# THE EFFECTS OF VALENCY ON THE COMPRESSIBILITY OF CLAYS

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**by**

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**İZMİR**

# Ms.Sc. THESIS EXAMINATION RESULT FORM

We certify that we have read the thesis, entitled **"The Effects of Valency on Compressibility of Clays"** completed by **Ali Hakan Ören** under supervision of Assistant Professor Abidin Kaya and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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# ABSTRACT

Many studies have been conducted to investigate the physicochemical behaviour of pure clay minerals and predict their engineering performance in the field. However, there is no clayey soil consisting of only a single clay mineral. In this study, the physicochemical properties of a clayey soil taken from Canakkale consists of different clay minerals, namely 40-50% montmorillonite, 20-30% illite and 10-15% kaolin was investigated. The CEC (Cation Exchange Capacity) of soil was determined 13 meq/ 100 g. The soil was washed with 1N ammonium acetate solution to purify the soil from cations presented in the exchangeable cation sites. Then, 1N chloride solutions of sodium, Na; calcium, $Ca^{+2}$; and aluminum, $Al^{+3}$ were used to make the soils homoionized.

The tested engineering properties are Atterberg Limits, hydraulic conductivity, sediment volume and consolidation behaviour. The results reveal that the liquid limit of soil increases with increasing in the cation valence; the plastic limit of the soils is also consistent with the liquid limit. Furthermore, the shrinkage limit of soil supports the general behavior of index properties. The hydraulic conductivity of the soil also increases with an increase in the valence of the cation at any given void ratio. There is no considerable change in the compressibility of the soil when the cation valence increased. However, trivalent clay consolidate six times faster than monovalent and two times faster than divalent clay. These properties of tested soils are similar to those of kaolinite.

The index properties of homoionized soil are also tested with different pore fluids such as n-hexane, ethanol and methanol. The volume basis liquid limit results of homoionized samples were compared while treating with different pore fluids. Decrease in the dielectric constant of the pore fluid results decrease in volume basis

liquid limit of homoionized specimens while treating with methanol. Then, volume basis liquid limit of homoionized specimens tend to increase when they were treated with ethanol. However, the volume basis liquid limit of samples decreased with n-hexane. On account of rapid evaporation of n-hexane, a correction was applied to the volume basis liquid limit values. Sedimentation test results were taken into consideration while applying the correction to the volume basis liquid limit of homoionized samples when treated with n-hexane. The obtained results are compared with the published data in the literature. The comparison revealed that the physicochemical behavior of the tested clay soil is, in general, between those of kaolinite and montmorillonite. However, when the pore fluid is inorganic the tested physicochemical parameters are close to those of kaolinite and when the pore fluid is organic the tested physicochemical parameters are close to those of either montmorillonite or kaolinite.

# ÖZET

Daha önce yapılan çalışmaların birçoğu, saf kil minerallerinin fizikokimyasal davranışlarının incelenmesi ve arazi performanslarının önceden belirlemesi üzerinedir. Fakat doğada saf halde (tek bir mineralden oluşmuş) kil bulabilmek mümkün değildir. Bu çalışmada kullanılan kil Çanakkale'den getirtilmiş olup, yapılan fizikokimyasal analizler sonucunda bünyesinde; 40-50% montmorillonit, 20-30% illit ve 10-15% kaolin bulunmaktadır. Katyon Değişim Kapasitesi de 13 meq/100 g olarak belirlenmiştir. Kili saflaştırabilmek için 1N'lik amonyum asetat çözeltisi kullanılmıştır. Daha sonra saflaştırılan kil, sırasıyla sodyum, Na; calsiyum, $Ca^{+2}$; ve aluminyum, $Al^{+3}$ iyonlarının klorürlü çözeltileriyle yıkanarak tek tip katyonla doyurulmuş kil haline getirilmiştir.

Farklı değerlikli katyonlarla doyurulan killerin Atterberg limitleri (kıvam limitleri), hidrolik iletkenlikleri, sediment hacimleri ve sıkışma davranışları gibi mühendislik özelikleri belirlenmiştir. Elde edilen sonuçların ışığında, katyon değerliğindeki artışla kilin likit limit değeri artmaya başlamış; aynı durum, plastik limit ve rötre limiti değerleri için de elde edilmiştir. Ayrıca, yine katyon değerliğindeki artış, kilin daha fazla geçirgen olmasına sebep olmuş; bir başka deyişle, hidrolik iletkenliği artmıştır. Kilin sıkışma miktarlarında fazla bir değişiklik olmamasına rağmen, aluminyumla doyurulan kilin sodyumla doyurulana göre altı kat, kalsiyumla doyurulana göre de iki kat daha hızlı konsolide olduğu gözlemlenmiştir. Bütün bu elde edilen sonuçların, literatürde kaolin kili ile yapılmış deneylerin sonuçlarına benzer sonuçlar verdiği görülmüştür.

Bu deneylere ilave olarak, farklı değerlikli katyonlarla doyurulan killerin indeks özelikleri, farklı dielektrik sabiti olan organik sıvıların (metanol, etanol ve n-hekzan) varlığında da belirlenmiştir. Likit limit sonuçları birbirleriyle hacimsel olarak karşılaştırılmıştır. Elde edilen sonuçlara göre, hacimsel esaslı likit limit değerleri

metanol sıvı kullanıldığında düşmüş; etanolle birlikte artma eğilimine girmiş; fakat n-hekzanla tekrar azalmıştır. n-hekzanın sıcaklığa bağlı olarak çabuk buharlaşmasının deney sonuçlarını etkilediği görülmüş ve sedimentasyon deneyi sonuçları da kullanılarak bir düzeltme yapılmıştır. Bulunan sonuçlar literatürdeki sonuçlarla karşılaştırılmış; ve killerin fizikokimyasal davranışlarının kaolinit ve montmorillonit arasında olduğu görülmüştür. İnorganik sıvı varlığında (saf su), elde edilen fizikokimyasal parametreler kaolinite benzer çıkmış; organik sıvı kullanıldığında ise bu parametrelerin hem montmorillonite, hem de kaoline benzediği görülmüştür.

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# CHAPTER ONE
# INTRODUCTION

## 1.1 Background

Contamination is a very important problem all over the world. Investigators evaluate the effect of pollution on daily life as well as on the performance of engineering structures such as pollution of groundwater, progressive failures of earth structures due to contamination etc. One of the areas affected from the contamination is subsurface. Geotechnical engineers concern with this problem and interested in the changes on the stability of soils and structures on it.

In geotechnical engineering, the behaviour of fine-grained soils, especially clays, is very important. Because of their high affinity for water, the engineering behaviour of clays is investigated under different conditions. The changes in the environment can affect the engineering behaviour to a marked point. For example, contamination of ground water may change the consistency limits, hydraulic conductivity, compression, and shear strength of clayey soils.

Change in environment can influence the fabric of clayey soils. Contamination in water (pore medium) can affect the particle orientation with respect to each other; that is particles tend to either attract or repulse each other. As a result, particle flocculation (either edge to face or face to face) or dispersion occurs. The new particle orientation because of change in pore medium, influences the engineering behaviour of soils significantly. Thus, the effects of contamination on the engineering behaviour of fine-grained soils will be investigated in this study.

### 1.2 Objective and Specific Approach

The overall objective of this research is to investigate the effect of cation valence and selected organic liquids as a pore fluid on a clayey soil consisting mixed minerals compare to DDI (Distilled Deionized) water.

In the literature, researchers conducted research either on kaolinitic soils or on montmorillonitic soils, however, in the nature, no clayey soil is made of a single clay mineral. Thus, to fill the gab, the behavior of clayey soil made of mixed minerals was investigated.

Initially, clay was treated with chemical solutions to make them homoionized. At the end, Na-clay was obtained with treating NaCl, Ca-clay was obtained with treating $CaCl_2.2H_2O$, and Al-clay was obtained with treating $AlCl_3$.

Index properties of each soil were determined. Specific gravity, consistency limit tests, sedimentation test, and consolidation test were performed on the homoionized soils. Only liquid and plastic limit tests and sedimentation test were conducted by some organic liquids having various dielectric constant.

