clay surface, the commonly accepted value for the thickness of the Stern layer. He found that zeta potential and the distance of slipping planes from the clay surface increased with decreasing NaCl concentration of montmorillonite with the constant surface charge density of 1.35×10^{-7} meq/cm^2. Specific results of this work is tabulated below:

Clay	NaCl conc. (N)	$\sigma\times10^{-7}$ (meq/cm2)	ζ (mV)	l (Angstrom)
Illite	0.02	1.50	-88	4.0
Bentonite	0.02	1.10	-78	5.0

σ=surface charge density, ζ=zeta potential, l=distance of slipping plane from the clay surface.

Yong and Sethi (1977) studied the basic mechanisms of dispersive clays with swelling or repulsive forces. They measured the turbidity and zeta potential of dispersive clays. The light transmittance technique was used to measure the turbidity.

The adsorption and desorption measurements of the suspensions at various low salt concentration indicated that the desorption of the adsorbed ions from the clay surfaces contributed to clay dispersibility through increases in the double layer thickness.

Chernoberezhskii (1982) studied the zeta potential of some clay minerals. He found that kaolinite had a zeta potential of -14.5 at pH 8.44, bentonite had a zeta potential of -18.9 at pH 7.8 and quartz had a zeta potential of -64.2 at pH 5.84.

Thompson and Pownall (1988) investigated the electrical state at the calcite aqueous solution interface using a streaming potential method applied to systems contaning no gas phase. They set up relationship between the zeta potential and solution pH. The formation of new surface material which modified the physical and electrical properties of calcite crystal surfaces seemed to be a common feature of aqueous calcite dispersions.

Xu and Yoon (1989) studied the coagulation behavior of silica samples using the classical Derjaguin Landau Vervey and Overbeek (DLVO) theory. It had been found that this theory was applicable to weakly hydrophobic solids but not to strongly hydrophobic ones. They showed that natural silica samples did not coagulate at any pH. This was difficult to explain on the basis of the DLVO theory. However, methylated silica coagulation occured over a wide pH range extending up to pH 10.7. At this pH, the zeta potential was as high as -51 mV. These findings suggested that there was a strong hydrophobic interaction force which was not considered in the classical DLVO theory.

Siffert et al. (1990) established a relationship between the electric charge and the stability of heavy oil distillation residues dispersed in organic medium. The origin of the electrical charge is a consequence of an electron transfer between the organic solid particles and the liquid organic phase. He concluded that the zeta potential strongly dependend on the electron donor and acceptor numbers of the dispersing medium. The stability of heavy oil distillation residues was given by the electrical charges on the surface of the particles.

2.3. MICROSTRUCTURE

Sediment microstructure is a function of the fabric and the physico-chemistry of the clay water system. Clay fabric is the orientations and arrangements of the particles. Investigation of original clay fabric can help to understand the effect of contaminants to the sediments and also to determine certain sediment properties.

Lambe (1953) showed the microstructure of some clays and suggested card-house fabric in a marine clay. Tan (1958) showed a network of edge-to-face oriented clay particles in clayey sediments. Rosenqvist (1959,1963) published electronmicrographs of undisturbed marine Oslo Blue clay. He supported the validity of the card-house arrangement in undisturbed sediment. Push (1962,1966,1968) studied the soft natural clays in the electron microscope and concluded that the structure of flocculated sediment is characterized by a network of large particles tied together by small particles arranged in groups or chains.

Bowles (1968) studied marine sediment from the Gulf of Mexico and showed that the microstructure of undisturbed marine sediment resembled a card-house or a honeycomb arrangement. Bowles, et.al (1969) suggested that unconsolidated sediments are also composed of packets of parallel oriented particles.

O'Brien and Harrison (1969) investigated a sensitive Pleistocene clay from the St. Lawrence river valley. The illitic clay had been deposited in a saline marine environment causing salt flocculation and resulting in a fairly random open structure. O'Brien (1970) showed that the fabric of uncompressed illite floccules formed under saline and salt-free conditions in the laboratory consisted of an open porous network mainly consisting of randomly oriented domains with face-to-face flocculated flakes.

Sides and Barden (1970) demonstrated that as the average clay particle size is reduced and the colloidal activity increased, the chemical additives became more effective in producing dispersed and flocculated structures. Thus the chemical additives had little visible effect on the structure of kaolinite clays whereas they did in illitic clays. In the case of montmorillonite clays definite conclusion could not be reached.

O'Brien showed (1971) that the repulsive forces between the kaolinite particles seem to be minimized so that the particles can attract each other in a face-to-face manner under conditions of either a large clay concentration in distilled water or low clay concentration in an electrolyte solution. O'Brien (1968) also investigated a consolidated Pennslyvania shale. Illitic clay was formed in a dispersing environment caused by the presence of organic material. Clay structure was highly oriented parallel to the horizontal bedding planes.

Lanier and Jones (1979) showed that sediment concentration (54g and 90 g/900l) and water salinity (0-5.4%/900ml) strongly influenced the flocculation and orientation of kaolinite clay sedimented under laboratory conditions. They correlated the development of grain aggregates and subsequent aggregate-to-aggregate orientations with increasing fluid salinity.

Pamukcu et al., (1990) studied the influence of municipal sludge, fuel oil, and flyash on the microstructure of consolidated and sedimented systems of pure clays. The sludge appeared to cause the formation of clay flocs and coating of these flocs with organic material. Specimens mixed with fuel oil exhibited loose and open microfabric.

Quigley and Fernandez (1990) studied the scanning electron photomicrographs which were obtained on specimens molded with water, alcohol, and benzene. The water compacted sample showed a clay platelet parallelism characteristic of dispersion whereas both the alcohol and benzene molded clays were highly flocculated and characterized by macropores that were especially well developed in the case of benzene.

2.4. GEOTECHNICAL PROPERTIES

The knowledge of clay microstructure indicates that the geotechnical properties of soft clayey sediments depend on the fabric, the particle contacts, and physicochemistry. Bennett et al. (1977) showed that the geotechnical properties of sediments can be related to fabric. Complex interrelation between sediment behavior and environmental effects can be understood through fabric.

Soil structure changes under different environmental conditions. Interparticle forces significantly changes the geotechnical properties of soils. Any changes in the soil-water system influence the double layer thickness and therefore effect the geotechnical properties. For example, the following changes usually reduce the shear strength of a clay (Lambe 1959): 1) Decrease of electrolyte concentration 2) Increase of dielectric constant of pore fluid 3) Adsorption of anions 4) Increase of pH of the pore fluid 5) Increase in water content Geotechnical properties such as Atterberg limits, shear strength, permeability, compressibility depend on the pore fluid composition. Pore fluid composition affects diffuse double layer thickness which decreases with increasing electrolyte concentration and increasing cation valence, and cation exchange capacity.

Ballou (1955) investigated the electroosmotic flow of water in kaolinite clay as a function of adsorbed counter-ion and the water content of the systems. He showed the aplicability of hydraulic permeability with the Helmholtz-Smoluchowski electrokinetic equations.

Mesri and Olsen (1971) studied the permeability of clays with polar and non-polar permeating fluids. They found coefficients of permeability of illite, kaolinite, and montmorillonite in water. The illite was about 200 times more pervious than the montmorillonite, and the kaolinite was about 200,000 times more pervious at the same void ratio. The permeability of montmorillonite was about 10^{-11} cm/sec, kaolinite was about 10^{-6} cm/sec, and illite was about 10^{-9} cm/sec, all at void ratio of 2. They indicated that the coefficient of permeability are largest for non-polar liquids, smaller for polar fluids of low dielectric constant and lowest for water which is polar and has a high dielectric constant. Reduction of electrolyte concentration tended to reduce the coefficient of permeability. However, the effect of electrolyte concentration vanishes as the valency of the cations increases. They also showed that the coefficient of permeability of the clays was the largest for benzene and tetrachlorite. When a fluid such as alcohol was used, the fluid was adsorbed either by the cations by the formation of hydrogen bonds with the surface and part of the flow channels was to be blocked which resulted in reduced permeability. However, all the clays had the same permeability, at around $10^{-5.5}$ cm/sec, at void ratio of 2 when non-polar fluids were used. This attributed to negligible adsorption of nonpolar fluids and no formation of diffuse double layer. The clay particles in non-polar fluids are randomly arranged in aggregates which are probably more or less spherical in shape. When the pore fluid is water, it is believed that aggregates of parallel particles, domains, are formed. In case of Ca-montmorillonite the water is adsorbed between the layers.Because the layers can not swell sufficiently to form diffuse double layers.

Koutsoftas and Fischer (1980) showed that at a given consolidation stress, overconsolidated specimens had higher shear modulus than normally consolidated specimens. The shear modulus was strongly influenced by the magnitude of the maximum past pressure and secondary compression.

Green et al. (1981) showed that hydrophobic or hydrophilic nature of the solvent was important to predict the solvent's rate of flow through clays. They also found that bulk density of clay was important to determine permeability of clay under a given solvent. Finally, they concluded that the effect of organic solvents on the coefficient of permeability might be estimated from the dielectric constant of the solvent and bulk density of the clay. They derived the following emprical relationship to estimate the coefficient of permeability:

$$\log k=1.17(\log(D^{0.75}/d^{7})) - 7.23$$

where, D is the solvent dielectric constant and d is the bulk clay density (g/cm^3)

Chassefiere and Monaco (1983) studied the Atterberg limits of marine sediments collected in the Mediterranean Sea. They found that the liquid limit and plasticity index determined by using salt water showed a variable drop compared to that of distilled water one.

Heath and Tadros (1983) investigated some characteristics of Na-montmorillonite dispersions as a function of pH and electrolyte (NaCl) concentration. Shear modulus of the clay increased with increasing electrolyte concentration. This was attributed to the reduction of double layer repulsion. If the shear wave velocity is related to changes in microstructure, the rate of shear wave velocity change should decrease with time. When primary consolidation is completed, shear wave velocity increases because of decreased particle spacing and higher particle contact stresses with rearrangement of particles.

Fernandez and Quigley (1985) determined the hydraulic permeability of natural Sarnia soils mixed with pure liquids at a void ratio of 0.8 yielded k values that increased from 5×10^{-9} to 1×10^{-4} cm/s as dielectric constant of the permeant decreased from 80 to 2. The higher values of permeability with lower dielectric constant were attributed to macropores between flocculation peds and double layer contraction. They calculated the double layer thickness assuming all chemical variables were held constant except D (dielectric constant) and plotted as a function of surface potential. They found that the double layer thickness of monovalent clay in a dilute water system (D=80) was 100 nm and for D=2 itwas 15 nm. On the basis of Gouy theory and the observed fabric of the soils, they concluded that for a given void ratio the high permeability directly related to low dielectric constant values which cause double layer contraction. From electromicrographs they also concluded that the benzene moulded samples are highly flocculated and contain large macropores compared to more dispersed water molded sample.

Bowders and Daniel (1987) permeated four organic chemicals through compacted specimens of kaolinite and illite-chlorite. They used methanol, acetic acid, heptane, and trichloroethylene as organic chemicals. Dilute organic chemicals had little affect on the hydraulic conductivity.

Acar and Olivieri (1989) investigated the effect of organic fluid permeation on the fabric of compacted clay. Consistency limit and free-swell tests on kaolinite, Ca-montmorillonite, and Na-montmorillonite with organic molding fluids indicate that the dielectric constant and the pH of the pore fluid strongly influence their interaction in these clay minerals. There was a significant decrease in hydraulic conductivity of kaolinite and Ca-montmorillonite when low solubility of organic fluids used.

Jose et al. (1989) conducted laboratory tests on compacted marine sediments to study the effect of salt concentration of permeating fluid on its permeability characteristics. They found that the permeability increased with increasing salt concentration at a given void ratio. Two clay particles begin to repel each other when their double layers come to contact each other. Increased electrolyte concentration depress the double layer which then promotes flocculation.

Muller-Vonmoos and Loken (1989) studied the shear behavior of kaolinite, illite and montmorillonite. They showed that the relatively high shear strength of kaolinite comes from the intergranular friction. The shear behavior of illite depended strongly on the counter ions. The shear behavior of montmorillonite was determined by the force by which the layers are held together.

Weiss (1989) studied about sealing of waste disposals by clays. He concluded that heavy metal ions and highly charged cations contracted the interlayer space of swelling montmorillonites and thus increased permeability.

Wetzel (1990) gave the following relationships between the Atterberg limits and specific surface area:

$$LL = 1.01\ S_g + 46.5, \qquad LL > 50$$

$$PL = 0.43\ S_g + 13.5, \qquad PL > 20$$

Where,

LL is the liquid limit, PL the plastic limit and S_g the specific surface area.

CHAPTER 3

MATERIALS AND METHODS

3.1. MATERIALS

In this section, the materials used for this study are investigated. Certain properties of clays, salt water, municipal sludge and crude oil are presented.

3.1.1. Clays and Saline Water

The major components of marine sediments are a complex mixture of different clay minerals with different properties. Several investigators have analyzed numerous samples collected from the major oceans around the world to estimate the relative distribution of major groups of clay minerals (Griffin et al., 1968; Rateev et al., 1968). The most common groups of clay minerals found in the marine environment are illite, montmorillonite, kaolinite and chlorite.

The distribution of clay minerals in the world oceans is closely related to geographical climate. Some of them, such as kaolinite and montmorillonite are formed in the zone of development of tropical lateritic soils. Others such as illite and chlorite are formed mainly in the soils of moderate and high latitudes.

Marine clay used in this study was prepared artificially mixing 50% illite, 21% Ca-montmorillonite, 16% kaolinite and 13% chlorite by weight. The percentages of clay minerals in the marine clay were based on average percentages of these clay minerals typically found in Atlantic Ocean clays (Emery and Uchupi, 1984). A summary of geotechnical and physico-chemical properties of these clays are gpresented in Tables 3.1, 3.2 and 3.3, respectively. Particle size distribution and specific gravity are presented in Table 3.1. Atterberg limits is presented in Table 3.2, and physico-chemical properties in Table 3.3.

3.1.1.1. Illite

Illite is a general term for the mica group of clay minerals that occur in many soils. The wide occurance of illite is probably a function of the abundance of muscovite micas in many coarse grained siliceous source rocks and its resistance to chemical weathering. Illite is one of the most abundant clay minerals present in marine sediments where it often composes 50% of the total sediment.

Illite is composed of a three- layer (2:1) structural sheets with potassium ions between the layers. A three-layer structural sheet consists of an octahedral sheet (alumina sheet) in the middle with one tetrahedral sheet (silica sheet) at the top and one at the bottom. The sheets are about 9.6 Angstrom thick. The small clear spacing between sheets (0.76 Angstrom) indicates that the potassium ions (radius=1.33 Angstrom) rest partially within the adjacent sheets. Potassium ions satisfy the charge deficiency and hold the illite sheets by ionic forces. They are distinguished from the montmorillonites primarily by the absence of interlayer swelling with water. Interlayer bond in illite is strong and water and other liquids are normally unable to penetrate between the layers.

Illite clay for this study was obtained by crushing 95% illite bearing shale from Fithian, Illinois, to passing No.100 sieve size. Illite, whose micelles are tightly bonded by potassium ions, has a moderate surface and edge-bond cation exchange capacity (CEC) ranging between 10 to 40 meq/100grs of dry clay. It can be seen from the x-ray diffraction spectrum in Figure 3.1 that illite clay used in this study is a complex of silica, aluminum, potassium and iron.

3.1.1.2. Ca-Montmorillonite

Ca-Montmorillonite is a typical weathering product of volcanic ash on both land and ocean floor. Montmorillonite is a clay mineral whose particles are relatively small, thin and filmy. The clay mineral is composed of three-layer structural sheets with water and exchangeable cations between the layers. The sheets are about 9.6 Angstrom thick. calcium is the predominant ion balancing charge on the alumina silicate lattice of the clay particles. Ca-Montmorillonite clays do not swell and respond less sensitively to changing water contents than Na-Montmorillonite clays. The magnitude of the attractive forces and their dependence on surface charge prevent Ca-clay crystals from swelling extensively. Its simplest form is $Ca{*}Al_2O_3{*}5SiO_2{*}nH_2O$. It can be seen from the x-ray diffraction spectrum in Figure 3. 2 that Ca-Montmorillonite has silica, aluminum, calcium and iron. Ca-Montmorillonite has considerable electrical unbalance in the crystal lattice and loosely held ions on its layer surfaces and between layers are rather easily displaced. Its CEC ranges from 60 to 100 meq/100grs of dry clay.

3.1.1.3. Kaolinite

The kaolinite clay mineral is a product of intense weathering of feldispathic rocks in high temperature, high rain fall regions. Particles of kaolinite are relatively large, thick and stiff. Kaolinite abundance ranges from 10 % to 20 % (average 15 %) of the total marine sediment. In kaolinite clays the pH may be the single most important factor controlling the fabric of sediments formed from suspension. Kaolinite is composed of a two-layer (1:1) structural sheet. A two-layer structural sheet is a combination of a silica sheet with an alumina sheet. The sheets are about 7.2 Angstrom thick. The linkage between adjacent sheets in a kaolinite crystal is hydrogen bonding.

The cation exchange capacity (CEC) is rather low because of the extremely small degree of isomorphous substitution. The crystal lattice of kaolinite clay is electrically balanced with a CEC largely along broken edge bonds. Its CEC ranges from 3 to 15 meq/100grs of dry clay. The cations are located on the exterior surfaces and the particles are thick. Kaolinite particles remain intact in natural aqueous medium. Because the hydrogen bonds between layers hold them together firmly. Its simplest form is Al_2O_3*$2SiO_2$*$2H_2O$.

3.1.1.4. Chlorite

Chlorite is an unstable clay mineral found where erosion is predominantly mechanical rather than chemical. Latitudinal dependence is strong and high concentrations of chlorite are found at high latitudes only when chemical weathering processes are less important than mechanical. Chlorite ranges from 10 % to 18 % (average 13 %) of the total marine sediment.

Chlorite clay minerals are found in high concentration both in the alluvial soils and in marine sediments. The chlorite minerals occur throughout the silt range. Chlorites are structurally related to the four-layer (2:1:1) sheets with a brucite sheet (magnesia sheet) between the layers. The sheets are 14 Angstrom thick. The x-ray diffraction spectrum in Figure 3.3 shows the constituents of chlorite clay mineral. Chlorite clay mineral consists of silicate, aluminum, magnesium and iron. Its simplest form is $3MgO$*Al_2O_3*$2SiO_2$*$3H_2O$. Its CEC ranges from 10 to 40 meq/100grs of dry clays.

3.1.1.5 Saline Water

Saline water was used in a number of experiments. The saline water solution was made by mixing a commercial product called "instant ocean" with tap water. The resulting solution had typical salt concentration of 38 g/l. Saline water was used to simulate the physico-chemical prospective of marine pore water. The pH of the resulting salt solution was measured 8.2. The contents of "Instant Ocean" product is listed in Table 3.4.

TABLE 3. 1. Particle Size Distribution and Specific Gravity of Clay Minerals.

Clay Mineral	Particle Size Distribution			Specific Gravity
	fine sand (%)	silt (%)	Clay (%)	
IILLITE	5	65	30	2.72
Ca-MONT.	4	66	30	2.50
KAOLINITE	0	8	92	2.60
CHLORITE	5	85	10	2.69
MARINE CLAY *	5	70	25	2.59

*Marine Clay=Illite (50%)+Ca-Montmorillonite (21%)+Kaolinite (16%)+Chlorite (13%)

TABLE 3.2. Atterberg limits of Clay Minerals.

Clay Mineral	Liquid Limit, LL (%) (measured/literature)	Plastic Limit, PL (%) (measured/literature)	Plasticity Index, PI (%)
ILLITE	31	20	11
Ca-MONT.	87/88[1]	58/54[1]	29
KAOLINITE	70/64[1] 69[2]	31/34[1] 31[2]	39
CHLORITE	---	---	Non-Plastic
MARINE CLAY	57	32	25

[1] Acar and Olivieri (1989); [2] Lagaly (1989)

TABLE 3. 3. Selected Physico-Chemical Properties of Clay Minerals.

Clay Mineral	Specific Surface Area (m^2/g) (measured/literature)	Cation Exchange Capacity (meq/100 g dry clay) (measured/literature)	Dielectric Constant (1mhz) (measured/literature)
ILLITE	22/80 - 100 [1]	20.1/10 - 40 [1]	8.92/9 - 10 [4]
Ca-MONT.	120/85 - 160 [2]	59/60 - 100 [3]	11.91/11.9 [1]
KAOLINITE	18/10 - 20 [1]	2.9/3 - 15 [1]	8.94/5 -12 [4]
CHLORITE.	6/5 - 50 [1]	6.9/10 - 40 [1]	7.65/7.9 [4]
MARINE CLAY	37/40 [5]	22/23.8 [5]	8.29/9.38 [5]

[1] Grim (1968); [2] American Petroleum Institute (1951); [3] Boyes (1975); [4] Olhoeft (1981);
[5] Calculated weighted average.

Example: 40=22x(%50)+120x(%21)+18x(%16)+9.6x(%13).

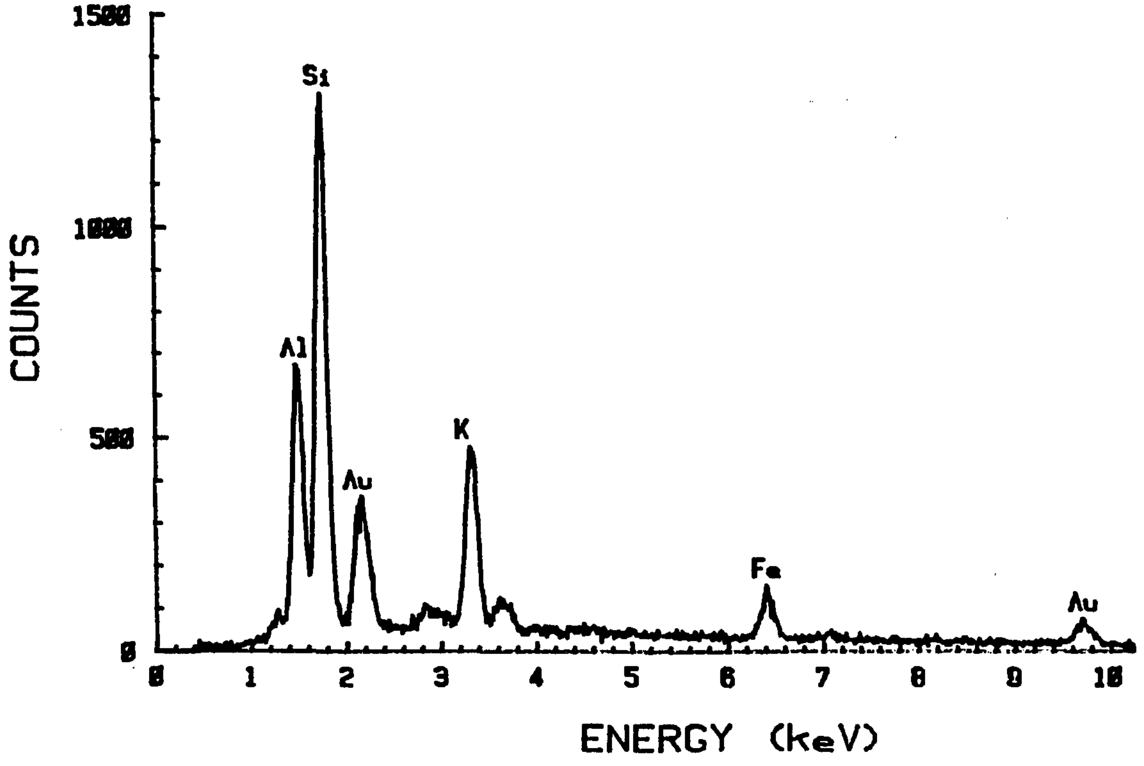


Figure 3.1. X-Ray Diffraction Spectrum (EDS) of Illite Clay Mineral.

TABLE 3.4. The Content of "Instant Ocean".

Major Ions	ppm
Cloride (Cl^-)	18.726
Sodium (Na^+)	10.374
Sulfate (SO_4^{--})	2.596
Magnesium (Mg^{++})	1.274
Calcium (Ca^{++})	429
Potassium (K^+)	387
Bicarbonate (HCO_3^{---})	197
Borate (BO_3^{---})	53.7
Strontium (Sr^{++})	10.2

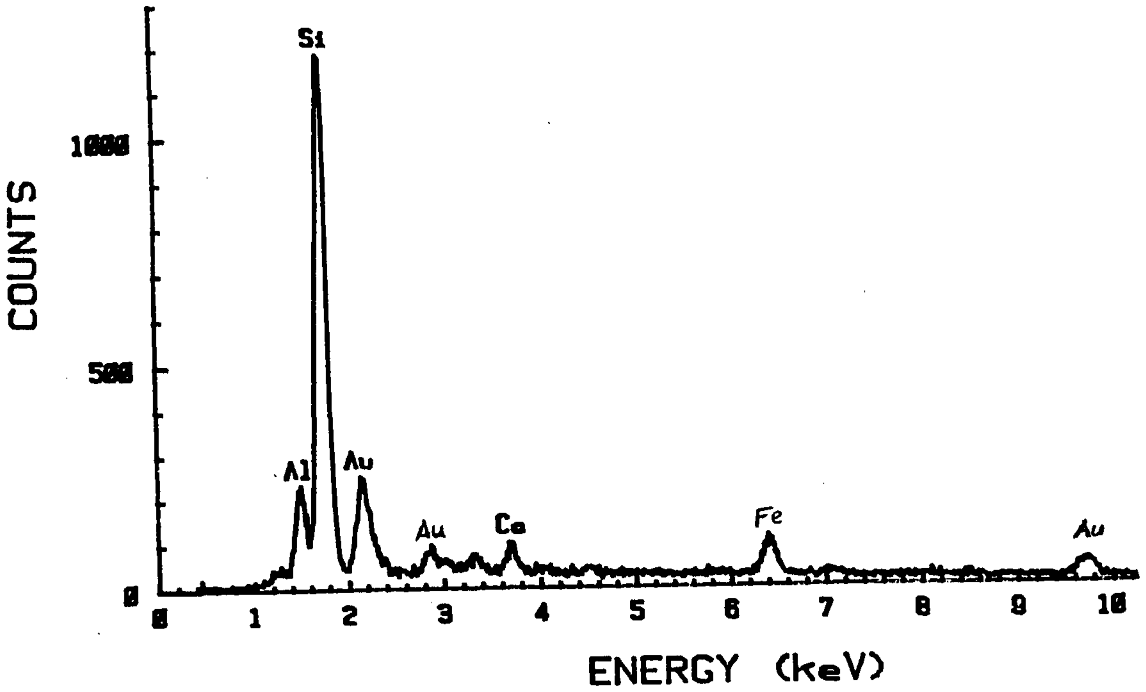


Figure 3.2. X-Ray Diffraction Spectrum (EDS) of Ca-Montmorillonite Clay Mineral.

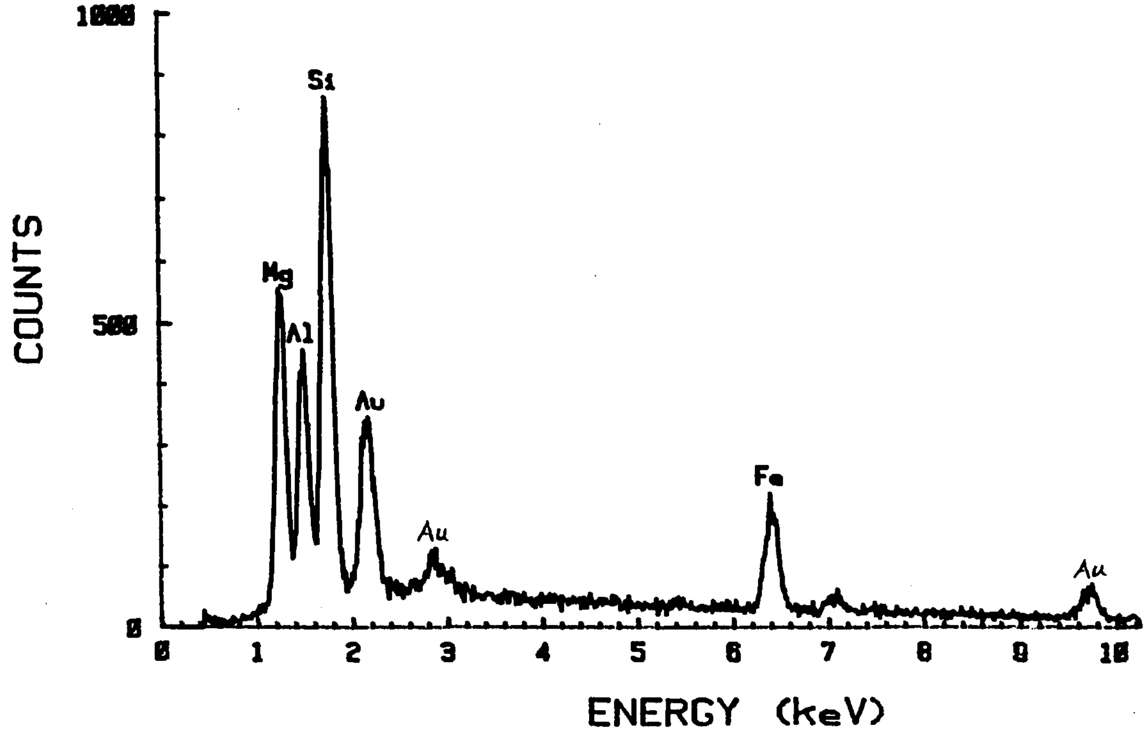


Figure 3.3. X-Ray Diffraction Spectrum of Chlorite Clay Mineral.

3.1.2. Contaminants

The contaminants were selected among the common products that have been disposed or spilled into the marine environment in the past and those that are being permitted for disposal presently. The most important sources of pollutants to the ocean are from municipal discharge and discharge of oil from ships, tankers and frighters. Therefore the selected contaminants included municipal sludge and crude oil.

3.1.2.1. Municipal Sludge

Sewage sludge, a concentrated semi-solid material resulting from sewage treatment, is often disposed of in the ocean. In this study, anaerobically digested sludge was obtained from the Allentown, Pennslyvania Waste Treatment Plant at Kline's Island. Raw sludge is obtained from sewage systems around the city. The raw sludge is then treated biologically to flocculate individual particles. The particles are allowed to settle. The liquid is then removed using trickling filters. The remaining block mass composed of fibrous solid particles in suspension is the digested sludge. A summary of the selected properties of this material is presented in Table 3.5.

3.1.2.2. Crude Oil

One of the most common pollutants in the marine environment are petroleum hydrocarbons in the form of crude oil. The crude oil for this study was obtained from J.C. Haab Co., Inc., in Philadelphia. In recent years there has been a great interest dealing with the influence of oil on marine sediments. Crude oil is a form of hydrocarbon which is immiscible with water and chemically inactive. Selected properties of the crude oil used in this work are given in Table 3.6.

TABLE 3.5. Properties of Anaerobically Digested Municipal Sludge.

Specific Surface Area	: 4.6 m^2/g
Cation Exchange Capacity (CEC)	: 134 meq/100 g dry sludge
Surface Charge Density	: 28 Coulomb/m^2
Zeta Potential (ζ)	: - 1.4 mV
Electrical Conductivity	: 5869 micro Simens/cm
Water Content	: 93 % (by dry weight)
Total Solids	: 7.0 %
Volatile Solids	: 73 %
pH	: 7.6
Heavy Metal Content:	**(ppm)**
Copper	: 1000-1139
Zinc	: 992-1147
Chromium	: 272-360
Manganese	: 201-243
Lead	: 122-185
Nickel	: 26-37
Cadmium	: 4.3-6
Cobalt	:0-4

TABLE 3.6. Selected Properties of A Typical Crude Oil.

Hydrocarbon Content	: 93 % [C (81%) and H (12%)]
API Gravity	: 11
Viscosity	: 173 sec.
Ash Content	: 6 %
Flash Point	: 185 °C
Pour Point	: 35 °C
Sulphur Content	: 0.93 %
Sodium Content	: 16.9 ppm
Vanadium Content	: 68 ppm

3.2. METHODS

3.2.1. Sedimentation Tank

In the laboratory sedimentation tanks were used to prepare marine sediment specimens. The experimental set up consisted of 6 rectangular sedimentation tanks. The sedimentation tanks were made up of translucent plastic sheets of 0.5 cm thickness. They were 0.3 m by 0.3 m in cross section and 0.6 m in height. They were equipped with sampling ports at 0.15 m intervals vertically. A schematic diagram of the sedimentation tank is shown in Figure 3.4.

3.2.2. Sample Preparation for Sedimentation

Typical Atlantic Ocean marine clay was prepared by mixing 50 % of illite, 21 % of Ca-montmorillonite, 16 % of kaolinite and 13 % of chlorite by dry weight. This clay was then mixed with saline water to prepare a slurry. The contaminants were mixed into the slurry in proportions of 5 % and 10 % by dry weight of the clay mixture. They were premixed into the marine clay with saline water to make a slurry.

3.2.3. Testing Procedure

The slurry of the manufactured marine clay and contaminant mixture was poured into the sedimentation tanks and mixed thoroughly with a tall hand-held mixer. The amount of solids in the mixture was controlled to attain a predetermined concentration when the level of the water in the tank was brought to a set level. The solids were allowed to settle under gravity until little variation was observed in the rate of settlement of the clay/water interface.

Settlement was measured by observing the downward movement of the clay water interface. When the interface was vague, the downward movement of a region, identified as the boundary, was observed. Samples were collected from the sampling ports periodically to determine the slurry concentration and other depositional properties. Finally, at the completion of settlement, water above the interface was drained through the sampling ports and undisturbed samples of the sediment were obtained. Samples were obtained by inserting a thin walled PVC tube into the sediment. Vacuum was applied at the end of the tube until the tube was retrieved and set on a flat surface. This process helped to retain the semi-solid sediment in the tube with minimum disturbance.

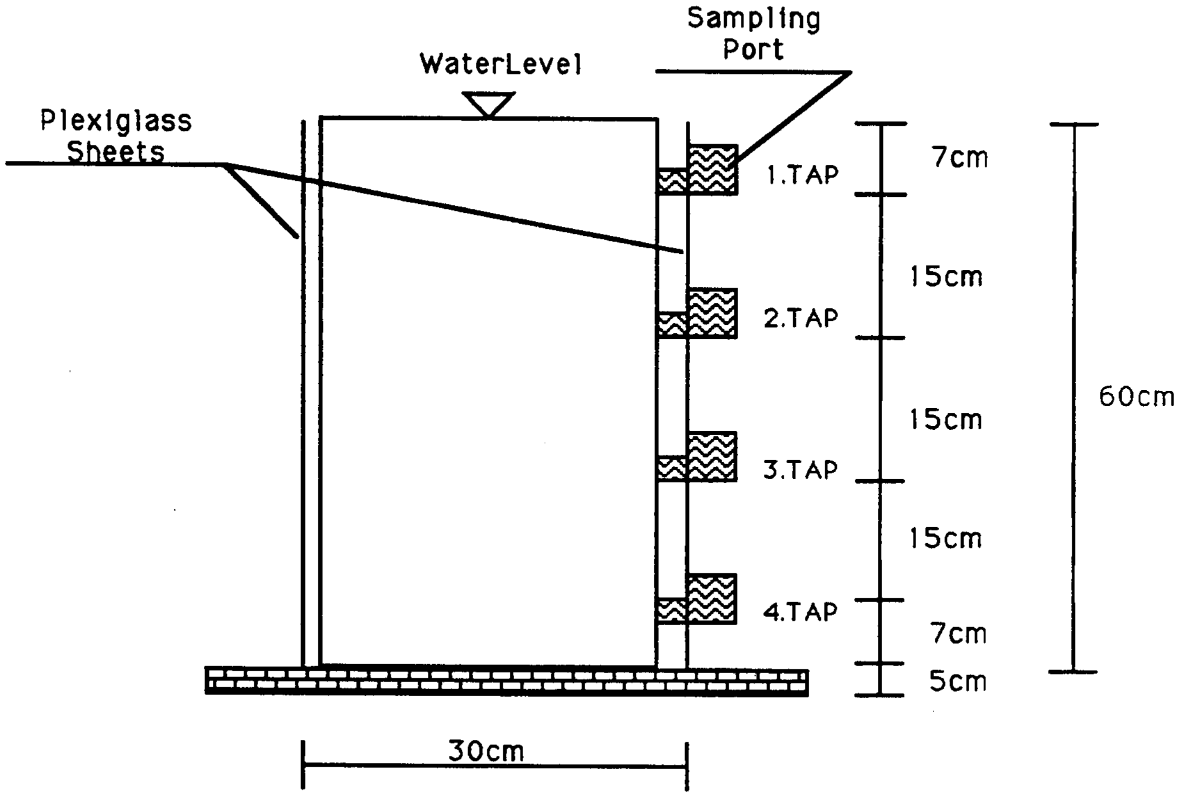


Figure 3.4. A Schematic Diagram of the Sedimentation Tank.

3.2.4. Preparation of Samples for Electron Microscopy

The undisturbed samples retrieved from the clay sediment were used to prepare specimens for scanning electron microscope (ETEC AUTOSCAN SEM) analysis. Preparation of a clay specimen for SEM involves complete drying of samples. Many clay soils show considerable volume decrease when air-dried and the fabric is affected by shrinkage. Therefore, clay samples were dried by employing "critical point drying method", (CPDM).

3.2.4.1. Drying Methods

Air-drying, oven-drying and freeze-drying clay specimens distort the fabric (Yong,1972 and Naymik,1974). Yong (1972) showed that air-dried montmorillonite clay samples had corn flake structure which was observed from photomicrographs. The clay flakes curl because of the surface tension at the fluid vapor interface. Naymik (1974) showed clearly that a large reduction of pore volume occured during air-drying and artifacts of drying formed during freeze drying. He found that the critical drying method was the most efficient method among them. He reported that there was no desiccation shrinkage in the samples by the critical point technique.

Luyet (1961) observed that ice crystals formed to some degree during the freeze drying process. Bound water sometimes do not freeze but dried at low temperature. This behavior contributes to a type of pseudo-freeze-drying.

Gillot (1969) discussed critical point drying and freeze drying methods for clay samples. He said that artifacts might be formed by ice crystallization during freeze drying which damages the original fabric. He also observed that clay fabric would be affected by shrinkage during air-drying.

O'Brien (1970) dried moist, unconsolidated, flocculated clay sediment by utilizing the freeze-drying method. He showed that this technique was better than air-drying procedures.

The freeze drying method was the most satisfactory technique for preparing clay samples for electron microscopy before the development of the critical point drying technique (Bennett and Hulbert, 1986).

3.2.4.2. Critical Point Drying Method (CPDM)

The critical point drying method (CPDM) is used for biological applications to preserve membrane tissues for electron microscopy (Hayat and Zirkon, 1973). Kistler (1932) used this technique for silica gel.

This method involves the replacement of pore fluid from water to liquid CO_2 as described by Anderson (1951) and Cohen et al. (1968). At a temperature and pressure above a critical point the physical properties of a liquid and its vapor become indistinguishable. The two phases are therefore no longer separated by a boundary layer and the surface tension forces vanish. Gillot applied this technique successfully to clay sediments using both alcohol and CO_2 for crtical point drying. Bennett (1976) used the CPDM technique, followed by sample impregnation with very low viscosity epoxy resin (SPURR) under vacuum to prepare samples for Transmission Electron Microscope (TEM) analysis.

At the critical temperature and pressure of a liquid, there is no boundary between the liquid and gas phase. When the temperature is held above the critical point, the gas may be released until atmospheric pressure is reached. Thus the sample is dried without having surface tension effects which is harmful for the clay fabric space. Acetone, alcohol, and amyl acetate are used as transition liquids. It is necessary to introduce these liquids between the aqueous phase of the sample and the liquid CO_2.

Marine clay specimens were dried by using Critical Point Drying Appratus (CPDA) with liquid CO_2. Specimens were initially treated with ethyl alcohol and then acetone. A CPDA was used to replace the acetone with liquid CO_2. The critical point of CO_2 occurs at 36^oC and 1400 psi pressure. When the temperature is held above the critical point, the gas can then be released until atmospheric pressure is reached. Thus the specimen can be dried without having surface tension effects. The specimens were then kept in a high vacuum desiccator for extended periods of time to ensure removal of all the water from the pore space before SEM observation. These specimens were coated with gold prior to SEM analysis to provide conductivity. Then the specimens were observed on SEM.

3.2.4.3. Scanning Electron Microscopy (SEM)

The instrument used in this study was scanning electron microscope (ETEC AUTOSCAN SEM). The scanning electron microscope is designed to produce a magnified image of a surface. Some of the main advantages of the instrument are as follows: (1) large depth of focus at high magnifications, which gives considerable perspective to the image, (2) the surface of the specimen is examined directly, (3) specimen appears as three-dimensional image, (4) the resolution is 100 Angstrom and the magnification ranges from 5X to 240,000X from the surface of the specimen for more accuracy.

3.2.4.5. X-Ray Diffraction Spectrum (EDS)

X-ray spectrum analysis shows the distribution of chemical elements in the microanalyzer. The process of x-ray spectrum is as follows: x-ray microanalysis is based on electronic transmissions between inner atomic shells. An electron from a scanning electron microscope ejects an electron from an inner shell of a sample atom. The resulting vacancy is then filled by an electron from a higher energy shell in the atom. This vacancy filling electron must give up some of its energy, which appears in the form of electromagnetic radiation.The radiation appears as x-rays. When excited by electrons of sufficient energy, every element in a sample will send out a unique and characteristic pattern of x-rays. The number of x-rays send out by each element gives direct relationship to the concentration of that element.

Electronic components convert these x-ray emissions to analyzable data. They produce a digital spectrum of the emitted radiation. The x-ray first creates a charge pulse in a semiconductor detector. The charge pulse is then converted into a voltage pulse whose amplitude reflects the energy of the detected x-ray. Finally, the voltage pulse is converted into a digital signal, which causes one count to be added to the corresponding channel of a multichannel analyzer. The accumulated counts from a sample produce an x-ray spectrum like the one in Figure 3. 1.

3.2.5. Determination of Physico-Chemical Properties

In this section, procedures and methods used to determine: (1) CEC, (2) surface area, (3) pH, (4) organic matter content, (5) electrical conductivity, (6) total dissolved solids, (7) particle size distribution, (8) turbidity, (9) dielectric constant, (10) zeta potential are presented briefly.

3.2.5.1. Determination of Cation Exchange Capacity (CEC)

Cation exchange capacity (CEC) was determined by sodium saturation method (Chapman, 1965). First, clay specimens were saturated with sodium acetate to replace the cations held on the surface and in the interlayer positions. Secondly, clay specimens were washed with isoproply alcohol to remove of the excess saturating salt. Thirdly, clay specimens were washed with ammonium acetate, by which adsorbed sodium was released into the solution. The amount of sodium was then determined by an atomic adsorption spectrometer. All the measurements were made at pH=7.