When the soils were tested with DDI water, the results showed that liquid limit, plastic limit, and shrinkage limits of homoionized clays increased linearly with increasing cation valence. Sedimentation tests indicate that flocculated particles have higher sediment height and sediment volumes in DDI water which is consistent with the shrinkage limit data. Cation valence does not considerable effect on the compressibility of homoionized clays. However, change in hydraulic conductivity is very significant. Increase in cation valence results increasing in hydraulic conductivity of homoionized clays. Thus, Al-clay consolidates almost six-times faster than Na-clay and three times faster than Ca-clay.

When treating the homoionized clays with organic liquids, results showed that particle flocculation occurred by decreasing the dielectric constant of the pore medium and there was a transition point in methanol while conducted the liquid limit test and sedimentation test. The liquid limit and sedimentation test results are consistent with each other when a correction was applied to the liquid limit of n-hexane on account of temperature effect on this liquid. Liquid limit and sediment volumes of homoionized clays decreased to the dielectric constant value of methanol and then increased while treating with ethanol and n-hexane. Plastic limit test results showed that homoionized clays act as non-plastic while treating with n-hexane.

### 1.3 Outline of Thesis

Chapter 2 discusses the observations made by previous researchers on the consistency, compression, strength and sedimentation behaviour of kaolinitic and montmorillonitic soils. It also describes the micro-structural changes in clays when exposed to such chemicals.

The properties of the materials used in the experiment and the experimental program of the study are described in detail in Chapter 3. This chapter consists of the washing procedure in order to obtain the homoionized clays and tests conducted to these samples to determine the variations in engineering properties, if there is any.

Chapter 4 discusses the results of the experiments and draws possible conclusions. Then, practical applications of the results are also discussed.

Chapter 5 summarizes the research program and lists the conclusions drawn from the work and suggestions for future work.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Clays

In soil mechanics, soils are divided into two groups: coarse grained and fine grained. Clayey soil falls in fine-grained group, and very important for geotechnical engineering applications because of their high affinity for water, due to electrical forces. It is well known that the engineering performance of clayey soils changes with water content.

According to the USCS (Unified Soil Classification System), 75 μm grain diameter is the borderline between coarse-grained and fine-grained. Soils above No. 200 (75 μm) sieve are known to be coarse grained; however, fine grained soils are soils passing through 75 μm. Under No. 200 sieve, hydrometer test is applied to determine the size distribution of the soil particles. Silts have almost no plasticity and water affects their engineering behaviour less than clays. Clays are described as not only by their size, but also by their mineralogical composition. Clay minerals are formation of chemical weathering of certain rocks and they are very tiny particles that cannot be seen with naked eyes.

### 2.1.1 Structure

As stated above, clay minerals are very tiny crystalline substances evolved primarily from chemical weathering of certain rock-forming minerals (Holtz & Kovacs, 1981). These minerals are composed of sheets and several bonds holding them to each other. There are two fundamental crystal sheets in clay minerals: silica unit (tetrahedron) and alumina unit (octahedron).

The silica unit consists of four oxygen atoms surrounded around a silicon atom (Lambe & Whitman, 1979). This form occurs in a tetrahedral unit. Oxygen to oxygen distances is the same. One of each oxygen at the base of the tetrahedral unit combines with the oxygen of another tetrahedral unit and forms honeycomb shape with a hexagonal hole. Two silicon atoms share each oxygen atoms at the base.

Oxygen in bases and tips are all in the same direction. Single and combined unit of tetrahedral forms are shown in Figure 2.1.

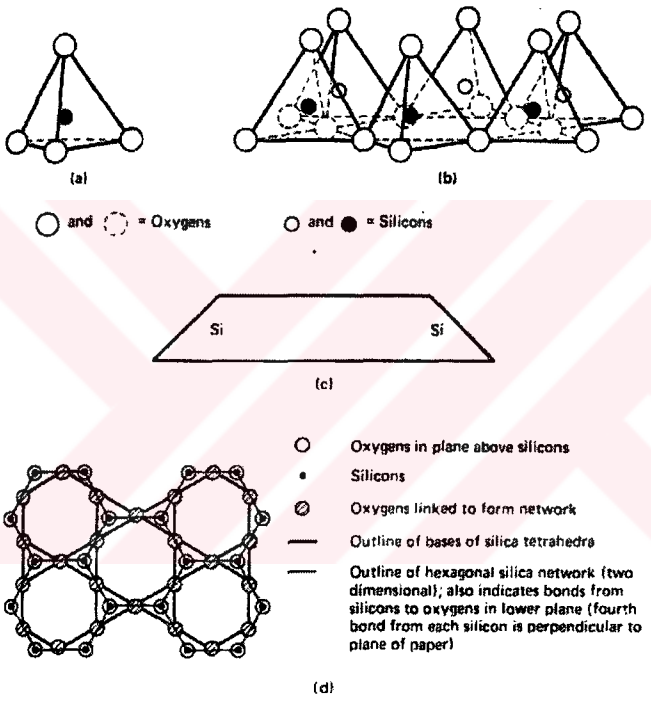



**Figure 2.1 (a) Single aluminum (or magnesium) octahedron. (b) Isometric view of the octahedral. (c) Schematic representation of the octahedral or alumina (or magnesia) sheet. (d) Top view of the octahedral sheet (Holtz & Kovacs, 1981)**

The octahedral unit consists of six oxygen and either an aluminum or magnesium atom at the center of this form. Again, two aluminum atoms share each oxygen atom. If two-thirds of the octahedral center are occupied by aluminum, then it is called gibbsite, with a chemical formula $Al_2(OH)_6$. If this center of octahedral form is full of magnesium atoms, then it is called brucite. $Mg_3(OH)_6$ is the chemical formula of

brucite (Yong & Warkentin, 1966). If the cation is trivalent, then normally only two-thirds of the possible cationic spaces are filled, and the structure is named dioctahedral. If the octahedrally coordinated cation is divalent, then normally all possible cation sites are filled, and the structure is called trioctahedral (Mitchell, 1993). Octahedral form is shown in Figure 2.2.

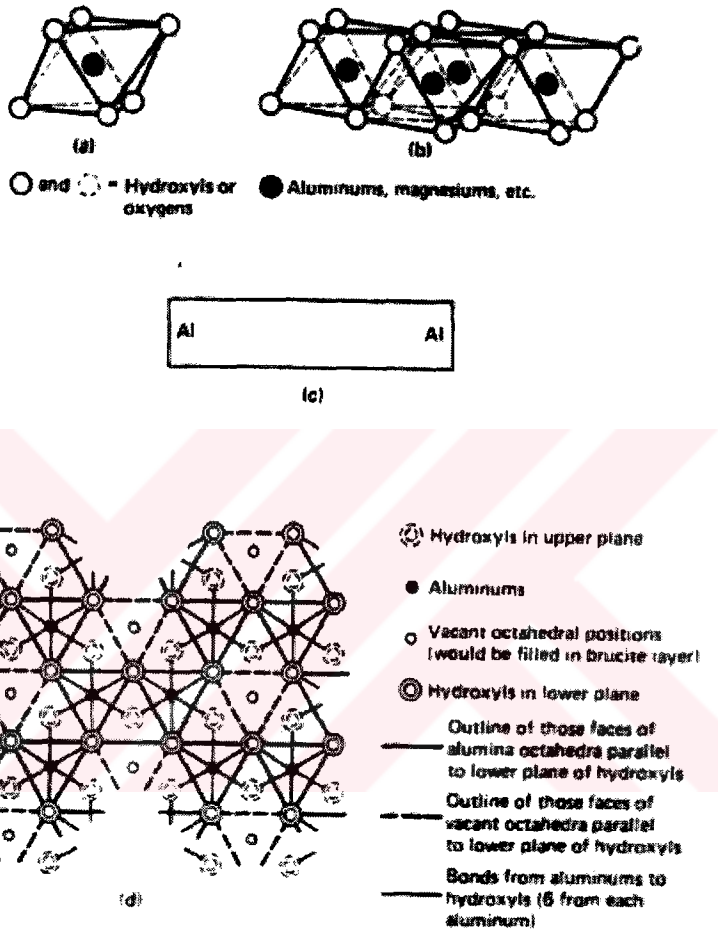



**Figure 2.2 (a) Single aluminum (or magnesium) octahedron. (b) Isometric view of the octahedral. (c) Schematic representation of the octahedral or alumina (or magnesia) sheet. (d) Top view of the octahedral sheet (Holtz & Kovacs, 1981).**