3.2.5.2. Determination of Surface Area

Surface area was determined using a Monosorb Surface Analyzer. The analyzer operates by measuring the quantity of adsorbate gas adsorbed on a solid face by sensing the change in thermal conductivity of a following mixture of adsorbate and an inert carrier gas. Usually the adsorbate is nitrogen and the inert gas is helium. The theoretical basis upon which the monosorb operates is the Brunauer, Emmett and Teller theory (B.E.T. theory) (Brunauer et al., 1938). B.E.T. theory is one of the most universal applied procedures for determining surface area. This method requires the prior removal of sorbed gasses, usually heating the specimen before measuring the sorption isoterm for the non-polar gas, often nitrogen.

3.2.5.3. Determination of Ignitable Organic Matter Content

The organic matter contents of the mixtures were determined by the ignition loss method. Contaminated clay specimens were pre-dried at 110°C for 24 hours. These specimens were then burned at 550°C for 2 hours. The loss of weight of the specimen as the result of the second heating was assumed to be primarily due to organic matter ignition.

3.2.5.4. Determination of Zeta (ζ) Potential

In this study, MATEC ESA-8000 system was used to measure zeta potential, conductivity and pH of the laboratory prepared marine clay suspensions. The MATEC ESA-8000 system can characterize colloidal suspensions by their electrokinetic sonic amplitudes (ESA). Measurements can be made in concentrated suspensions, up to 50 % by volume, and with particles ranging in size from 150 microns to moleculer dimensions. Measurements can be made in aqueous or non-aqueous systems as well. All measurements were made in a 250 ml capacity teflon beaker at 25 °C. After the sample was placed in the beaker, it was then mixed with a stirrer continually during measurements. Zeta potential, conductivity, pH and temperature were measured simultaneously throughout the experiments as the pH of the system was varied by adding concentrated acid or base.

3.2.5.5. Determination of Dielectric Constant

Dielectric constant measurements were made by using Impedence/Gain-Phase Analyzer (Hewlett-Packard Model 4194A). The HP 4194A features eleven impedence and four gain-phase measurement functions and covers a frequency range of 100Hz to 40 MHz for impedence, and from 10Hz to 100MHz for gain-phase.

A special container was made to measure the dielectric constant of slurry specimens. The container was made out of 0.3 cm thick, 1.9 cm by 2.5 cm arcylic sheets.

Two silver electrodes were placed into the container with a 0.7 cm distance as shown in Figure 3.5. Electrodes were connected to the analyzer with wires. Specimens were placed into the container between the silver electrodes to measure the dielectric constant. Dielectric measurements of suspensions were made at 100 Hz. When an alternating electrical field is applied to a clay-water-electrolyte system, a response is produced which can be measured in terms of a resistance, R, and capacitance, C_S. The measured value of the capacitance can then be converted into a quantity known as the dielectric constant, D. The following formula was used to calculate the dielectric constant;

$$D = \frac{C_s d}{A \varepsilon_0} = 2.775 \bullet C_s$$

where,

D = Dielectric constant

C_s = Capacitance, F

d = Length of a sepecimen, 0.7 cm

A = Cross-Section area of specimen, 2.85 cm^2

$\varepsilon_0 = 8.85 \times 10^{-14}$ F/cm

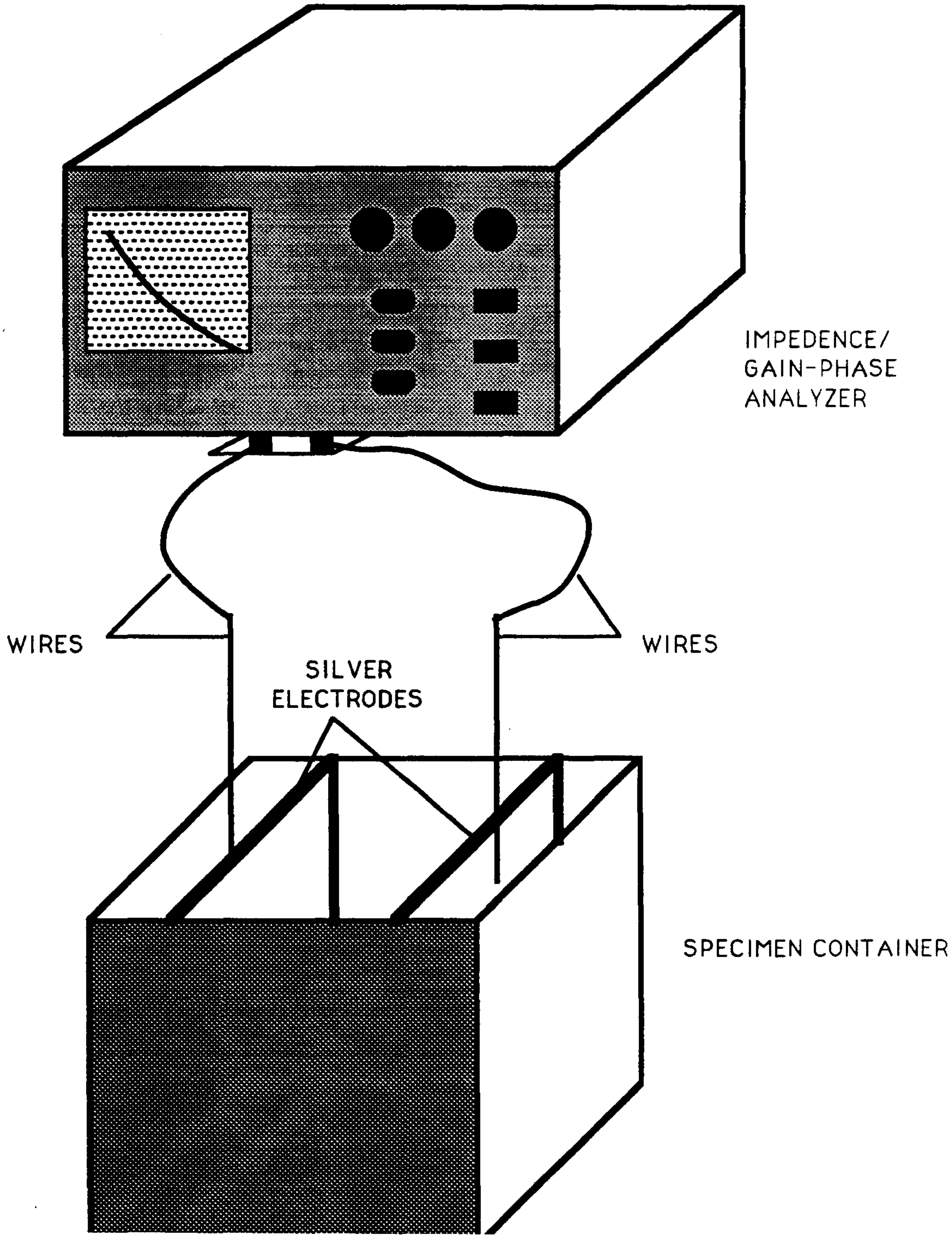


Figure 3.5. The Schematic of the Dielectric Constant Instrument.

3.2.5.6. Determination of Electrical Conductivity and Total Dissolve Solids (T.D.S.)

Conductivity and total dissolved solids (T.D.S.) of the suspensions were measured by Extech Model 695 Combined T.D.S. and Conductivity meter. Conductivity can be measured over 5 ranges for maximum accuracy and covers the range 0.1 to 200,000 microsimens/cm. T.D.S. ranges between 10 and 20,000 ppm.

3.2.5.7. Determination of Particle Size Distribution

Particle size of the suspension solids was determined by Particle Counter Model ILI 1000. This instrument is designed to permit inspection of bottled liquids without removing any of the contained liquid. A laser beam is provided to permit observation of small particles by near-forward light scatter. In addition, a scanning and detection system is provided to automatically quantify the number of small particles in one milliliter of the contained liquid. Particle size measurement is based on the amount of scattered light reaching the collection system. The laser inspection technique is very sensitive and permits observation of very small particles. This instrument uses basic light source of Helium-Neon laser (wavelength 632.8nm).

3.2.5.8. Determination of Turbidity of the Suspension

Turbidity was determined by turbidimeter Model 2100A. This instrument is a laboratory nephelometer calibrated for measuring turbidity in liquids. It is suitable for a broad range of turbidity measurement with ranges of 0-0.2, 0-1.0, 0-10, 0-100 and 0-1,000 Nephelometric Turbidity Units (NTU).

An intense beam of light is directed up through the bottom of a glass cell containing the test specimen. Light scattered by particles in the specimen is detected by a sensitive photomultiplier tube at a 90^{o} angle from the incident light beam. The amount of light reaching the photomultiplier tube is proportional to the sample turbidity. The photomultiplier tube converts the light energy into an electrical signal which is amplified and displayed on the instrument meter.

3.2.5.9. Determination of pH

pH of the suspensions was measured by pH meter (Fisher Model 900 Accumet). The pH of crude oil mixed marine clay and sludge mixed marine clay specimens was measured using special probes for oil (Beckman Electrode 39537 S006A) and for sludge (Beckman Electrode 39848 S002A).

3.2.6. Determination of Geotechnical Properties

In this section, determination of hydraulic permeability, shear strength and dynamic properties are given briefly.

3.2.6.1. Determination of Hydraulic Permeability of Marine Sediment

Permeability tests were performed using a flexible wall triaxial permeability system. Details of operation of this equipment is given elsewere (Evans and Fang, 1986). Specimens were normally consolidated under $1 kg/cm^2$ pressure. Tests were performed using saline water as the permeating fluid for saline water mixed marine clay mixtures.

3.2.6.2. Determination of Dynamic Properties of Marine sediment

Shear modulus and shear wave velocity were determined by piezoceramic bender elements (Dyvik and Madshus, 1986). The technique involves the use of piezoceramic bender elements at each end of a soil specimen. The bender element at one end of the specimen is used to generate a shear wave pulse which propagates along the length of the specimen and the other element is used to determine the arrival time of the shear wave. The travel time along a known specimen length produces a direct measurement of the shear wave velocity, V_S, and, in turn, shear modulus, G_S, for the soil. The travel time, t, of the shear wave is determined on the oscilloscope as the time difference between the rise of a square wave signal and first significant jump in the receiver signal. The shear wave velocity, V_S, for the soil can be calculated from the expression;

$$U_s = \frac{L}{t}$$

where,

L= the length of travel of the shear wave or
the length of the specimen
t= the travel time of the shear wave

The shear modulus, G_S, was then calculated from the expression;

$$G_s = \rho \bullet (U_s)$$

where ρ is the bulk unit density of the soil.

3.2.6.3. Determination of Shear Strength of Marine Sediment

Shear strength of the saturated soft laboratory prepared marine sediment was determined using the laboratory vane shear apparatus according to standard procedure of ASTM, D-2488. This apparatus includes the use of both conventional calibrated torque spring units and electrical motorized vane. The vane shear test consists of inserting a four rectangular bladed vane in the end of an undisturbed tube sample and rotating it at a constant rate to determine the torque required to cause a cylindrical surface to be sheared by the vane. This torque is then converted to a unit shearing resistance of the cylindrical surface area. The torque is measured by a calibrated torque spring that is attached directly to the vane. The shear strength can be determined by;

$$\tau = \theta \bullet R$$

where,

τ= Shear strength

θ=Deflection in degrees

R= Equipment constant

(function of spring, stiffness and vane size)

CHAPTER 4

BASE EXPERIMENTS

4.1. PHYSICO-CHEMICAL PROPERTIES OF CLAYS

4.1.1. Components of the Marine Clay

Four types of clay minerals were used in this study to make up the artificial marine clay. These are illite, Ca-Montmorillonite, kaolinite and chlorite. The composition of marine clay was 50 % illite, 21 % ca-montmorillonite, 16 % kaolinite and 13 % chlorite. Some physico-chemical properties of each of these minerals including the marine clay mixture were investigated and the results are presented here. The relationship between the measured specific surface area (SSA) and cation exchange capacity (CEC) based on data for illite, Ca-Montmorillonite, kaolinite, chlorite, and marine clay is given in Figure 4.1. A review of Figure 4.1 shows that increasing specific surface area relates to increasing cation exchange capacity. The greater specific surface area of Ca-Montmorillonite is due to its lattice expansion and exposure of internal surfaces, which is not so in the case of kaolinite. Measured specific surface area of illite is significantly less than the literature reported specific surface area of illite (literature reported values are given under chapter 3) . This is because the illite sample used in this work was obtained by on illite rich rock to -No 100 mesh size. Therefore, the particle sizes obtained may be larger than most naturally found illite clay. The CEC of kaolinite is rather low (around 3 meq/100g dry kaolinite) because of small degree of isomorphus substitution.

4.1.1.1. Illite

It can be observed from Figure 4.1 that the cation exchange capacity (CEC) of illite is smaller than that of Ca-montmorillonite, even though illites have a higher degree of isomorphous lattice substitution (van Olphen, 1963). This is probably due to the large size of illite particles used in here. ζ-potential versus pH relationship for illite is shown in Figure 4.2. When different concentrations of illite clay suspensions in distilled water are titrated with hydrochloric acid, the ζ-potential vs pH curves intersect at or very close to a common pH point around 4. Initial ζ-potential value of illite is around -80 mV at pH 9.5. Clays with high ζ-potential contain easily exchangeable ions. According to ASTM D-4187 Standart Test Methods for Zeta Potential of Colloids in Water and Waste Water, if a colloidal solution has a ζ-potential more than -60 mV, its stability is ranked excellent stability. According to Riddick (1968), the stability characteristics of the illite solution may be termed as excellent.

Illite is slightly soluble in acids. When acid is introduced, it appears that the alkaline earths are removed more rapidly than the aluminum or iron (Grim, 1968). When the solution pH increases ζ-potential of the solution also increases. The ζ-pH curves show an inversion as pH decreases. This phenomena is attributed to "anion adsorbtion". This phenomenon will be explained in more detail under the section on marine clay. Conductivity increases with decreasing solution pH as shown in Figure 4.3.

4.1.1.2. Ca-Montmorillonite

The ζ-potential versus pH relationship for Ca-montmorillonite is shown in Figure 4.4. A review of ζ-potential is shown to decrease to a minimum value at approximately a pH of 2.0. After that the curve raised to an asymptotic at a ζ=12 mV. As the concentration of solids increases, ζ-potential decreases. Coughanour and Utter (1944) showed that the ζ-potential decreases with increasing particle size and clay concentration. At the begining ζ-potential of Ca-montmorillonite is around -15 mV at pH 5.5. According to ASTM D-4187 Standart Test Methods for Zeta Potential of Colloids in Water and Waste Water, its stability is incipient instability. According to Riddick (1968), the stability of Ca-Montmorillonite may be characterized as at the threshold of agglomeration or flocculation.

The distance between unit layers in Ca-montmorillonite is too small for the formation of a complete diffuse double layer (Kjellander et al., 1988). Divalent calcium ions are held more strongly onto the clay, therefore the effective net negative charge on each clay particle was reduced. In general when calcium is present in sufficient quantities, the thickness of the double layer is reduced and face to face contact of clay particles can occur and form flocs. The formation of flocs is called flocculation (EPA, 1984).

Conductivity increases with decreasing solution pH as shown in Figure 4.5. When Ca-montmorillonite is added to water, it dissociates into a calcium cation and bentonite micelle. The conductivity of the cation and the electrophoresis of the micelle increase the conductivity of the solution.

4.1.1.3.Kaolinite

Kaolinite is less soluble than the three-layer clay minerals in hydrochloric acid (Grim, 1968). The solubility of all clay minerals is based on their cation solubility. A positive edge double layer is responsible for the adsorption of anions acting as counter-ions. Buchanan & Oppenheim (1972) showed that at pH=2.25 the aluminum species and at pH=6.00 the silicon species are the more soluble ions. At low pH the positively charged edges and the negatively charged faces of the particles can link together to form a card-house structure (Nicol & Hunter, 1970). When pH is increased, OH^- ion adsorption takes place on both the edges and surfaces of the kaolinite particles. Therefore, ζ-potential increases because of the increasing electrostatic repulsion between the particles. Increasing pH also breaks down the card-house.

ζ-potential versus pH for kaolinite is shown in Figure 4.6. ζ-potential decreases with decreasing pH, and it decreases with increasing solid concentration. Initial ζ-potential of kaolinite is around -13 mV at pH 5.6. Its stability is incipient instability according to ASTM D-4187 Standart Test Methods for Zeta Potential of Colloids in Water and Waste Water as Ca-Montmorillonite. Conductivity increases with decreasing pH as shown in Figure 4.7. In addition, when the solid concentration changes, conductivity remains more or less constant.

4.1.1.4. Chlorite

Chlorites are more soluable than kaolinite in hydrocloric acid. For chlorite, the aluminum in octahedral coordination is more soluble in hydrochloric acid than the aluminum in tetrahedral coordination. Chlorites have very low water adsorption properties. ζ-potential vs pH relationship is given in Figure 4.8. Below, approximately a pH of 7, ζ-potential increases sharply with decreasing pH. This behavior is attributed to the adsorption of chloride ions with the addition of HCl.

ζ-potential decreases with increasing solid concentration. Initial ζ-potential of chlorite is around -30 mV at pH 9.4. Its stability is ranked moderate stability according to ASTM D-4187 Standart Test Methods for Zeta Potential of Colloids in Water and Waste Water. According to Riddick (1968), its stability is characterized to be at the plateau of slight dispersion. Conductivity increases with decreasing pH as shown in Figure 4.9.

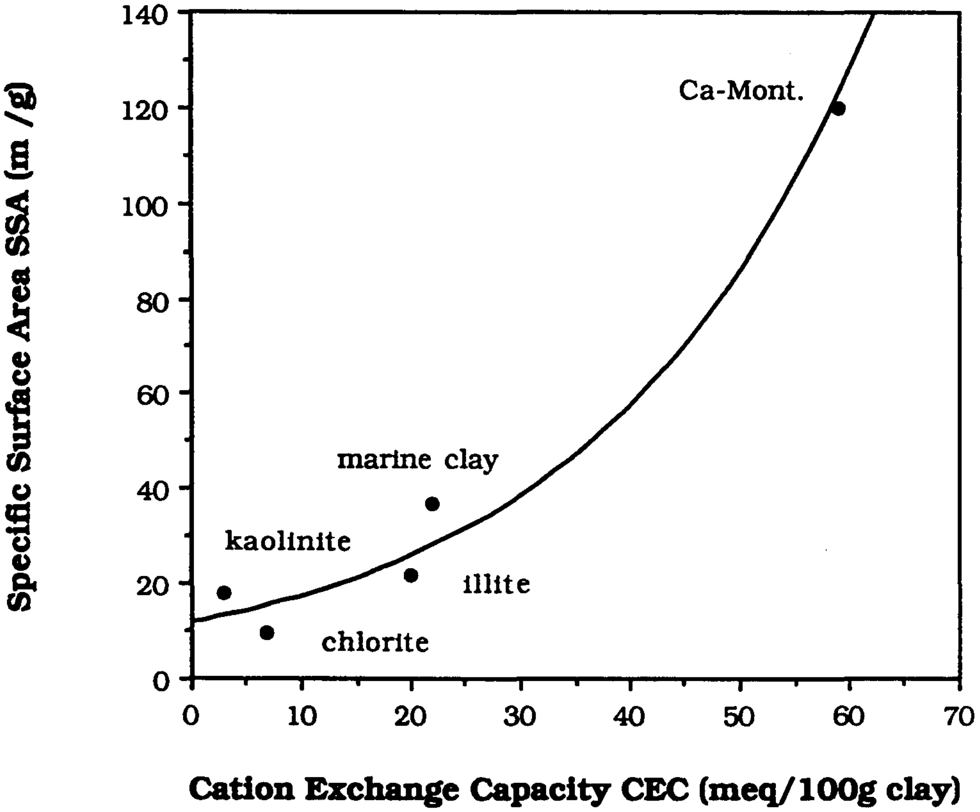


Figure 4.1. Specific Surface Area versus Cation Exchange Capacity

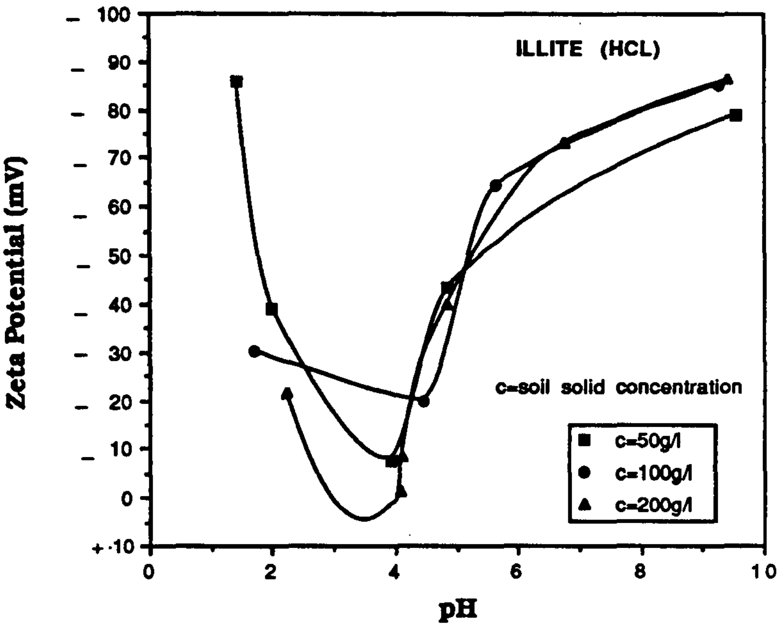


Figure 4.2. Zeta Potential versus pH for Illite Clay Suspension

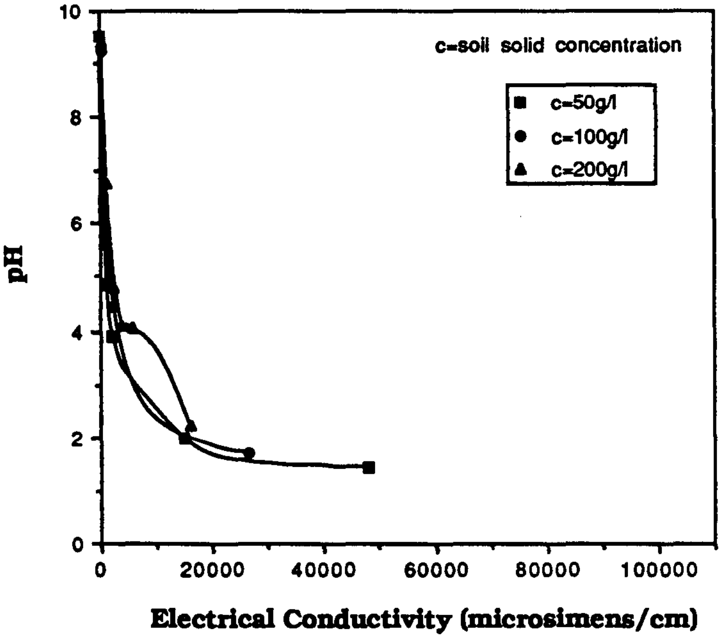


Figure 4.3. pH versus Conductivity for Illite Clay Suspension

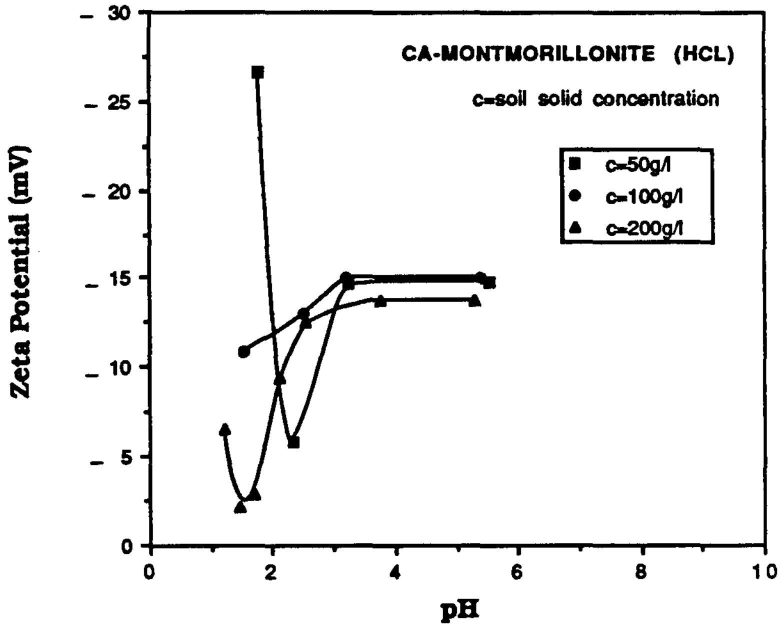


Figure 4.4. Zeta Potential versus pH for Ca-Montmorillonite Clay Suspensions

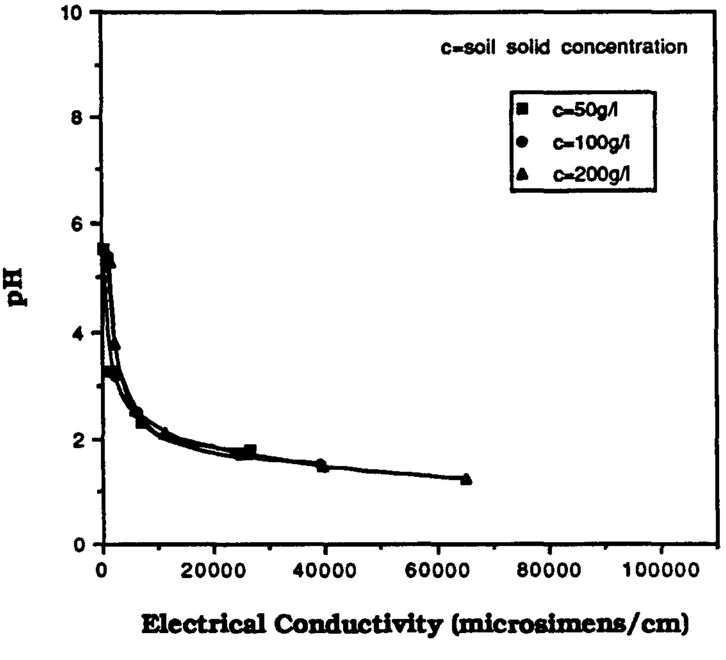


Figure 4.5. pH versus Conductivity for Ca-Montmorillonite Clay Suspensions

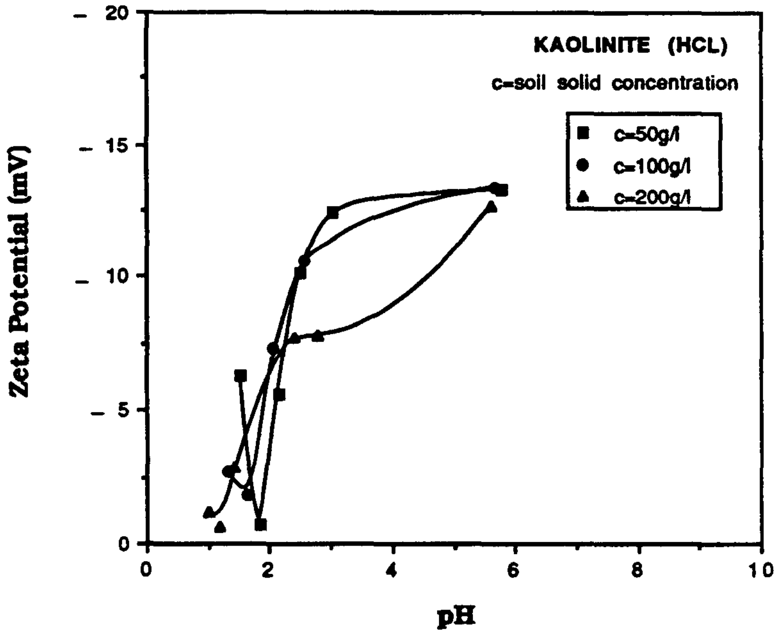


Figure 4.6. Zeta Potential versus pH for Kaolinite Clay Suspension

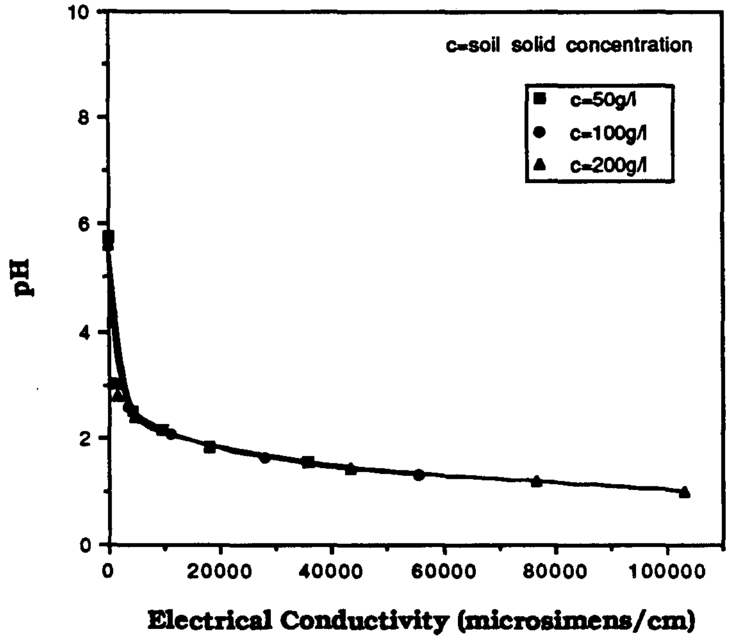


Figure 4.7. pH vs Conductivity for Kaolinite Clay Suspension

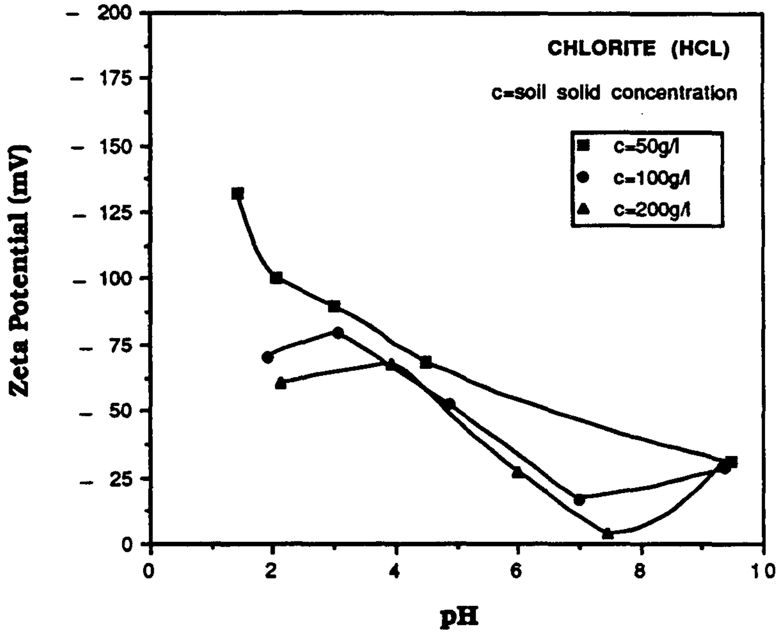


Figure 4.8. Zeta Potential versus pH for Chlorite Clay Suspension

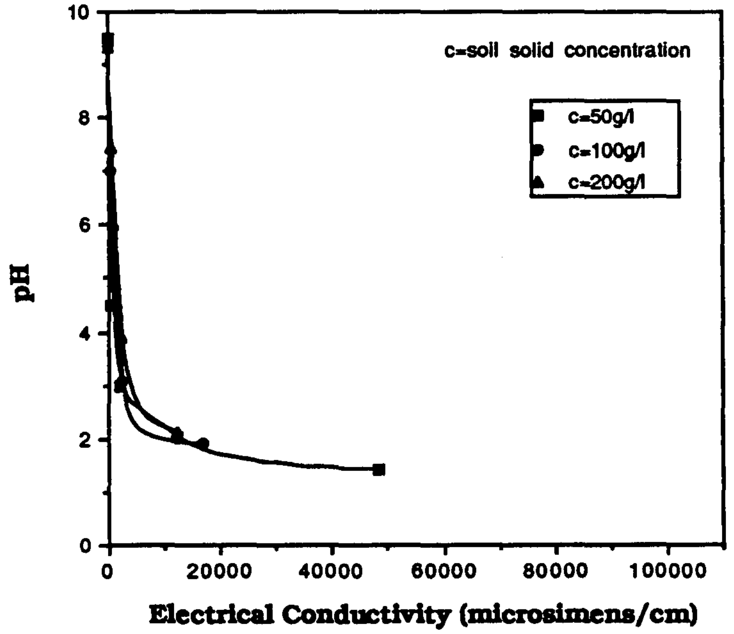


Figure 4.9. pH versus Conductivity for Chlorite Clay Suspension

4.1.2. Zeta (ζ) Potential Measurements for Marine Clay

The ζ-potential was plotted as a function of pH for different solid concentrations of the marine clay as shown in Figure 4.10 and 4.11. Each measurement is the average of a number of zeta potential measurements for each pH value. The experimental results shown in Figure 4.10 and 4.11 were obtained by adjusting the initial pH between 7.0 and 8.0 and then lowering the solution pH by successive additions of hydrochloric acid or nitric acid. The solution temperature was maintained at around 25 ^{o}C during these measurements.

The ζ-potential of the marine clay mixture decreased with decreasing pH until around pH value of 3.0. This was expected since ζ-potential decreases upon the addition of acids due to the shift of counter -ions toward the diffuse double layer. Acid attacks the less stable minerals and releases cations such as Ca, Fe, Al, and others into the solution (Lambe,1958). Therefore hydrogen ions alone do not determine the effect of the electrolyte on the clay minerals, but also the other cations released from the clays. As pH increases, anions increase in the solution. The density of the cations near the clay surface decreases as a thicker layer of cations is needed to screen the negative charge on the clay particle and thus the double layer thickness increases. The thicker the double layer, the higher is the ζ-potential.

ζ-potential decreases sharply with decreasing pH solution. ζ-potential is expected to decrease with increasing electrolyte concentration. The lowering of the ζ-potential as a result of addition of electrolytes is because of a decrease in the diffuse double layer. There is no isoelectric point at which the ζ-potential attains zero value, but there is a minimum value of ζ-potential in the region of pH (3.0-4.0) for HCl and in the region of pH (2.0-3.0) for HNO_3. When the ζ-potential is around zero, the adsorbed ions are held so tightly that they can not be exchanged. As the solution pH decreases beyond these regions, zeta potential starts to increase.

Beyond the minimum point there is a characteristic turn of the zeta potential to more negative values with decreasing pH. This may be called an "inversion" of the ζ-potential - pH curve. The ζ-pH inversion can be explained as follows: At high pH values, ζ-potential is high because of the hydroxyl ions in the solution. High solution pH also disperses clay particles and increases the negative charge on the clay surfaces, which results in increased repulsion between the particles. With decreasing pH, ζ-potential decreases sharply because of the adsorption of the cations such as the trivalent aluminum ions. Acid then attacks on clay minerals releases aluminum, calcium, iron and other cations into the solution. The presence of cations reduce repulsive forces, promote flocculation, and compressed double layers. Below a certain critical pH value, the increasing anion adsorption appears to dominate the effect of increasing hydrogen ion adsorption onto the clay particles. Below this critical pH the ζ - pH curve inversion occurs. Anions tend to enlarge the thickness of the double layer and subsequently raise the ζ-potential. Adsorption of anions such as chloride is greatest under strong acid environments.

For example when Cl^- gets adsorbed onto a clay mineral it interchanges with OH^-, as follows:

$$\text{Clay - OH + HCl ---------> Clay - Cl + HOH}$$

Both HCl and HNO_3 acids were used to obtain the typical ζ-potential versus pH curves. The inversion occured in both case and the trends were similar as indicated in Figures 4.10 and 4.11, respectively. Hence the results confirm each other. ζ-potential versus clay concentration at different solution pHs are shown in Figure 4.12 and 4.13. When the solution pH is between 3 and 5, ζ- potential decreases with increasing clay concentration because of the increasing cation concentration in the solution as explained in the previous paragraphs. When the solution pH increases to about 7, ζ-potential of the solution increases at lower concentrations of the solids because of the increasing hydroxyl ions. At higher concentrations there is little decrease in zeta potential for pH values of 6 and 7.

The results show that addition of HCl and HNO_3 to the marine clay solutions decreases the ζ-potential of the solutions but increases the conductivity of the solutions as expected. For both of the acids used to vary pH of the clay-water systems, data showed that below a pH value in the region of 2 to 4, ζ-potential increases with decreasing solution pH. The inversion of the curve is attributed to the anion adsorbtion on the clay in the presence of strong acids such as HCl and HNO_3. In overall analysis ζ-potential decreases with increasing particle size, pH and clay concentration.

4.1.3. Electrical Conductivity Measurements for Marine Clay

Conductivity measurement results are shown in Figure 4.14 and 4.15. The conductivity of a solution is a measure of its ability to carry an electrical current, and varies both with the number and type of ions that a solution contains. Conductivity of marine clay solution increases with decreasing solution pH as expected. When the clay concentration is increased, it dissociates into ions and clay-water micelle. The ions and the electrophoresis of the micelle increase the conductivity of the solution. At higher pH clay forms a gel and decreases the conductivity of the electrolyte. At lower pH, the clay dissociates and increase the conductivity of the solution (Dakshinamurti, 1960).

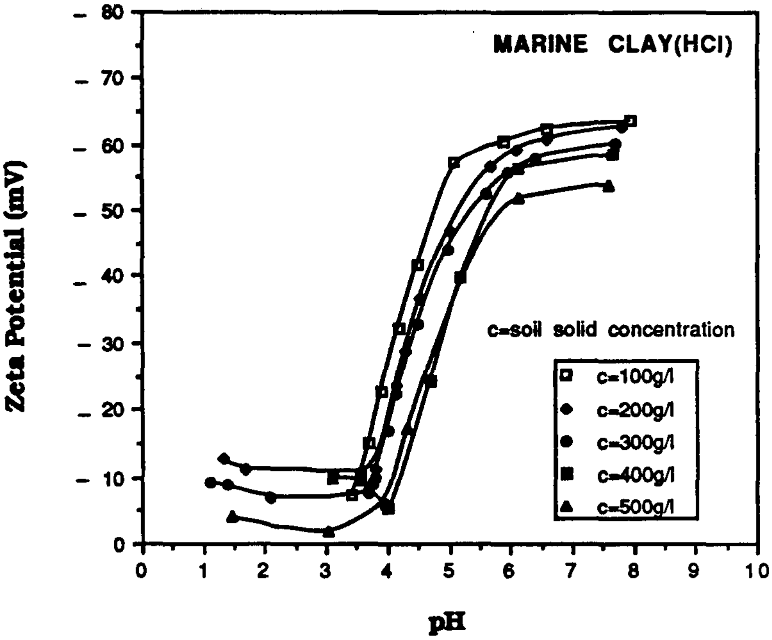


Figure 4.10. Zeta Potential versus pH for Marine Clay Suspensions (HCl)

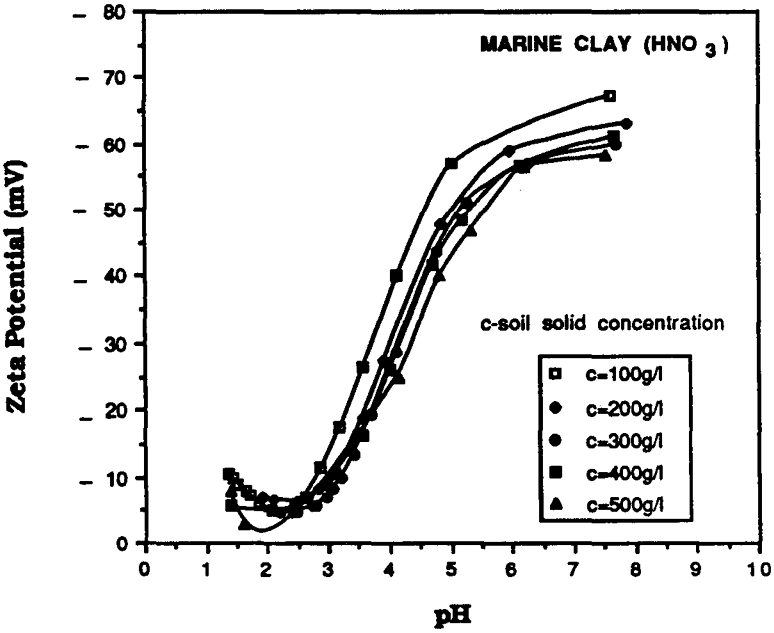


Figure 4.11. Zeta Potential versus pH for Marine Clay Suspension (HNO_3)

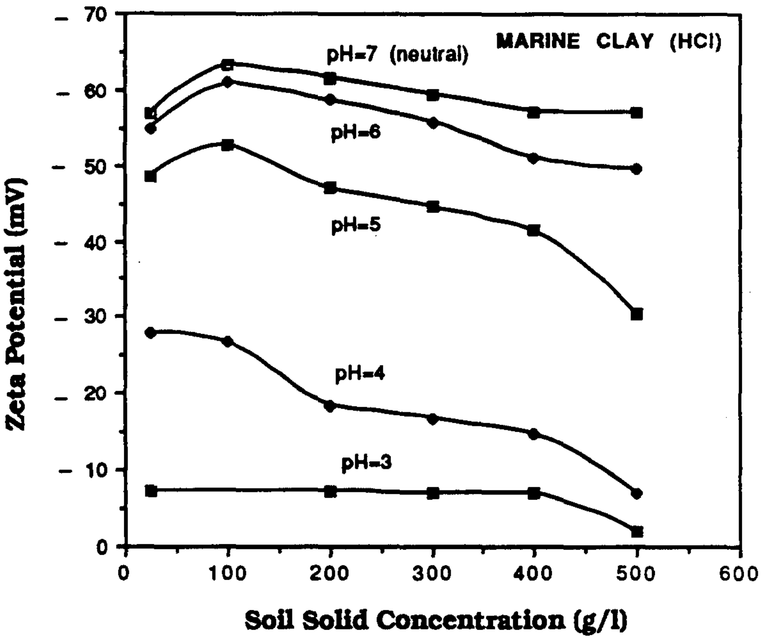


Figure 4.12. Zeta Potential versus Solid Concentration for Marine Clay Suspension (HCl)

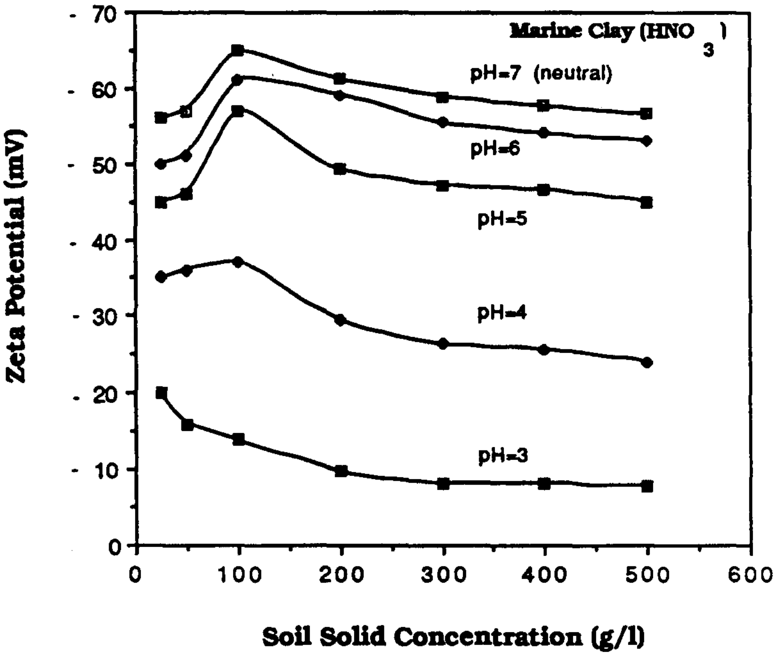


Figure 4.13. Zeta Potential versus Solid Concentration for Marine Clay Suspensions (HNO_3)

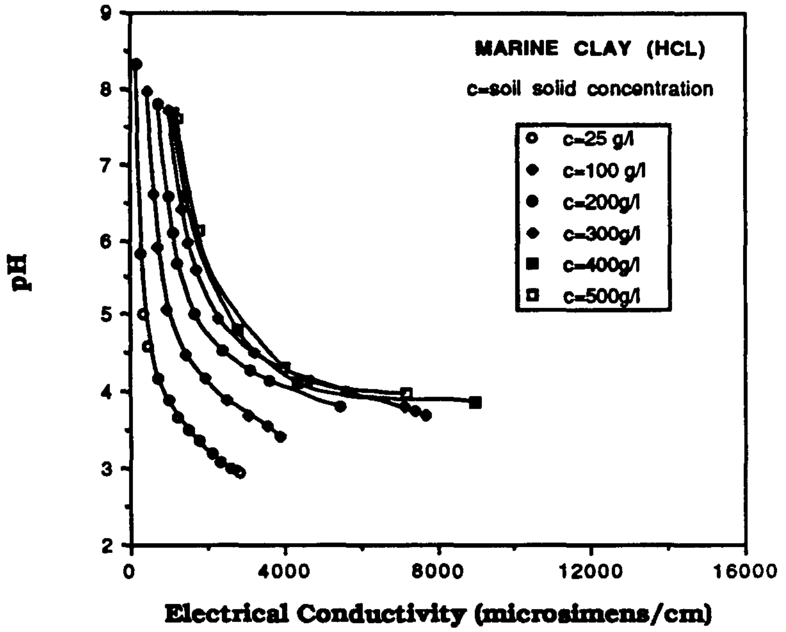


Figure 4.14 pH versus Conductivity for Marine Clay Suspension (HCl)

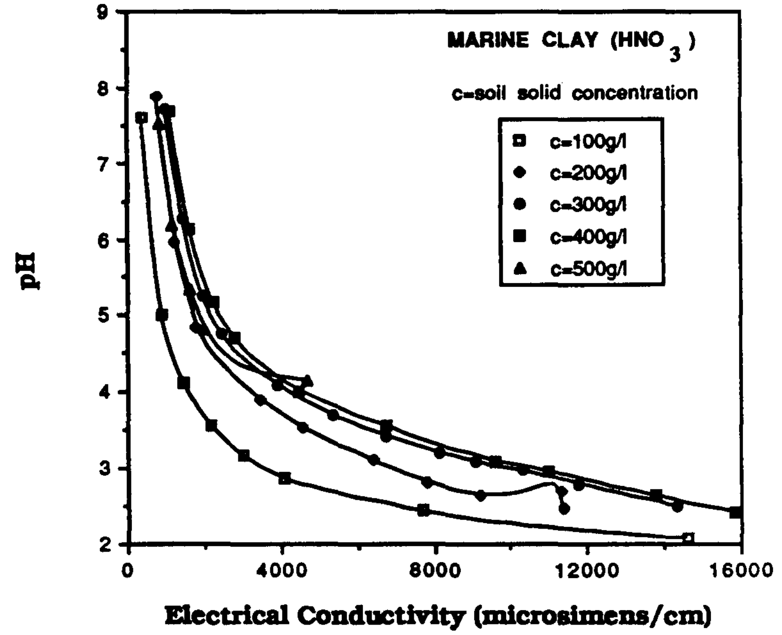


Figure 4.15 pH versus Conductivity For Marine Clay Suspension (HNO_3)

4.1.4. Dielectric Constant Measurements for Marine Clay

Measurement of dielectric constant provides an information about the thickness of the double layer attached to colloidal particles. Factors which influence the dielectrical constant can be divided into the following three catagories: (1) The chemical composition of the material, (2) The crystal structure of the material, (3) The relationships between the various constituents of the soil.

The effect of pH on the dielectric constant of of a solution of distilled water mixed with marine clay along with distilled water alone is shown in Figures 4.16 and 4.17, respectively. A review of Figures 4.16 and 4.17 shows that the dielectric constant increases with decreasing pH of the solution. Dielectric constant measurements made on clay suspensions at low frequencies give strangely high values. This is because of the heterogeneity of the medium. Sachs and Spiegler (1964) found that wet soils and rocks had dielectric constants larger than 1000 while the dielectric constants of most dry soils and water were lower than 10 and 80, respectively. Myers and Saville (1989) found that there was a tremendous change in dielectric constant because of the addition of colloidal particles. They reported dielectric constant of 800 for a colloidal solution which is 10 times larger than that of pure water. Chew (1984) also reported high values of dielectric constant of 1000 for a solution of clay particles which was immersed in an electrolyte solutions.

Dielectric constant decreases as the frequency increases. The chemical composition of the water affects the dielectric constant because adsorbed water has a lower dielectric constant than free pore water. When a heterogeneous system is considered such as clay-water-electrolyte system, current density varies from point to point as charges accumulate at the interfaces between the clay particles and the surrounding solution. When the frequency is increased, there will be less time for the charges to accumulate at the interface. This decreases the system's ability to store electrical energy, and thus decreases the dielectric constant. At high frequencies, the effects of conductivity and interfacial polarization become less important. Polarization is the separation of the positive and negative charges of a molecule. The magnitude of the polarizability of a material is reflected by the dielectric constant. Larger particles allow greater displacement of adsorbed cations along the surface and therefore their polarizability is larger.

Dielectric constant increases with decreasing pH of the solution. The double layer is reduced as a consequence. The adsorbed water structure adjacent to the surface may become less viscous and ions may move parallel to the surface. Polarization and frequency increase. Therefore dielectric constant increases. Dielectric constant of the distilled water increases with an increase in the electrolyte concentration as shown in Figure 4.18. The electrolyte would be expected to influence the dielectric properties of the solution in two ways: (1) Its ions may dissociate and produce ion pairs and these ion pairs make their own contribution to the dielectric constant, (2) The ions in the medium influence the solvent's molecular interactions; solvent molecules may be firmly bonded to the ions and therefore giving rise to new characteristic molecules of the solution.

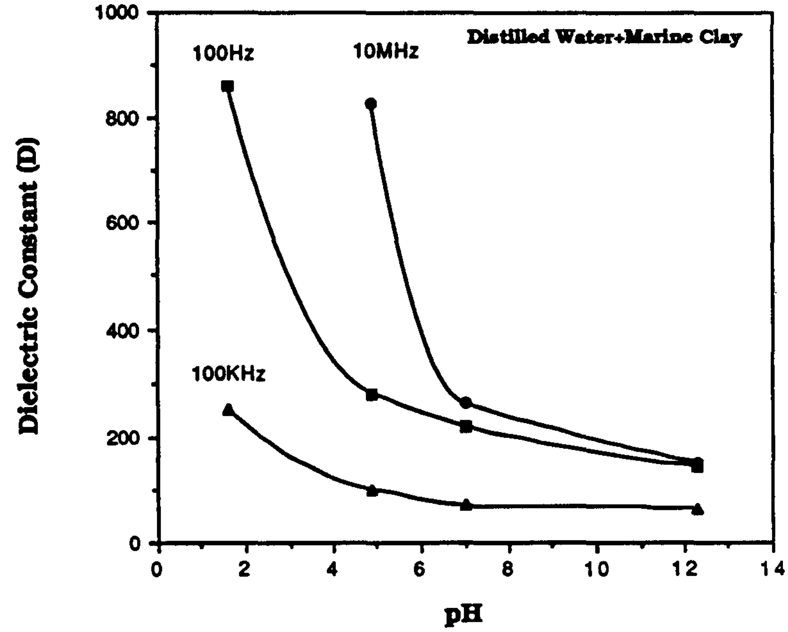


Figure 4.16. Dielectric Constant versus pH for Marine Clay+Distilled Water

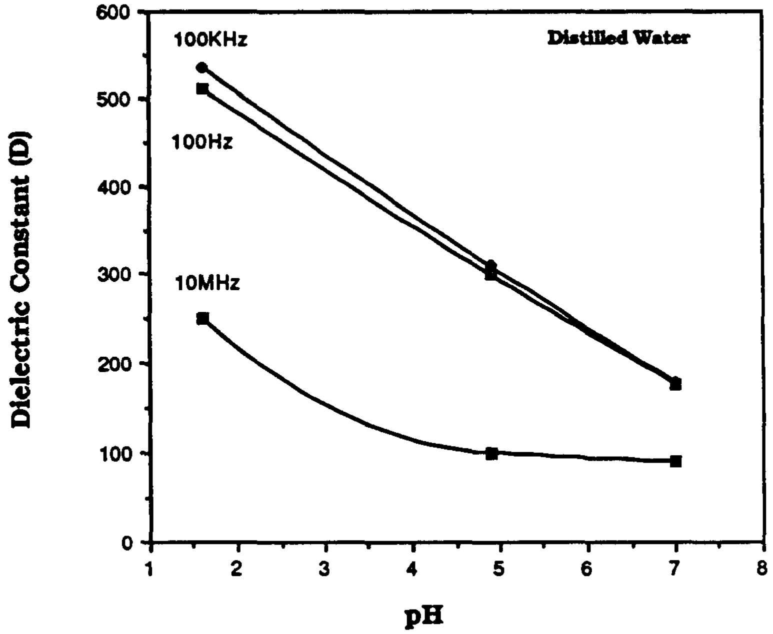


Figure 4.17. Dielectric Constant versus pH For Distilled Water

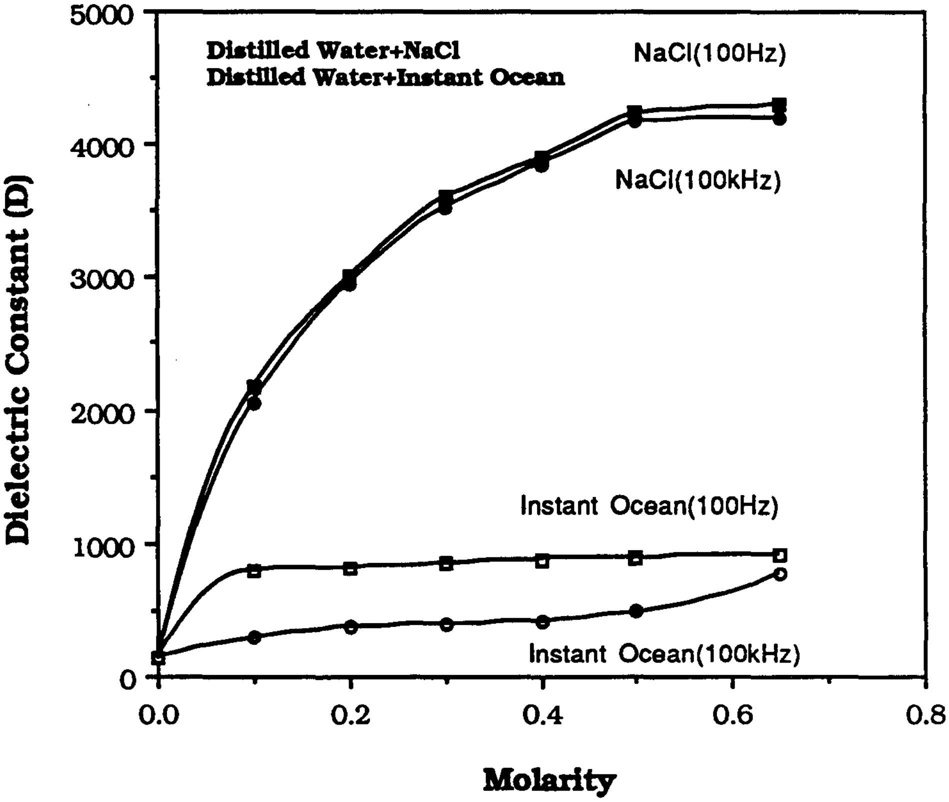


Figure 4.18. Dielectric Constant versus Molarity of NaCl and Instant Ocean

4.1.5. Double Layer Thickness For Marine Clay

Double layer thickness of marine clay was calculated according to Gouy-Chapman theory under changing electrolyte concentrations (Equation [2]). Increasing acid concentration decreases the diffuse double layer as shown in Figures 4.19 and 4.20. In these predictions the pH variability of the dielectric constant (100KHz) of the suspension (approximately 250 g/l concentration) was incorporated (see Figure 4.16). When an acid is added to water, hydrogen ion concentration increases in the solution which eliminates the repulsive forces between the particles and the suspension coagulates or flocculates.

Flocculation or coagulation occurs because of the compression of the electrical double layer around the clay particles. When the flocculation is increased, the system will be unstable. Addition of hydrogen ions increases the concentration of cations in the solution. Because hydrogen ions are adsorbed on clay exchange sites releasing aluminum and other cations into the solution. Therefore, addition of hydrogen ions releases cations from the clay surface so that the diffuse double layer is compressed. This then causes the ζ-potential decrease as shown in Figures 4.21 and 4.22. The ζ-potential-double layer thickness variations were predicted from the previous pH dependent correlations.

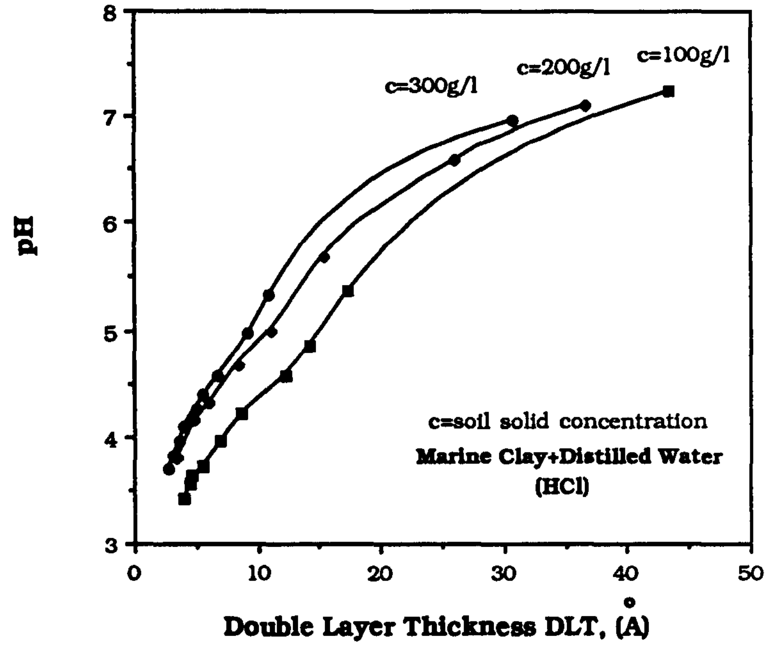
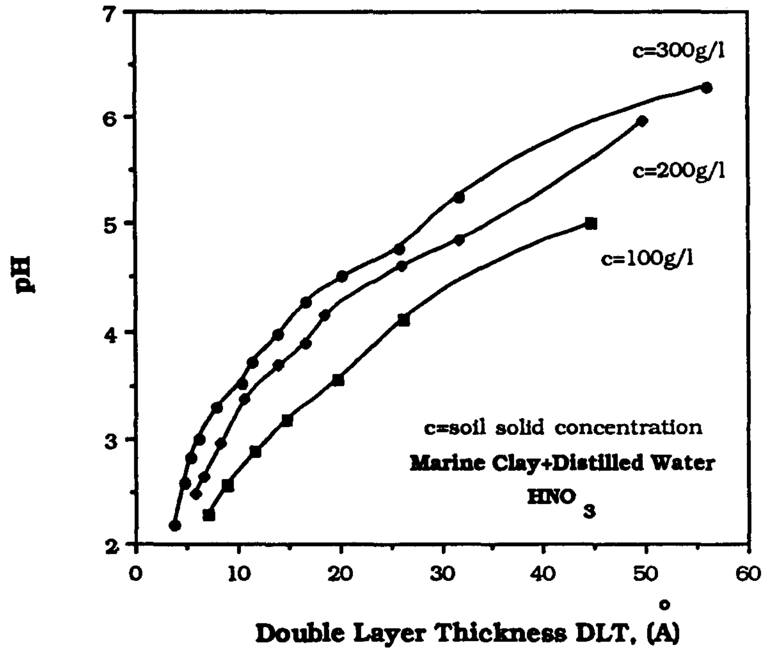


Figure 4.19. pH versus Double Layer Thickness for Marine Clay



FFigure 4.20. pH versus Double Layer Thickness for Marine Clay

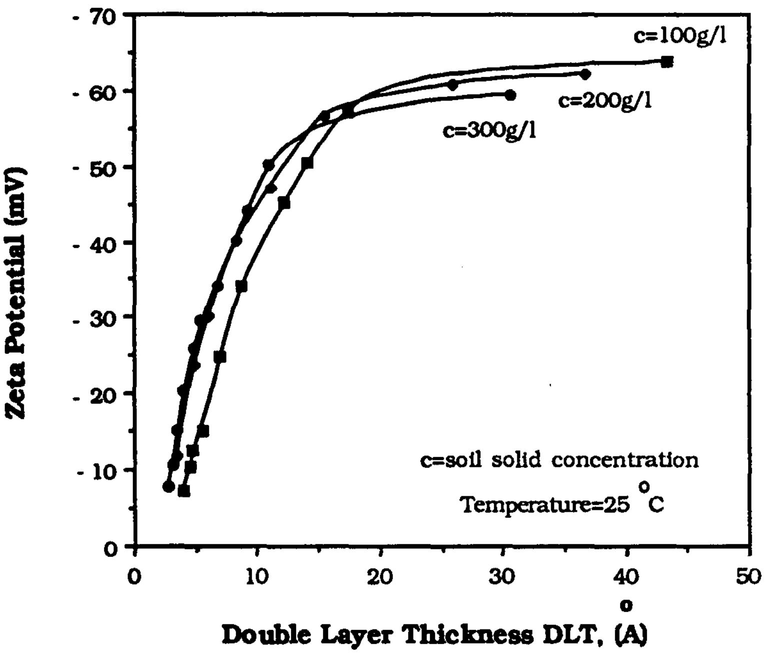


Figure 4.21. Zeta Potential versus Double Layer Thickness for Marine Clay (HCl)

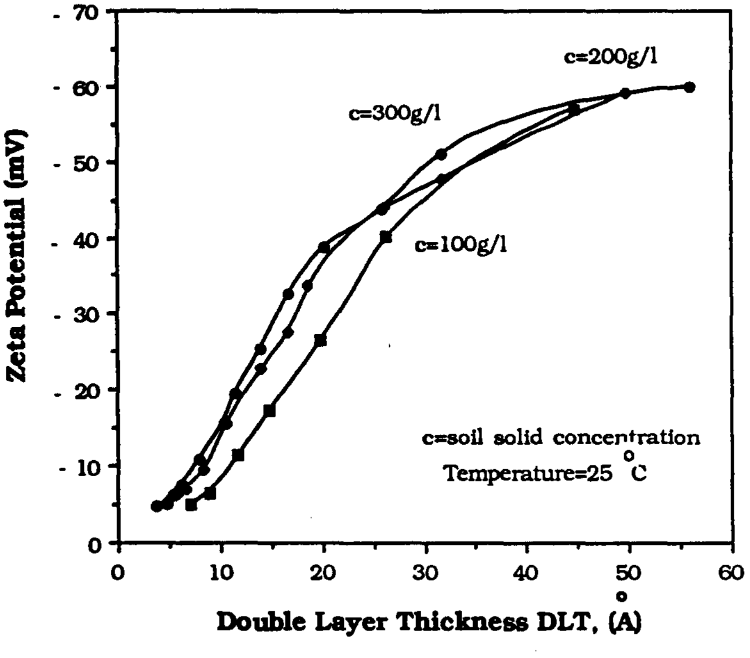


Figure 4.22. Zeta Potential versus Double Layer Thickness for Marine Clay (HNO_3)

4.2. PHYSICO-CHEMICAL PROPERTIES OF ADDITIVES MIXED MARINE CLAY

4.2.1. Specific Surface Area

Specific surface area is an important property of finely divided and porous solids. The reason for theis are the following: (1) flocculation, dispersion and ion exchange depend on surface phenomena, (2) specific surface is related to the particle size and shape of clay minerals. The specific surface area of a soil is a fundamental property which has been found to correlate with important phenomena such as the cation exchange capacity (CEC), retention and release of various chemicals, retention of water, physical and mechanical properties such as strength, permeability, plasticity and cohesion of natural clays.

Figures 4.23 and 4.24 shows the relationship between specific surface area and percentage of sludge and crude oil, respectively. Specific surface area decreases with increasing percentage of sludge and crude oil. Organic matter is assumed to coat and agglomerate the clay particles (Pamukcu, et al., 1990 and Tuncan, 1989). This brings small particles together creating "appearent" large particles. Specific surface area of the crude oil mixed marine clay is considerably lower than that of the sludge mixed marine clay. The specific surface area of 15% crude oil mixed marine clay is around 1 m^2/g which is the same as the specific surface of fine sand. It has been observed that the color of crude oil mixed clay is brownish and clay flocs can not be crushed easily after drying, possibly due to the "gluing" effect of the oil. This phenomena may be similar to the "spherical agglomeration" discussed by Puddington and Sparks (1975).

In the spherical agglomeration process, colloidal particles in liquid suspension are treated with a bridging liquid, which preferentially wets the colloidal particles and is immiscible with the water. An important aspect of the spherical agglomeration process is the relative wettability of the suspended solids by the two immiscible liquids. Another causes of decreasing specific surface area in the sludge mixed material might be the inclusion of larger and fibrous particles in the sludge. A detailed discussion of spherical agglomeration and the effect of fibrous particles are presented in later sections.

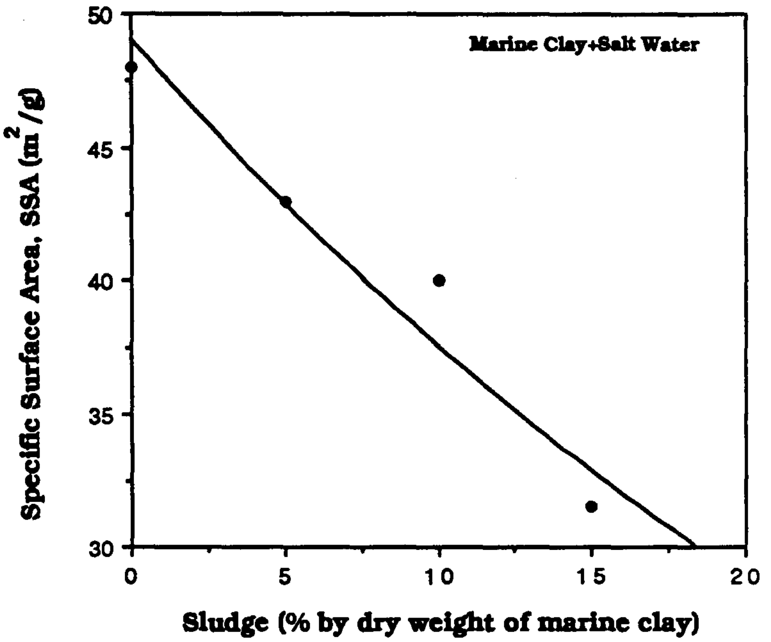


Figure 4.23. Specific Surface Area versus Sludge for Marine Clay

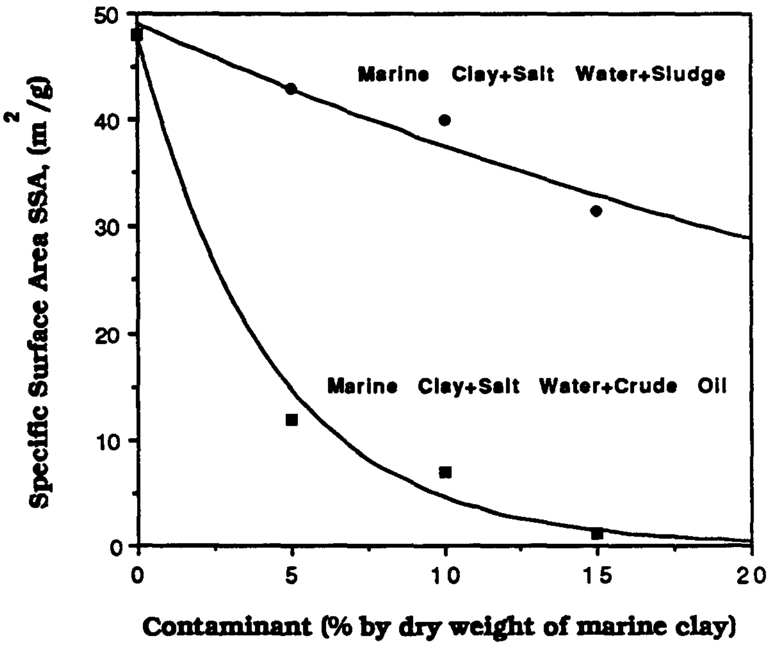


Figure 4.24. Specific Surface Area versus Contaminants for Marine Clay

4.2.1.2. Cation Exchange Capacity (CEC)

Cation exchange phenomena is important for the fundamental understanding of the differences in the nature and development of electric charges between the clay particles which affects the flocculation and dispersion processes in clay systems. CEC is a measure of the degree of the isomorphous substitution which gives a net negative charge to clay particles (van Olphen, 1963). Cations are attracted and held onto the surfaces and edges to preserve electrical neutrality (Mitchell, 1975). These cations are exchangeable cations because they can be replaced by cations of another type.

The relationship between cation exchange capacity (CEC) and the percentage of sludge and crude oil mixed marine clay are presented in Figures 4.25 and 4.26, respectively. Cation exchange capacity (CEC) increases with increasing percentage of sludge because of the humic matter in the sludge. Humic matter is an important cation exchanger in soils. Organic particles are adsorbed onto the clay mineral surfaces and edges and act as exchange locations (Aiken, et al., 1963; Grim, 1968). Cation exchange capacity decreases with the increasing percentage of crude oil. This is probably due to the blanketing or coating of the clay exchange sites by large hydrocarbon molecules. This would inhibit the magnitude of measuredexchange potential.

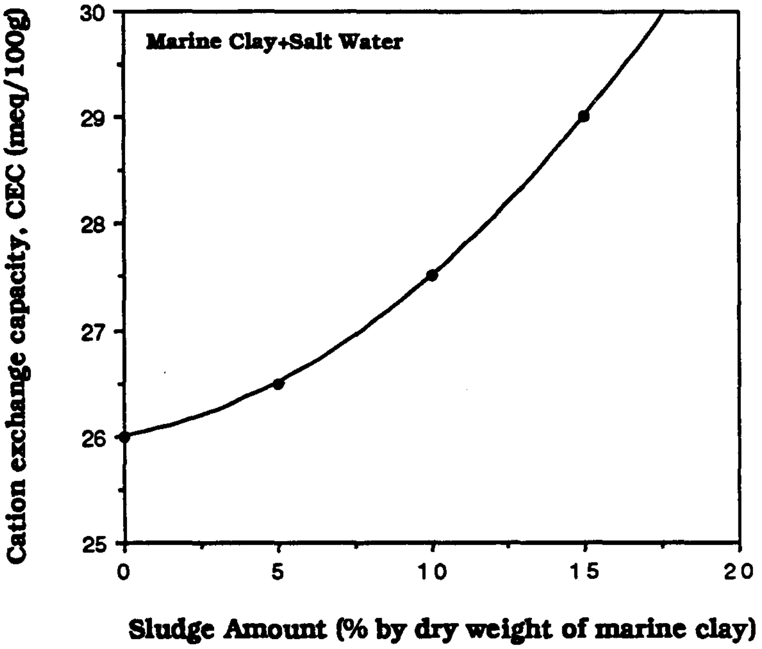


Figure 4.25. Cation Exchange Capacity versus Sludge Amount for Marine Clay

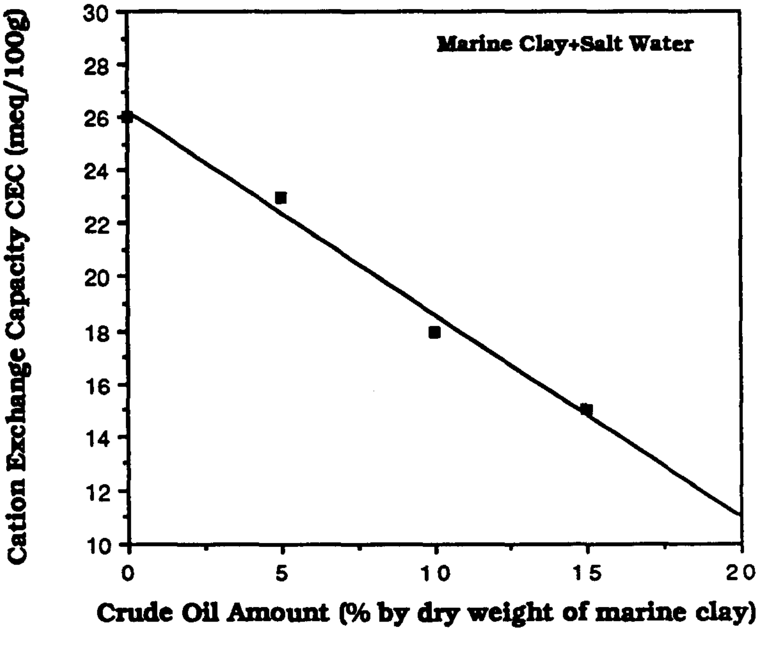


Figure 4.26. Cation Exchange Capacity versus Crude Oil Amount for Marine Clay

4.2.1.3. Ignitable Organic Matter Content

The relationship between the organic matter and the percentage of sludge and crude oil for marine clay are shown in Figures 4.27 and 4.28. A review of Figures 4.27 and 4.28 show that organic matter content increases with increasing sludge and crude oil in the mixture. High specific surface area of clay minerals makes organic matter an important constituent of particles. Most organic matter has electrostatic and steric cation retention characteristics, and they are often adsorbed onto clay minerals due to electrostatic adsorption and chemical bonding..

The humic substances or organic compounds found in sludge which are similar in chemical structure to natural humic substances can be adsorbed onto clay particles as macromolecular complexes bonded together by di- and trivalent cations or hydrogen bonding (Pamukcu, et al, 1990). The adsorption of humic substances onto kaolinite, montmorillonite and illite clay minerals increases with increasing salinity and dissolved humic substance concentration. Adsorption increases in the following order: montmorillonite> illite> kaolinite. This order is directly related to the increasing CEC of these clay minerals (Aiken, et al, 1963). Organic matter also contributes to the CEC of the clay minerals. This contribution comes from the humic acids. The greater the degree of humification, the higher is the CEC due to the retention of cations onto the clay particles.

Crude oil is a petroleum hydrocarbon. The hydrocarbons contain mainly carbon and hydrogen along with some other elements such as nitrogen, sulphur, and sodium. The adsoption of high molecular weight components such as the hydrocarbon chains of crude oil onto clay surfaces causes wettability to change from water-wet to oil-wet (Cristenson, 1987). The adsorption of these components creates an adsorbed layer around the particles. This adsorbed layer is not water soluable and are not displaced by water. Thus exchange sites become coated by molecules. This reduces CEC of crude oil contaminated clays.

The variation of specific surface areas with the measured cation exchange capacity of the sludge and crude oil contaminated marine clay mixtures is shown in Figures 4.29 and 4.30. The data shows that the specific surface area ranges between 0 and 20 for crude oil contaminated clay and it ranges between 30 and 50 for the sludge contaminated clay. The trend for the crude oil contaminated clay complies with the findings reported in Tables 1 and 2, namely as the specific surface increase so does the cation exchange capacity. However, this is not so with the sludge contaminated clay. This is because the humic particles in the sludge attach themselves onto the clay reducing the specific surface, but also act as exchangers in the system increasing the overall cation exchange capacity of the system. It should be noted that the cation exchange capacity of the sludge itself is rather high also, on the order of 134 meq/100g. This explains the trends of surface charge density with increasing contamination with sludge and crude oil.

4.2.1.5. Zeta (ζ) Potential, Electrical Conductivity and pH

The effect of sludge on the measured zeta potential of the marine clay and sludge mixture is shown in Figure 4.31. ζ-potential decreases with the increasing amount of sludge. This shows that addition of sludge increases the tendency of the system to flocculate and the suspension becomes less stable. The reduction of ζ-potential with sludge content appear to be slightly more with higher clay concentration, which also supports the flocculation tendency.

Sludge has humic acids. Therefore, solution pH decreases with increasing sludge content as shown in Figure 4.32. Lowering the pH results in an increased adsorption of humic acid on clay minerals. Because the clay dissolutionintroduces buffering capacity to the system, the pH reduction is less with the higher clay concentration specimen. Conductivity is shown to increase with an increasing percentage of sludge in Figure 4.33.

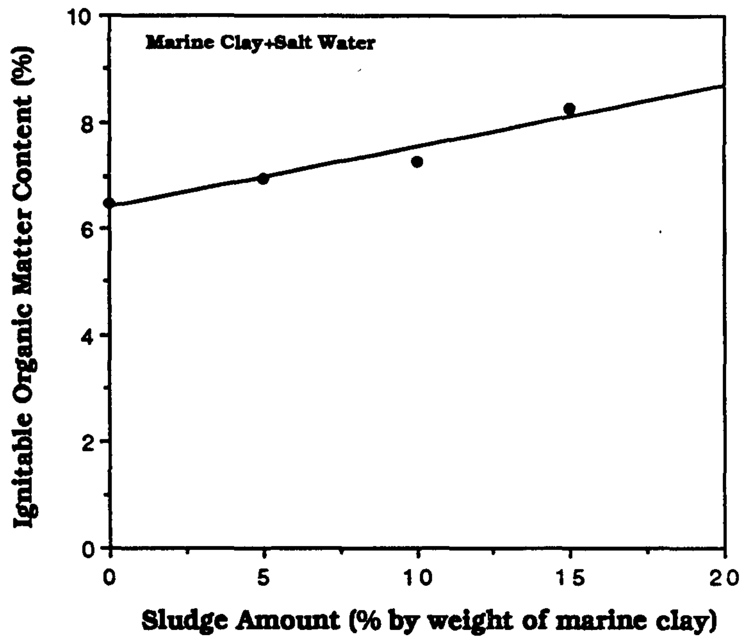


Figure 4.27 Organic Matter Content versus Sludge Amount for Marine Clay

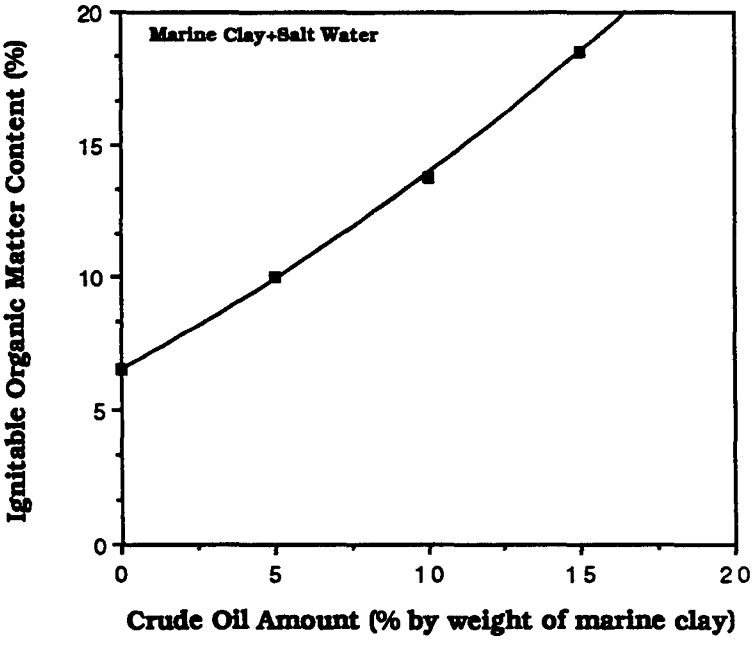


Figure 4.28. Organic Matter Content versus Crude Oil Amount for Marine Clay

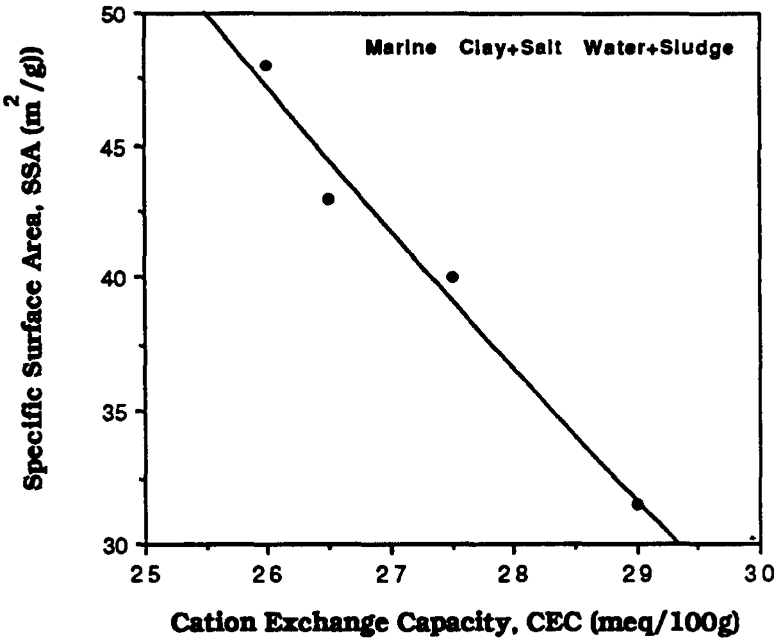


Figure 4.29. Specific Surface Area versus Cation exchange Capacity for Marine Clay Mixed with Sludge

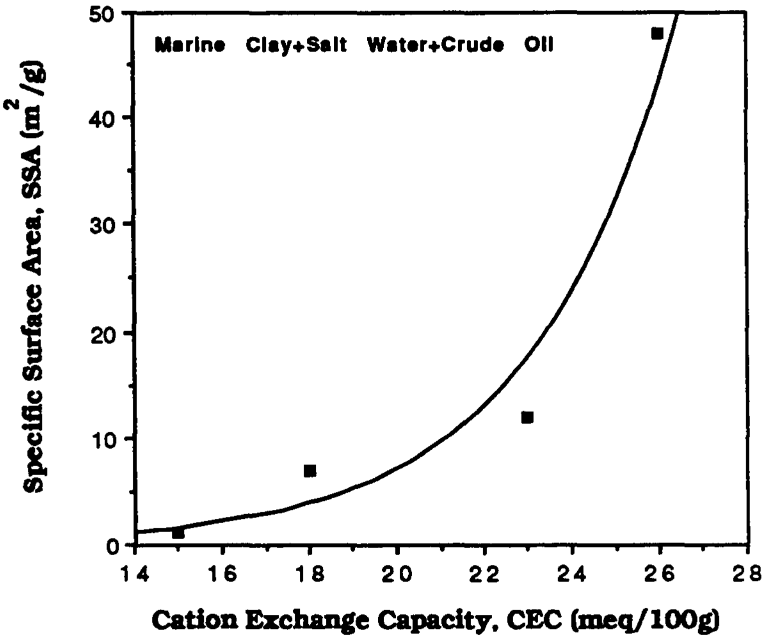


Figure 4.30. Specific Surface Area versus Cation Exchange Capacity for Marine Clay Mixed with Crude Oil

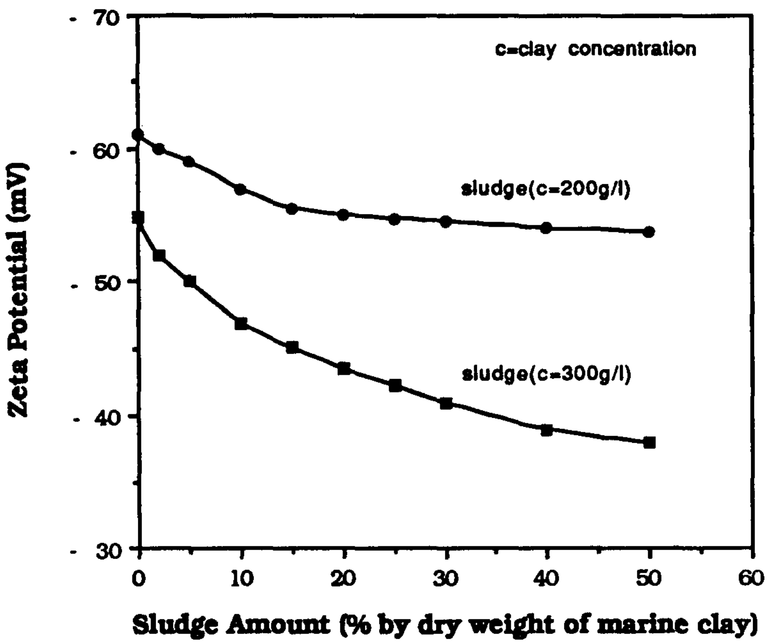


Figure 4.31 Zeta Potential versus Sludge Content For Marine Clay

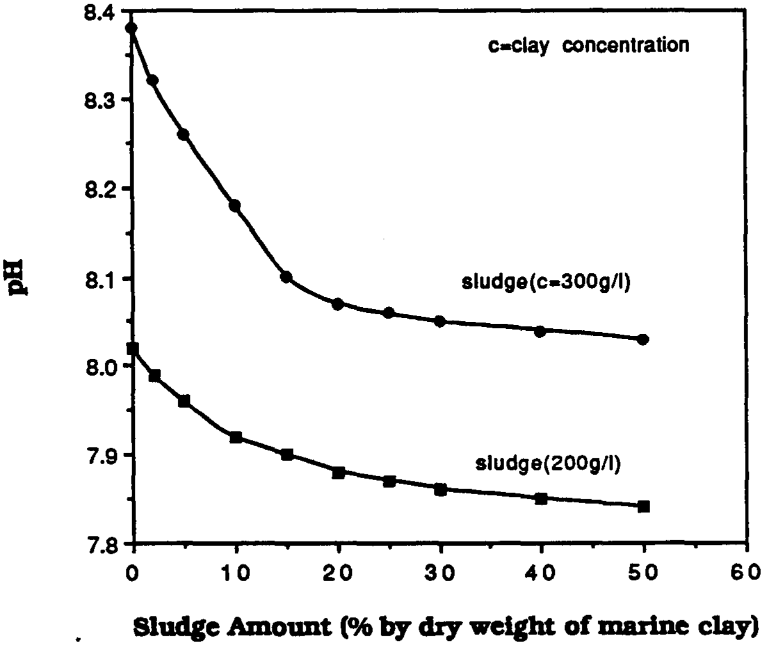


Figure 4.32 pH versus Sludge Content For Marine Clay

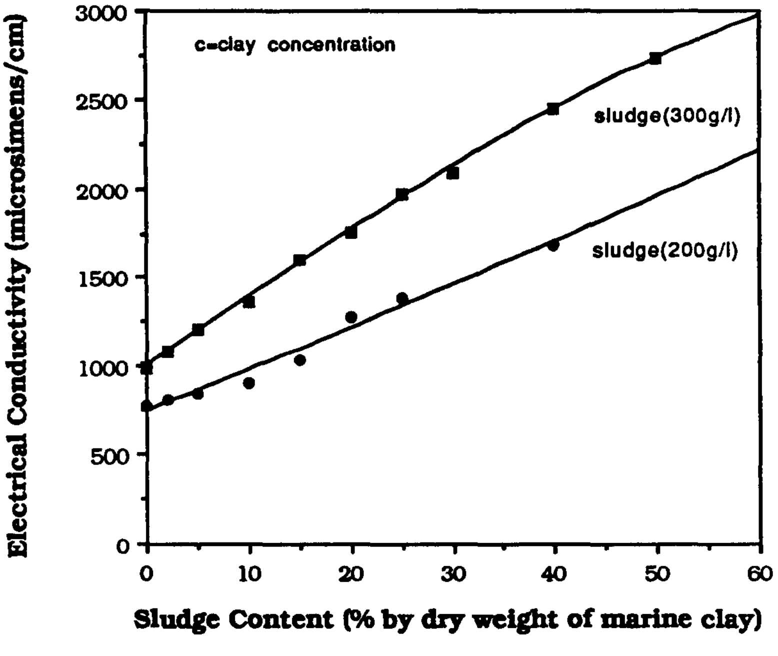


Figure 4.33 Electrical Conductivity versus Sludge Content For Marine Clay

4.3. DEPOSITIONAL PROPERTIES

4.3.1. Rate of Sedimentation

Settlement-time curves were generated for the marine clay mixtures. Figures 4.34, 4.35, 4.36 and 4.37. show the settlement versus time measurements for marine clay (MC) with tap water (TW) and with saline water (SW); marine clay, saline water and sludge (5%and 10%); marine clay, saline water and crude oil (5% and 10%); and also combined representation of these three curves, respectively.