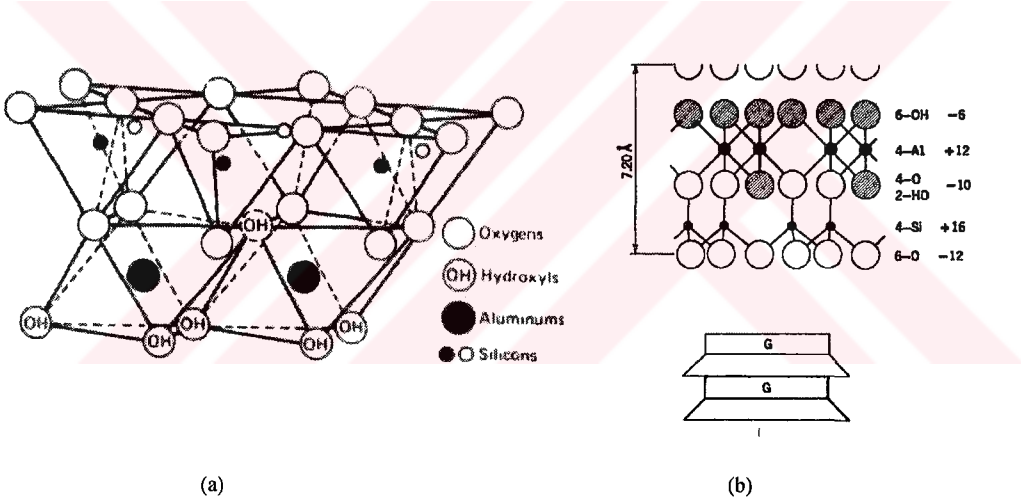
In the clay minerals, some of tetrahedral and octahedral spaces are not only occupied by silicon (either aluminum or magnesium atoms), but also some other cations may enter these spaces. Isomorphous substitution is an important factor in

the structure and properties of clay minerals, which occurs due to deficiencies in the structure (Mitchell, 1993). Isomorphous substitution may be an important factor in cation exchange capacity of clay minerals.

If clay minerals wanted to be narrowed down for geotechnical purposes, there are three most common clay minerals; namely, kaolin, montmorillonite and illite, described in detail in the following paragraphs.

#### 2.1.1.1 Kaolin

Kaolin is called as 1:1 mineral. It means, tips of tetrahedral sheet and upper side of the layers of octahedral sheet is in the same direction and held together. Composed of octahedral and tetrahedral crystal sheets form layers. One layer is about 0.72 nm thick and continues in the other two directions. Typical form of kaolin is shown in Figure 2.3.




(a) (b)

**Figure 2.3 (a) Diagrammatic sketch of the kaolin (Mitchell, 1992) (b) Atomic and symbolic structure of kaolin (Lambe & Whitman, 1979)**

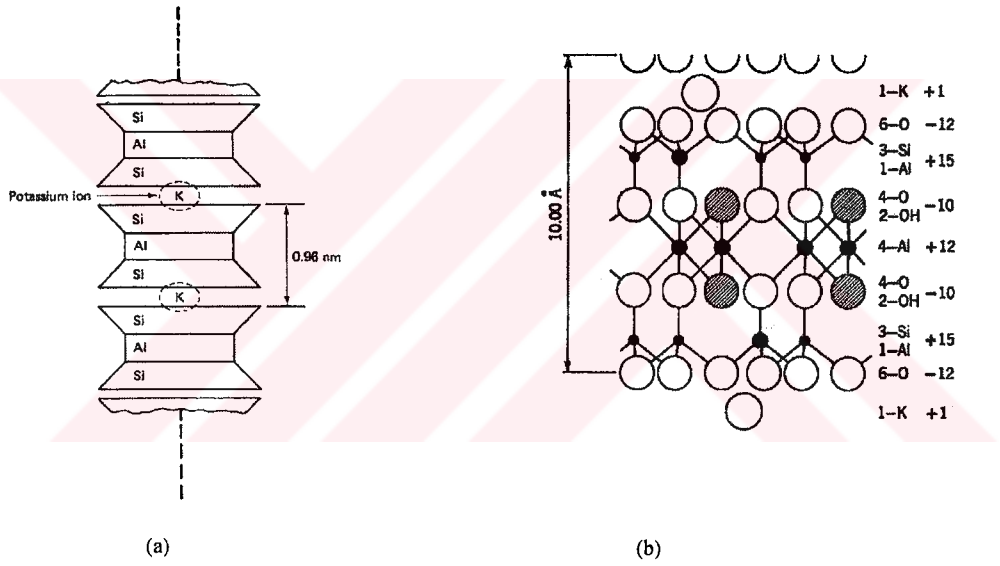
On account of hydrogen bonding between layers, kaolin is not a swelling clay. This strong bonding restricts the water adsorption between the layers.

The physical properties of kaolin are as follows: Values of cation exchange capacity for kaolin in the range of 3-15 meq/100 gm. The lateral dimensions of plates

range from about 0.1 to 4 μm, and their thickness are from about 0.05 to 2 μm. The specific surface area of kaolin is about 10 to 20 $m^2$/gm of dry clay (Mitchell, 1993).

### 2.1.1.2 Illite

Illite is a 2:1 mineral. Octahedral sheet is sandwiched between two silica sheet and these combined sheet layers are held each other by potassium ions, $K^+$. Potassium ions are fixed in the hexagonal hole and bond layers strongly together. Thickness of one layer is about 1 nm. Illite is a mineral that shows a between characteristics of kaolin and montmorillonite. Schematic diagram and atomic structure of illite are shown below.




(a) (b)

**Figure 2.4 (a) Schematic diagram of illite (Holtz & Kovacs, 1981) and (b) Atomic structure of illite (Lambe & Whitman, 1979)**

Its structure is similar to the mica minerals but with less isomorphous substitution and less potassium ions. On the other hand, it is chemically much more active than other micas (Holtz & Kovacs, 1981).

The physical properties of this mineral are as follows: the cation exchange capacity of illite is less than that of the smectites, amounting 10 to 40 meq/100 gm. If

well crystallized, the flaky particles may have hexagonal outline. The long axis dimension ranges from 0.1 μm or less to several micrometers, and the plate thickness may be as small as 30 $A^{o}$. The specific surface area of illite is between 65 $m^2$/ gm and 100 $m^2$/ gm (Mitchell, 1993).

### 2.1.1.3 Montmorillonite

Montmorillonite is a 2:1 mineral like illite. One octahedral sheet combines with the tips of two silica sheets and forms a layer. Layers are held together by van der Waals forces. Because of these weak forces and some charge deficiencies in the structure, water can easily penetrate between layers and cations, which balance the deficiencies.

On account of water adsorption, montmorillonite is high plastic clay. Not only montmorillonite has high affinity for water but also very sensitive to the changes in the environment; which is very important for geotechnical applications. Figure 2.5 shows the atomic and symbolic structure of montmorillonite.

The physical properties of montmorillonite are as follows: have high cation exchange capacities, generally in the range of 80-150 meq/100 gm; particles range in thickness from 10 $A^{o}$ unit layers upward to about 1/100 of the width, the long axis of the particle is usually less than 1 or 2 μm; and the surface area exclusive of interlayer zones, ranges from 50 to 120 $m^2$/gm (Mitchell, 1993).

The relative sizes of three common clay minerals and their specific surfaces are shown in Figure 2.6.