4.3.1.1. MC+TW and MC+SW

Mixing marine clay with saline water promotes flocculation and therefore slightly faster deposition as observed in Figure 4.34. This is because salt removes the energy barrier that tends to keep the particles apart. The flocculation of the clay particles leads to the deposition of homogeneous (nonstratified) sediments with open microstructure.

On the other hand, mixing marine clay with tap water promotes dispersion and slower deposition. It promotes clay particles to be oriented parallel to each other. Because the particles must overcome an energy barrier to aggregate, the distance between particles is determined by minimization of their potential energy . The tap water mixed marine clay also has a higher pH value than the salt water mixed marine clay, as expected. High solution pH tends to disperse colloidal particles by increasing the negative charge on clay particles which then increases repulsion between them.

4.3.1.2. MC+SW+Sludge 5% and MC+SW+Sludge 10%

Figure 4.35 shows time versus settlement depth variation for sludge mixed marine clay specimens. It can be observed that 10% sludge mixed clay has a faster rate of deposition than the 5%sludge mixed clay. The lower pH values of the 10% sludge mixed marine clay may explain its faster rate of deposition since at low pH values clay particles would tend to flocculate. The physico-chemical properties discussed before also support the flocculation tendency with sludge and therefore faster rate of deposition.

4.3.1.3. MC+SW+Crude Oil 5% and MC+SW+Crude Oil 10%

Figure 4.36 shows the time versus settlement depth variation for crude oil mixed marine clay specimens. It can be observed that the 10% crude oil mixed clay has a faster deposition rate when compared to the 5% crude oil mixed clay. Oil tends to coat and agglomerate the clay particles. This increases the apparent particle size and weight and thus promotes faster deposition. 10% crude oil mixture has a lower pH value than the 5% crude oil mixture, which again may explain the difference in their settlement rates. Once again, the physico-chemical changes discussed earlier support the agglomeration and flocculation tendency of the clay suspension with the introduction of crude oil into the system.

4.3.2. Total Solids Concentration

4.3.2.1. MC+TW and MC+SW

Figure 4.38 and 4.39 show the total solids concentration versus depth measurements for MC+TW and MC+SW mixtures, respectively. While the sediment concentrations from the first three sampling ports decrease, the concentration of the forth tap increases in time. This is expected as the settlement continues. Some information is replotted in Figure 4.40 and 4.41 in which the variation of concentration in the sedimentation tank with time. As observed, the concentration of salt water mixed marine clay decreases considerably faster than the tap water mixed marine clay. This difference between the two specimens is evident even with the trend of the TSC versus time curve for the last tap at which the concentrationincreases with time.

4.3.2.2. MC+SW+Sludge (5%) and MC+SW+Sludge (10%)

Figures 4.42 and 4.43 show the concentration versus depth measurements for the 5% sludge and the 10% sludge, respectively. The concentrations of the top two sampling ports decrease faster than that of the third sampling port in both cases.

The total solids concentration versus time curves for the 5% and 10% sludge mixed samples are given in Figures 4.44 and 4.45, respectively. As observed, the trends of the curves are very similar but with slightly more solids accumulated at the forth tap at the end of the seventy hours for 10% sludge mixed material. Organic matter and heavy metal ions have a high tendency to be adsorbed onto the clay particles. In addition, organic matter and mucus may coat the particles which would make them larger and also heavier. Surface adsorbtion of ionic species and organic matter also promotes flocculation by reducing the repulsion between the particles. These explain the higher concentration of solids in the settled mixture of the higher percentage sludge mixed clay.

4.3.2.3. MC+SW+Crude Oil (5%) and MC+SW+Crude Oil (10%)

Figures 4.46 and 4.47 show the total solids concentration versus depth measurements for crude oil mixed specimens. Concentration of the 10% crude oil slurry column decreases significantly faster than the 5% crude oil mixed slurry for the first, second and the third ports. Oil coats and agglomerates clay particles, apparently increasing their size and weight and causing them to settle faster. Oil also acts as a "bridging agent" which coagulates particles. The solids concentration versus time curves for the crude oil samples given in Figures 4.48 and 4.49 confirms the faster deposition for the 10% crude oil mixed clay. The final solids concentration in the settled mass is also significantly higher in the 10% oil mixed clay than the 5% oil mixed clay.

4.3.3. pH Variation

pH of solution has a profound effect on the adsorption characteristics of organic matter on clay minerals. Acidity promotes adsorption because of the development of positive charges at the edges of clay minerals in acid conditions.

4.3.3.1. MC+TW and MC+SW

Figures 4.50 and 4.51 show the pH versus depth measurements for tap water mixed marine clay and saline water mixed marine clay, respectively. Initial measurements show that pH increases slightly with increasing depth of the sampling ports for both the tap and the saline water samples. While the pH of the first three sampling ports change, the pH of the forth sampling port remains more or less constant. The reason for this is probably that the solid concentrations of the first three sampling ports change considerably while the change at the forth tap is slightly incremental over the initial concentration.

pH of saline water column changes between 7.2 and 8.1, and the pH of the tap water column changes between 7.55 and 8.0. The former is slightly a wider range than the latter. Figures 4.56 and 4.57 show the pH variation with time. In Figure 4.57, the pH values are normalized by the ones measured in the corresponding ports in the uncontaminated tap water column. There is a consistent trend of pH change with time at the level of the top three taps of the sedimentation column, as observed in Figure 4.56. It appares as the clay phase settles out of the suspension, there is a steady climb of pH probably due to the down of the dissolved cationic species with the clay particles.

In salt water, pH again increases with time throughout the column. However, these pH variations show an opposite trend to those of tap water column when the pH values are normalized with tap water column values, as observed in Figure 4.57. Once again, the pH of settled mass stays more or less constant with time, while the pH of the upper tap waters first increase and then decrease slightly after 24 hours. It appears that the clay particles act as transfer agents for salt ions through the settling column. As they become removed downward in the water column, the pH of the column increases with respect to the tap water cause.

4.3.3.2. MC+SW+Sludge 5% and MC+SW+Sludge 10%

Figures 4.52 and 4.53 show the depth versus pH variation during sedimentation for the 5% and the 10% sludge mixed marine clays, respectively. pH increases with time and the depth in the settling column. Activated sludge is known to become acidic in time. Therefore as sludge settles out of the water column it might decrease at the pH of the system in the lower levels. Lowering of the pH probably resulted in an increase in the amount of organic matter adsorption.

The normalized pH vs time curves of the mixtures in the sedimentation tanks are given in Figures 4.58 and 4.59. These pH values are normalized by the pH values measured at the corresponding ports in the uncontaminated saline water column. The normalized pH values of the 10% sludge mixed marine clay are lower than that of the 5% sludge mixed marine clay. pH decreases with increasing time during the first 24 hours. However, the normalized pH starts increasing after the first 24 hours. The pH of the forth tap stays constant more or less. During sedimentation, particles would tend to adsorb the organic substances in the water column. The particles also exchange ions. These may be some of the causes of pH variation in time. However, when compared with that of salt water column pH, these variations appear to be controlled more by the salt water and clay interaction than the organic matter interactions.

4.3.3.3. MC+SW+Crude Oil (5%) and MC+SW+Crude Oil (10%)

Figures 4.54 and 4.55 show the pH versus depth variation for the 5% and the 10% crude oil mixed marine clays, respectively. The pH of the columns increase for the top three ports initially and then stay constant. The pH of the settled mass decrease, unlike the other suspensions of the clay mixtures. Clay particles may adsorb significant amount of oil onto their surfaces. Oil may also envelop particles which then settle to the bottom.

The normalized pH versus time curves of the mixtures in the sedimentation tanks are given in Figures 4.60 and 4.61. The initial reduction of pH in the sedimented mass may be due to entrapment of some of the ionic species in an clay-oil-water matrix.

4.3.4. Variation of Dielectric Constant of the Suspension

The dielectric constant is a measure of the ability of the clay particles to store electrical potential energy under the influence of an electrical field. The dielectric constant of the electrolyte-pore fluid system can influence both the surface potential and the double layer thickness of the clay. According to Gouy-Chapman theory the thickness of the double layer decreases when the dielectric constant of the medium is reduced. Such a reduction can be due to the addition of water miscible solvents. All the dielectric constant measurements of the suspensions made in this work were conducted at 100Hz. Suspensions of colloidal particles in aqueous electrolyte solutions generally have unusually high dielectric constants at low frequencies.

In most fine-grained materials there is a concentration of electrical charges adjacent to the surface of the particles. This charge depends on particle surface structure, the number of unsatisfied surface bonding sites and the net electrical charge of the particle itself. Polarization is the separation between centers of positive and negative charge at any instant. The composition and structure of the material determines the magnitude of polarizability. The magnitude of polarizability of a material is reflected by the dielectric constant.

Increase in electrolyte concentration causes the diffuse cation layer to depress toward particle surfaces. The adsorbed water structure adjacent to the clay surfaces may become disrupted and less viscous and ions may have greater freedom for movement parallel to the surfaces. Therefore, polarization increases.

In a media of low dielectric constant, an attraction may exist between the particles. Therefore flocculation takes place. The dielectric constant of the flocculated soil is less than the dielectric constant of the dispersed soil. This is due to the differences in the proportion of water to solid in the clusters.

4.3.4.1. MC+TW and MC+SW

Figures 4.62 and 4.63 show the depth variation of the dielectric constant of the tap water and the saline water mixed marine clay, respectively. The dielectric constant of the tap water mixed marine clay slurry is large compared to the salt water mixed marine clay slurry. For the tap water mixed marine clay slurry the dielectric constants for the first three sampling ports are approximately the same, however it is considerably high at the forth sampling port .

Dielectric constant decreases with decreasing solid concentration in the suspension. Therefore dielectric constant for the top three ports reaches to a constant value at approximately 80 in time, as expected (dielectric constant of distilled water is 80). However, dielectric constant increases for the forth tap. Increasing the particle size increases dielectric constant. Larger particles allow greater displacement of adsorbed cations along the clay surfaces, rendering larger polarizability.

Dielectric constant of salt water mixed marine clay slurry increases with time, whereas it decreases with time for the tap water mixture. When salt particles are dissolved in solution, the dissolved ions separate and are free to move in the solution. Cations go into the inner part of the double layer and their concentration in the diffuse double layer decreases. At high salinity, the platey shape particles can quantitatively explain the large values of dielectric constant.

4.3.4.2. MC+SW+Sludge 5% and MC+SW+Sludge 10%

Figures 4.64 and 4.65 show the variation of dielectric constant with depth. Dielectric constant decreases sharply with the depth of settling column at the beginning of the test for both of the sludge mixed marine clays slurries. There is considerable fluctuation of the dielectric constant along the length of the column with time. This may be due to the fluctuation of pH at the same time. However, there is a general decreasing trend in dielectric constant with time. This indicates decrease in polarization which is probably due to reduced electrolyte and particle concentration as they settle out of the water column.

4.3.4.3. MC+SW+Crude Oil (5%) and MC+SW+Crude Oil (10%)

Figure 4.66 and 4.67 show the time variation of dielectric constant of crude oil mixed marine clays. Dielectric constant increases with time for the top three ports but stays constant for the forth tap. The oil in the water column first decreases the overall dielectric constant. As it settles out the dielectric constant increases as it does in the saline water, marine clay suspension.

4.3.5. Electrical Conductivity of the Suspension

Conductivity is a numerical expression of the ability of a medium to carry an electric current. This number depends on the total concentration of ionized substances dissolved in the medium and the temperature at which the measurement is made.

4.3.5.1. MC+TW and MC+SW

Conductivity of the tap water mixed marine clay increases with the depth of the sampling ports. The top three port conductivity values decrease with time as shown in Figure 4.68. Clay particles settle carrying the electrolytes with time therefore decreasing conductivity. However, conductivity increases with time for the forth tap. When the clay concentration increases, clays start to dissociate into ions and clay-water micelle. The conductivity of the ions and the electrophoresis of the micelle increase the conductivity of the solution.

Conductivity of salt water mixed marine clay increases with the depth of the sampling ports and with time as shown in Figure 4.69. Conductivity of salt water mixed marine clay is significantly higher than that of the tap water mixed marine clay as expected. Conductivity increases with the increased salt ion concentration in the solution.

4.3.5.2. MC+SW+Sludge (5%) and MC+SW+Sludge (10%)

Conductivity of sludge mixed marine clay increases with time, however stays approximately constant with depth. Addition of sludge to marine clay decreases the conductivity of the solution as shown in Figures 4.70 and 4.71. This may be due to organic adsorption of ionic species in the water column. As the organics settle the ionic concentration in the water column may increase from dissolution and diffusion of bottom layers which would then explain the slight increase in the conductivity.

4.3.5. 3. MC+SW+Crude Oil(5%) and MC+SW+Crude Oil (10%)

Conductivity of crude oil mixed marine clay decreases with time for the upper ports, and increases for the lowest port as shown in Figures 4.72 and 4.73. The decrease may be caused by the adsorbtion of salt ions by the oil which settles and removes them from the upper water column.

4.3.6. Turbidity of the suspension

Turbidity is a method of determining the quantities of substances in the form of fine, suspended precipitates. Turbidity in water is caused by the presence of suspended matter, such as clay particles, finely divided organic matter and other particulate substances. Turbidity is an expression of the optical property that causes light to be scattered and adsorbed rather than transmitted in straight lines through the sample.

4.3.6.1. MC+TW and MC+SW

Turbidity of the tap water mixed marine clay decreases with depth and time except for the forth port as expected (Figure 4.74). Turbidity of saline water mixed marine clay is slightly higher than the tap water mixed marine clay at the lower ports. This is probably because of the reduced repulsion between the colloids in the presence of salt as shown in Figures 4.74 and 4.75.

4.3.6.2. MC+SW+Sludge (5%) and MC+SW+Sludge (10%)

Turbidity of the sludge mixed marine clays are higher than the saline water mixed marine clay initially. They reach to about the same distribution as in saline water mixture in about two days. These data are shown in Figures 4.76 and 4.77.

4.3.6.3. MC+SW+Crude Oil (5%) and MC+SW+Crude Oil (10%)

Turbidities of the crude oil mixed marine clays are higher than the saline water mixed marine clay as shown in Figures 4.78 and 4.79. The time rate of change of the turbidity measurements are similar to those of the sludge mixed clays. In both cases, however, the lower percentages of the contaminant produce higher turbidity initially.

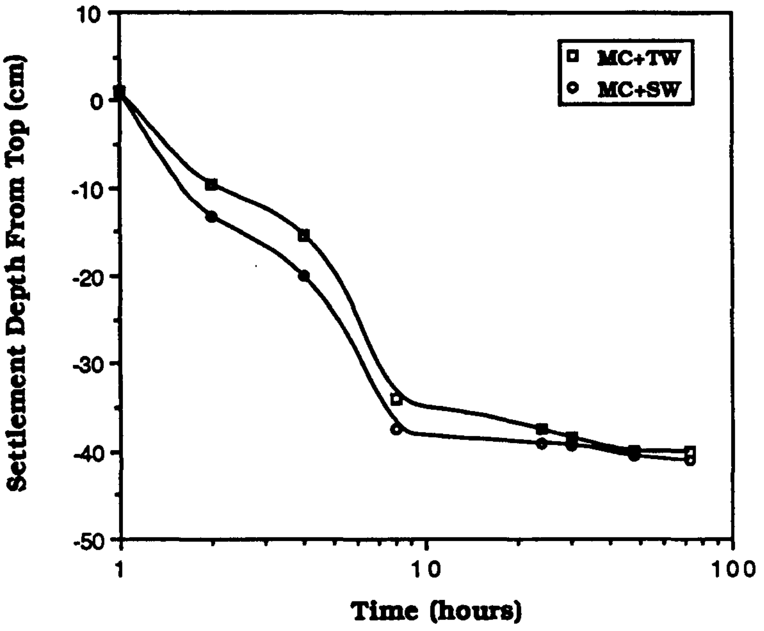


Figure 4.34. Settlement versus Time for MC+TW and MC+SW

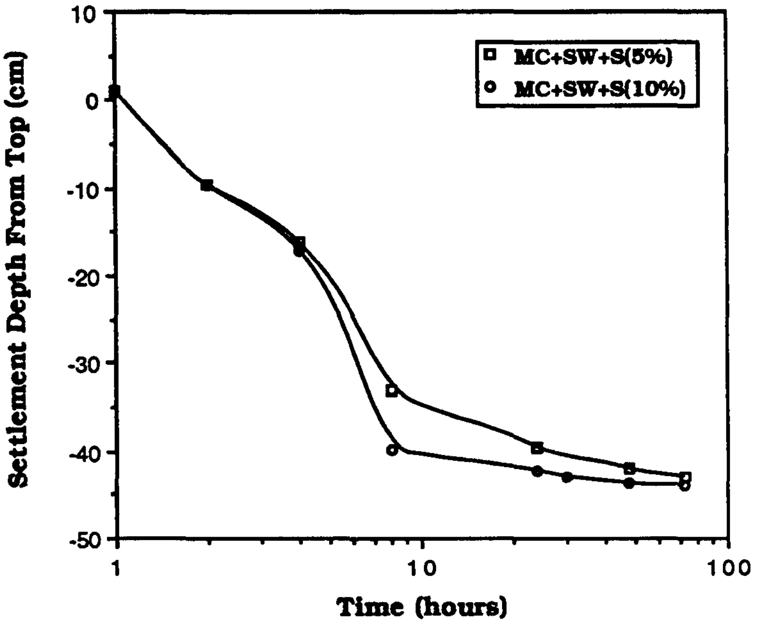


Figure 4.35. Settlement versus Time for MC+SW+SLUDGE(5%) and MC+SW+SLUDGE(10%)

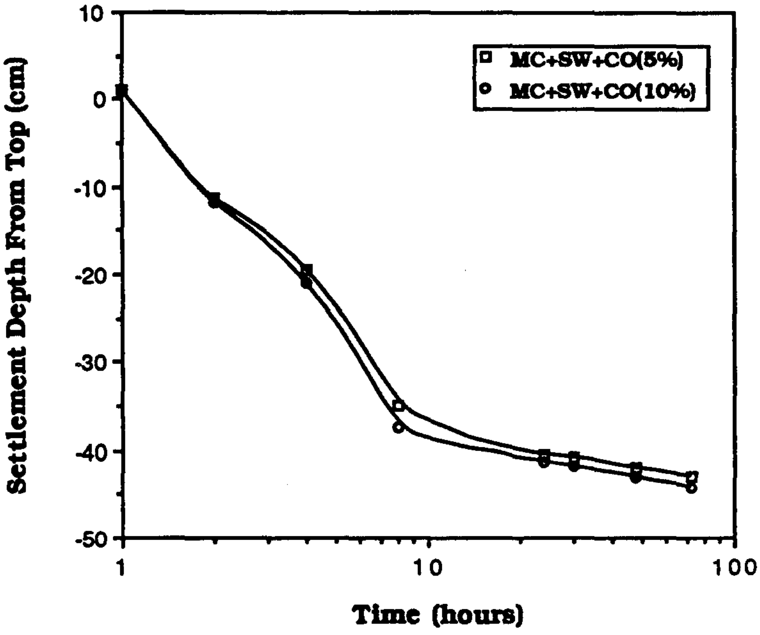


Figure 4.36. Settlement versus Time for MC+SW+CRUDE OIL (5%) and MC+SW+CRUDE OIL (10%)

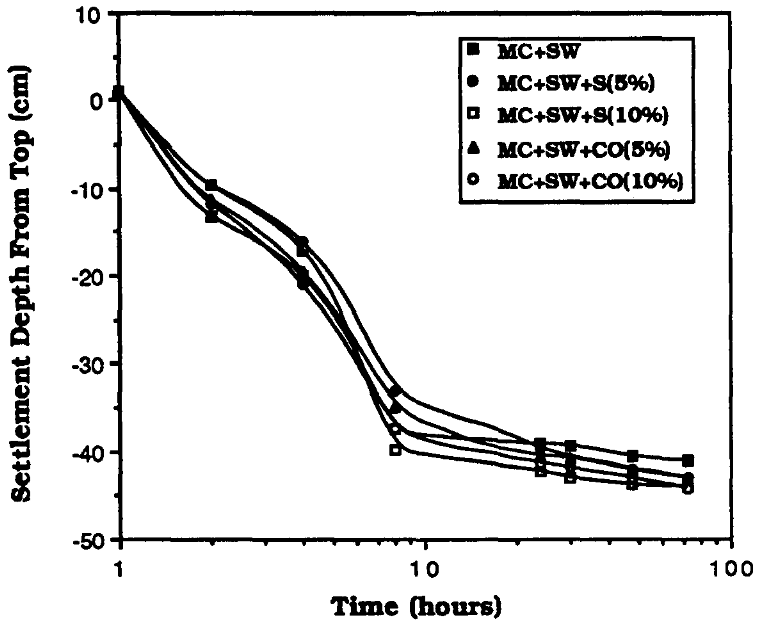


Figure 4.37. Settlement versus Time for MC+SW+ADDITIVES

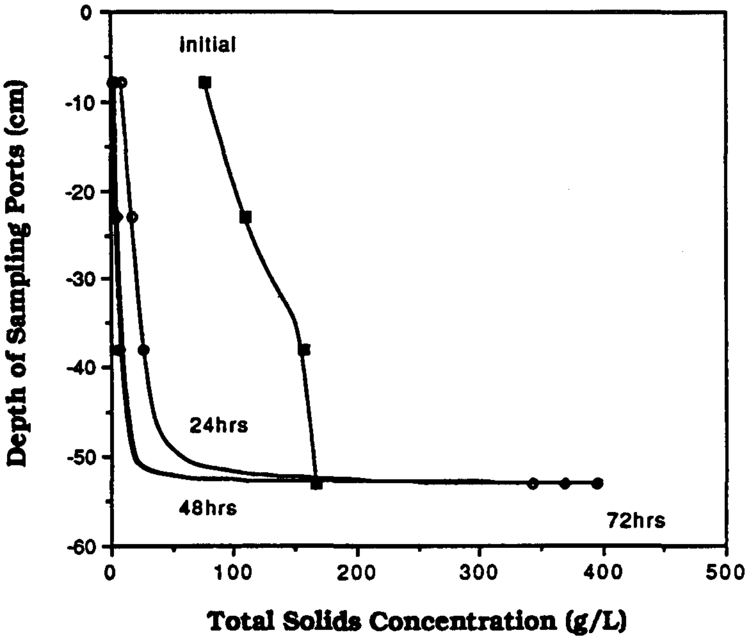


Figure 4.38 Depth versus Total Solids Concentration for MC+TW

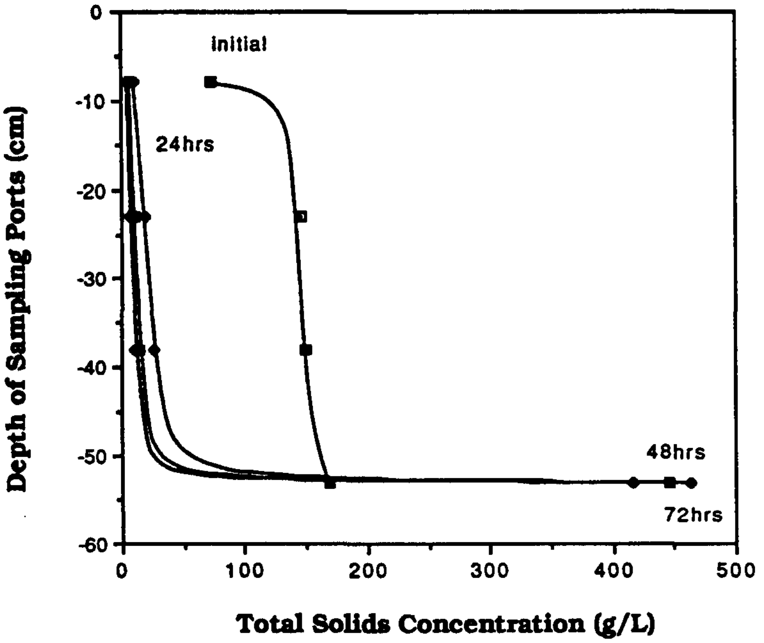


Figure 4.39 Depth versus Total Solids Concentration for MC+SW

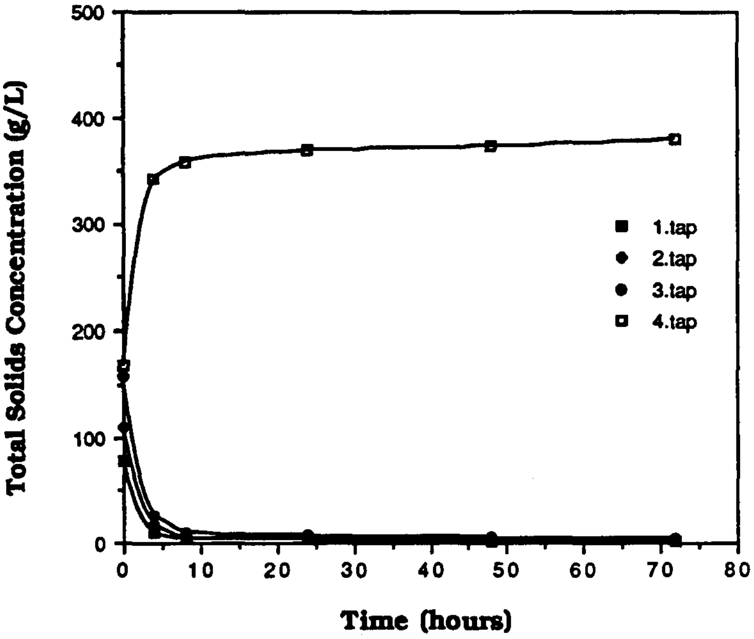


Figure 4.40 Total Solids Concentration versus Time for MC+TW

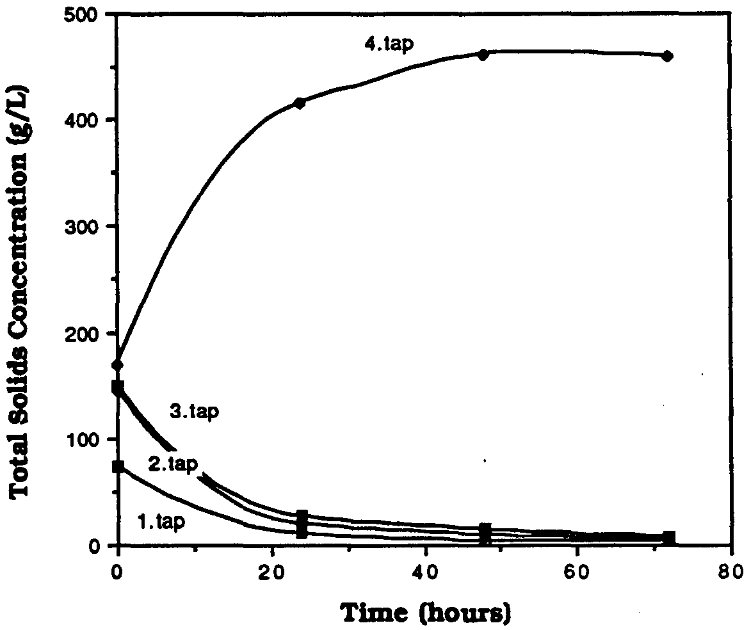


Figure 4.41 Total Solids Concentration versus Time for MC+SW

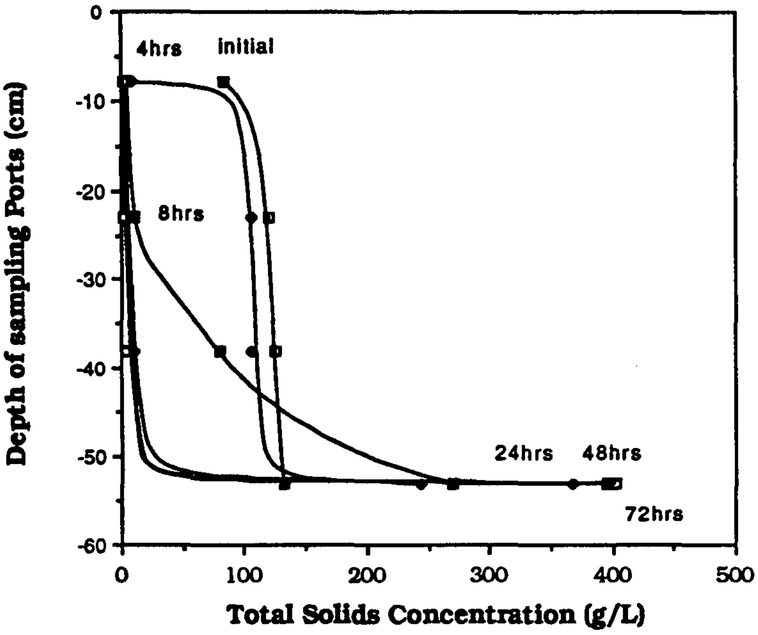


Figure 4.42. Depth versus Total Solids Concentration for MC+SW+SLUDGE (%5)

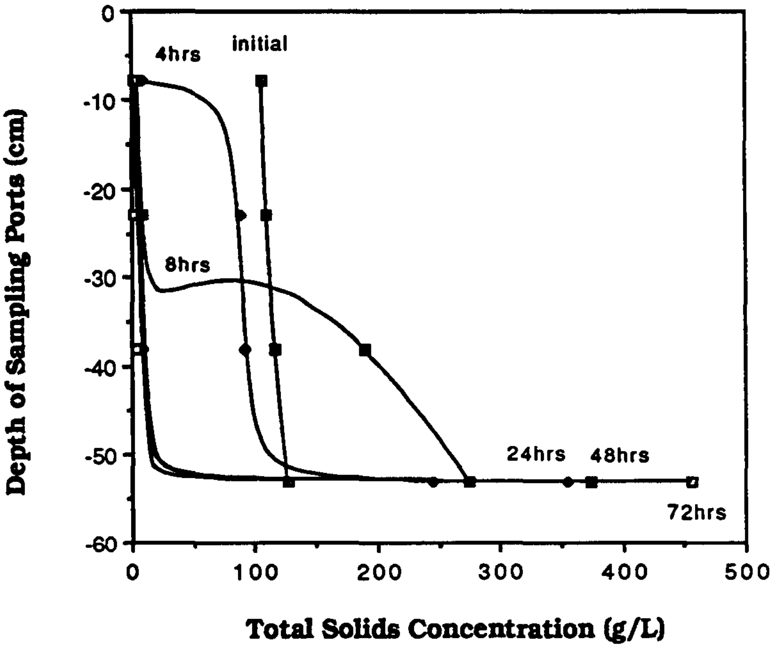


Figure 4.43. Depth versus Total Solids Concentration for MC+SW+SLUDGE (10%)

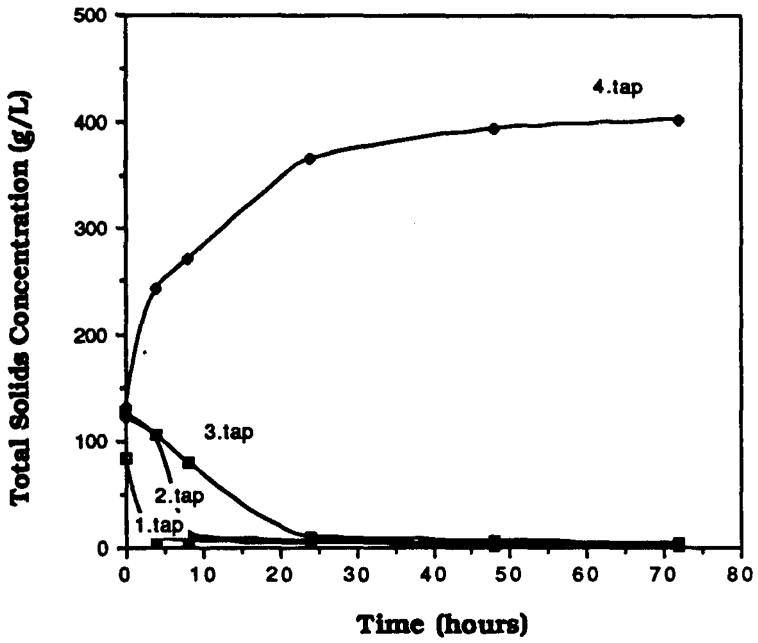


Figure 4.44. Total Solids Concentration versus Time for MC+SW+SLUDGE (5%)

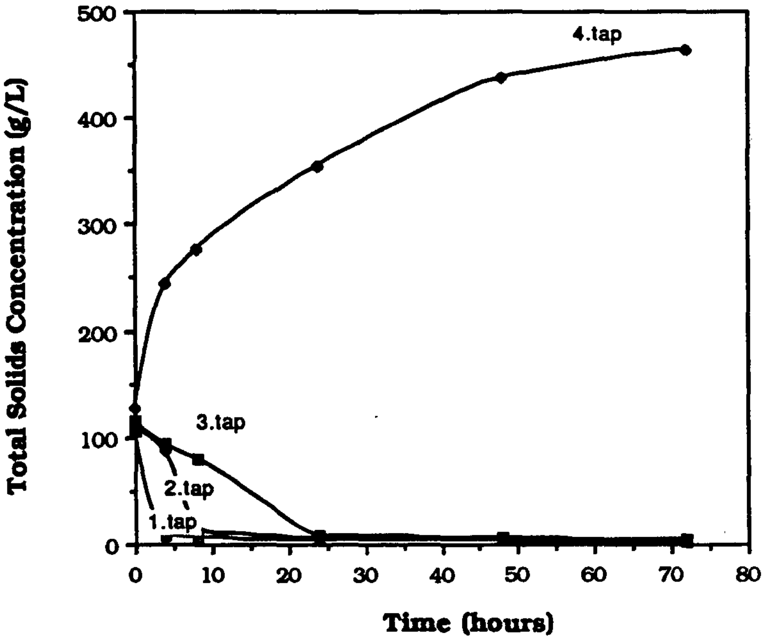


Figure 4.45. Total Solids Concentration versus Time for MC+SW+SLUDGE (10%)

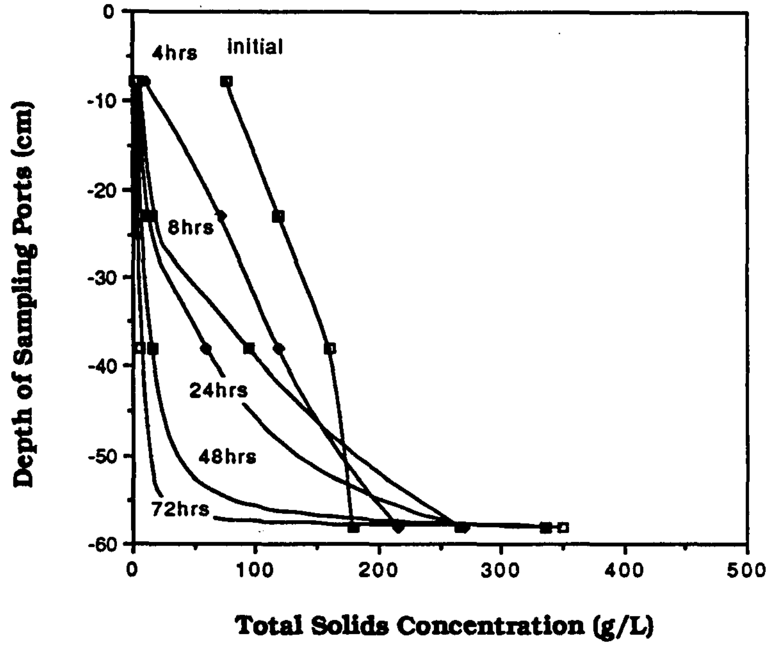


Figure 4.46. Depth versus Total Solids Concentration for MC+SW+CRUDE OIL (5%)

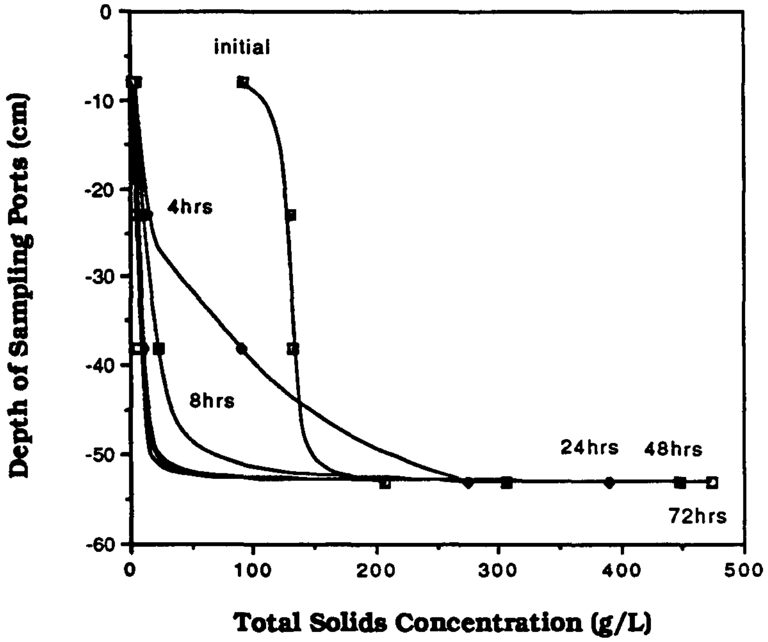


Figure 4.47. Depth versus Total Solids Concentration for MC+SW+CRUDE OIL (10%)

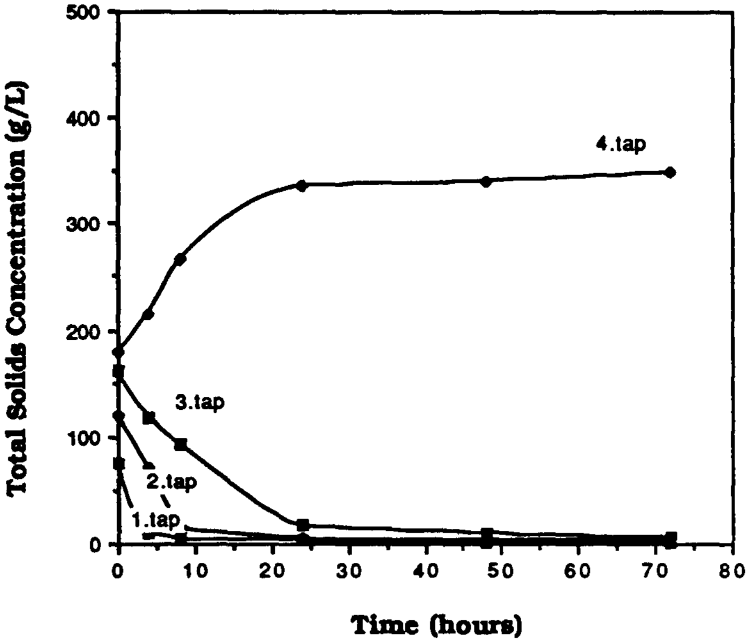


Figure 4.48. Total Solids Concentration versus Time for MC+SW+CRUDE OIL (5%)

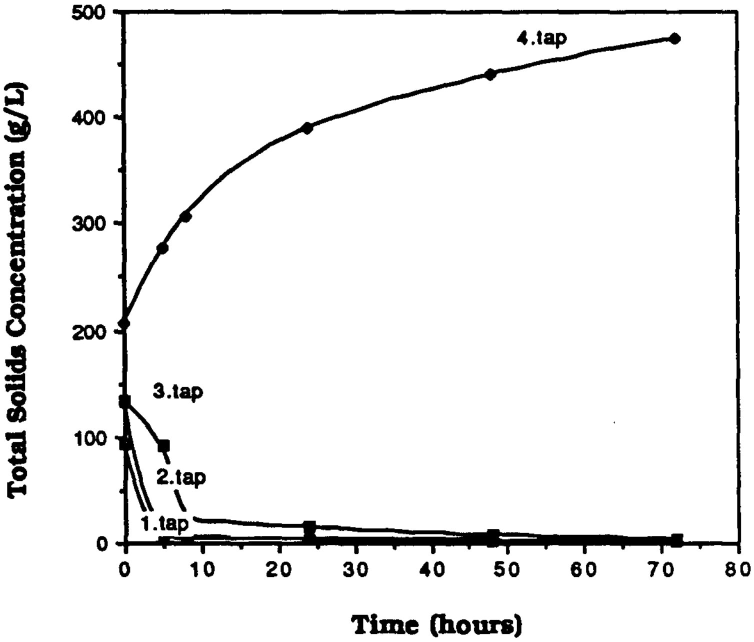


Figure 4.49. Total Solids Concentration versus Time for MC+SW+CRUDE OIL (10%)

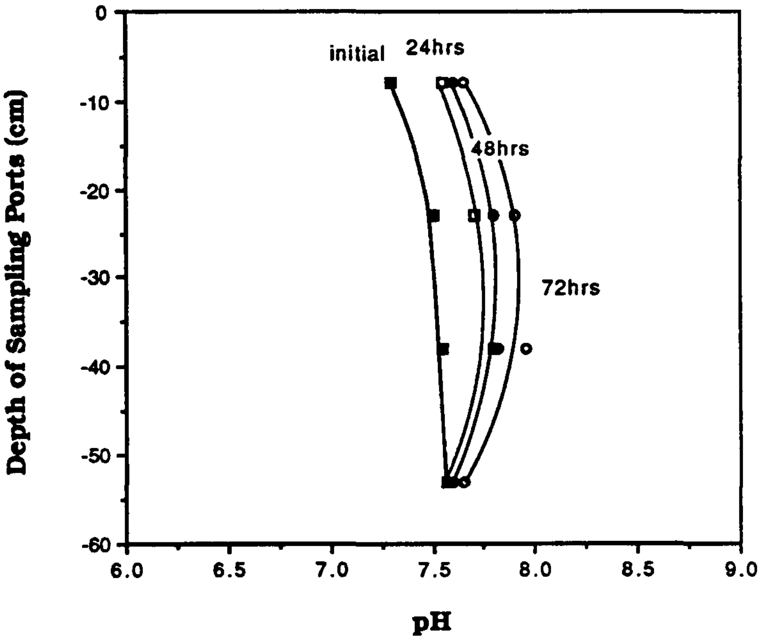


Figure 4.50 Depth versus pH for MC+TW

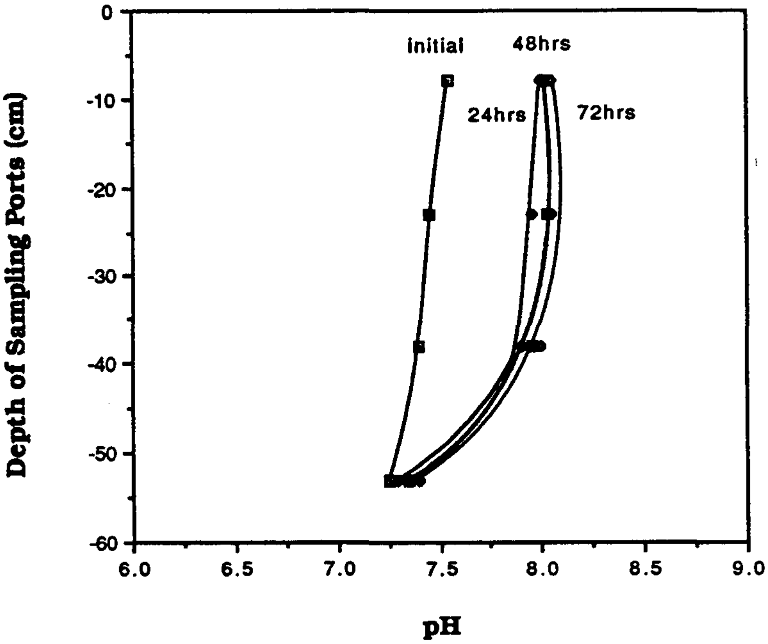


Figure 4.51 Depth versus pH for MC+SW

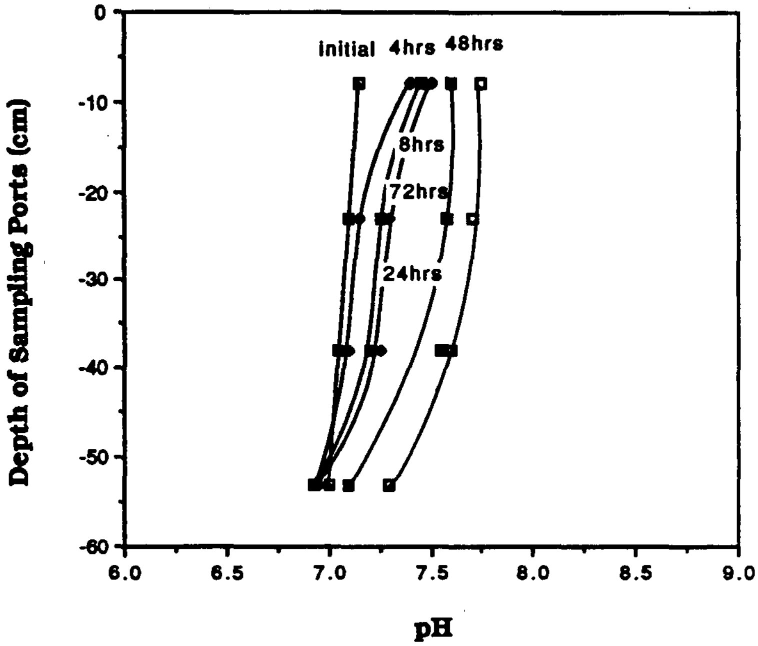


Figure 4.52 Depth versus pH for MC+SW+SLUDGE (5%)

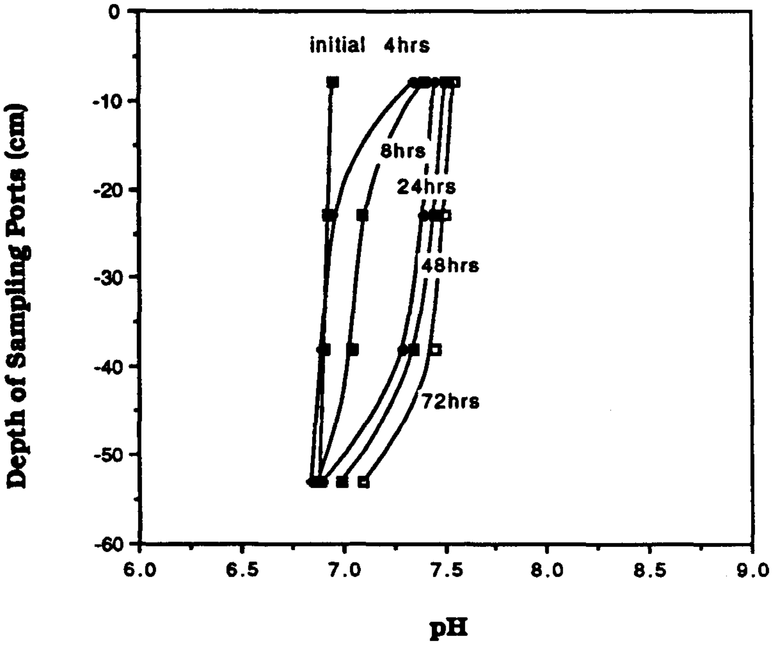


Figure 4.53 Depth versus pH for MC+SW+SLUDGE(10%)

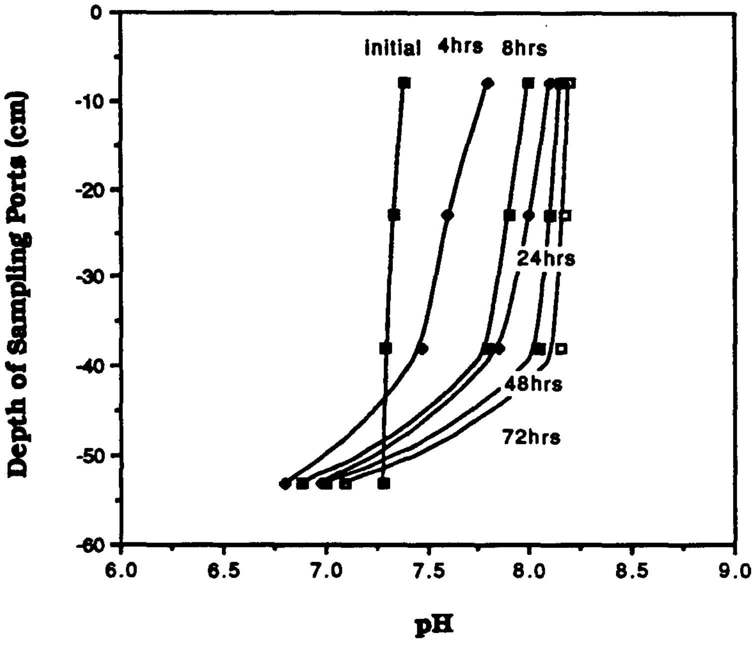


Figure 4.54 Depth vs pH For MC+SW+CRUDE OIL (5%)

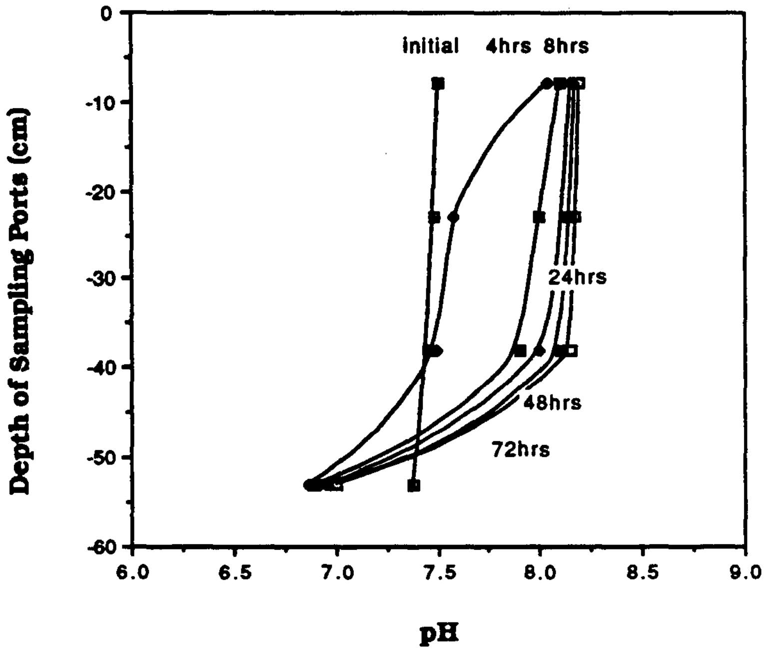


Figure 4.55 Depth versus pH for MC+SW+CRUDE OIL (10%)

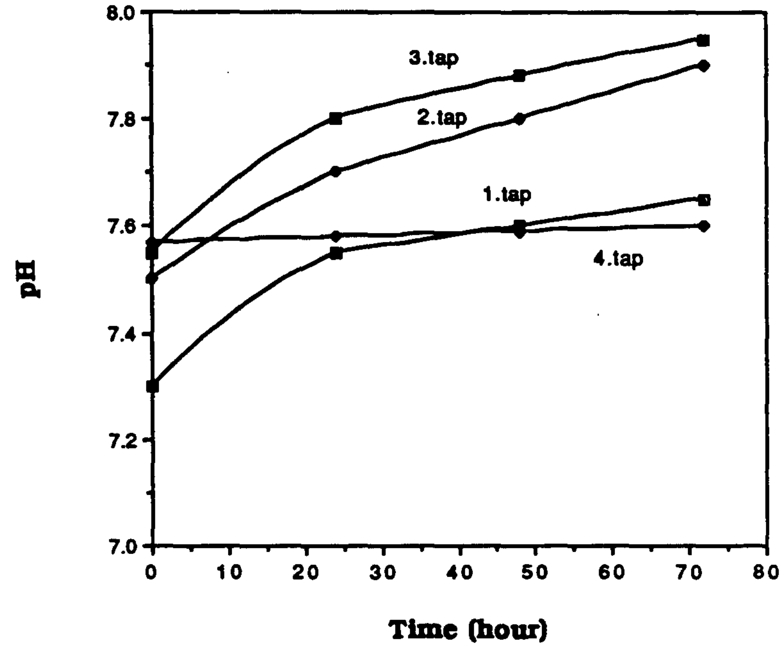


Figure 4.56 pH versus Time for MC+TW

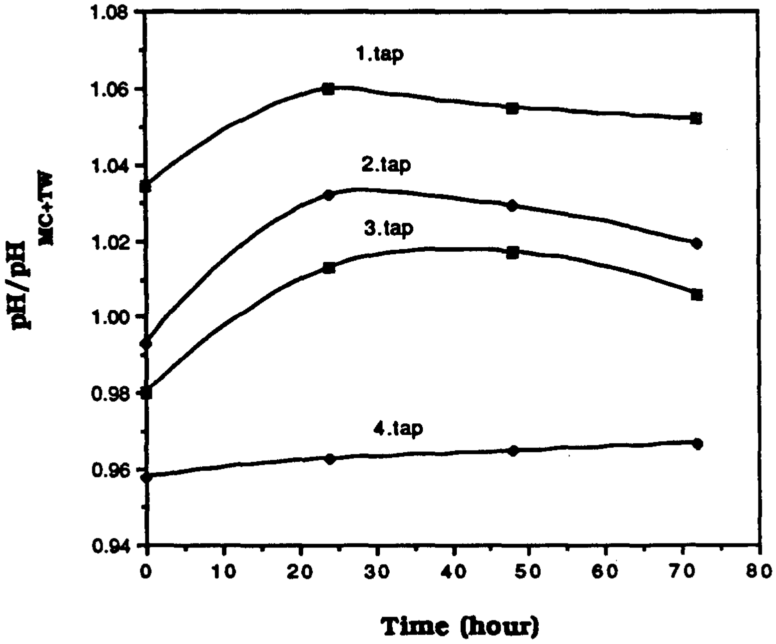


Figure 4.57 pH versus Time for MC+SW (Normalized with MC+TW)

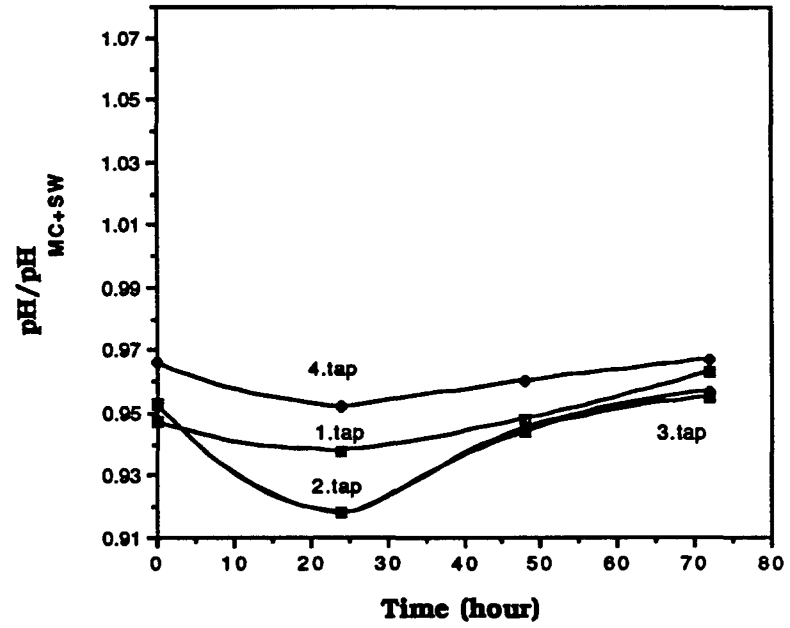


Figure 4.58. pH versus Time for MC+SW+SLUDGE(5%) (Normalized with MC+SW)

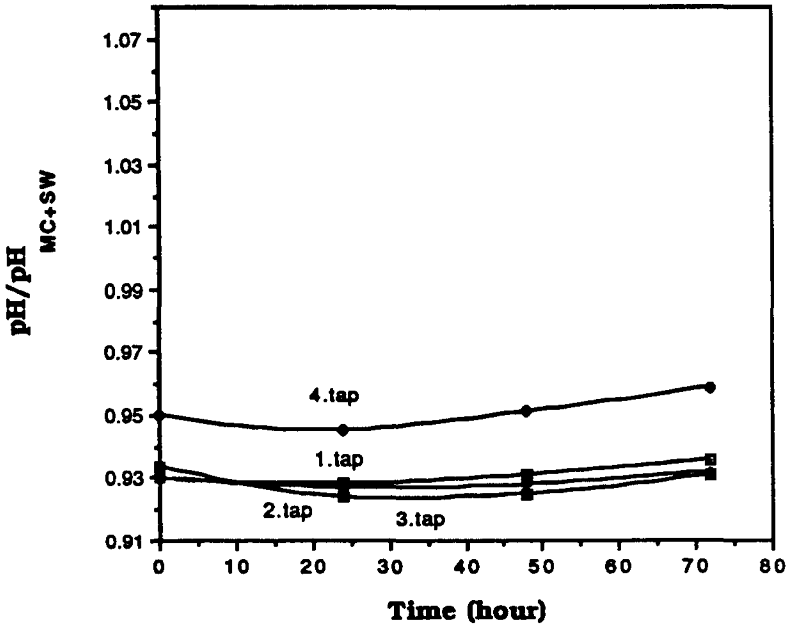


Figure 4.59. pH versus Time for MC+SW+SLUDGE(5%) (Normalized with MC+SW)

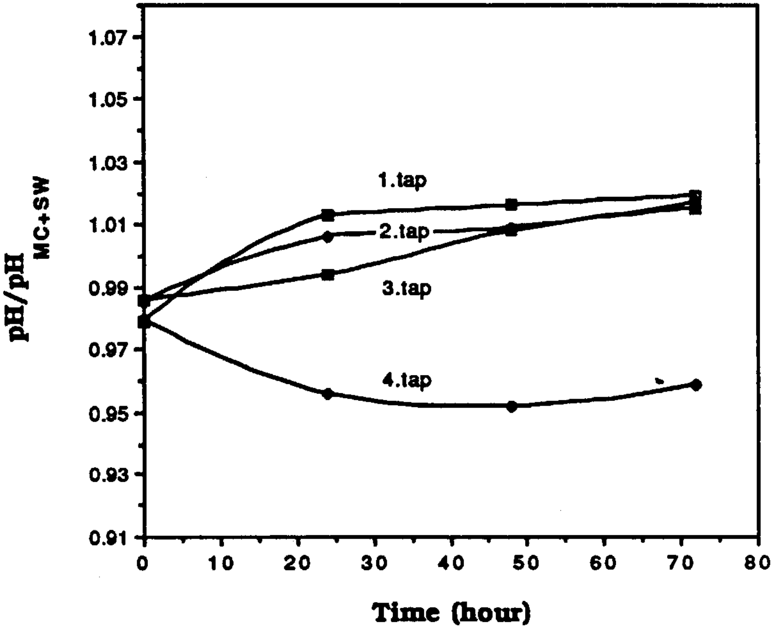


Figure 4.60. pH versus Time for MC+SW+CRUDE OIL(5%)
(Normalized with MC+SW)

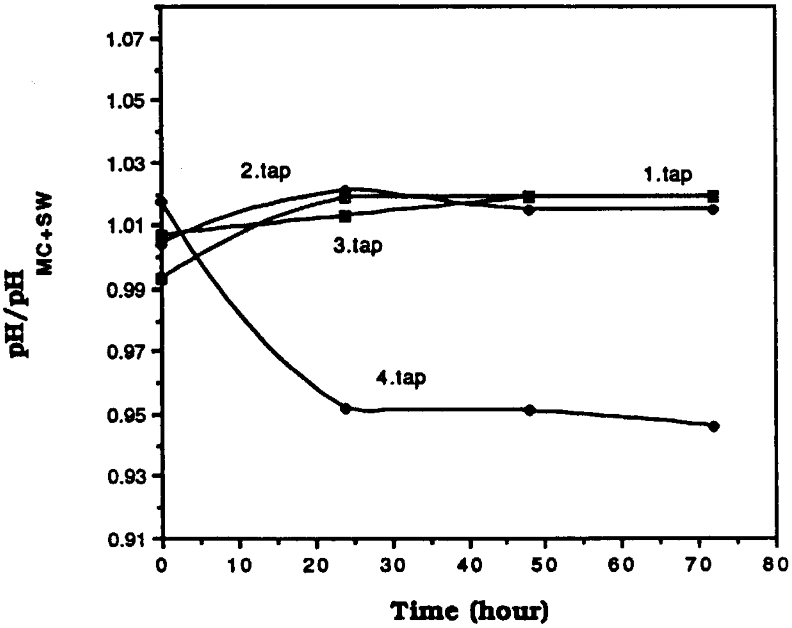


Figure 4.61. pH versus Time for MC+SW+CRUDE OIL(10%)
(Normalized with MC+SW)

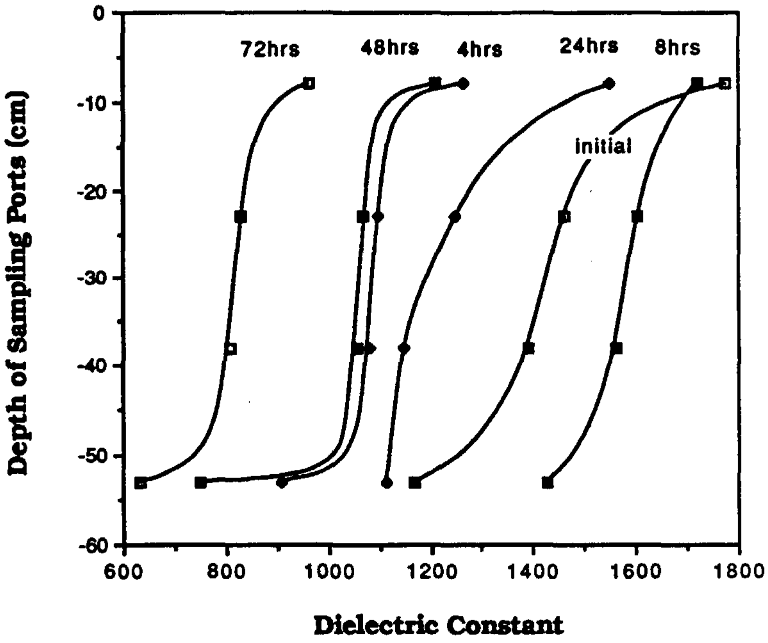


Figure 4.64. Depth versus Dielectric Constant for MC+SW+SLUDGE (5%)

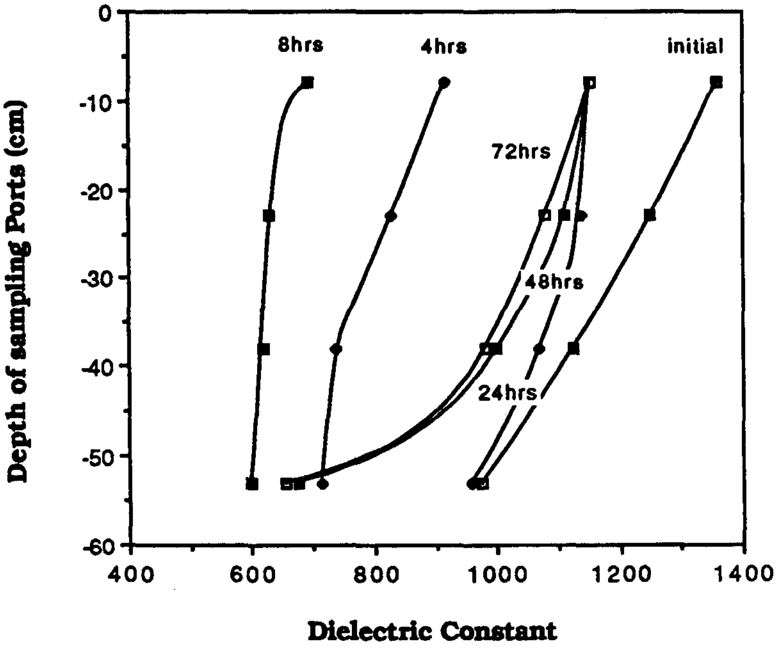


Figure 4.65. Depth versus Dielectric Constant for MC+SW+SLUDGE (10%)

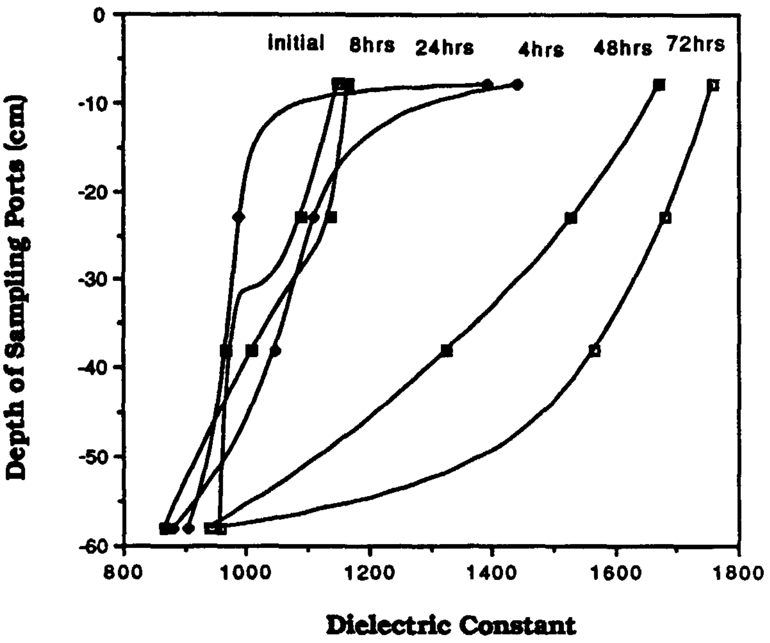


Figure 4.66. Depth versus Dielectric Constant for MC+SW+CRUDE OIL (5%)

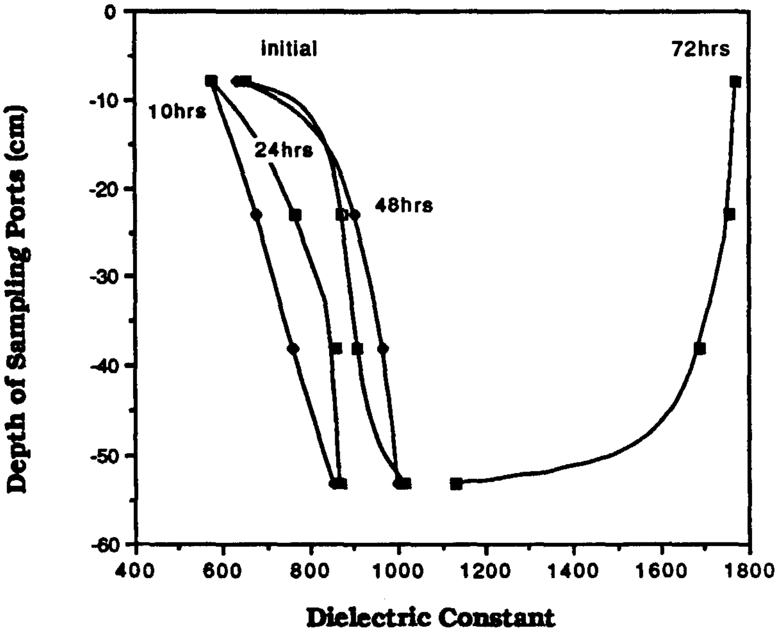


Figure 4.67. Depth versus Dielectric Constant for MC+SW+CRUDE OIL (10%)

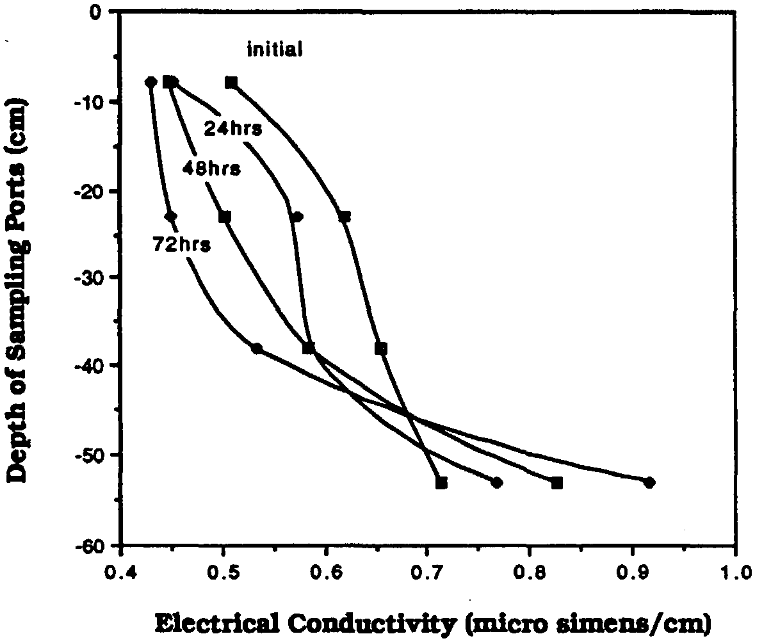


Figure 4.68 Depth versus Electrical Conductivity for MC+TW

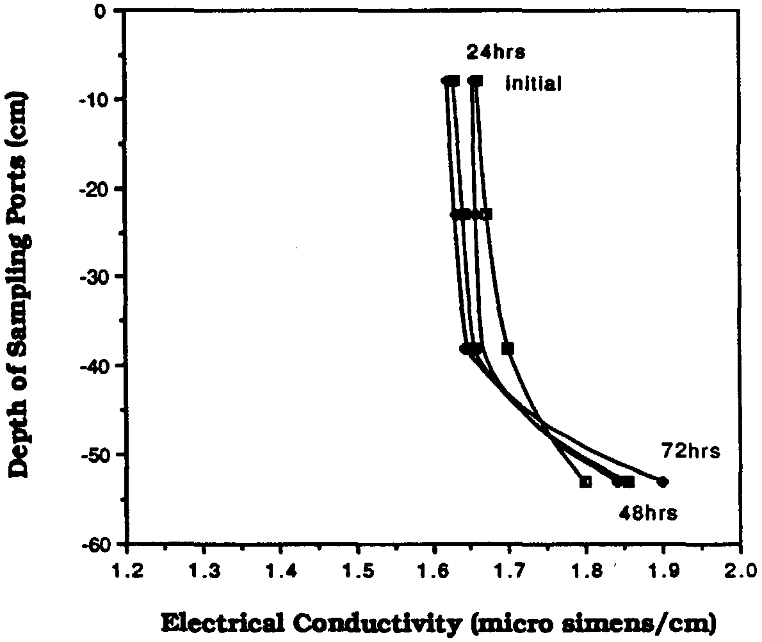


Figure 4.69 Depth versus Electrical Conductivity for MC+SW

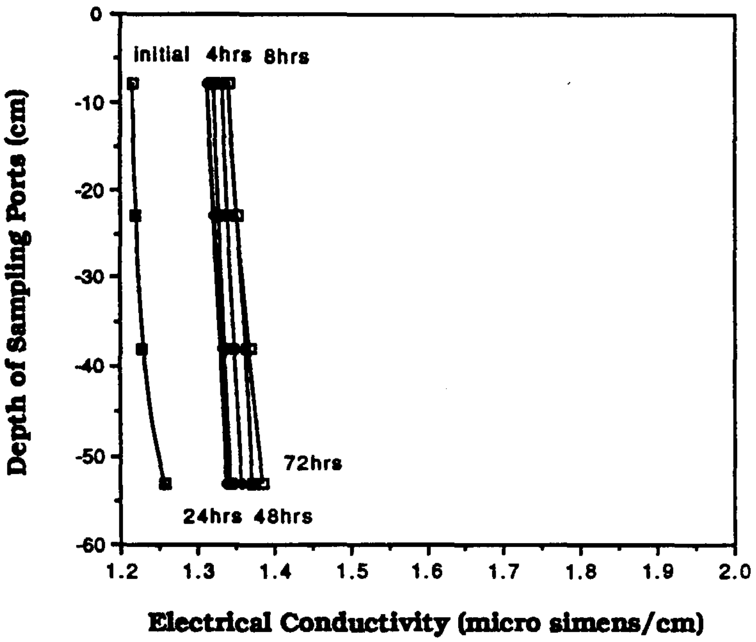


Figure 4.70. Depth versus Electrical Conductivity for MC+SW+SLUDGE (5%)

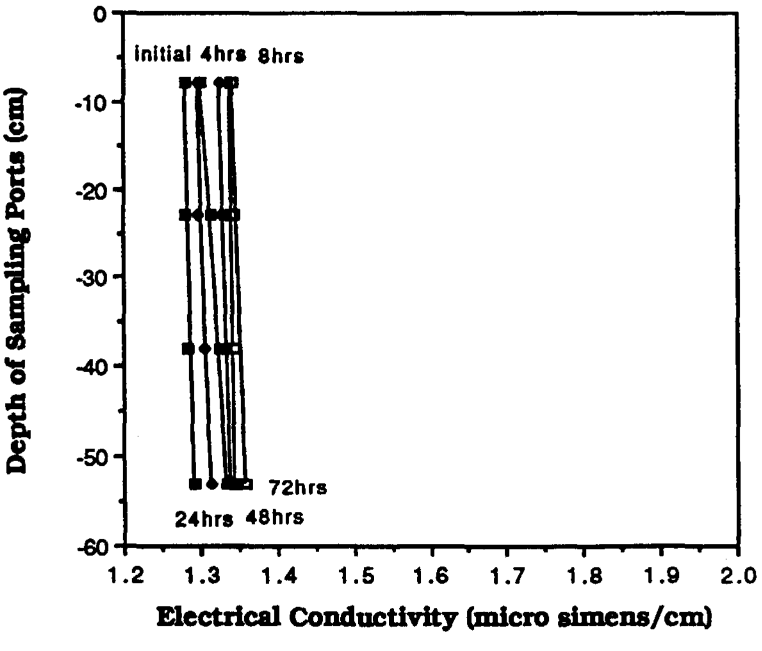


Figure 4.71. Depth versus Electrical Conductivity for MC+SW+SLUDGE (10%)

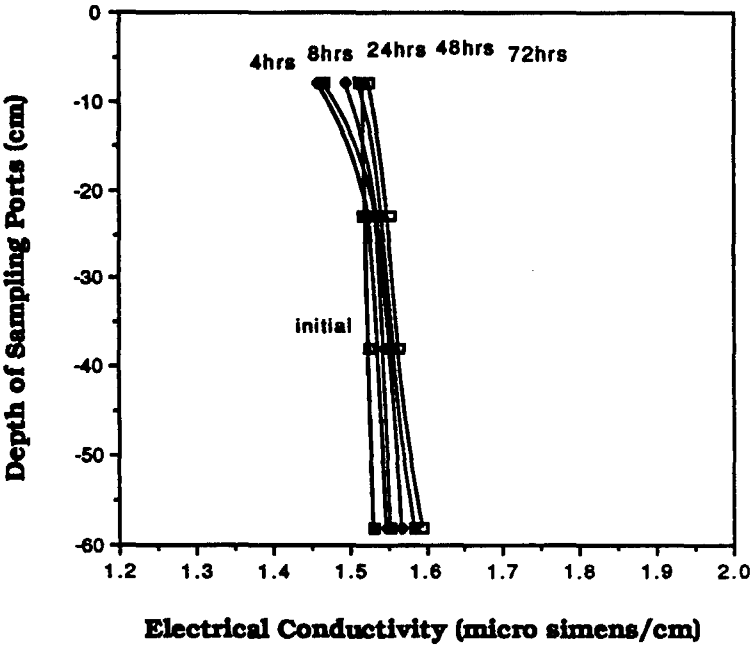


Figure 4.72. Depth versus Electrical Conductivity for MC+SW+CRUDE OIL (5%)

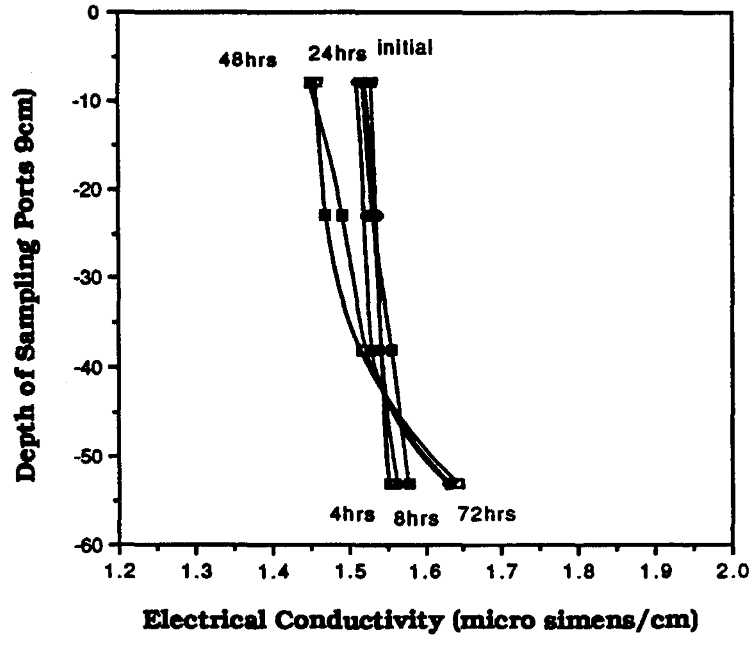


Figure 4.73. Depth versus Electrical Conductivity for MC+SW+CRUDE OIL (10%)

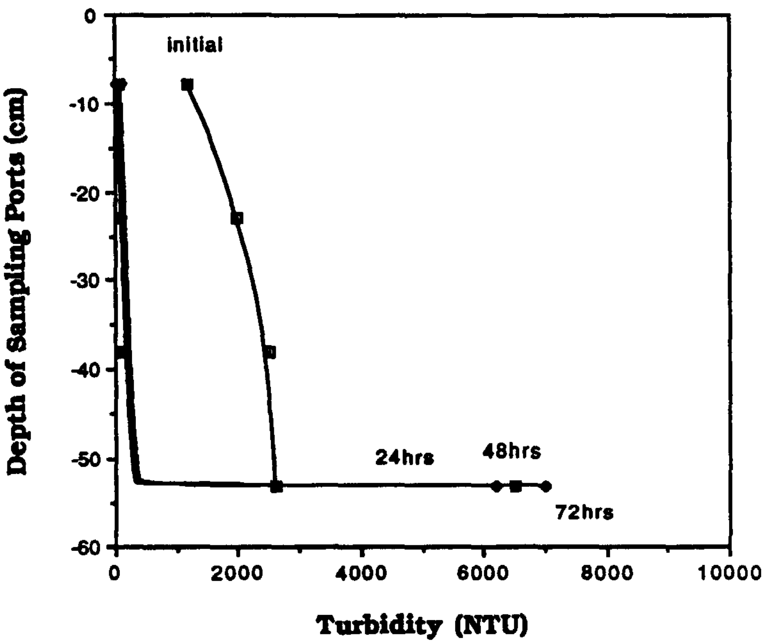


Figure 4.74. Depth versus Turbidity for MC+TW

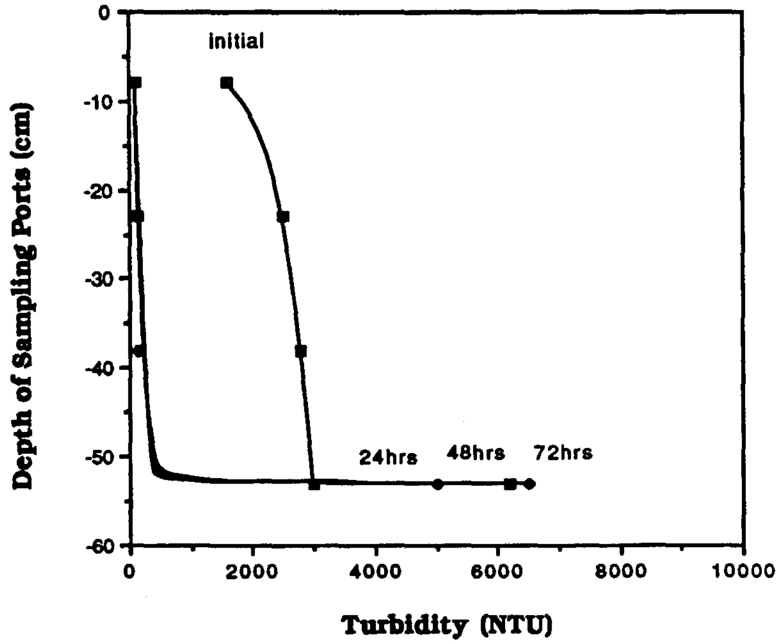


Figure 4.75. Depth versus Turbidity for TW+SW

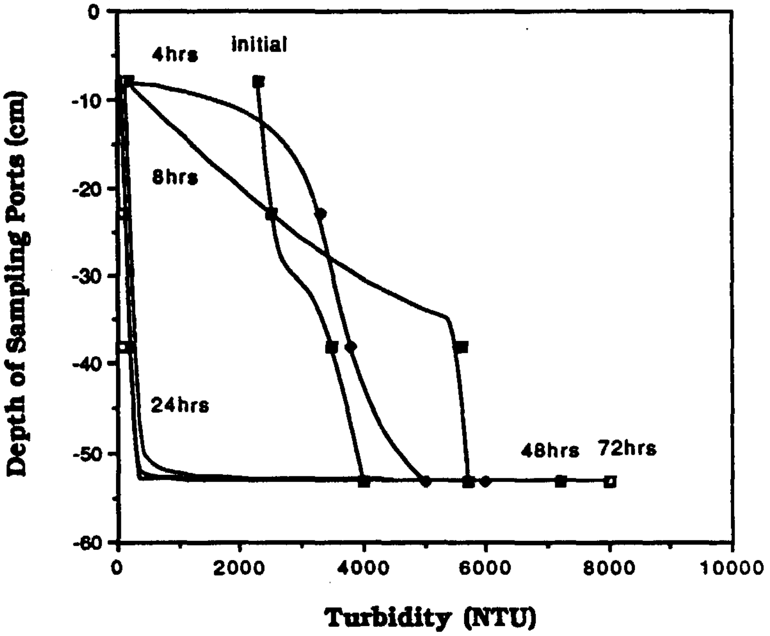


Figure 4.76. Depth versus Turbidity for MC+SW+SLUDGE(%5)

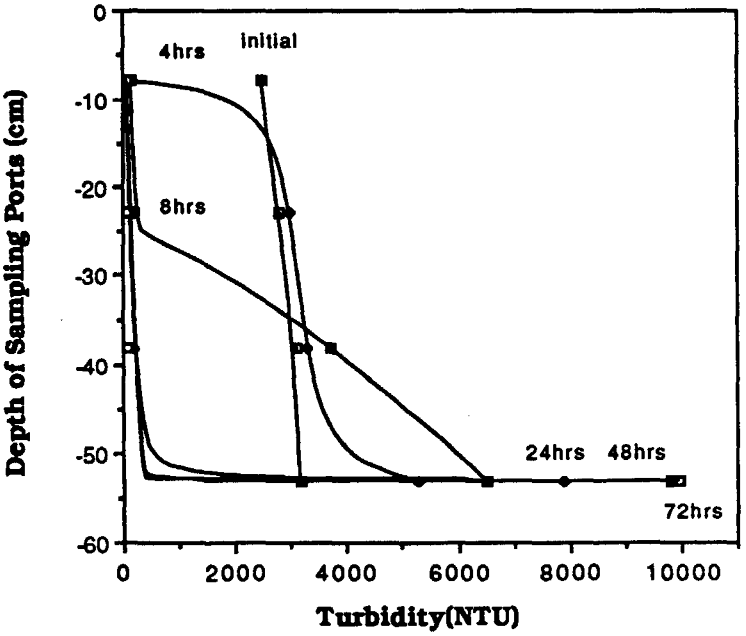


Figure 4.77. Depth versus Turbidity for MC+SW+SLUDGE(10%)

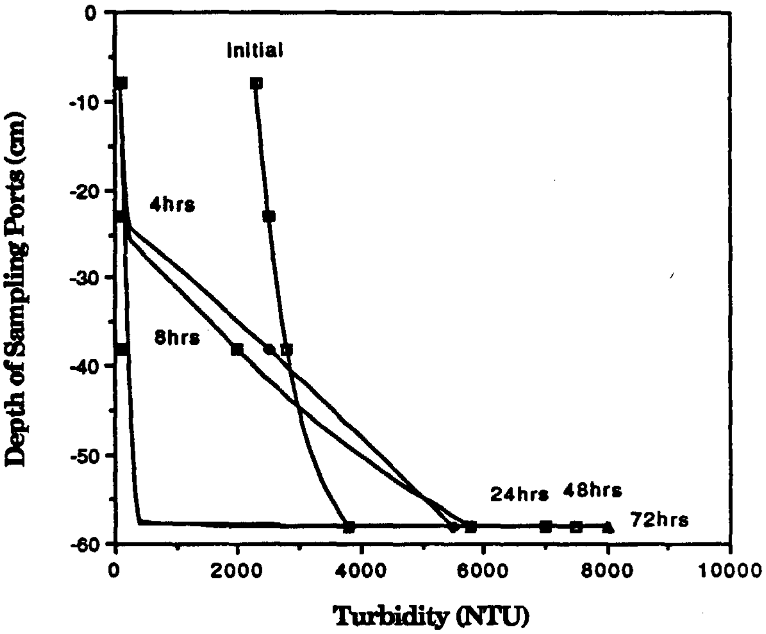


Figure 4.78. Depth versus Turbidity for MC+SW+CRUDE OIL(5%)

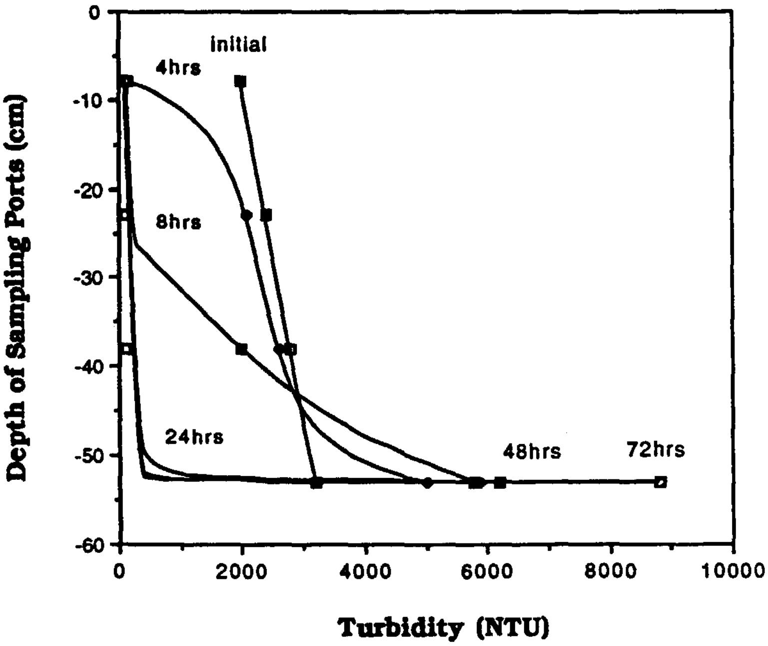


Figure 4.79. Depth versus Turbidity for MC+SW+CRUDE OIL(10%)

CHAPTER 5

PREDICTED MECHANISMS OF INTERACTION OF MARINE CLAY BASED ON MICROSTRUCTURE

Introduction

Scanning electron microscope is an ideal tool to illustrate the features of fabric of fine grained soils. Sediment microstructure is a function of the fabric and the physico-chemistry of the clay water system. Microstructural units are composed not only of single clay particles but also compound particles held together by physico-chemical forces. Compound particles are domains, aggregates, floccules, clusters and organic compounds. Clay fabric is defined as the orientation and arrangement of clay particles and particle to particle relationships. Physico-chemistry describes the interparticle forces between the particles. Physico-chemical forces are responsible for aggregating clay particles in suspension and holding the sediment together when the it is formed. If the physico-chemistry and fabric effects on the properties and mechanics of marine clay are understood, sediment behavior can be estimated more realistically under changing environmental conditions.