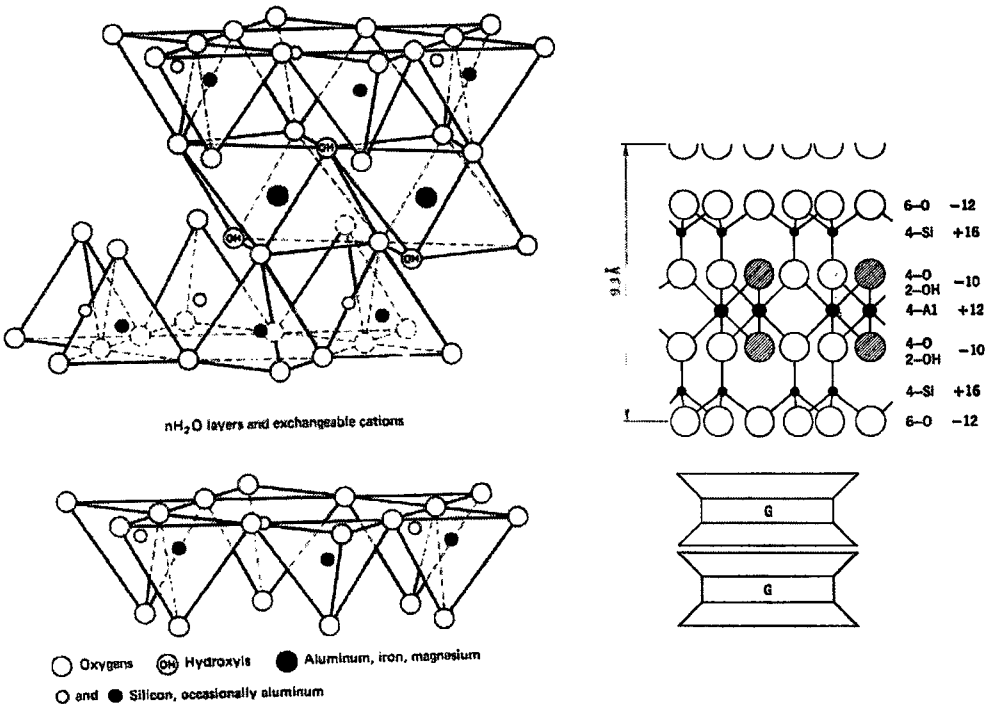



**Figure 2.5 (a) Atomic structure of montmorillonite (Holtz & Kovacs, 1981) and (b) Atomic and symbolic structure of montmorillonite (Lambe & Whitman, 1979)**

| Edge View | Typical Thickness (nm) | Typical Diameter (nm) | Specific Surface ($km^2/kg$) |
|---|---|---|---|
| Montmorillonite | 3 | 100-1000 | 0.8 |
| Illite | 30 | 10000 | 0.08 |
| Kaolinite | 50-2000 | 300-4000 | 0.015 |

**Figure 2.6 Average values of relative sizes, thickness, and specific surfaces of the common clay minerals (Holtz & Kovacs, 1981).**

## 2.2 Factors affecting engineering behaviour of clays

The engineering properties of fine-grained soils are strongly dependent on water content. They are easily affected from changes in external pressure, chemistry of pore medium, wetting and drying cycles and temperature (Sridharan, 1990).

Herein, only, how clays are affected from environmental conditions will be briefly discussed. Clays are very sensitive to chemical changes in the presence of water. For example, compositionof pore fluid in clay can easily change its engineering behaviour. Similarly, dielectric constant of pore medium also affects the microstructure of clays; in turn, engineering behaviour.

Clays have generally flaky or plate shapes. Surface of clays are negatively charged and these negative surfaces are neutralized by the cations within the system. However, changes in the environment of clays directly influence the microstructure of them. These changes allow them to be flocculated or dispersed, depending on the environment.

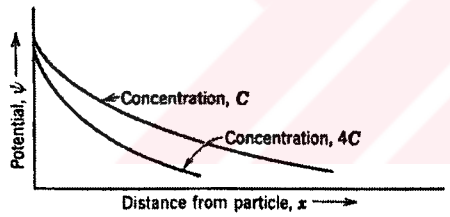
Concentration of cations in the pore medium affects the electrical potential of clays. If cation concentration increases, the electrical potential of clay decreases. That means, increase in cation concentration allow them to be flocculated; or decrease in cation concentration results more dispersed clays than that of high concentration.

Some of cations are also strongly attracted by the negatively charged clay surface and forms a dense layer, which is full of cations. This compacted layer is called Stern Layer. After this, layer ions are freely diffuse to the outside of clay particle surface. Both of these layers are called Electrical Diffuse Double Layer. From Coulomb theory, the potential energy of these ion layers is inversely proportional to the distance between them. For this reason, the cations in the Stern Layer are strongly attracted than those in diffuse layer. If the concentration of cations in the pore

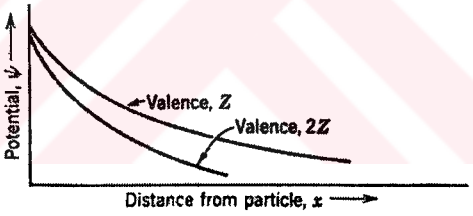
medium is increased, the cations in the Stern Layer also increase until all adsorbed surfaces is filled by cations. Then, no more cations can be hold at the Stern Layer. As the cation adsorption increases, the diffuse double layer compresses, resulting a flocculated structure.

Valence of cations also influences the diffuse double layer thickness. If the valence of cation increases, the potential energy of clays will also increase; again resulting flocculation of particles. But trivalent cations are much more attracted to the clay surface than those of divalent, and divalent cations are strongly held to the surface than monovalent cations. That means if valence of cations in the pore medium increases, then, particles attract each other more strongly than lower valence cations. Thus, dispersion is higher for lower valence cations than those of higher ones.

The effects of changes in the soil-liquid system properties on double layers are shown in Figure 2.7. That shows the changes between potential, $\psi$ vs. distance from particle, $x$, under different concentration, valence, and dielectric constant.




(a)

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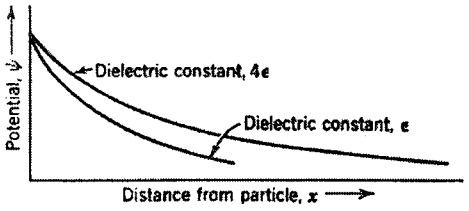


(c)

**Figure 2.7 The effects of changes in system properties on double layers. (a) Concentration only variable. (b) Valence only variable. (c) Dielectric constant only variable (Lambe & Whitman, 1979).**

Another factor affecting the behaviour of clay is the size of hydrated ions. The effect of size can be seen well for monovalent cations, which have different hydrated ionic radius than that of divalent and trivalent. According to the Gouy-Chapman Model, positive ions diffuse in the layer around the clay particle. For Stern Model, cation can approach to the clay surface only to a distance of its radius; thus, the higher the ionic radius, the less amount of the hydrated ions in the Stern Layer. Decrease in hydrated ionic size results more attracted cations to the surface and more compacted layer around a clay particle.

The explanation presented above is also true for dielectric constant of pore medium. Decrease in dielectric constant of pore medium results particles attraction and thus, more flocculated clay particles occur. On the other hand, increase in dielectric constant allows particles to be oriented.

Decrease in pH causes to flocculation of particles. This is because the amount of hydrogen ions increases due to pH decreasing; clay particles attract these cations to their surface. Then, particles tend to be flocculated.

Increase in anion adsorption also changes the behaviour of clay particles. Negative forces on the clay repel the anions in the pore medium. Repulsive forces control the flocculation in this situation and dispersion is more effective than attractive forces.

At last, temperature of pore medium also affects the clay structure: flocculation or dispersion. If temperature increases, flocculation occurs between clay particles. Factors affecting the clay structure are summarized in Table 2.1.

## 2.3 Homoionized Clays

Homoionized clays means, most of the exchangeable sites are occupied by one type of cation. In nature, it is impossible to find homoionized clays. In practice, homoionized clay is prepared by using the chloride solution of desired cations and then, removing the chloride by washing with distilled deionized water.

**Table 2.1 Factors affecting particle flocculation in soil-liquid system.**

| | | |
|---|---|---|
| Increase in | Electrolyte Concentration | Flocculation |
| | Ion Valence | Flocculation |
| | Temperature | flocculation |
| Decrease in | Dielectric Constant | flocculation |
| | Hydrated Ionic Size | flocculation |
| | PH | flocculation |
| | Anion Adsorption | flocculation |

### 2.3.1 Methods of Preparation

Replacing one cation with another is not an easy process. Some cations have higher replacement power than others. The list below is in approximate order of cation replacement ability. The specific order depends on the type of clay, and the concentration of the various ions in the water (Holtz & Kovacs, 1981).