The behavior of clay particles in the ocean is important to understand the physico-chemical properties of marine sediments which cover the sea floor. Suspended particles enter the sea by rivers, costal erosion, aeolian transport and submarine volcanic eruptions. Sediment fabric can be used to understand the various depositional environments. Clay fabric is useful to understand the particle-to-particle and particle-to-contaminant interactions which may be related to their physical and mechanical properties. In addition, the clay fabric provide a framework for the behavior of clay sediments under static and dynamic loads in different environmental conditions.

The clay microstructure of suspended sediments and sedimentary deposits depends on the clay type and the environmental conditions at which they are deposited. These factors produce the depositional and post-depositional sediment properties in time. Clay particles exhibit electrical forces on their surfaces. These forces are important in determining the fabric of the sedimented material. When the deposition is completed post-depositional processes come into play. The clay fabric and particle-to-particle and particle-to-contaminant arrangements and interactions control many geotechnical properties. The chemical environment of clay particles is critical during the depositional stage of fabric formation in the water column and at the sediment-water interface. The chemical nature of the fluid medium strongly affects the electrostatic interactions among suspended clay particles. Clay fabric are composed of not only single particles but also various combination of particles such as domains, aggregates, floccules and clusters. Some key terms used in this work are given below to describe the fabric of marine clay and its interaction with contaminants:

1. "PARTICLE" is a single clay plate. The particle can be considered as the fundamental element of clay fabric.
2. "DOMAIN" a perfect stack of face-to-face clay plates with some slight face-to-face association. Domain can be formed from flocculation, consolidation and during the deposition of clay plates in different environmental conditions.
3. "CLUSTER" is a group of particles which has a random or almost random internal structure.
4. "CHAIN OR LINKING CHAIN" is a series of particles which are face-to-face and edge-to-edge contact. This may terminate in contact between larger units such as flocs or larger particles.
5. "OIL BRIDGE" is a long thin connection between a clay particle and oil surface.

6. "FIBRE " is a solid sludge particle.

Particle associations in clay suspensions can be described as follows:

1. A "DISPERSED" soil structure is one in which the electrical forces between adjacent particles at the time of deposition produce repulsion. Dispersed structures are those in which particles tend to move apart.

2. A "FLOCCULATED" soil structure is one in which the net electrical forces between adjacent particles at the time of deposition produce attraction. Therefore, flocculated structures are those in which particles tend to join together such as edge-to-edge or edge-to-face association of particles.

3. The soil structure is said to be "AGGREGATED" if the net electrical forces are the net attractive forces during deposition. Therefore there is face-to-face association of several clay particles.

4. The soil structure is said to be "AGGLOMERATED" if the clay particles are held together by surface tension, organic cohesion and adhesion. This can be spherical agglomeration in case of oil mixed clay particles.

All these structures can be found in natural soils. Their presence depends on the type of clay minerals found in the environment and the environmental conditions. The structure formed is mainly controlled by the surface properties of the clay minerals. When two clay minerals approach each other face-to-face or edge-to-edge, similar electrostatic charges come into close contact and a repulsion force is created. Increasing electrolyte concentration of the surrounding medium compresses the double layer neutralizing charge sites and van der Waals attraction dominates. If two particles approach face-to-edge, the particles attract each other. If the ions in the surrounding medium are movable, the cations at the face and anions at the edge are pressed out and face-to-edge contacts of the clay particles are formed by electrostatic attraction. Therefore, card-house structure is formed (van Olphen, 1956). The porosity of this structure is high. In nature, card-house structures are formed when the sedimentation of clay takes palace in saline water or sea water. The high electrolyte concentration of the surrounding solution copresses the diffuse double layer therefore, face-to-edge contacts are formed.

5.1. Tap Water Mixed Marine Clay

If the electrolyte concentration in a suspension is low, the clay tends to disperse and when it settles out the resulting sediment is dense and compact. Clays deposited in tap water showed dispersed structure and settled with a slower velocity than salt water mixed marine clay. A greater degree of parallel particle orientation was observed in these specimens as shown in the micrographs in Figures 5.1, 5.2, 5.3 and 5.4. This occurs because the particles first must overcome an energy barrier to aggregate. When clay particles approach face-to-face, energy is minimized due to the lack of electrical attraction between the particles. At this stage the only attractive force between the particles is the van der Waals attraction. Such a system is called colloidally stable or deflocculated. More dense and compact structure can be seen in the micrograph in Figures 5.1 and 5.2.

Figure 5.1. SEM Micrograph of Tap water mixed Marine Clay Sedimented Specimens (Magnification: 5000X).

Figure 5.2. SEM Micrograph of Tap water mixed Marine Clay Sedimented Specimens (Magnification: 8000X).

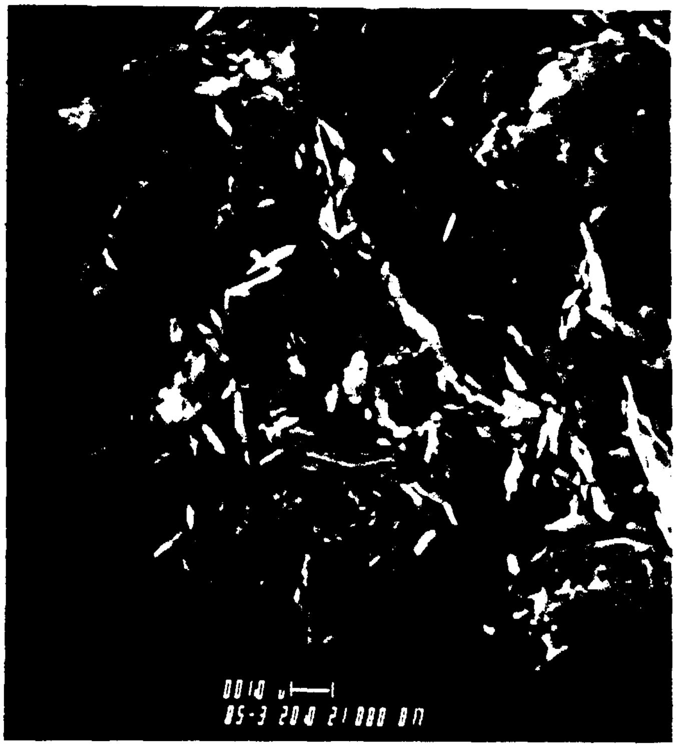


Figure 5.3. SEM Micrograph of Tap water mixed Marine Clay Sedimented Specimens (Magnification: 5000X).

Figure 5.4. SEM Micrograph of Tap water mixed Marine Clay Sedimented Specimens (Magnification: 7000X).

5.2. Salt Water Mixed marine Clay

When the pore water electrolyte concentration is high, the soil flocculates into agglomerations and settles into an open structure. Diffuse double layers around the clay particles are compressed allowing the particles to approach each other at edge to face configuration. When individual particles aggregate together in flocs, the resulting suspension is characterized as colloidally unstable. In the flocculated state, positively charged particle edges may be bound with the negatively charged particle faces. Such edge-to-face orientations can be observed in the electron micrographs of the salt flocculated marine clay sediment samples shown in Figures 5. 5 and 5.6.

In the laboratory sedimentation columns, due to the high electrolyte and high clay concentration, the double layer of each clay particle may have been compressed significantly. In such cases, van der Waals forces of attraction promote single particle chains as indicated in Figures 5.7. The fabric of the sedimented marine clay floccules formed in saline water consists of an open porous network with randomly oriented domains and clusters which can be observed readily. The results of these experiments agree with the fabric given by others in the honeycomb or cardhouse models of clay flocs in saline environments (O'Brien and Harrison, 1969; O;Brien, 1970; Lanier and Janes, 1979). Salt flocculation shows domains, often containing a few particles with overall arrangement of random and open structures dominated by large interdomain macrovoids and cavities. These features are readily observed in the micrograph in Figure 5.8.

Figure 5.5. SEM Micrograph of Salt water mixed Marine Clay Sedimented Specimens (Magnification: 5000X). F: Flocculation (Edge-to-Face), D: Domain

Figure 5.6. SEM Micrograph of Salt water mixed Marine Clay Sedimented Specimens (Magnification: 5000X). F: Flocculation (Edge-to-Face), D: Domain

Figure 5.7. SEM Micrograph of Salt water mixed Marine Clay Sedimented Specimens (Magnification: 10000X). F: Flocculation (Edge-to-Face)

Figure 5.8. SEM Micrograph of Salt water mixed Marine Clay Sedimented Specimens (Magnification: 5000X). F: Flocculation, D:Domain, C: Chain, M: Macrovoids

5.4. Municipal Sludge and Salt Water Mixed Marine Clay

The municipal sludge contain organic particles, fibres and humic substances which are probably similar in chemical structure to the naturally occuring humus in soil. Organic compounds can be adsorbed onto clay mineral surfaces as macromolecular complexes bound with cations. Humic substances are heterogeneous organic substances that are generally characterized as high molecular weight compounds with negative surface charge. The sludge itself had zeta potential measured in the negative millivolts (see Table 3.5) which showed that the overall surface charge of the compounds in the sludge was negative. Since sludge compounds and clay minerals are both negatively charged they are expected to repel each other. However, a wide variety of cations are adsorbed on clay minerals by cation exchange reactions. These cations play an important role in adhesion or coating of organic material on mineral surfaces. In other words, these cations act as bridges that strongly bind the organic and the mineral together. This mechanism is given in Figure 5.9, which shows the interaction of clay particle and municipal sludge through cations.

The SEM photo micrograph of solid particles of sludge is shown in Figures 5.10, 5.12. From these micrographs it can be observed that sewage sludge possesses large particles (50-500 μm) and fibrous substances. In entirety, sewage sludge consisted of a low concentration of these organic particles suspended in water with heavy metals in the parts per million range concentrations (see Table 3.5), and also dissolved organic compounds. The x-ray diffraction spectrum (EDS) of sludge particles (Figure 5.10) and sludge fibre (Figure 5.12) are shown in Figures 5.11 and 5.13. It can be seen that the municipal sludge used in this study have following inorganic elements predominantly: aluminum, silica, cobalt, cadmium, copper, chromium, sulphur, manganeze, zinc and iron.

Fibrous particles attract the clay particles and act as reinforcing members or "bridges" between the flocculated domains (Figure 20). The mechanism is given in Figure 5.14, which shows the interaction of clay particle and fibrous particle through cations. The SEM photo micrograph of sludge mixed marine clay is shown in Figure 15.The x-ray diffraction spectrums of sludge mixed marine clay as indicated by an x in Figures 5.16 and 5.18 are given in Figures 5.17 and 5.19, respectively. The EDS in

Figure 5.17 shows predominantly silica on a selender shaped particlesThis indicates that fibrous particle of sludge is probably coated by clay particles. The EDS in Figure 5.19 shows elements similar to those occuring in solid sludge particles, which indicates that the selender particle is probably sludge fibre. The constituents of sludge also seem to promote face-to-face agglomeration of the particles in an oriented fashion as shown in Figures 5.21 and 5.22. Sludge agglomerates and "glues" the particles into domains such that these particles are cemented or bounded together by dissolved organic matter.

Municipal or sewage sludge consists of organic particles suspended in water. The natural organic particles in municipal sludge contain heavy metals and synthetic organics that are present in all foods, the human body, and human wastes. The humic substances or organic compounds have similar chemical properties to the humic substances present in the sludge. Humic substances are the heterogeneous organic substances that can be characterized black in color and high molecular weight. Those substances can be adsorbed onto clay mineral surfaces as macromolecular complexes bound with some cations.

Sludge compounds and clay minerals are both negatively charged. They are expected to repel each other. Positively charged metals neutralize the charges and link the clay particles and sludge compounds together. The mechanisms of reactions between the sludge compounds and clay minerals are varied and many. Both, physical and chemical forces may take place in the formation of sludge-clay complexes.

Chemical Bonds

The chemical bonds formed between clay minerals and sludge compounds might be ionic bonding and hydrogen bonding.

Ionic Bonds: The cations are adsorbed on clay minerals by cation exchange reactions. These exchangeable cations play a leading role in binding organic matter on mineral surfaces. Polyvalent cations such as iron and aluminum provide good and stable linkages. They can act as bridges between sludge compounds and clay mineral surfaces. Cation exchange capacity of sludge is high at around 134 meq/100gr dry clay. Sludge has also heavy metals. When sludge compounds react with clay minerals in the presence of exchangeable cations, cation bridging is probably the dominant mechanism of reaction. Cation bridge formation can also help the adsorption of uncharged polar organics by clay minerals.

Hydrogen Bonding: Hydrogen bondings are formed between the molecules of organic substances and clay mineral components. Sludge compounds are linked through exchangeable cations by means of hydrogen bonding or water bridge. Hydrogen bonding to the clay surface is strong in three-layer clay minerals.

In addition to these main mechanisms of chemical reactions between organic matter and clay mineral surfaces, other chemical bondings such as covalent bonds might also be formed. Covalent bonding is a type of linkage where the reacting atoms contribute one electron each, forming a two electron bond.

Physical Bonds

Organic compounds can be held on clay mineral surfaces by physical forces as well as chemical forces. One of the physical forces is the intermolecular attraction or linkage by van der Waals forces. van der Waals forces are the mutual attraction of positively and negatively charged particles forming dipoles.

If electrolytes are introduced in the solution, they modify the colloidal properties of clay minerals and organic matter. Electrolytes decrease the electrostatic repulsion between the clay minerals and sludge components which promotes physical interaction. Physical reactions improve the conditions for chemical bond formation between the sludge and charged sites of the clay minerals. Since the presence of cations act as a linkage between sludge material and clay minerals, the dissolved salts of marine waters play an important role in adsorbing of organic matter on clay minerals.

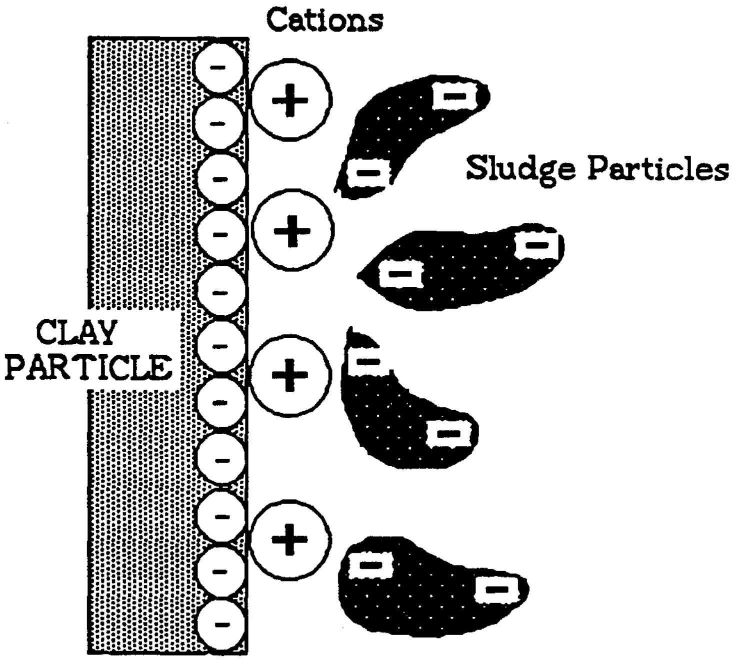


Figure 5.9. A Schematic Representation of Predicted Interaction Between Clay and Municipal Sludge Particles.

Figure 5.10. SEM Micrographs of Solid Municipal Sludge Particles (Magnification: 100X). P: Particle (Sludge), F: Fibre

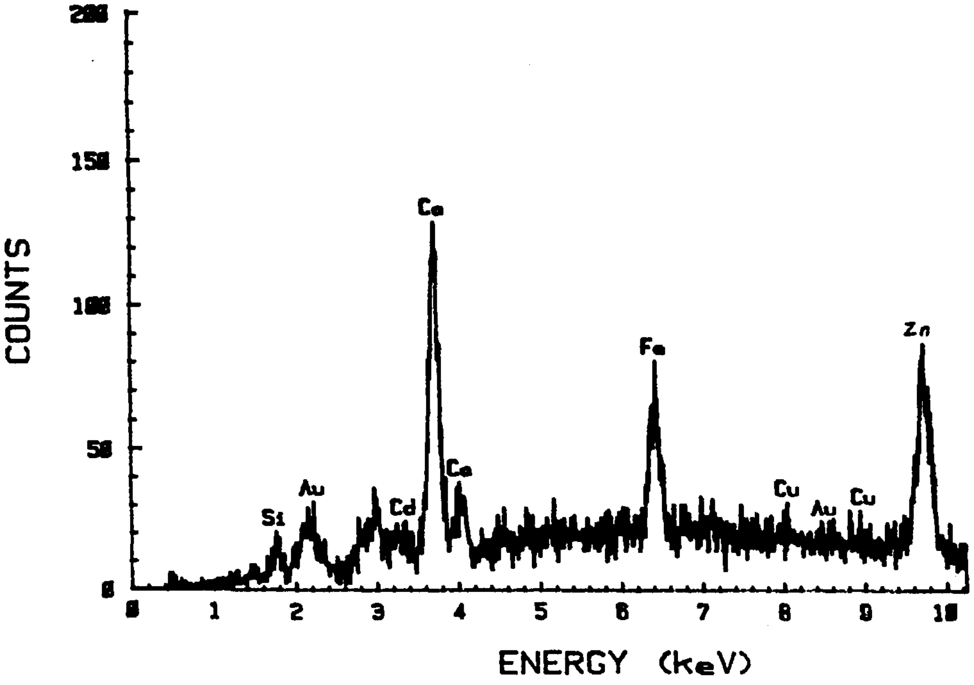


Figure 5.11. X-Ray Diffraction Spectrum of Solid Sludge Particle at Location X.

Figure 5.12. SEM Micrograph of Municipal Sludge (Magnification: 70X).
F: Fibre (sludge), X: X-Ray Diffraction Spectrum Location.

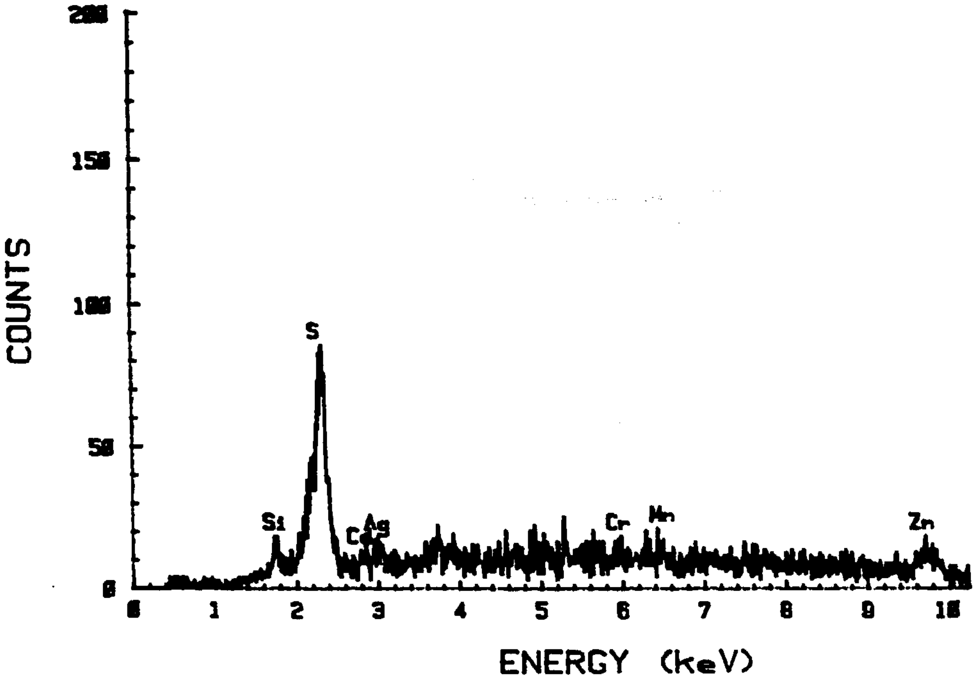


Figure 5.13. X-Ray Diffraction Spectrum of Fibrous Sludge Particle at Location X.

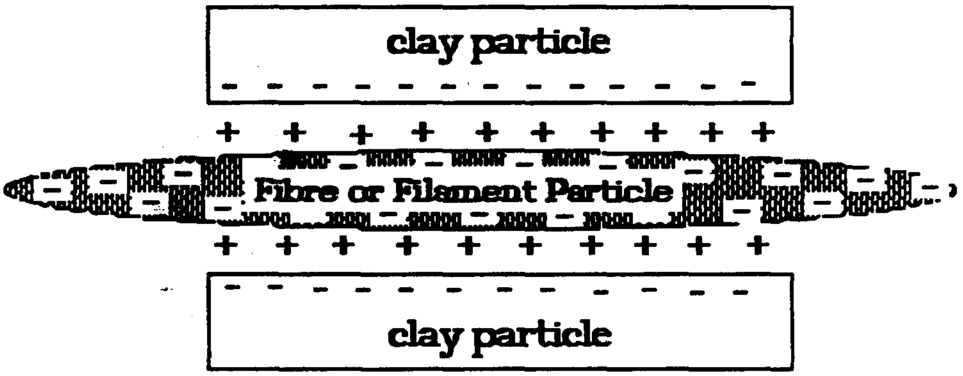


Figure 5.14. A Schematic Representation of Predicted Interaction Between Clay and Fibrous Particle.

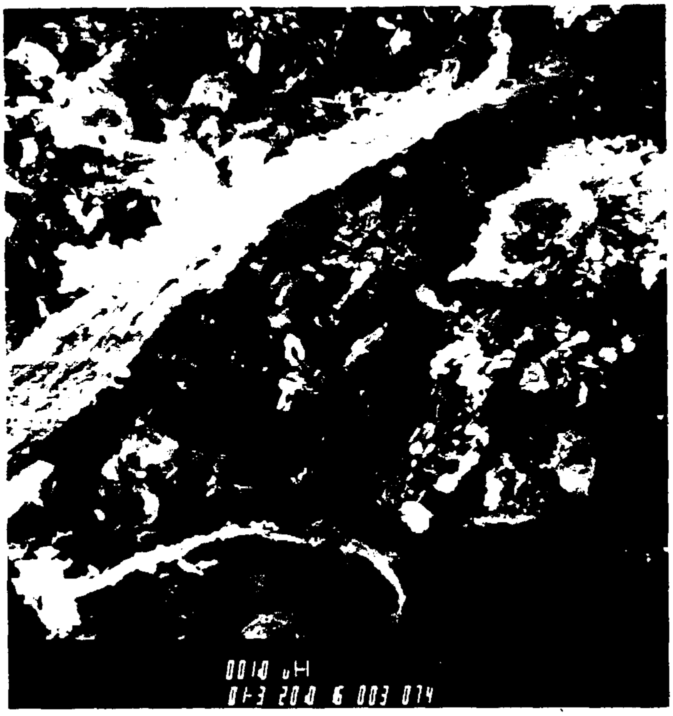


Figure 5.15. SEM Micrograph of Municipal Sludge + Salt Water Mixed Marine Clay Sedimented Specimens (Magnification: 1000X).

Figure 5.16. SEM Micrograph of Municipal Sludge + Salt Water Mixed Marine Clay Sedimented Specimens (Magnification: 1000X).
F: Fibre , D: Domain

Figure 5.17. SEM Micrograph of Municipal Sludge + Salt Water Mixed Marine Clay Sedimented Specimens (Magnification: 2000X).
F: Fibre (coated by clay particles), X: X-Ray Diffraction Spectrum

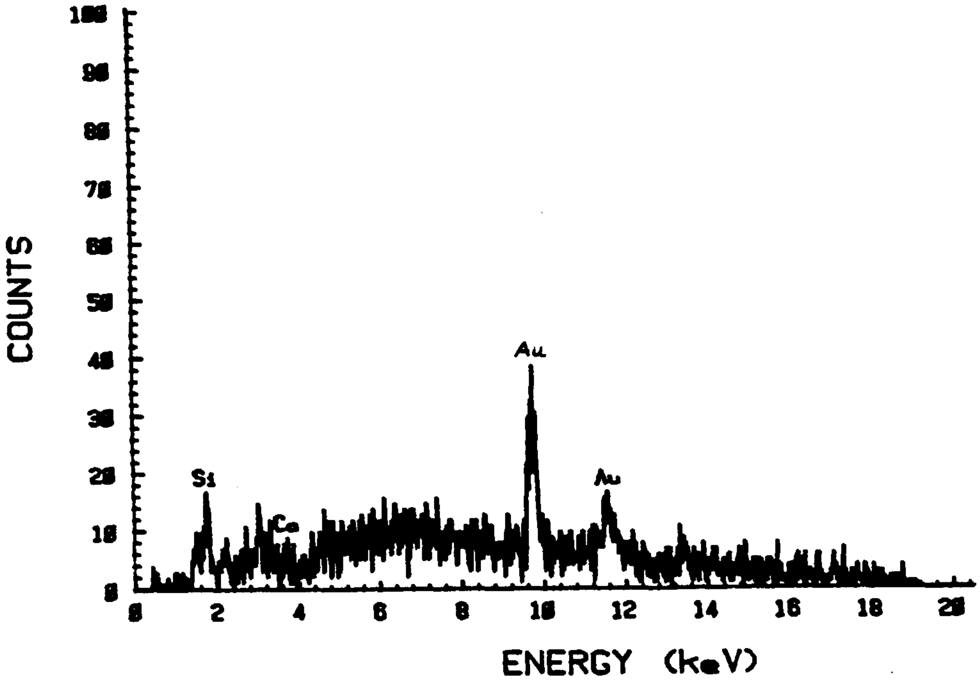


Figure 5.18. The X-Ray Diffraction Spectrum of Sludge Mixed Marine Clay + Salt Water at Location X.

Figure 5.19. SEM Micrograph of Salt Water + Sludge Mixed Marine Clay Sedimented Specimens (Magnification: 5000X).

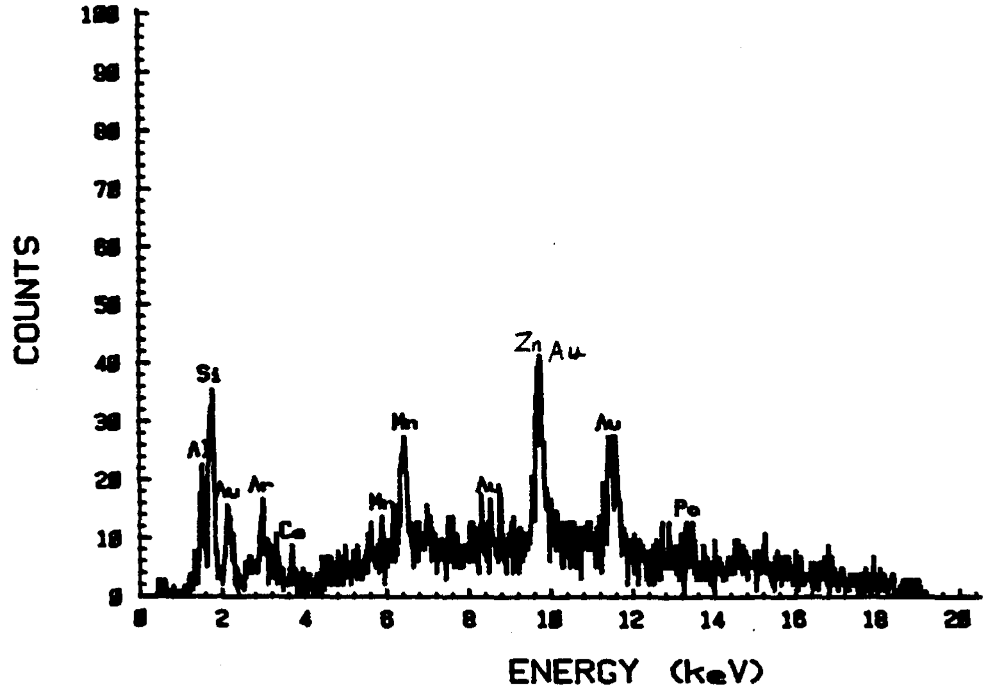


Figure 5. 20. X-Ray Diffraction Spectrum of Sludge Mixed Marine Clay at Lacation X.

Figure 5.21. SEM of Salt Water + Sludge Mixed Marine Clay Sedimented Specimens(Magnification: 1000X).

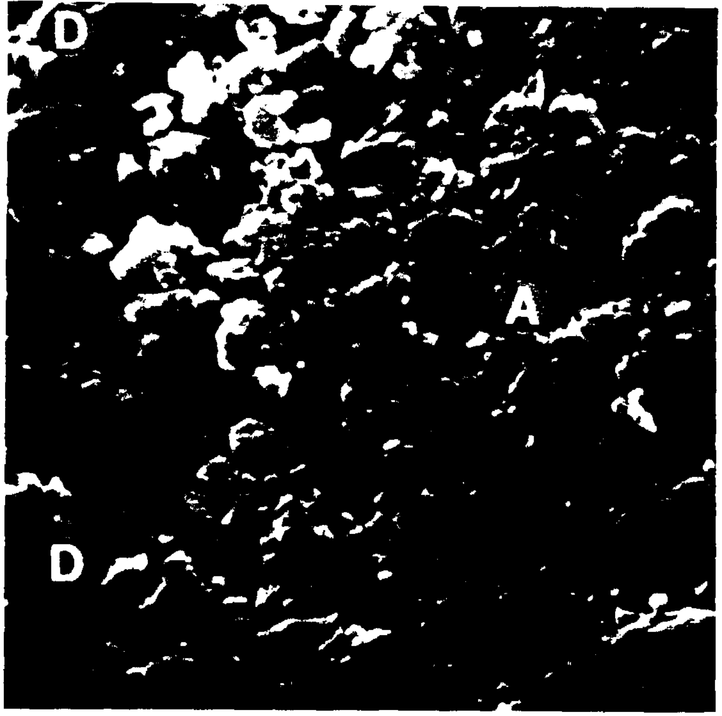


Figure 5.22. SEM of Salt Water + Sludge Mixed Marine Clay Sedimented Specimens(Magnification: 1000X). D: Domain, A: Agglomeration

5.3. Crude Oil and salt Water Mixed Marine Clay

When an oil is released into water, it often spreads and floats on the surface to form an oil slick due to its low specific gravity and low solubility. Oil particles are then dispersed in the water column and come into contact with suspended clay and colloidal particles. The suspended clay particles and sea water act as a transfer agent of oil to the bottom. Clay particles can adsorb large quantities of petroleum hydrocarbons. This adsorption increases with salinity probably due to the cationic bridges formed between oil and mineral surfaces. If the quantity of suspended particles is high, so is the extent of oil transfer to the bottom sediments. Approximately 50 % by weight of oil is volitalized. Some part is digested by bacteria and some part is deposited on the sediment layer where they may remain there for many years.

Oil wets the clay particle surfaces promoting flocculation and agglomeration of the particles which subsequently sink to the bottom with an increased rate of sedimentation. The adsorbtion of oil components onto clay particles causes the wettability to change from water-wet to oil-wet. The adsorbed layers increase the viscosity of the oil near the surface. This adsorbed layer can not be replaced or removed by water. The resulting interaction between clay and oil in water has been characterized as "spherical agglomeration" (Puddington and Sparks, 1975).

5.3.1. Mechanism of Spherical Agglomeration

In the spherical agglomeration process, clay particles in liquid suspension are treated with a bridging liquid which wets the clay particles and is immiscible with the first liquid. An important aspect of the spherical agglomeration process is the relative wettability of the suspended clay particles by the two immiscible liquids. When the bridging liquid is water, it is adsorbed on the surface of the clay particles. When two or more suspended clay particles collide, adhesion occurs forming water bridges between the particles. The bonding force between the clay particles is due to the interfacial tension of the liquids involved. Larger spherical particles need more bridging liquid for their formation. The amount of bridging liquid required for the agglomeration depends on the geometry of the particles. Flat surfaces require less bridging liquid to have a very strong adhesive bond than spherical surfaces. If water is the suspending medium, the most suitable bridging liquids that would cause spherical agglomeration are organic compounds such as oil which is insoluble in water. The surface of the solid must be hydrophobic to form an agglomeration. Clay minerals are hydrophobic and therefore will form spherical agglomeration in presence of oil in a water suspension.

The clay particles in water immiscible liquids are believed to be randomly arranged and the agglomerations are more or less spherical in shape. When oil drops and clay particles are mechanically agitated as in the case of preparing oil mixed water suspensions of clay in the settling columns, the total energy of interaction between the double layers together with the forces due to particle and oil drop motion is responsible for bringing the oil drops and clay particles into sufficiently close proximity. This mechanism is given in Figure 5.23.

The mechanism of interactions between oil and clay constituents in a given mixture can be understood with a simple diagram shown in Figure 5.24.

At equilibrium:

$$T_{co} - T_{cw} = T_{ow} \cos\theta$$

Where,

Tco = Surface tension at the interface of the clay and oil.
Tcw = Surface tension at the interface of the clay and water.
Tow = Surface tension at the interface of the oil and water.
θ = Contact angle measured in the liquid.

The following conditions may apply :

1. If $\theta<90^o$, the particle will tend to be drawn into the aqueous phase.

2. If $\theta=90^o$, the particle will tend to remain concentrated at the interface.

3. If $\theta>90^o$, the particle will tend to be drawn into the oil phase.

Spherical agglomeration occurs when contact angle, θ, is greater than 90^o. In this case, the clay particles migrate into the oil phase becoming absorbed by the oil. This starts the agglomeration process which can be evidenced in the photomicrograph given in Figure 5.25. In this figure an oil drop is partially coated by clay particles. A full coating could be presented by the diagram in Figure 5.26. A good example of such coating is evident in the photomicrograph in Figure 5.27, where the inside of a spherical shell of clay is exposed when the inner oil drop was removed, probably during sample preparation. This is a good example of particle adhesion and adsorption by oil.

Crude oil mixed marine clay, appeared to have loose and "spongy" structure in general as observed in Figure 5.28. Studying the photomicrographs of oil contaminated clays, it appeared that several mechanisms of interaction between clay and oil may be occuring simultaneously. One mechanism is the spherical agglomeration as discussed before. Micrographs in Figures 5.29 and 5.30 present more examples of the agglomeration. The average diameter of these spherical drops range from a fraction of a micron to several microns. The coating of oil surfaces with clay particles is checked by EDS analysis of the surface marked by X in Figure 5.31. As observed the x-ray diffraction spectrum records in Figures 5.32 and 5.33 of the "so called "oil surfaces indicate no dominant presence of a mineral and therefore are interpreted as oil. There is a characteristic arching of the record which was associated with pure oil earlier.

It can be seen from Figures 5.34 and 5.35 that oil bridges may form between oil surface and clay particles. There is also adhesion between these oil bridges and clay particles forming a different type of agglomeration referred to as " rod " agglomeration in this work.

Another mechanism of clay-oil interaction is when the oil is incorporated in the sediment as an irregular shaped mass or a thin layer of material, as shown in Figure 5.36. There is adhesion between these oil surfaces and the clay particles. X-ray diffraction spectrums of the oil surface and the clay surface shown Figure 5.36 are given in Figures 5.37 and 5.38, respectively. It can be seen from these records that x-ray of oil surface and x-ray of clay surface are significantly different. Oil surface has small amount of silica, aluminum and iron. This is because of the small fractions of clay particles on the oil surface or the ash present in oil. The shape of the x-ray for oil exhibits the characteristic arching, while the x-ray of clay surface is very similar to that of illite clay (Figure 3.1).

The micrographs of more oil surfaces with associated EDS records are presented in Figures 5.39 through 5.50. The x-ray diffraction spectrums for Figure 5.41 are given in Figures 5.42, 5.43 and 5.44. A hole was detected on the oil surface which was confirmed by the signature obtained in the EDS records, where barely any response was recorded. Therefore, these records show the difference between a hole and oil surface clearly. The x-ray of oil bridge (Figure 5.44) is similar to that of oil surface given in Figure 5.42. This record support that the filament is an oil surface. Representative photomicrographs of oil surfaces showing various mechanisms of interaction with clay are presented in Figures 5.45 through 5.52.

Such oil surfaces blanket the void spaces and prevent water from flowing through the soil, therefore result in the net effect of lowered permeability. Finally, visual observation and handling of the crude oil mixed marine clay specimens indicated that crude oil reduced the cohesionness of the clay, probably due to the agglomeration of clay into flocs and significant reduction of the effective specific surface area of the material.