$Li^+ < Na^+ < H^+ < K^+ < NH_4^+ << Mg^{++} < Ca^{++} << Al^{+++}$

Methodology for preparing homoionized samples is almost same for all researchers, yet it may show minor variations. For example, Sridharan et al. (1988), and Rao & Mathew (1997), used the same procedure during sample preparation. First of all, soil was washed by 1N ammonium acetate ($CH_3COONH_4$) solution. This is because, ammonium can replace easier with other cations present in the soil and all exchangeable sites occupied by this cation. After successive ammonium acetate treatments, soil was washed with 1N chloride solution of desired cations such as Na (sodium), K (potassium), $NH_4$ (ammonium), Li (lithium), Mg (magnesium), Ca (calcium), Al (aluminum) and Fe (iron) successively. In addition, the samples were

washed with distilled water until the filtrate gave no detectable chloride precipitates upon adding silver nitrate solutions.

### 2.4 Consistency Limits of Homoionized Clays

Clays are divided into two groups: swelling clays and non-swelling clays. Kaolinite is an example for non-swelling clays whereas montmorillonite is the example for swelling-clays. To determine the clays either swelling or non-swelling free-swell test is conducted on clay specimens. This test is a kind of sedimentation test in a polar and non-polar liquid. According to Sridharan (1991), if the value of sediment volume in a non-polar liquid (carbon tetrachloride, $CCl_4$) is higher than in a polar liquid (water), then it can be said that the clay is non-swelling clay (i.e. kaolinite). That shows, double layer theory is not applicable for kaolinitic soils. Lower dielectric constant of $CCl_4$ results particle flocculation, so higher sediment volume occurs. Double layer theory can be adapted to monmorillonitic soils. Sedimentation is higher in water than in $CCl_4$; this was attributed to the diffuse double layer, which is covering the particle.

#### 2.4.1 Kaolinitic Soils

Liquid limit of kaolinitic soils is investigated by many researchers (Sridharan et al.; (1988), Sridharan & Prakash; (1998), Anson & Hawkins; (1998), Mathew & Rao; (1997), Kaya & Fang; (2000)) . The liquid limit of a soil is defined as the water content above which the soil behaves as a viscous liquid (i.e. a soil-water mixture with little measurable shear strength) (Sridharan et al., 2000).

Sridharan et al. (1988), evaluated the index properties of kaolinitic soils. They found almost a linear relationship between liquid limit and shrinkage limit; and also between liquid limit and sediment volume. However, when their results are closely studied, the results reveal that the higher the liquid limit, the higher the shrinkage limit is more right instead of saying a linear relationship between them. According to the authors, for kaolinitic soils, interparticle forces have an important role in determining the liquid limit. Particle flocculation surrounds larger void spaces for

water entrapment and exhibit larger liquid limit values. Change in clay fabric governs the liquid limit of kaolinitic soils.

Rao & Mathew (1997) investigated the effect of cations on some engineering properties of a marine clay from India. It was mentioned that clay was made of swelling chlorite, kaolinite, and illite and associated mineral quartz and feldspar. They reached the same conclusion as Sridharan et al. (1988) did based on the studies on montmorillonite. Liquid limit of marine clay was decreased when an increase was seen in the valence. For the same valence, hydrated ionic size has an important role. Authors mentioned that diffuse double theory is effective on account of swelling chlorite.

Rao et al. (1990) investigated the effect of drying on the liquid limit of another marine clay. XRD (X Ray Diffraction) of soil showed that smectite and kaolinite minerals were predominant in clay, having calcium and magnesium are the major cations. Liquid limit and plastic limit of air-dried and oven dried samples were different. These cations allow particles to be strongly flocculated, resulting an aggregated structure. This aggregated structure causes significant development of capillarity stresses that permit intimate contact of particles and growth of strong van der Waals' and Coulombic bonds, which are not easily reversed. The resultant particle aggregation reduces the available surface for interaction with water (Rao et al.,1990).

Kaya & Fang (2000) also investigated particle arrangement in different dielectrical constant of pore medium for kaolinite, bentonite and a local soil of Bethlehem, PA. For lower dielectric constants, clays behave like non-cohesive sand or fine-grained silty soil. The index properties of tested soils were supported by $\zeta$ (zeta potential), pore medium size, CEC (cation exchange capacity) of soils. The data obtained for kaolinite is consistent with Sridharan's (1991) data which is lower dielectric constant of pore medium leads to higher liquid limit values.

### 2.4.2 Montmorillonitic Soils

The mechanism governing the engineering properties of montmorillonite is attributed to the diffuse double layer surrounding this type of clay mineral. Sridharan et al. (1991) investigated the effects of cations on diffuse double layer of montmorillonite. Change in cation type, in turn in the diffuse double layer thickness affects the consistency limit values, especially liquid limit. The higher the dielectric constant of pore medium, the higher the liquid limit of montmorillonitic soils. This is because higher dielectric constant allows montmorillonite to be more dispersed than that of lower one. Opposite behaviour can be seen between kaolinite and montmorillonite. This conclusion is also supported by Kaya & Fang (2000).

Maio (1996) studied the changes in the engineering properties of bentonite when it is exposed to salt. She treated the soil with $K^{+}$ and $Ca^{++}$. Obtained liquid limits were in line with other researchers.

Sridharan et al. (1987) investigated the fluoride effect on bentonite and an Indian local soil. Liquid limit value of untreated bentonite was 495%. After treatment of fluoride, the value had been decreased to 256%. The liquid limit of the local soil changed from 124% to 81%.

Sridharan et al. (1986) conducted experiments to evaluate the effects of cation valence on engineering behaviour of homoionized bentonite. The results indicated that liquid limits of lithium and aluminum treated bentonite were 675% and 108%, respectively. On the other hand, plastic limit values were 49.1% to 63.5%, respectively. From the results, aluminum decreases the liquid limit while it increases the plastic limit.

## 2.5 Compressibility Behaviour of Homoionized Clays

Compressibility behaviour of clays which treated with different chemicals shows interesting results. Valence has great importance on the compressibility of clayey soils as well as other engineering properties. The valence effect is more clear on montmorillonitic soils, thus most researchers conducted experiments on this soil.

### 2.5.1 Methods of Testing

Classical one-dimensional consolidation tests were conducted to find compressibility characteristics of clays. For consolidation, samples were prepared nearly at their liquid limit water contents for remoulding easily. To avoid entrapped air in the samples, they were placed under vacuum and agitated periodically. After deaeration, the moist specimens had been hand remoulded in the consolidation ring. Filter papers was put between sample and placed bottom and top porous stones. Ring had been fixed in the consolidation cell and cell was filled with distilled water. Loading was initiated from very low pressure to high ones (0.0625 $kg/cm^2$ to 4.0 $kg/cm^2$). Finally, samples had been waited one day to reach the equilibrium (Sridharan et al., 1986). In general, the ASTM Standards (American Society of Testing Materials) were followed by all researchers.

### 2.5.2 Effects of Valence on the Compressibility of Homoionized Clays

Different valence of homoionized specimens has different compressibility behaviour. Compressibility of soils with monovalent cations is higher than that of divalent and trivalent. The effect of valence is more pronounced on montmorillonitic soils than kaolinitic ones. As stated above, increase in valency leads particles to be more flocculated. For the same valency, hydrated ionic radius becomes important. Smaller dehydrated radius of an ion has greater tendency to attract water to be hydrated than ions having larger dehydrated radius. Thus, the smaller the dehydrated ionic radius, the larger the hydrated ionic radius. An ion of larger hydrated radius is held loosely by clay surface than is an ion of smaller hydrated radius, because smaller ones can approach clay surface more closely. Thus their coulombic attraction

by the surfaces is increased (Bohn et al., 1985). Table 2.2 presents the dehydrated and hydrated ionic radii of various cations.