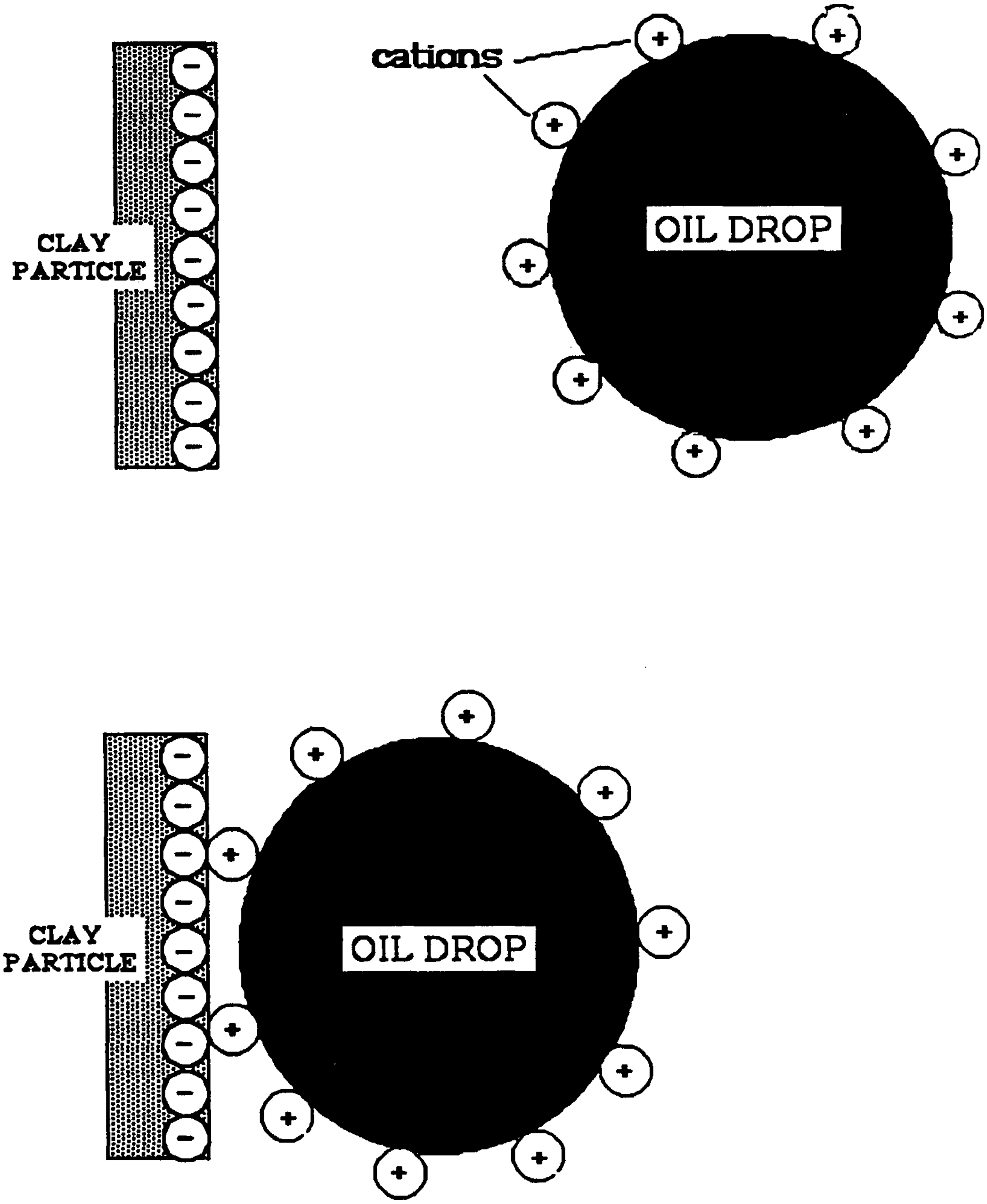


Figure 5.23. The Mechanism of Adhesion between Oil Drop and Clay Particle.

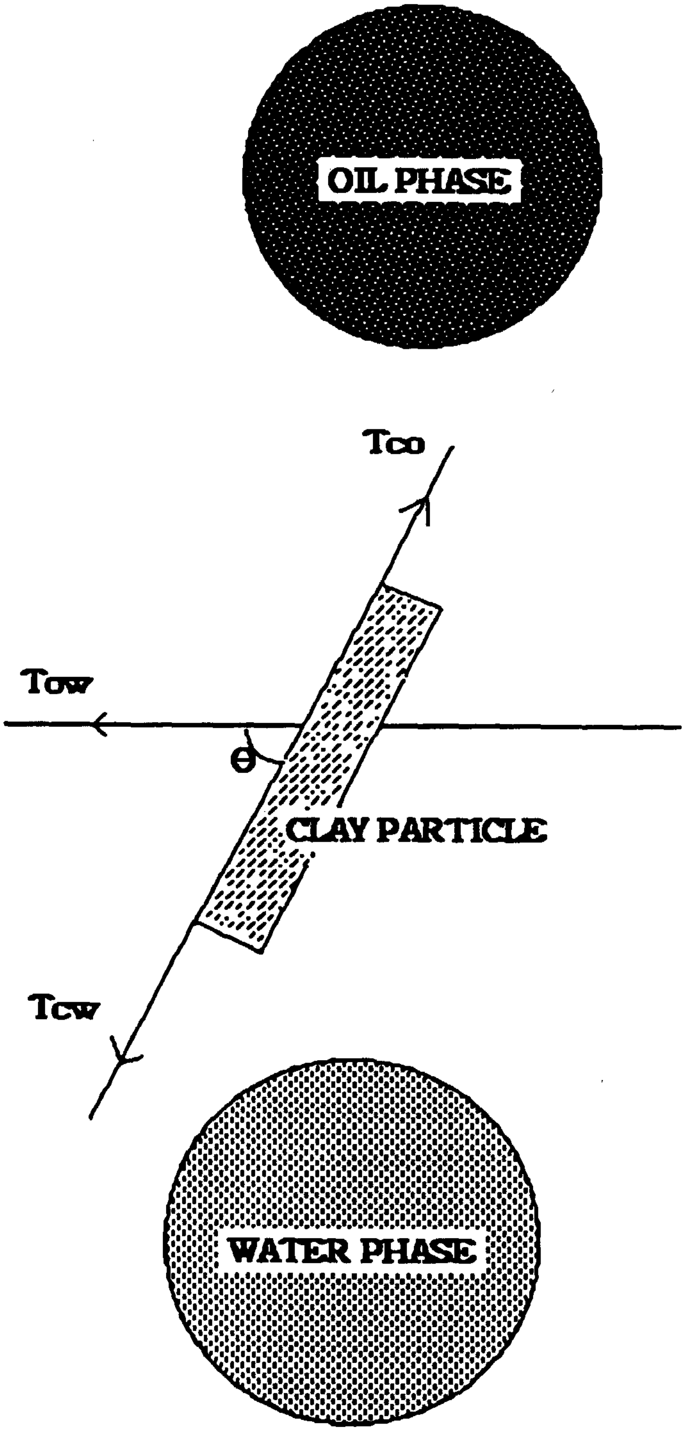


Figure 4.24. The Mechanism of Spherical Agglomeration between Oil Drop and Clay Particles.

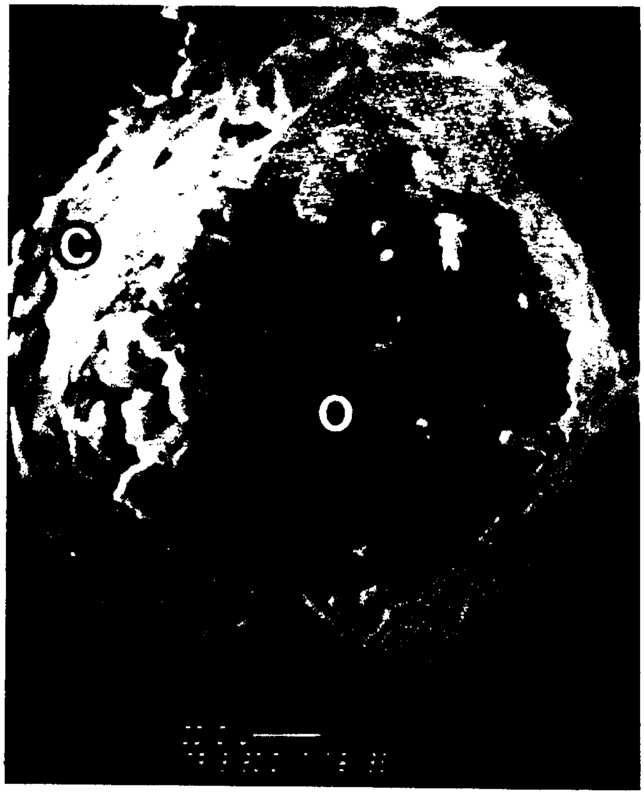


Figure 5.25 SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification:9000X) C: Clay Particle, O: Oil Surface

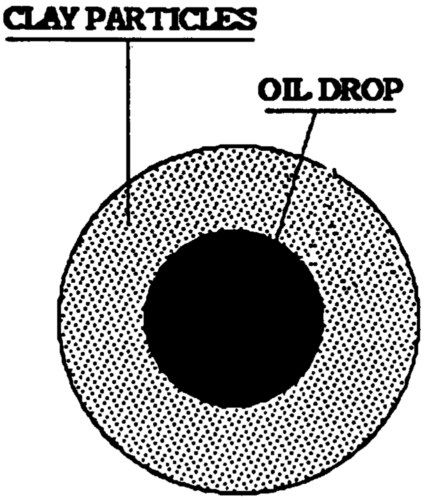


Figure 5.26. The Mechanism of Coated Oil Droplet by Clay Particles.

Figure 5.27. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 1000X). S: Spherical agglomeration

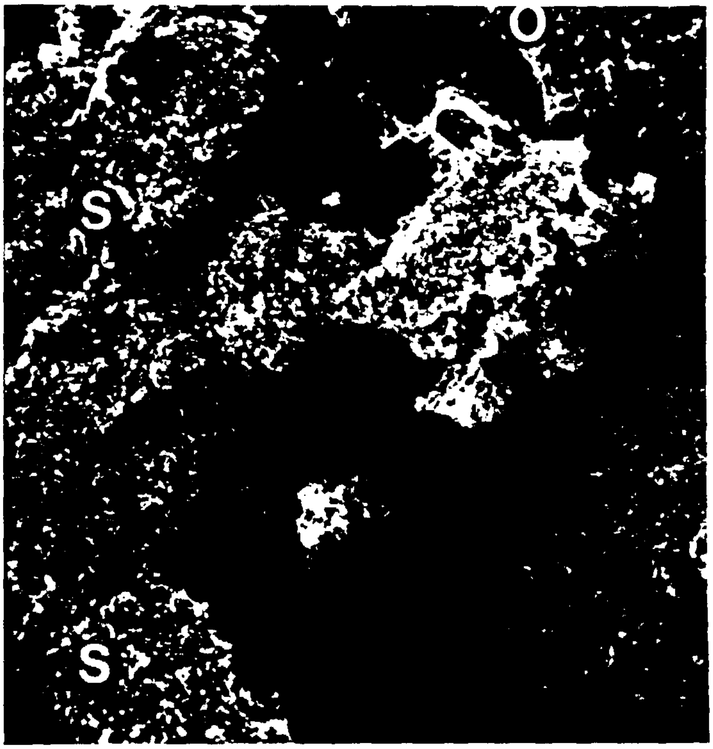


Figure 5.28. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 100X). S: Spherical Agglomeration, O: Oil Surface

Figure 5.29. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 2000X). S: Spherical Agglomeration

Figure 5.30. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 5000X). S: Spherical agglomeration

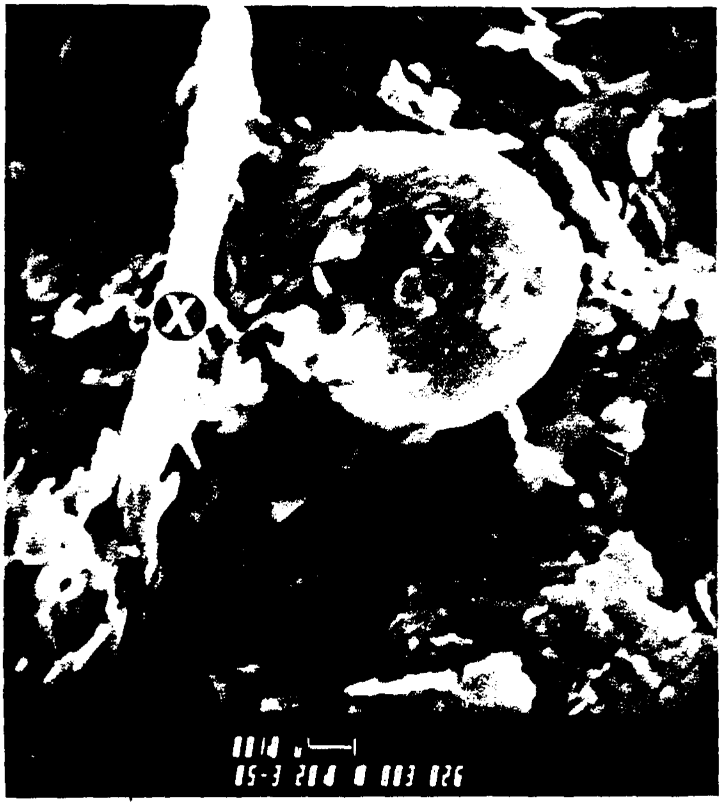


Figure 5.31. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 5000X) X: X-Ray Diffraction Spectrum

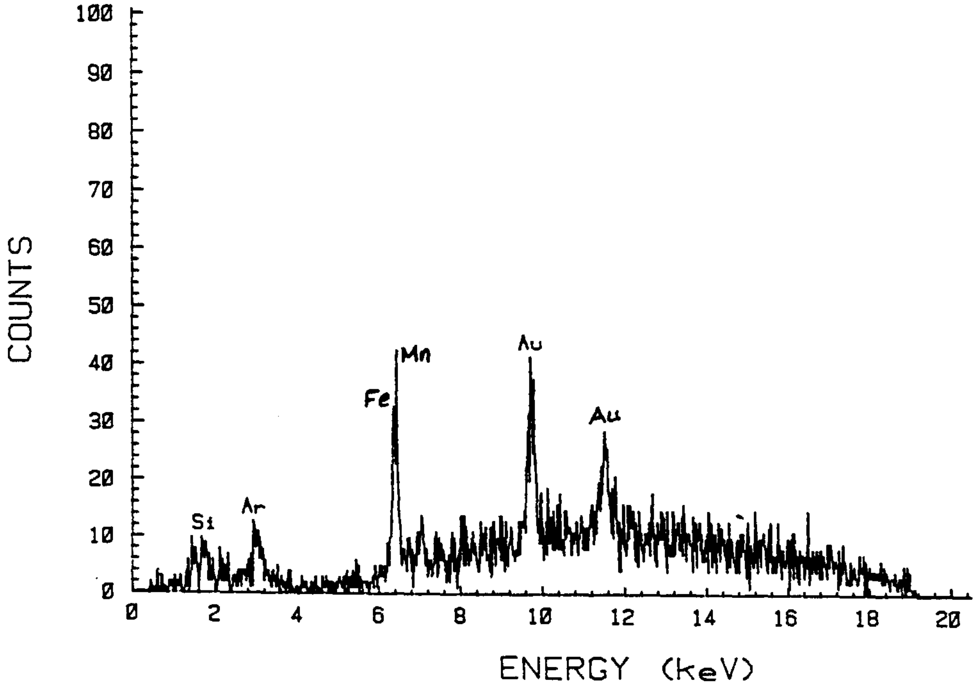


Figure 5.32. X-Ray Diffraction Spectrum of the surface of a Spherical Agglomeration in Figure 5.31.

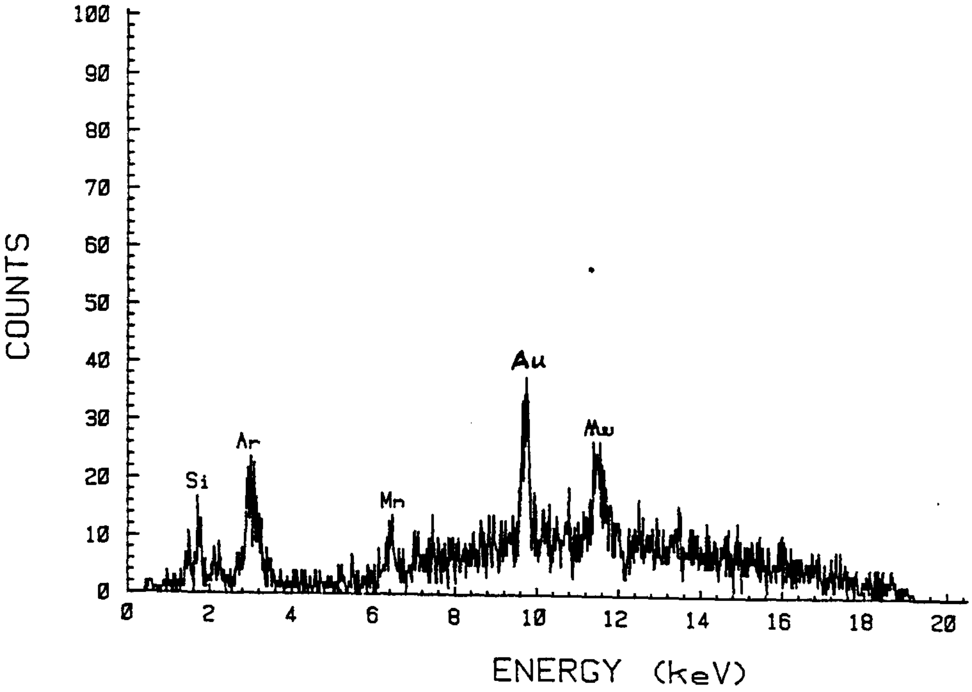


Figure 5.33. X-Ray Diffraction Spectrum of the Surface of the Selender Feature (Oil Filament) in Figure 5.31.

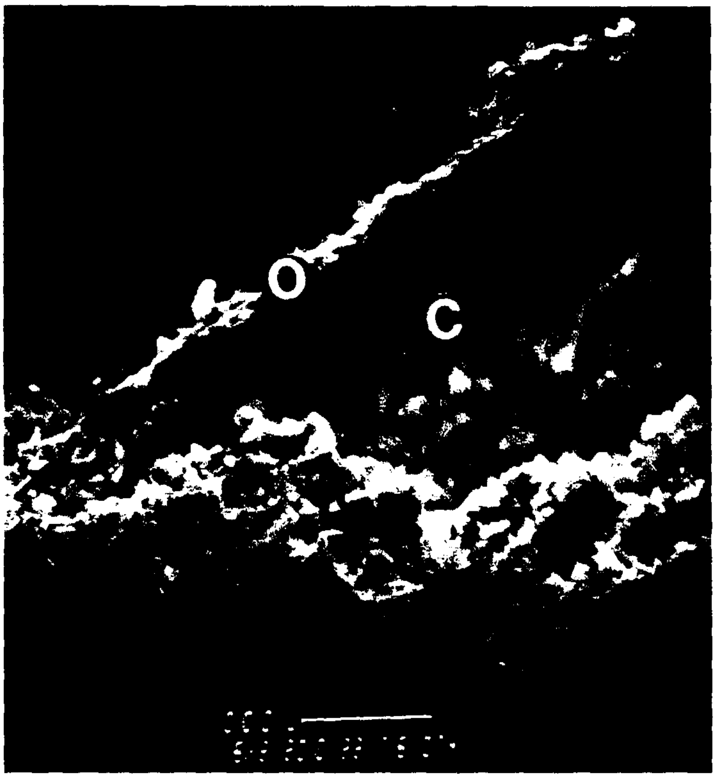


Figure 5.34. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 1600X). O: Oil Bridge, C: Clay Particle

Figure 5.35. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 1000X). O: Oil Surface

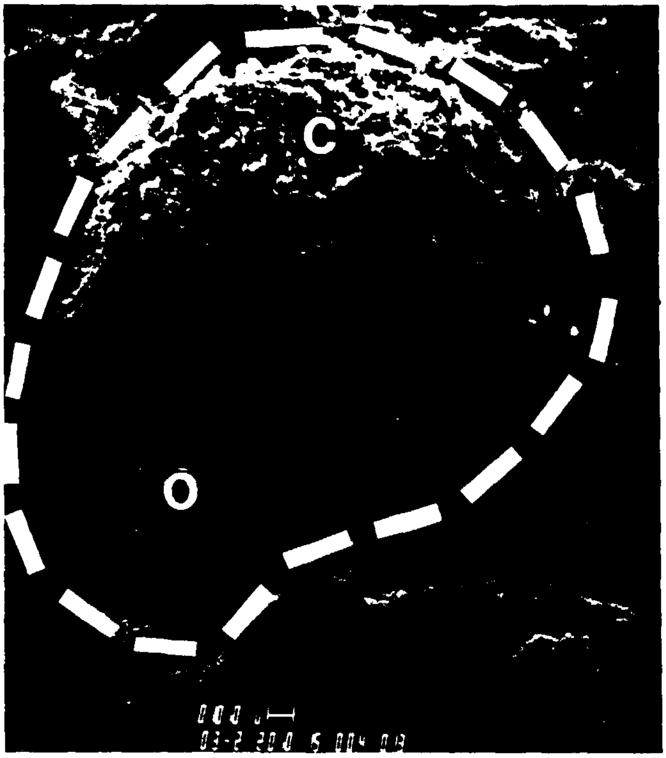


Figure 5.36. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 300X) . O: Oil Surface, C: Clay Particle

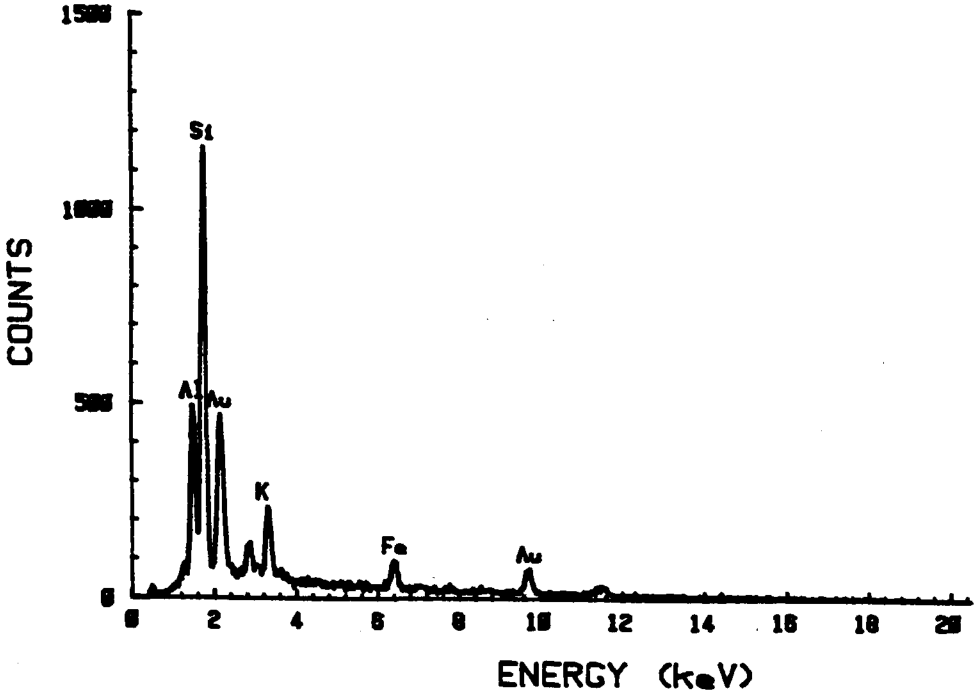


Figure 5.37. X-Ray Diffraction Spectrum of Clay surface in Figure 5.36.

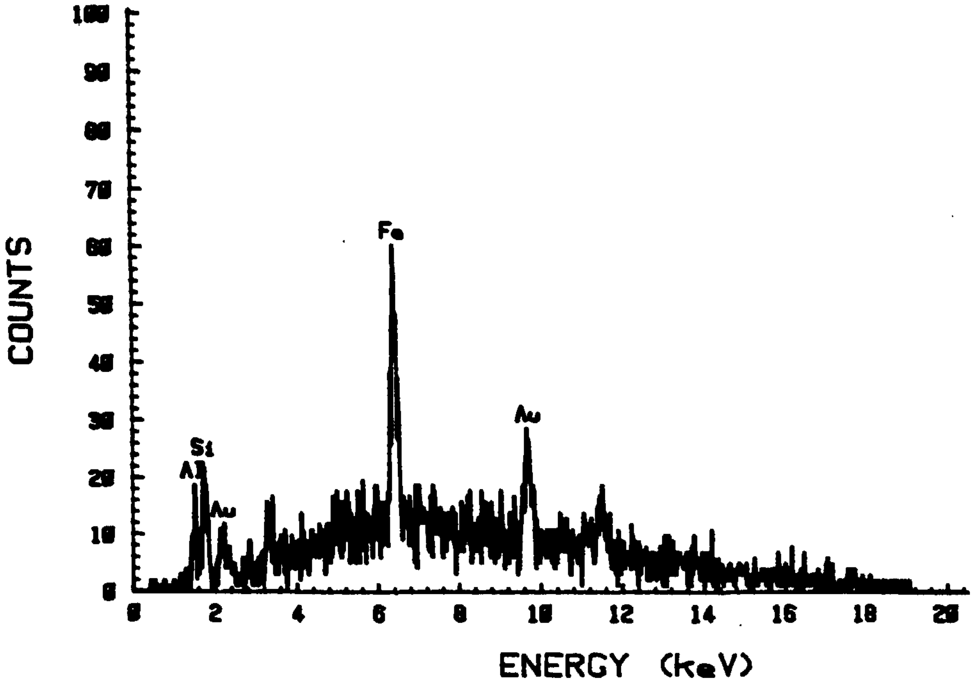


Figure 5.38. X-Ray Diffraction Spectrum of Oil Surface in Figure 5.36.

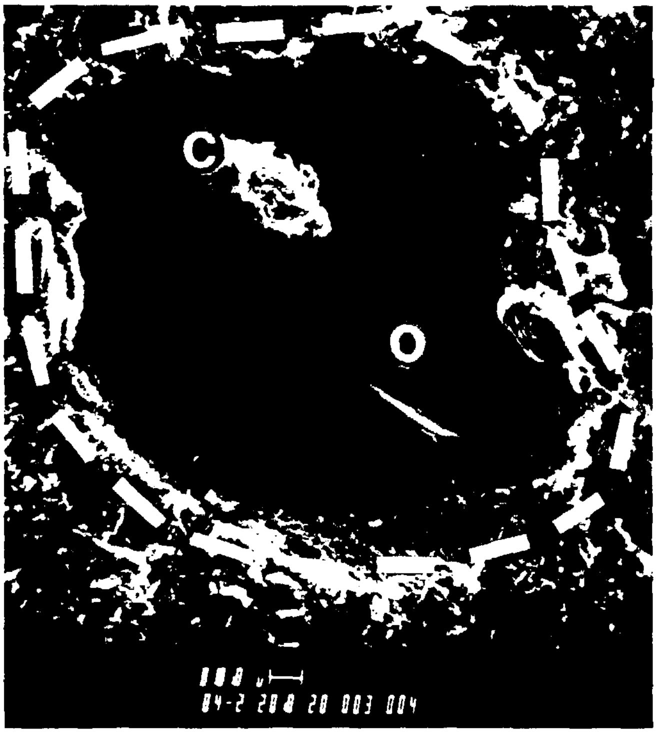


Figure 5.39. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 400X). C: Clay particle, O: Oil Surface

Figure 5.40. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 300X). O: Oil surface

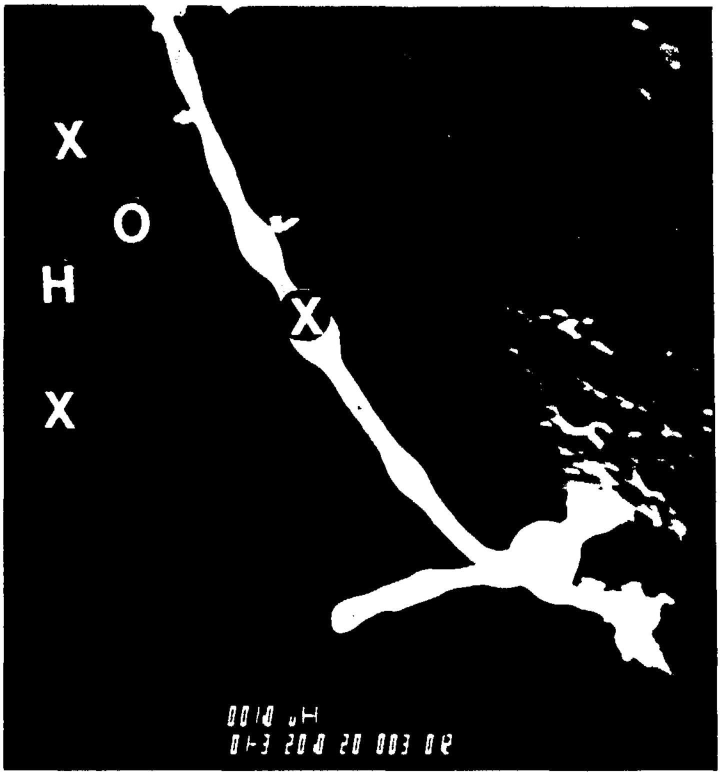


Figure 5.41. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 1000X) O: Oil Surface, H: Hole on the Oil Surface, X: X-Ray Diffraction Spectrum

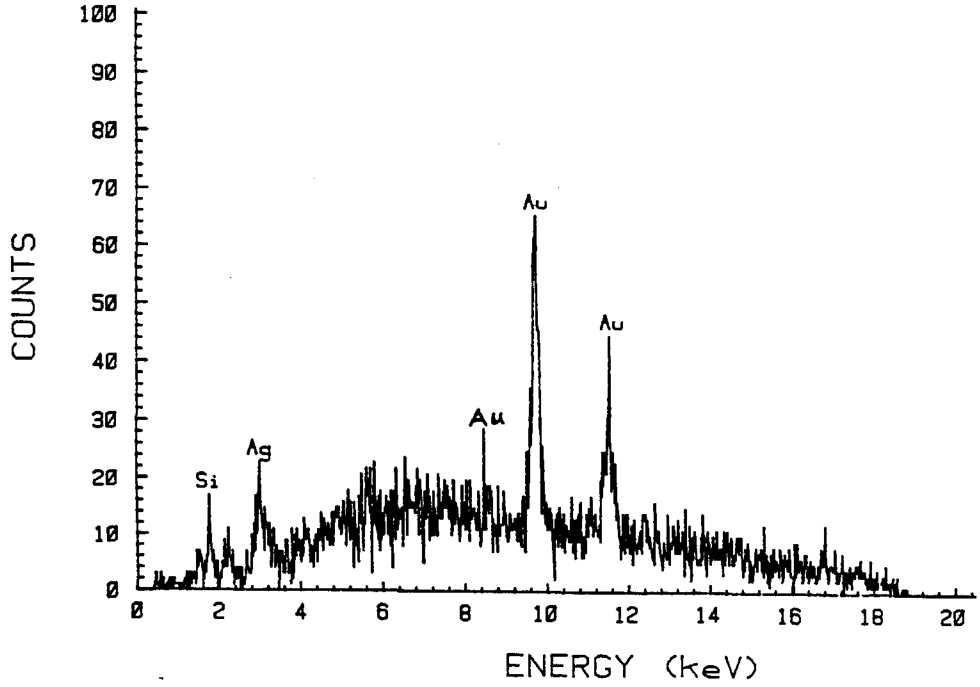


Figure 5.42. X-Ray Diffraction Spectrum of Oil Surface in Figure 5.41.

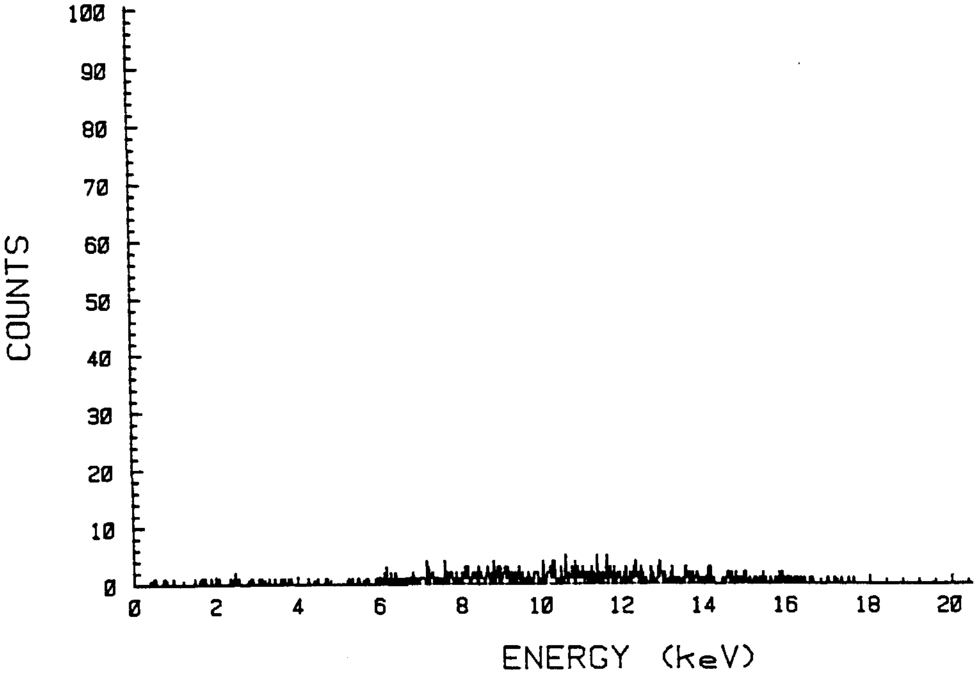


Figure 5. 43. X-Ray Diffraction Spectrum of Hole on the Oil Surface in Figure 5.41.

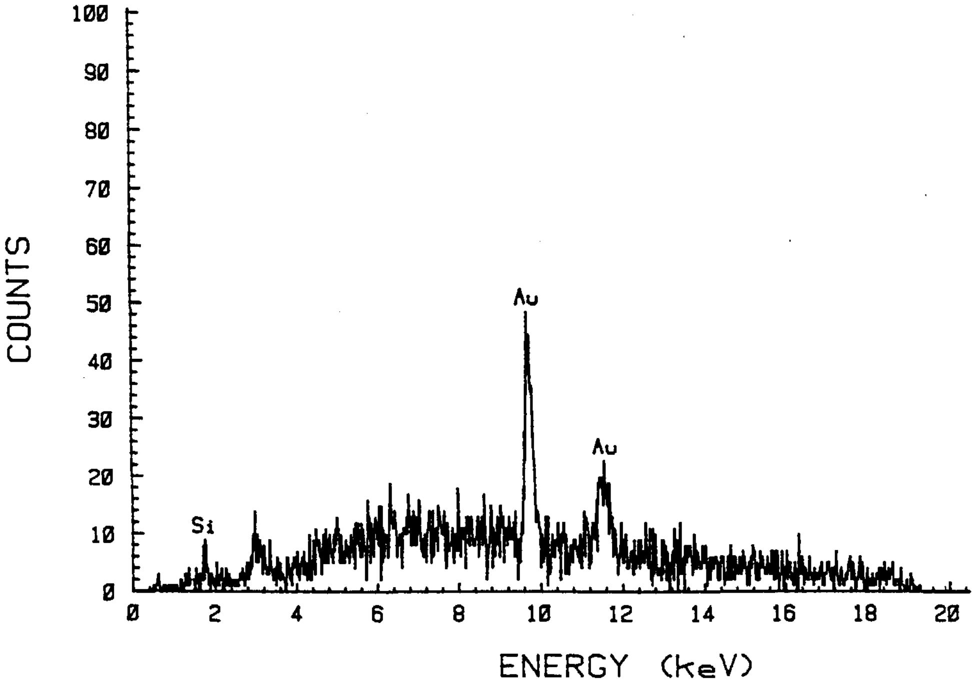


Figure 5.44. X-Ray Diffraction Spectrum of Oil Filament in Figure 5.41.

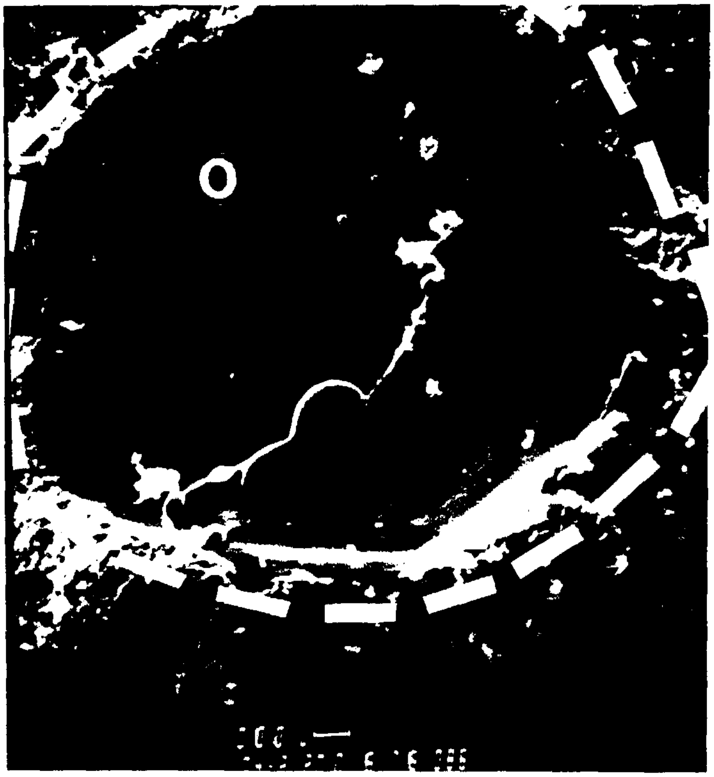


Figure 5.45. SEM Micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 400X). O: Oil Surface

Figure 5.46. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 1000X). O: Oil Surface

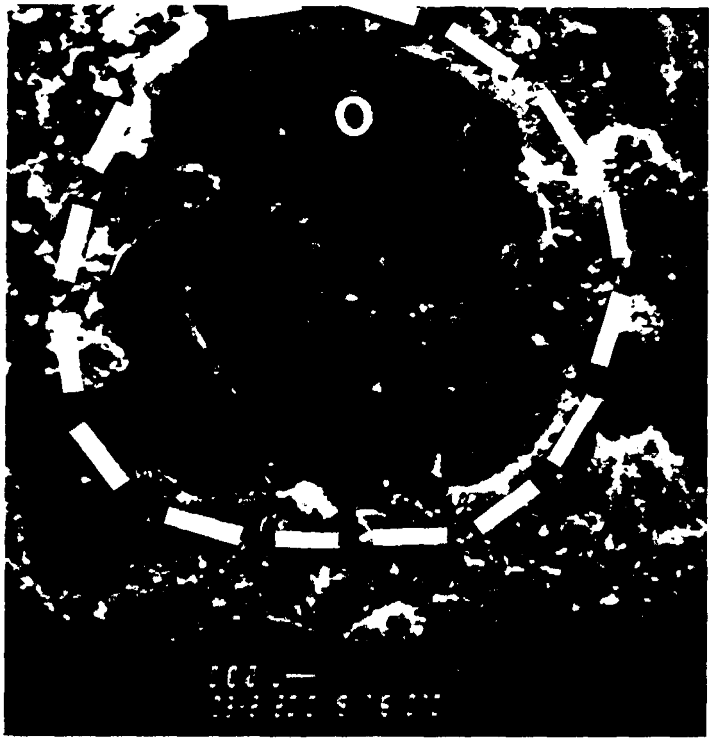


Figure 5.47. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 300X). O: Oil Surface

Figure 5.48. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 400X) O:Oil Surface, H:Hole

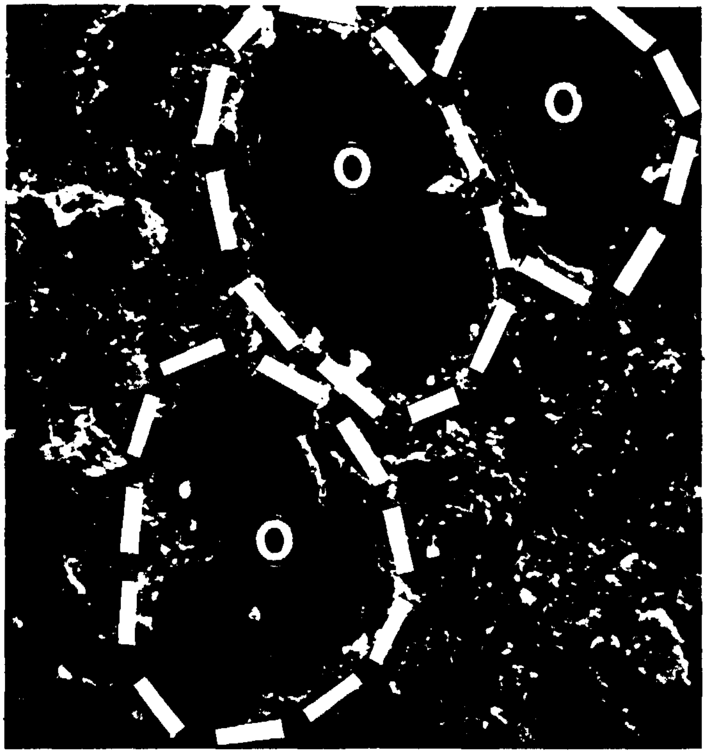


Figure 5.49. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 200X). O: Oil Surface

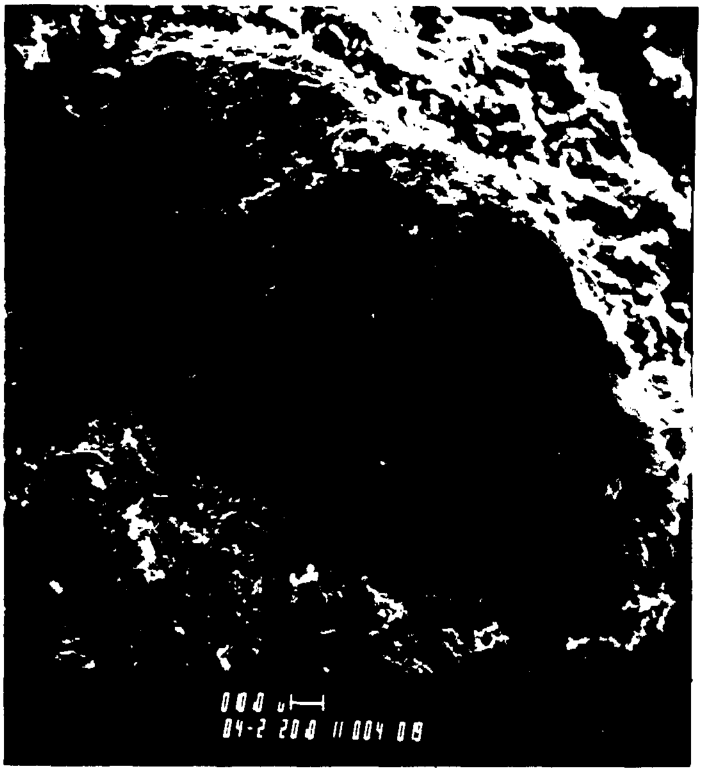


Figure 5.50. SEM micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 400X)

Figure 5.51. SEM Micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 2000X).

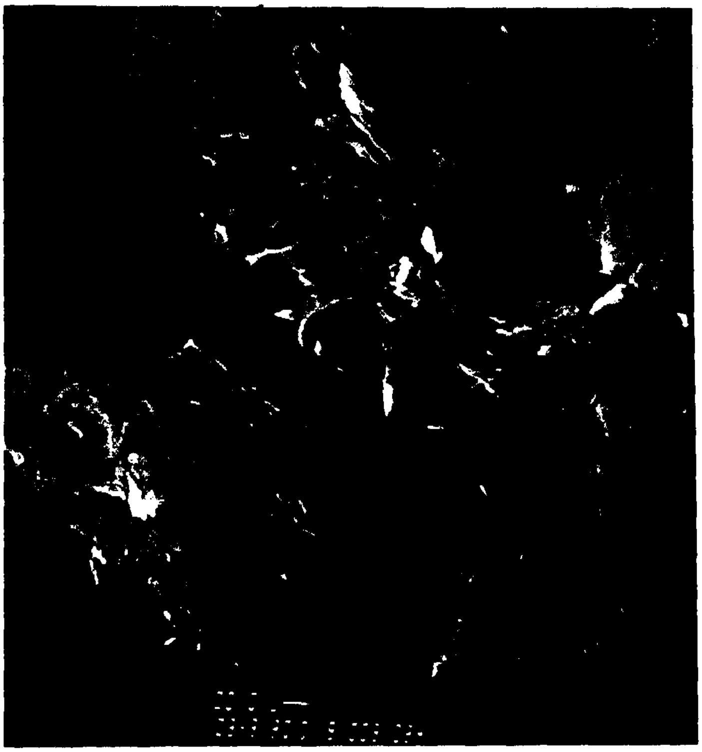


Figure 5.52. SEM Micrograph of Salt Water + Crude Oil Mixed Marine Clay Sedimented Specimens (Magnification: 3000X).

CHAPTER 6

GEOTECHNICAL PROPERTIES

Introduction:

A number of physical and mechanical properties characterized as geotechnical properties were measured for the contaminated sediments. These properties were measured to investigate the influence of microstructure and physico-chemical changes on the physical and mechanical behavior of the sediments. The measured index and mechanical properties of the sediments are given in Table 6.1 and 6.2, respectively. These properties were measured using the core specimens retrieved from the sedimented mass.

6.1. Index Properties

6.1.1. Water Content

The water content of soil shows the amount of water present in the voids relative to the amount of solids. As observed in Table 6.1, marine clay, salt water and 10% crude oil mixture has the highest water holding capacity compared to the others. Marine clay and tap water mixture has the lowest water content due to its denser structure.

6.1.2. Bulk Density

The bulk density of the sediments were determined from the retrieved core specimens in which the natural structure of the sediments were assumed to be undisturbed. The 5% sludge mixed specimens exhibited the highest average bulk density while the 10% crude oil mixed specimens showed the lowest average bulk density. However, in overall analysis, there was little variation in the bulk densities of the specimens with contaminants at the percentages mixed.

6.1.3. Specific Gravity

Specific gravity of a crude oil contaminated marine clay was lower than the sludge contaminated marine clay. In either case, addition of the sludge and crude oil decreased the specific gravity of the clay mixtures.

6.1.4. Atterberg Limits

The water contents that correspond to the boundaries between various states of consistency are the Atterberg limits. Atterberg limits depend on the type and amount of clay fraction, exchangeable cations and pore water chemistry. Addition of salt to pore water decreased the plasticity index of the clay mixtures as shown in Table 4. Chassefiere and Monaco (1983) observed a similar occurance where the liquid limit and plasticity index of a clay determined by using saline water as mixing water decreased compared to those of distilled water mixed clay. As observed from Table 4, addition of sludge increased the plasticity of marine clays slightly, whereas addition of crude oil decreased the plasticity, which may be attributed to loss cohesion in latter case.

6.1.5. Ignitable Organic Matter Content

Organic content was determined by the ignition loss method. Sediment samples were pre-dried at105^{o}C for 24 hours. These samples were then heated at 550^{o}C for 2 hours. The loss of weight as a result of the second heating was assumed to be due to loss of organic matter only. Ignitable organic matter content increased with addition of sludge and crude oil as expected. This increase was larger with the crude oil. Organic content also appear to correlate well with the measured water content. As organic matter increases so does the water content which may be due to entrapment of water inside oil-clay or organic matter-clay domains.

6.1.6. pH

pH of the pore fluid influences the behavior of sediments. Low pH promotes flocculation and causes the formation of loose structures while high pH promotes dispersion and dense sediments. Although a significant change in pH was not observed with contamination, some general trends could be detected. For example, saline water mixed marine clay had the lowest pH and tap water mixed marine clay had the highest pH and it increased with increasing organic matter content.

Table 6.1 Measured Index Properties of Contaminated Sediments

Mixture	Water Content (by dry weight) (%)	Bulk Density (g/cm3)	Specific Gravity	Liquid Limit (%)	Plasticity Index (%)	Ignitable Organic Content (by dry weight) (%)	pH
MC + TW	82-99	1.42-1.62	2.63-2.65	51-53	20-21	5.36	7.45
MC + SW	89-96	1.52-1.60	2.50-2.53	48-50	16-17	6.50	6.70
MC + SW + 5%S	97-105	1.56-1.60	2.30-2.45	49-50	17-20	7.29	6.75
MC + SW + 10%S	91-99	1.42-1.53	2.46-2.49	51-53	20-24	8.11	6.80
MC + SW + 5%CO	100-101	1.47-1.50	2.21-2.25	45-47	15-17	10.10	6.90
MC + SW + 10%CO	102-120	1.44-1.49	2.37-2.40	42-44	12-14	12.00	7.10

MC=Marine Clay, S=Sludge, CO=Crude Oil, TW=Tap Water, SW=Salt Water

6.2. Mechanical properties

6.2.1. Shear Strength

Shear strength is a varient property of the contaminated sediments. The shear strength parameters of fine grained sediments are influenced by void ratio, water content, interparticle forces or cohesive bonds and also pore fluid chemistry. The shear strength of the marine clay samples were determined by laboratory vane shear tests. The sedimented loose marine clay had virtually no shearing resistance. Therefore these samples were initially consolidated under a triaxial consolidation pressure of 14 kPa.

The shear strength of themarine clay, salt water and crude oil samples are significantly smaller than the others as shown in Table 6.2. This is mainly because of the reduced cohesion in the presence of hydrocarbons. However, marine clay, salt water and sludge samples exhibited the highest shear strengths which is probably due to increased interparticle bonding between the clay particles and also the reinforcing effect of fibrous inclusions in the clay matrix. Shear strength of marine clay with salt water is higher than marine clay with tap water, as expected. This is attributed to salt flocculation.

6.2.2. Coefficient of Permeability

Permeability is a soil property which describes how fast the water flows through soil. Pore fluid migration through clays is a complex phenomenon because of the electrochemical interactions between the particles and pore fluid constituents. In the case of contaminated pore fluid the complexity probably increases due to the induced changes in the chemical environment.

Permeability tests were conducted using triaxial permeability apparatus (Evans amd Fang, 1986). Samples were isotropically consolidated under 14 kPa. All tests were performed using saline water as the permeating fluid except for the tap water mixed samples.

Salt water mixed samples exhibited the highest permeability probably because of the open structure produced by salt flocculation. marine clay, salt water and crude oil samples exhibited the lowest coefficient of permeability, approximately one order of magnitude lower than that of marine clay and saline water mixture. This is because oil tends to trap water and create discontinuous channels by blocking the voids. The presence of sludge tends to reduce the net negative charge of particles, therefore they may move closer together in a face-to-face arrangement reducing the space for free water flow. Acar and Olivieri (1989) showed similar results in which there was a decrease in hydraulic conductivity of kaolinite and Ca-montmorillonite when low solubility organic fluids were permeated through compacted samples of these clays.

6.2.3. Compressibility

The compression characteristics of a sediment can provide an understanding of its depositional process and stress history. The compressibility of the sediment sample were determined by means of a standard consolidation test in which a sediment volume is compressed by applying different known stresses axially while the sample is constrained laterally. The sediment compressibility is quantified by the compression index, C_c.

Compression tests were carried out on undisturbed samples of the sedimented clays. The marine clay and tap water sediment samples exhibited higher compressibility than the marine clay and salt water samples as shown in Table 6.2. This may again be due to the salt flocculation of the latter one. Compression index appears to decrease slightly with the addition of sludge and crude oil to the marine clay, which is probably due to flocculation and agglomeration caused by these two agents.

The more compressible the material is, the more pronounced the effect of adsorbed cations and the electrolyte concentration. During consolidation, the particles come closer together, causing an increase in the interparticle forces. As two soil particles approach each other, their exchangeable cations repel each other. However, when particles are close enough, any reduction of particle spacing results in an increase of attractive forces. As a result, less compressible structures tend to be flocculated, often with an edge to face configuration.

6.2.4. Porosity

Porosity is a fundamental property of sediments. The porosity of sediments when correlated with other geotechnical parameters may reflect the compositional and depositional environment of the sediments. Changes in the porosity may also reflect the changes in some basic physical properties such as consistency and compressibility. The computed porosity for the samples tested in this work did not show appreciable variation. In the overall analysis, however, addition of increased percentages of sludge and crude oil increased the porosity of samples slightly.

6.2.5. Shear Modulus

Dynamic soil properties such as shear modulus and shear wave velocity are some of the basic soil properties required in the design of foundations for offshore structures. Many marine sediments have low strengths and high compressibilities that require accurate evaluation for design purposes. Shear moduli of the laboratory prepared marine sediments appeared to be strongly influenced by the presence of sludge and crude oil in their matrix. Shear moduli of the marine clay samples with and without contaminants, as determined from unconsolidated undrained (UU) and consolidated drained (CD) tests are given in Figures 6.1 and 6.2, respectively. These tests were conducted using piezo electric elements (Bender element) installed at top and bottom plattens of a triaxial cell, a wave generator and a storage oscilloscope. Principles of using this test set-up to measure shear modulus are given elsewhere (Dyvik and Madshus, 1986).

When tested in the unconsolidated undrained condition, shear moduli of the clays decreased with the increasing confining pressure and percentage of crude oil and sludge as well. These tests were conducted by first allowing the retrieved specimens to consolidate under 14 kPa. Following consolidation, the confining pressure was increased in steps and the modulus measurement was made at each pressure increment while the sample was kept under undrained conditions. The tap water mixed marine clay exhibited the lowest shear moduli, whereas the crude oil mixed marine clay exhibited the highest shear moduli as observed in Figure 6.1. Essentially little or no variation was observed in shear moduli with increasing confinement for the tap water mixed clay.

In the consolidated drained condition for which the specimens were allowed to consolidate at each pressure increment, densification of the specimens resulted in an increase in the value of shear wave velocity. This is due to the decreased particle spacing and larger percentage of particle to particle contact area. Shear moduli with and without contamination increased with increasing consolidation pressure but decreased with sludge or oil contamination. In this case, crude oil mixed marine clay exhibited the lowest shear modulus values.

The response of shear moduli to confining stress in the undrained testing is affected by progressive pore pressure buit up. As the confining stress effect diminished with pore water pressure built up, the shear moduli decreased significantly. The interesting phenomenon observed was the initial peaking of the moduli values due to the confinement only, which indicates little or no effect of pore water pressure at low confining pressures. The higher values of moduli obtained for the oil and also sludge mixed clays may be attributed to the agglomeration of particles in presence of these substances. When particles agglomerate and form domains, they may act as large size particles in the range of silt and sand sizes. Since in the UU tests no volume change was allowed, the soil matrix remained the same with increasing confinement but progressively build up pore water pressure. Therefore the initial response of high shear moduli to apparent increased particle size drops with the increasing pore pressure response.

Comparing the moduli values obtained from the undrained and the drained tests, the shear modulus of clay with 10 % oil is on the order of 2000 MPa at 400 kPa confining pressure for the UU tests, whereas it is on the order of 4000MPa at the same confining pressure for the CD test specimen. Initially, however, these values are on the order of 5000 MPa and 1500 MPa for the UU and the CD tests, respectively at the confining stress of 50 kPa. This is because, under the increased compression, the agglomerations and domains crush and break apart releasing the oil from within these domains, which results in the lower shear modulus. However, as compression and densification continues, it progressively increases to around 4000 kPa. The increase of Gmax with consolidation pressure is an expected behavior. It is interesting to note the significant variation of the moduli response between the salt and tap water mixed specimens which is probably due to the slightly higher density of the former, and their flocculated structure which results in edge to face proximity of the particles.

Table 6.2 Measured Mechanical Properties of Contaminated Sediments

Mixture	Vane Shear Strength (kPa)	Coeff. of Permeability kx10-7 (cm/s)	Compression Index Cc	Coeff. of Consolidation Cv (cm2/min)	Porosity n (%)
MC + TW	21.72	1.15	0.75	0.05	69.7
MC + SW	35.37	3.10	0.51	0.06	67.6
MC + SW + 5%S	36.20	2.96	0.52	0.10	67.5
MC + SW +10%S	43.44	1.80	0.56	0.06	69.3
MC + SW + 5%CO	19.31	0.66	0.52	0.04	66.5
MC + SW +10%CO	14.48	0.32	0.53	0.15	70.7

MC=Marine Clay, S=Sludge, CO=Crude Oil, TW=Tap Water, SW=Salt Water

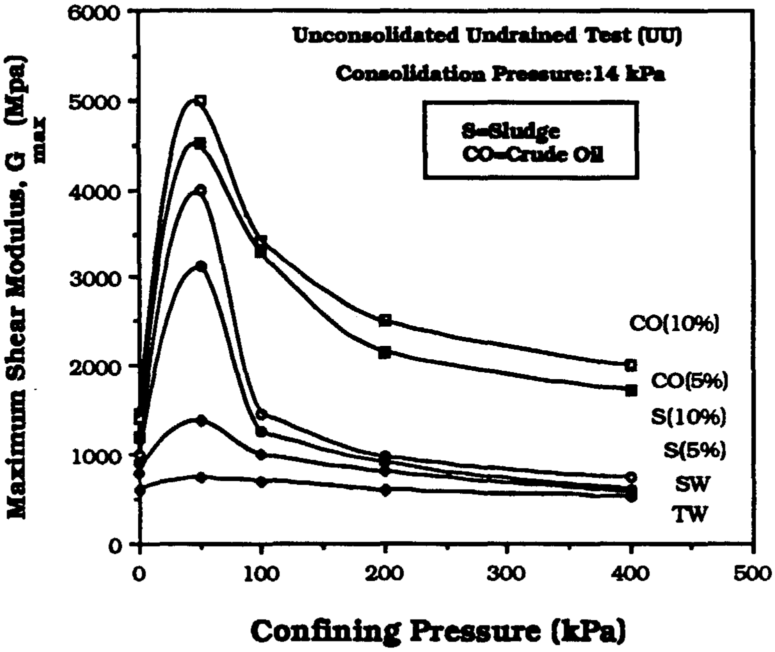


Figure 6.1. Shear Modulus versus Confining Pressure for Sedimented Specimens

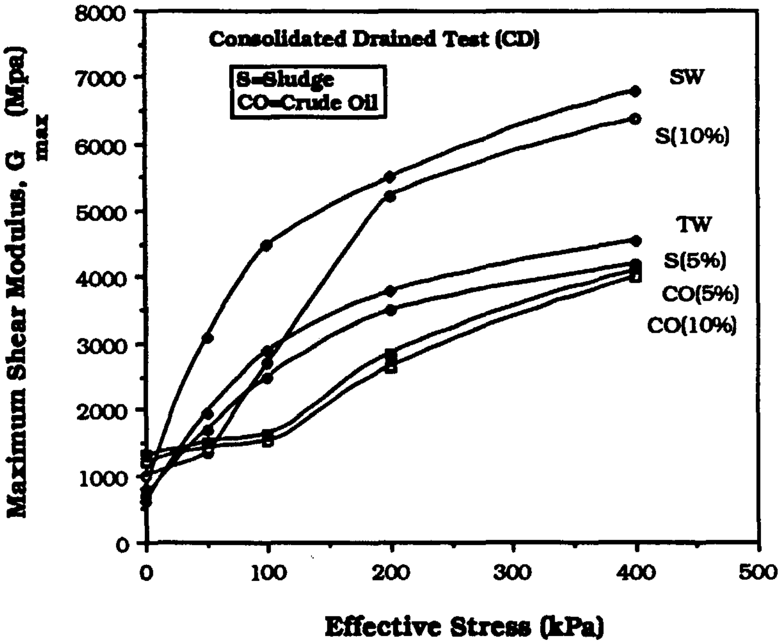


Figure 6.2. Shear Modulus versus Consolidation Pressure for Sediment Specimens

CHAPTER 7

THE INFLUENCE OF CRUDE OIL AND SLUDGE ON THE DOUBLE LAYER THICKNESS OF MARINE CLAY

Introduction

Finally, the influence of municipal sludge and crude oil on the thickness of the computed thickness of the clay double layer is examined. The empirical relationships between the degree of crude oil or municipal sludge contamination and the double layer thickness are developed. In addition the empirical and qualitative relationships between the double layer thickness and clay microstructure, strength, and permeability properties of marine sediments are also developed.

The qualitative influences of crude oil and municipal sludge on clay double layer thickness and geotechnical properties are summarized in Table 7.1. These correlations are also confirmed with the observed microstructure and fabric features of the contaminated marine clay sediments, as discussed in the previous two chapters. Thickness of the double layer is calculated based on the Helmholtz theory.

Table 7.1. The Proposed Effects of Salt, Sludge and Crude Oil on Properties of Marine Clay

MIXTURE*	Double Layer Thickness	Clay Microstructure	Strength	Permeability
MC+SW **Addition of Salt to MC+TW**	DECREASES	OPEN FABRIC LOOSE SEDIMENT FLOCCULATION	INCREASES	INCREASES
MC+SW+SLUDGE **Addition of Sludge to MC+SW**	DECREASES	CLOSE FABRIC DENSE SEDIMENT AGGLOMERATION	INCREASES	DECREASES
MC+SW+CRUDE **Addition of Crude Oil to MC+SW**	DECREASES	OPEN FABRIC LOOSE SEDIMENT AGGLOMERATION LARGE OIL SURFACES	DECREASES	DECREASES

*MC: Marine Clay, SW: Salt Water, TW: Tap Water

Application of the Helmholtz theory to clay particles allows the double layer thickness to be used in the quantitative description of certain properties of clay suspensions and clay sediments. The following equation, which is also given in chapter 2, was used to calculate the double layer thickness.

$$\delta = \frac{\zeta \varepsilon_0 D}{\sigma_0} \qquad [1]$$

where,

δ= Double layer thickness, m

ζ= Zeta potential, mV

ε_0= permittivity of vacuum = 8.854×10^{-12} Coulomb/Vm

D = Dielectric constant of the medium

σ_0= Surface charge density, Coulomb/m^2

σ_0 is given by the following expression (Mitchell, 1976):

$$\sigma_o = \Gamma \bullet F$$

$$\Gamma = \frac{\text{Cation Exchange Capacity}}{\text{Specific Surface Area}}, \text{meq}/\text{m}^2$$

$$\text{F} = \text{Faraday Constant} = 96.5 \text{ Coulomb/meq}$$

7.1. The effect of Municipal Sludge and Crude Oil on Double Layer Thickness (DLT)

7.1.1. The Effect of Municipal Sludge

The effect of municipal sludge on the double layer thickness is shown in Figure 7.1. The salt water modifies the properties of sludge particles and clay minerals. The electrolytes compress the thickness of the double layer and decrease the repulsive forces but increase the van der Waals forces. The van der Waals forces are attractive forces which bring the molecules closer. This would result in greater physical adsorption. This initial physical adsorption allows the subsequent chemical reactions between the sludge compounds and clay minerals. Different cations act as bridging ions. The polyvalent cations such as iron and aluminum play an effective role in binding the organic and inorganic molecules. The divalent cations such as calcium and magnesium, which are abundant in salt water, also play an effective role in the adsorption of organic matter on clay minerals. When the adsorption reaction progresses, the size of the sludge mixed marine clay complex increases forming flocs. This means that specific surface area of marine clay decreases with increasing amount of sludge.

The heavy metals present in the sludge and the electrolytes present in the salt water neutralize the negative charges on the clay particles. Neutralizing the charges allows the sludge particles and clay minerals to come in close proximity to each other forming flocs. Contact develops between heavy metals, electrolytes and clay particles in such a manner that flocculation and coagulation occurs decreasing the thickness of the double layer. It is predicted that sludge compounds are associated with clay mineral surfaces through formation of clay-metal/salt ion-sludge complex. Clay particles and sludge complex are negatively charged. Positively charged metal and salt ions neutralize the charges and at the same time link the clay particles and sludge forming a complex together.

Rashid (1985) calculated the thickness of the double layer for both kaolinite clay and humic acid. He found that in a 35 g/l sodium chloride solution the thicknesses of the double layer of kaolinite and humic acid were 12 and 8 Angstrom, respectively. In this study, it was found that in a 38 g/l salt solution (predominantly sodium chloride) the thickness of the double layer of marine clay only and marine clay with 5% sludge and 10 % by weight sludge added are 9, 6.8 and 6.1 Angstrom, respectively.

7.1.2. The Effect of Crude Oil

The effect of crude oil on the thickness of double layer is shown in Figure 7.2. It can be seen from this figure that increasing percentage of crude oil decreases the double layer thickness significantly more than does sludge. Clay minerals adsorb petroleum hydracarbons. Adsorption increases with salinity, because salinity concentrates the clay particles in the oil phase. Ina saline water-oil mixed system, cations dissolve in the oil phase and chloride ions remain in the water. This causes the oil phase to be positive with respect to water. Adhesion occurs between the clay particle surface and oil. Therefore, clay particle surfaces become wetted by oil. The large specific surface area of the marine clay and its composition also affect the oil retention on clay particle surfaces. Among the clay constituents is illite which is particularly active to oil retention. The EDS records of the clays adsorbed on the oil surfaces showed that similarities to pure illite records which strenthens this conclusion. Therefore, agglomeration and flocculation are increased.

Agglomeration brings small particles together creating large particles. The specific surface area of a mixture of crude oil and marine clay is approximately 1 m^2/g which is similar to the specific surface area of fine sand. This is because of the spherical agglomeration and large oil surfaces on the clay particle surfaces. That is why the double layer thickness of the crude oil mixed marine clay is so low compared to that of sludge mixed marine clay. The forces at the oil-water-clay interfaces are wettability, adhesion and surface tension forces. Scanning electron micrographs of mixture of crude oil and marine clay support these explanations.

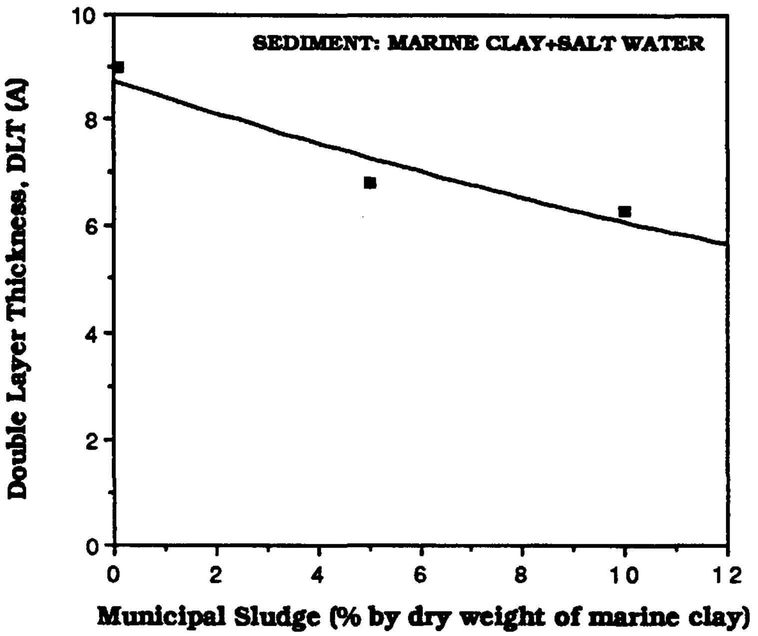


Figure 7.1. Double Layer Thickness versus Sludge Contamination

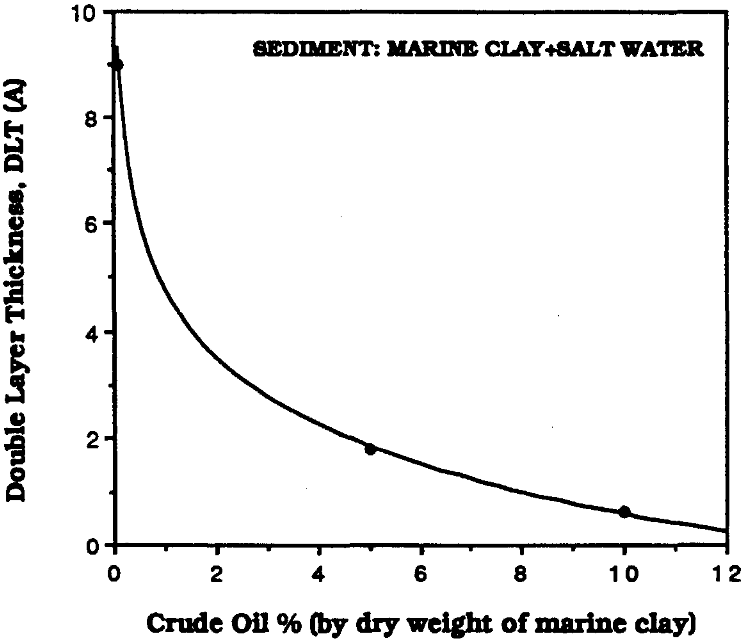


Figure 7.2. Double Layer Thickness versus Crude Oil Contamination

7.2. Correlations between the Double Layer Thickness and the Geotechnical Properties

7.2.1. Strength

Shear strength decreases with increasing double layer thickness as shown in Figure 7.3. Addition of sludge to salt water mixed marine clay increases the strength and decreases the double layer thickness as expected. Clay microstructure of sludge mixed marine clay also shows that the fabric is denser and tighter compared to that of uncontaminated clay. There is an interparticle bonding between the clay particles due to the organic matter. Sludge increases the cohesion between the clay particles. There is also bonding between the flocs because of the fibrous particles in the sludge. Fibrous particles act as reinforcing members between the clay particles and the flocculated domains. Therefore, the strength of the sludge marine clay mixture is increased. It was also observed that when the sludge mixed samples were oven dried, they remain intact and did not pulverized easily. This indicated that sludge probably promoted cementation between the clay particles.

Addition of crude oil decreases both the shear strength and the double layer thickness of marine clay as shown in Figure 7.4. Addition of crude oil to marine clay reduces the cohesion by increasing particle size and reducing the specific surface area. Crude oil mixed marine clay appeared "spongy" with loose, open fabric and porous structure which were evident in the micrographs. Oven dried specimens of crude oil mixed clay pulverized easily which indicated destruction of cohesion between the clay particles.

7.2.2. Permeability

Permeability of sludge mixed marine clay decreases as the double layer thickness decreases as shown in Figure 7.5. The presence of sludge reduces the net negative charge of clay particles. Therefore clay particles move closer to each other in a face to face arrangement reducing the space for free water flow.

Addition of crude oil to marine clay also reduces the permeability and double layer thickness significantly as shown in Figure 7.6. Crude oil traps water and creates discontinuos channels. It can be seen from micrographs that there are large oil surfaces which may block the water channels. Even though the clay fabric is open and porous, the permeability of crude oil mixed specimens were low probably because of these oil blocks. Study also shows that the permeability of the sediment decreases further when the crude oil percentage is increased.

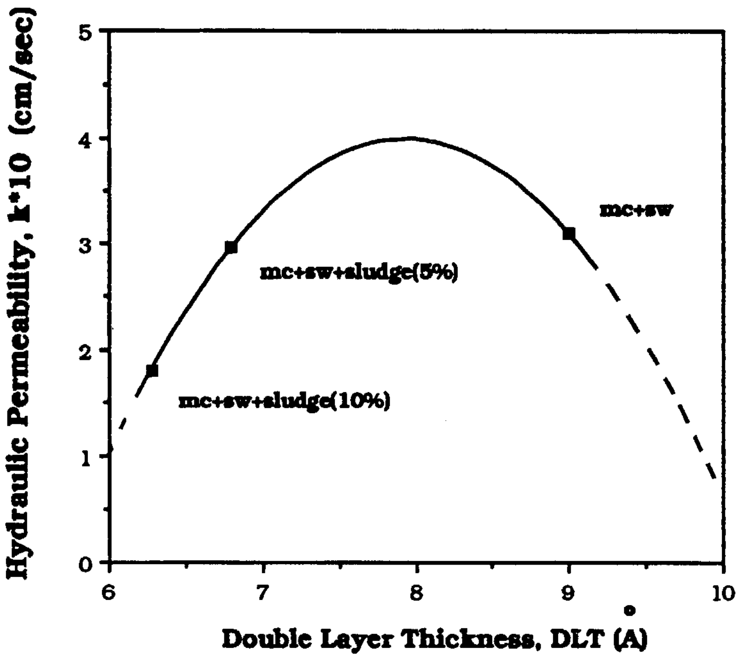


Figure 7.5. Hydraulic Permeability versus Double Layer Thickness for MC+SW+SLUDGE

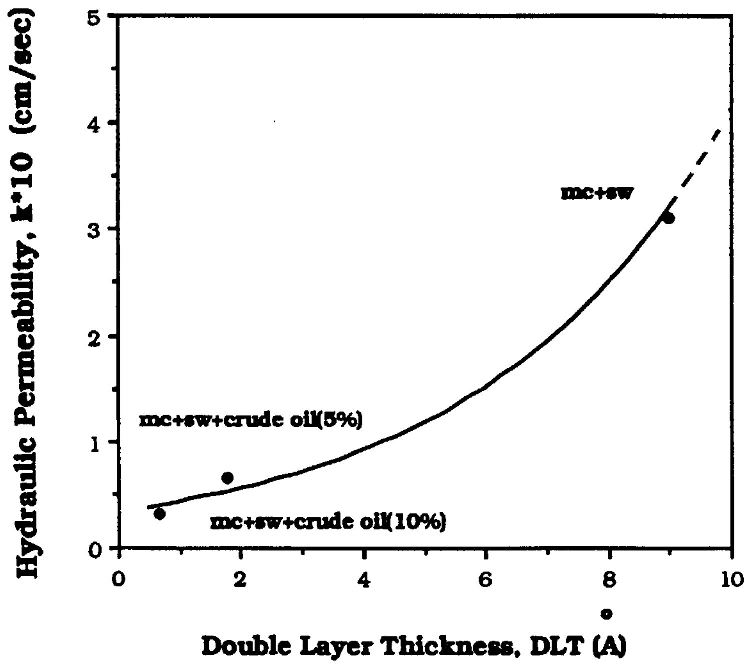


Figure 7.6. Hydraulic Permeability versus Double Layer Thickness for MC+SW+CRUDE OIL

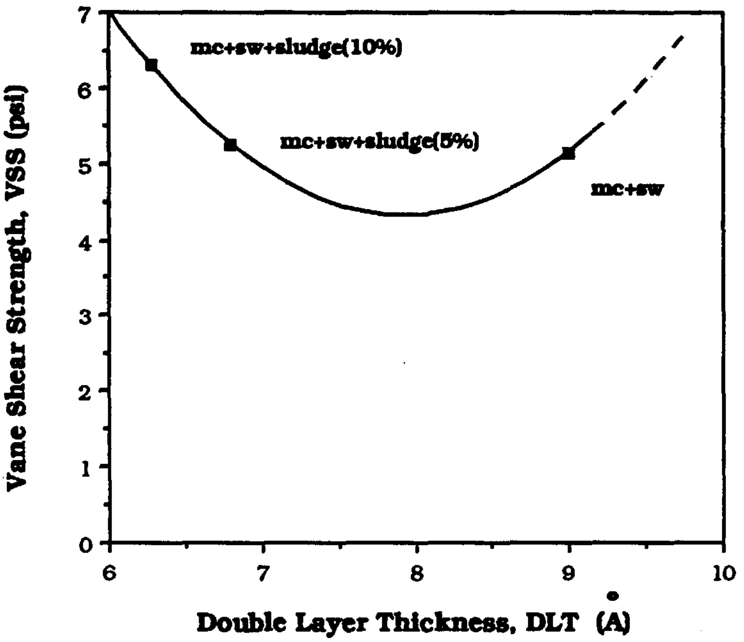


Figure 7.3. Shear Strength versus Double Layer Thickness for MC+SW+SLUDGE

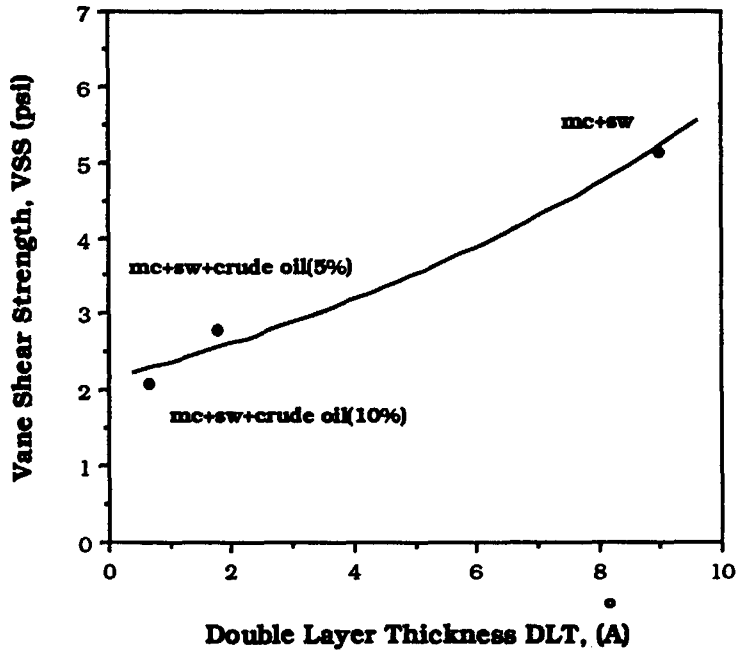


Figure 7.4. Shear Strength versus Double Layer Thickness for MC+SW+CRUDE OIL

7.3. Conclusions

A clay particle double layer thickness is important to its mechanical and permeability behavior. The double layer thickness is both a measure of the amount of immobilized fluid around the particle and also a measure of the repulsive force between particles. The chemical nature of the fluid medium during and after sedimentation is important with respect to electrostatic interactions between clay particles. If the double layer thickness is known, mechanical and hydraulic engineering properties and their effect on material behavior can be predicted and better understood under changing environmental conditions.

Crude oil has significant influence on the thickness of the double layer. However, municipal sludge does not have as much influence. Crude oil interactions create bigger particles because of the spherical agglomeration and there are also large oil surfaces in corporated in the clay both which work toward decreasing the specific surface area available for chemical or physical exchange. These were confirmed with the observed microstructure of the contaminated marine clay sediments.

Addition of municipal sludge to salt water mixed marine clay promotes formation of dense sediment with close fabric. However, addition of crude oil to salt water mixed marine clay creates loose sediment with open fabric. Vane shear strength of the clay increases in the case of sludge mixing while it decreases in the case of crude oil mixing. Sludge increases the cohesion and reinforces the domains, however, crude oil destroy the cohesion between the particles. Hydraulic permeability decreases for both cases. In case of crude oil, this reduction is significant because of the void blocking action of oil surfaces.

In Figure 7.7, the coefficient of hydraulic permeability, k, versus DLT data for sludge and crude oil mixed clays are superimposed to derive an emprical correlation between the two properties. This correlation is given below, which is based on the fitted curve to the data. The goodness or R^2 value of this fit is 0.938. It should be noted that this correlation is valid for clays prepared and tested in the manner described in here and should not be generalized to other cases.

$$k = 0.338 \times 10^{[0.119(DLT)]} \times 10^{-7} \qquad [6]$$

where,

k= Coefficient of Hydraulic Permeability, cm/sec

DLT= Double Layer Thickness, (Angstrom)

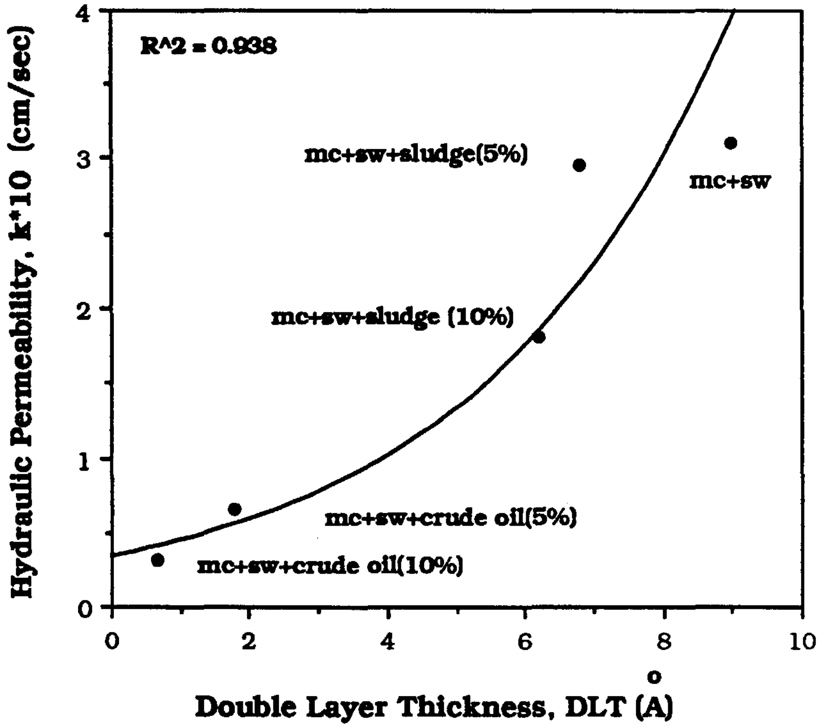


Figure 7.7. Hydraulic Permeability versus Double layer Thickness foe MC+SW+SLUDGE & MC=SW+CRUDE OIL: Predicted Correlation

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

In this study, physico-chemical, microstructure and geotechnical properties of municipal sludge or crude oil contaminated marine clays were studied using laboratory prepared mixtures of pure clays. Correlations between the percentage of municipal sludge or crude oil to the thickness of the double layer and geotechnical properties were established. These correlations were confirmed with the observed microstructure and fabric features of the contaminated marine clay specimens.

This study shows that there are significant influences of disposed or spilled waste products on the geotechnical properties of marine clay sediments. Emphasis was given to the impact of sludge and crude oil on physico-chemical properties and microstructure formation which subsequently influence the following geotechnical properties: strength, permeability, compressibility, shear strength, plasticity and porosity.

8.1. Physico-Chemical Properties

Addition of municipal sludge to salt water mixed marine clay increases the rate of deposition as shown in Table 8.1. Decrease in pH, dielectric constant and electrical conductivity and increase in turbidity, particle size distribution and cation exchange capacity values of sludge mixed marine clay can explain its fast deposition. Clay particles tend to flocculate at low pH values. The flocculated sediment settles out of water faster than the dispersed one. Addition of sludge to marine clay also increases ζ-potential thus decreasing the thickness of double layer. Addition of sludge to marine clay appears to promote agglomeration through coating of the particles and also decreasing the double layer thickness of the clay particles. Decrease in double layer thickness allows the particles to approach each other closely and adhere to each other.

Addition of crude oil to salt water mixed marine clay increases the rate of sedimentation as shown in Table 8.1. Crude oil tends to agglomerate and coat the clay particles. This increases the apparent particle size, turbidity and decreases specific surface area and cation exchange capacity significantly. The larger particle size and decrease in pH explain fast deposition of these clays. Addition of crude oil also decreased the double layer thickness considerably, because of agglomeration and retention of specific surface area.

8.2. Geotechnical Properties

Addition of sludge to salt water mixed marine clay increases the plasticity, vane shear strength, compressibility, porosity. However, it decreases permeability and shear modulus as shown in Table 8.2. Addition of sludge increases interparticle bonding. Presence of sludge tends to reduce the net negative charge of clay particles. Clay particles move closer in a face to face arrangement reducing the space for free water flow. Fibrous particles of sludge also appeared to promote cementation and bonding between the clay particles.

Addition of crude oil to salt water mixed marine clay increases compressibility and porosity, but decreases considerably the plasticity, vane shear strength, permeability and shear modulus as shown in Table 8.2. Addition of crude oil to marine clay tends to destroy the cohesion between the particles which results in the strength reduction. Therefore the strength of the clay decreased. Additon of crude oil also decreased the permeability due to large oil surfaces blocking the water channels in the sediment. Addition of crude oil appeared to cause the formation of a looser and more porous structure with increased water holding capacity in marine clay sediments.

8.3. Clay Microstructure

Addition of sludge to marine clay appeared to promote face to face agglomeration through coating and cementing of the particles with humic substances and dissolved organic matter. Sludge mixed marine clay showed a tighter structure and more orientation. The fibrous particles reinforced the clay causing increased strength and stiffness relative to those measured with oil cotaminated clay.

Addition of crude oil appeared to cause the formation of an open "spongy" structure with a number of mechanisms of interaction between clay and oil evidenced in the micrographs. Two types of adsorption mechanisms were observed. One is the adsorption of clay particles by the oil and the other one is the adsorption of oil by the clay particles. As a result of these mechanisms there different interactions were observed between oil and clay particles. These were the spherical agglomeration of clay particles, clay coating of of the oil drops and adhesion of oil layers or sheet structures to clay surfaces.

SUMMARY AND RECOMMENDATIONS:

This study has generated fundamental information on the physico-chemical interaction of clay constituents of marine sediments with two selected organic contaminants: municipal sluge and crude oil. The information is evaluated on the basis of the impact of these contaminants with respect to the physical and mechanical properties of a typical marine clay sediments. The two most important conclusions of this study are that:

1) The organics contaminants influence clay through surface interactions and therefore specific surface area becomes one of the critical factors in evaluation of the impact on clay behavior.

2) The organic contaminants influence water column chemistry with respect to dielectric constant and ionic concentration the most.

Based on these general conclusions, it is recommended that further studies on geotechnical properties of contaminated clays be focused on the influence of the specific surface area, dielectric constant and ionic concentration of pure clay and organic compound systems.

Table 8.1. The Proposed Effects of Municipal Sludge and Crude Oil on Depositional Properties of Marine Clay

MIXTURE	Rate of Sediment.	pH	Dielectric Constant	Elect. Conduct.	Turbidity	Particle Size	Cation Exchange Capacity	Zeta Potent.	Double Layer Thickness
MC+SW+SLUDGE	INCR.	DECR.	DECR.	DECR.	INCR.	INCR.	INCR.	DECR.	DECR.
Addition of Sludge to MC+SW									
MC+SW+CRUDE OIL	INCR.	DECR.	DECR.	DECR.	INCR.	INCR.	DECR.*	DECR.	DECR.
Addition of Crude Oil to MC+SW									

* Exchange sites become coated

Table 8.2. The Proposed Effects of Municipal Sludge and Crude Oil on Geotechnical Properties of Marine Clay

MIXTURE	Strength	Permeability	Compressibility	Shear Modulus		Plasticity	Porosity
				Undrained	Drained		
MC+SW+SLUDGE	INCR.*	DECR.	INCR.	INCR.	DECR.	INCR.	INCR.
Addition of Sludge to MC+SW							
MC+SW+CRUDE OIL	DECR.	DECR	INCR.	INCR.	DECR.	DECR.✱	INCR.
Addition of Crude Oil to MC+SW							

* Fibre reinforcement and dense structure

✱ Decrease in specific surface area

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