**Table 2.2 Relation of crystallographic and hydrated ionic sizes**

| ION | CRYSTALLOGRAPHIC (DEHYDRATED) RADIUS (nm) | HYDRATED IONIC RADIUS (nm) |
|---|---|---|
| $Li^+$ | 0.068 | 0.73-1.03 |
| $Na^+$ | 0.097 | 0.56-0.79 |
| $K^+$ | 0.133 | 0.537 |
| $NH_4^+$ | 0.143 | 0.38-0.532 |
| $Mg^{+2}$ | 0.066 | 1.08 |
| $Ca^{+2}$ | 0.099 | 0.96 |
| $Ba^{+2}$ | 0.134 | 0.88 |
| $Al^{+3}$ | 0.051 | - |

Sridharan et al. (1986) determined compressibility behavior of some homoionized bentonites. As mentioned before, compressibility for monovalent specimens is more than that of divalent and trivalent. However, divalent and trivalent specimens consolidate much faster than monovalent samples. Also, these specimens are more permeable than monovalent ones. Divalent and trivalent cations change engineering behaviour of clay more than monovalent one due to higher flocculation. For the same valence cations, especially monovalent, hydrated ionic size controls the behaviour, which is in agreement with the Stern Layer Model. Smaller hydrated radius means, more cations present in the Stern Layer. On the other hand, $K^+$ and $NH_4^+$ treated homoionized samples have the lowest double layer thickness among other monovalent specimens. In addition to hydrated ionic size, fixation of unhydrated $K^+$ and $NH_4^+$ in the hexagonal hole of silica sheet leads the lowest compressibility in monovalent specimens. Mathew & Rao (1996), found similar trend for a local marine clay from India. They investigated consolidation behavior of homoionized soils with different chemicals. Trivalent samples had been compressed

more than divalent, and divalent samples had been consolidated more than monovalent samples. The conclusion is same as Sridharan's, (1986), which is explained above.

Grain size distribution and hydraulic conductivity behaviour of marine clay have also been investigated by Mathew & Rao, 1995. The results revealed that the higher the valence homoionized samples, the higher the permeability values. The grain-size distributions of these homoionized samples obtained using hydrometer test were also varied. As it is expected, the more flocculated particles (i.e. trivalent samples) have the lowest percent finer than monovalent samples. Dispersed particles tend to pass easier than flock particles. Percentage finer of $Na^{+}$ clay is higher than that of $Al^{+3}$ (Mathew & Rao, 1995).

Sridharan et al. (1987), investigated the fluoride effect on the compressibility of montmorillonitic soils. Fluoride causes particle flocculation. However, lower compressibility had been seen for fluoride treated samples because of flocculated particles and thus, lower equilibrium void ratio. Permeability of fluoride treated sample has higher permeability values than that of untreated.

Sridharan et al. (1991) also conducted some experiments with various pore fluid or replacing the pore fluid during load increment in consolidation test. The results of these tests were also very indicative for double layer effect on montmorillonitic soil specimens.

Azam et al. (2000) determined the changes occur in swelling potential of expansive soils when they were interacted with calcium sulfate phases, especially gypsum and anhydrite. The swelling potential of clay-calcium sulfate decreases as the amount of calcium sulfate increases. This was explained in terms of cementation of clay particles by calcium sulfate. In addition to conventional odometer ring, they had also used large-scale circular mold and large-scale square mold for better simulation of in-situ conditions. The results showed that the use of large-size

specimens better simulates the in-situ conditions since such simulation allows taking into account the effect of fissures and joints in natural soils.

Abdullah et al. (1997) investigated the effects of the clay-water electrolyte system and the temperature on primary and secondary compressibility of soils. $Na^{+}$, $Ca^{+2}$ and $K^{+}$ cations were used in the experiments to make the soils homoionized. The potassium dominated clay caused fundamental changes in the properties with comparison to the untreated soil; such as decrease in PI (Plasticity Index) from 66% to 13%, free swell from 10.5% to 1.7% and increase in coefficient of permeability about 10-fold.

Maio (1996), investigated the compressibility and strength behavior of bentonite. Bentonite was exposed to NaCl, KCl, $CaCl_2$ solutions and direct shear tests and oedometer tests had been applied. The experimental results were consistent with the double layer theory. Compaction of double layer had led to decrease in consolidation and increase in residual shear strength.

Sridharan & Prakash (1999) investigated the valence effect on sediment volumes of montmorillonitic and kaolinitic soils. Size effect is more pronounced for monovalent than divalent montmorillonitic samples. Valence effect was not effective (negligible) for these soils. For kaolinitic soils, flocculation governs the sediment volume thickness. The samples with low valence cations have more sediment volume than those of high valence cations. They also noted that hydrated ionic radius was more pronounced for monovalent kaolinitic samples.

Mathew& Rao (1997) observed the diffusion of lime into the marine clay, which was placed in a test tank. Some lime columns placed on the marine clay with equal distance from each other. Observation and measurements were taken at determined points and layers (upper most, middle and lower most). Then, the changes in lime content, pH, and cation exchange capacity (CEC) with time were investigated. Lime content was increased with the time and the same results were obtained with pH vs. time and CEC vs. time. The differences between the layers were negligible.

Effect of interaction between clay particles and $Fe^{3+}$ ions on colloidal properties of kaolinite suspensions was investigated by Ma & Pierre (1997). Sedimentation test was conducted on kaolinite in the $FeCl_3$ solution to observe the differences in sediment thickness by using unaged and aged $FeCl_3$ solutions. The tests were conducted with various Fe concentrations and pH. Three sedimentation behaviours were observed: accumulation; flocculation and mixed flocculation-accumulation. The data of zeta potential was also used to predict the type of sedimentation behavior. Then, results were supported by the SEM (Scanning Electron Microscopy) data.

The similar study was conducted on kaolinite and montmorillonite with $AlCl_3$ solution. The results were in agreement with the previous ones, which supported by SEM data (Pierre & Ma, 1999).

Effects of organic cation such as BTEA (benzyltriethylammonium chloride), TMA (tetramethylammonium bromide), decyltrimethylammonium bromide (DTMA), and hexadecyltrimethylammonium bromide (HDTMA), with a different chain length, on the behavior of organobentonites was investigated by Soule & Burns (2001). Specific gravity, liquid limit, plastic limit, compressibility and shear strength (angle of internal friction) of modified and unmodified bentonites were compared. There are considerable changes between treated and untreated bentonites. Specific gravity of organobentonites decreased with the chain length. Liquid limit of unmodified bentonite reduced from 458% to 52-65% in organobentonites. The exchange of the organic cations on the bentonite significantly reduced the compressibility of the clays. However, the direct shear friction angle value of four organobentonites was found much higher than unmodified bentonite.

# CHAPTER THREE
# EXPERIMENTAL PROGRAM

## 3.1 Overview

The effects of cations on physicochemical properties of mixed minerals were investigated. Since most of the previous studies were conducted either on kaolinitic soils or montmorillonitic soils, herein, engineering behaviour of mixed-mineral (i.e. montmorillonite, kaolin and illite are found in the mineralogical composition) of clayey soil was investigated. In this regard, consistency limits, sedimentation tests, and consolidation tests were conducted on the homoionic samples. For consistency limits, not only water was used as pore liquid, but also some organic liquids having lower dielectric constant than water, such as methanol, ethanol and n-hexane, were used.

The samples were washed with 1N ammonium acetate ($CH_3COONH_4$) solution to move out cations found in the exchangeable sites. This kind of sample was considered as pure clay. After obtaining pure clay, other samples were prepared after washing 1N chloride solution of $Na^+$, $Ca^{+2}$ and $Al^{+3}$. Then, washed with distilled deionized (DDI) water in order to remove the chloride in each soil, one type of cation was accepted to be placed in the exchangeable sites named as Na-clay, Ca-clay, Al-clay. These cations were chosen in order to determine the valence effects on mixed mineral clay.

### 3.2 Materials used, their properties and uses

#### 3.2.1 Soil

The soil was obtained from Kale Seramik, Canakkale. The chemical composition of the soil was determined by "Whole Rock ICP Analysis" and is presented in Table 3.1.

**Table 3.1 Chemical composition of the soil (Acme Analytical Laboratories Ltd, Canada)**

| Sample | $SiO_2$ % | $Al_2O_3$ % | $Fe_2O_3$ % | MgO % | CaO % | $Na_2O$ % | $K_2O$ % |
|---|---|---|---|---|---|---|---|
| Illite | 58.77 | 23.50 | 2.57 | 0.90 | 0.08 | 0.13 | 1.88 |
| Re Illite | 59.18 | 23.56 | 2.58 | 0.90 | 0.07 | 0.10 | 1.65 |

X-Ray Diffraction patterns of homoionized samples were determined at Mining Department of College of Engineering, Dokuz Eylul University. Based on X-Ray diffraction results, the soils consist of 40-55% montmorillonite, 20-30% illite, 10-15% kaolinite, and 2-3% quartz.

The cation exchange capacity of soils were determined using Na-method at the Soil Laboratory of College of Agriculture, Ege University. Table 3.2 shows the CEC values of homoionized samples.

**Table 3.2 CEC values of homoionized samples**

| | Na-clay | Ca-clay | Al-clay |
|---|---|---|---|
| CEC (meq/100g) | 13.04 | 13.04 | 11.96 |

### 3.2.2 Chemicals used

As it is mentioned above, soil was washed with ammonium acetate ($CH_3COONH_4$) solution. Then, NaCl was used for preparing the Na-clay; $CaCl_2.2H_2O$ used for Ca-clay; $AlCl_3$ used for Al-clay. As pore fluid, water, methanol, ethanol and n-hexane were used.

## 3.3 Washing Procedure

Soil was washed with DDI water during sieving from No.200. The passed soil was collected into the metal dish and dried in an oven at 105°C for 24 hours. After collecting 500 g of dry soil in a basin, 1N ammonium acetate ($CH_3COONH_4$) solution was used for washing. In another words, 500 g dry soil was washed with 1N ammonium acetate solution every time. Mixture was stirred with a wooden stick about ten minutes and the soil particles allowed to settle; then, the supernatant was discharged. Before discharging, electrical conductivity of the supernatant was measured. The process was repeated until the electrical conductivity became constant. Washed soil was dried in an oven at about 80°C. The dried soil was named pure-clay. However, 2 kg dried pure-clay was put in the basin and washed with 1N chloride solution of $Na^+$, $Ca^{+2}$, and $Al^{+3}$ separately. Mixture was stirred about ten minutes and electrical conductivity measurements were taken after settling the particles. After successive treatments of those solutions, soils were washed, with distilled deionized water until filtrate gave no detectable chloride. Chloride was detected by adding silver nitrate solution to the supernatant. Electrical conductivity of supernatant solution was decreased to very low values during washing with distilled deionized water.

After obtaining Na-clay, Ca-clay, and Al-clay, soils were put into the oven to be dried at 80°C. The dried soils were taken off from the oven, pulverized in a mortar and then sieved from No. 40 mesh.

### 3.4 Conducted Tests on Homoionized Soils

ASTM Standards were conducted to all homoionized samples. Atterberg Limits of soils and compressibility behavior were determined individually. In addition to these, sediment volumes of homoionized specimens were investigated.

#### 3.4.1 Index Properties of Homoionized Soils

The specific gravities of the homoionized clay specimens were determined using a pycnometer as specified by the American Society for Testing and Materials (ASTM, D 854-92).

Fall cone (or cone penetrometer) was conducted to all clay specimens. This test depends on some conditions: The values of liquid limit obtained by this method are influenced by surface roughness of the cone, the cone angle and the problem of liquefaction (Sridharan & Prakash, 1998). The point of the cone can become blunted from excess use (Bowles, 1992).

Plastic limits and shrinkage limits were determined according to the ASTM Test Method, D 4318-98 and D 427-93, respectively.

The liquid limits were determined to obtain a minimum of four points between 15 and 25-cone penetration for plotting the flow curve (Sridharan, 2000). In this study, minimum three points were obtained between 15 and 25 mm penetration depth. Tests were conducted by using distilled deionized (DDI) water and some organic liquids such as n-hexane, ethanol, and methanol as pore fluid.

#### 3.4.2 One Dimensional Consolidation Tests

The homoionized clay specimens' consolidation behaviours were determined according to the ASTM, D 2435. The clays were tested in the EL25-0402

Consolidation Apparatus. It is a standard fixed ring consolidometers. Rings are 7.5 cm in diameter and 2.0 cm in height. To minimize the friction between the ring and the specimen, grease was used for lubricating the inside of the ring.

Specimens of Na-clay, Ca-clay, and Al-clay were prepared in an easily remoldable state. In another words, clays were prepared at near their liquid limits. First, specimens were mixed at higher water content such as 300-400%. Then, plexiglas cell was taken and porous stone and a filter paper were placed under the cell. It is connected to the permeability apparatus to allow water easily driven out and deaeration easily under vacuum. After preparing the specimen, it was placed into the plexiglass cell and allowed to settle down under gravity. After the settlement of the specimen, clear liquid above sediment was discharged and another filter paper and porous stone placed over the specimen. To obtain samples near the liquid limit, height of the specimen at its liquid limit was calculated and marked on the plexiglass cell; then, loading was adapted to the specimen in the plexiglass cell in order to reach the liquid limit value of specimens. When reaching the liquid limit, the specimens in the plexiglass cell carefully taken off and placed into the consolidation ring without any air entrapment and consolidation test was initiated. Loading was started at a low pressure of 0.125 $kg/cm^2$ and finished at a maximum of 8.0 $kg/cm^2$.

### 3.4.3 Determining Sediment Volume of Homoionized Clay Specimens

10 g samples of Na-clay, Ca-clay, and Al-clay were taken and placed into the 100 ml graduated cylinder. 100 ml DDI water was added to the graduated cylinder and each cylinder was covered with a piece of parafilm in order to prevent evaporation. The mixtures were shaken with hand about 10 minutes letting it to settle; then, shake for another ten minutes. This process repeated a few times to prevent any flocculation may take place. Test was begun at the same time for three homoionized clay specimens and the sedimentation behaviour was recorded.

At the second part of this test, sedimentation behavior was observed in organic liquids individually. Then, sediment volumes were calculated for all and compared with each other.

# CHAPTER FOUR
# RESULTS AND DISCUSSIONS

## 4.1 Characterization of Soil

### 4.1.1 Consistency Limits

The consistency limits of the soil, as it is received, are as follows: Liquid limit 74%, and plastic limit 36%. When these values are plotted on the Casagrande Plasticity Chart, it is seen that the soil fell close to the A-line and can be named as an illitic soil. Figure 4.1 indicates the location of the tested soil on Casagrande Chart.

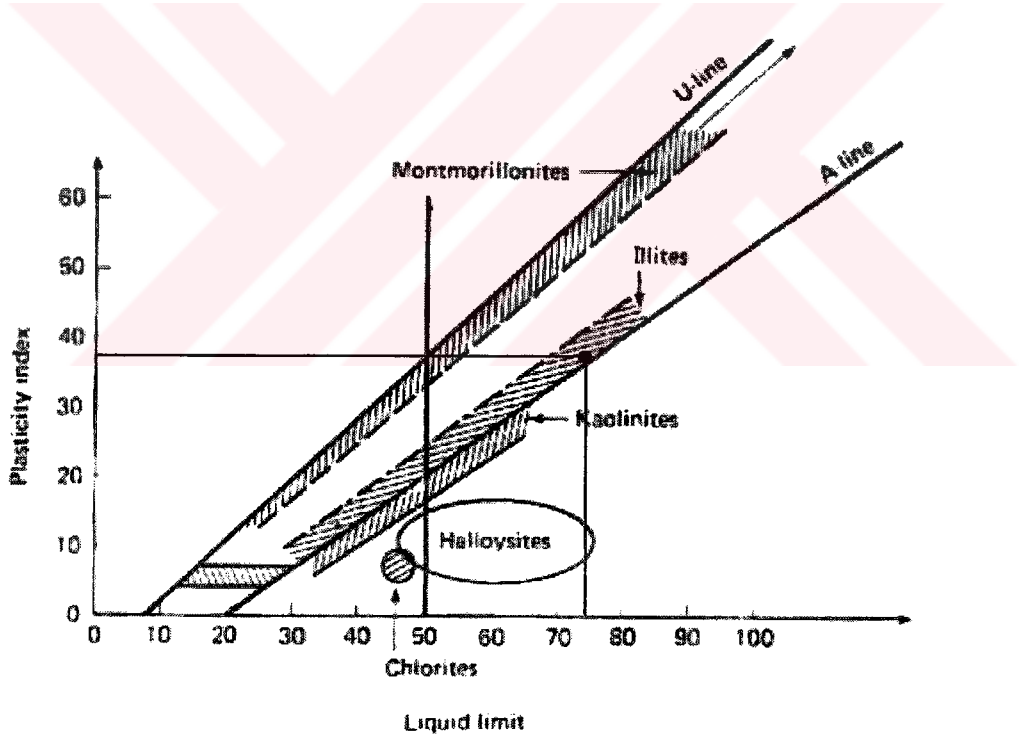


**Figure 4.1 Location of tested sample on Casagrande's Plasticy chart**

Considering that the soil consists of 40-55% montmorillonite, 20-30% illite, 10-15% kaolin, and 2-3% quartz, it plots as an illitic soil on Casagrande Chart. This is because mixed minerals can present the behavior of any mineral (Mitchell, 1992).

### 4.1.2 Consistency Limits in Polar Liquid

DDI water was used as a pore fluid in the first part of the tests. Table 4.1 presents the specific gravity, liquid limit, plastic limit and the shrinkage limit values of the homoionized clays and Figure 4.2 shows the conducted fall cone test results for each homoionized specimen. The liquid limit values of homoionized clay specimens are an average of two trials and the variation between two trials was about 1% for pure-clay, 1.5% for Na-clay and Ca-clay and %2.5 for Al-clay. The specific gravity values are an average of two tests and individual determinations differed from the mean by less than 1%.

There is not a consistent pattern between specific gravity of homoionized clays and cation valence. However, liquid, plastic, and shrinkage limits of the homoionized clays increase with increasing in cation valence.

**Table 4.1 Effect of valence of the adsorbed cations on the index properties of clay**

| Clay type | Specific Gravity | Liquid limit: % | Plastic Limit: % | Shrinkage Limit: % |
|---|---|---|---|---|
| Sodium | 2.65 | 61.6 | 30.1 | 20.7 |
| Calcium | 2.65 | 64.2 | 31.3 | 21.9 |
| Aluminum | 2.67 | 69.5 | 32.7 | 24.1 |

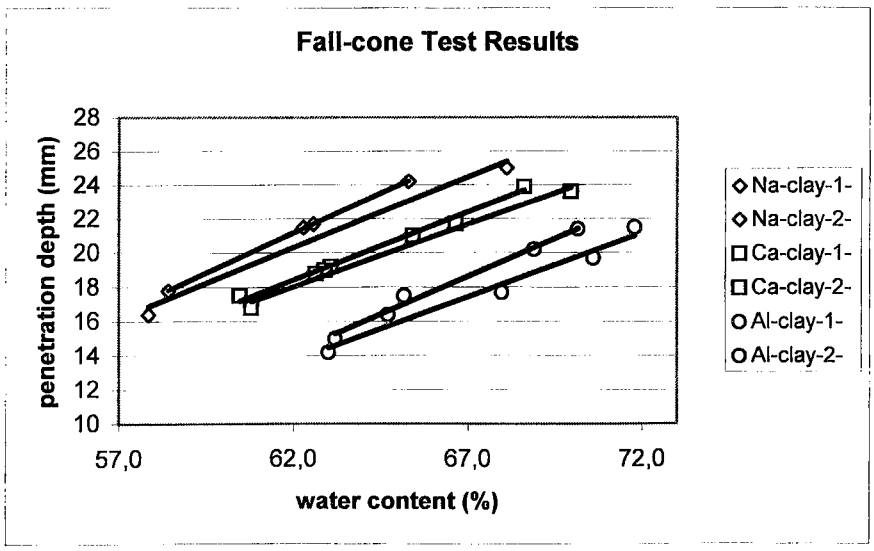


**Figure 4.2 Fall-cone test results for each homoionized specimens**

There are linear relationships between LL (Liquid Limit) and PL (Plastic Limit), LL and SL (Shrinkage Limit), and PL and SL of the Na-clay, Ca-clay and Al-clay. These relationships are shown in Figure 4.3.

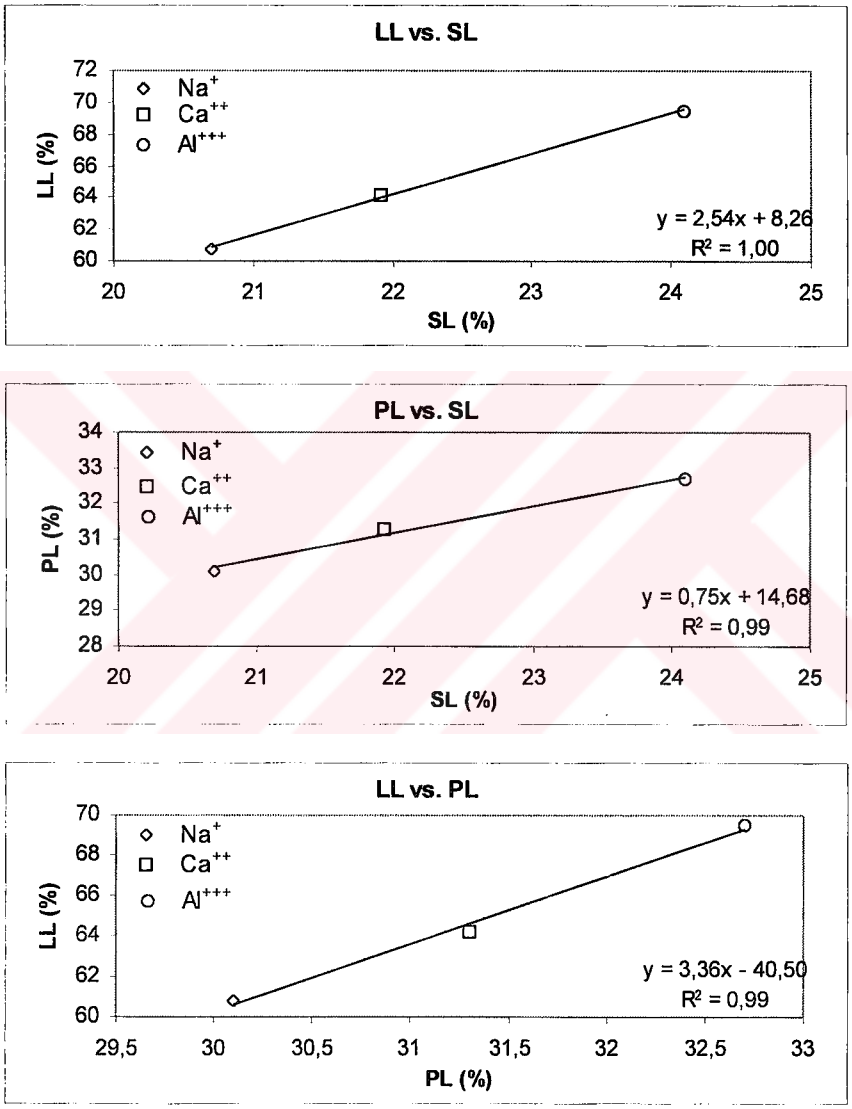


**Figure 4.3 Consistency test relationships between homoionized clays**

For kaolinitic soils, particle arrangement governs the engineering behaviour of clay (i.e. the fabric). Void spaces will be entrapped within the flocculated particles and those spaces lead higher liquid limit values. However, flocculated particles have higher shrinkage limit value than dispersed particles.

The support to explain the presented results comes from the literature; for example, Yong & Warkentin (1966) suggested that when kaolinite is saturated with divalent and trivalent cations, electrostatic attraction is developed between positive and negative faces, leading to an open-structured, flocculated particle arrangement. This results in a higher liquid limit, as water becomes entrapped within the void spaces of the flocculated structure (Anson & Hawkins, 1998).

The liquid limit behaviour of kaolinitic soil is opposite of montmorillonitic soils, because diffuse double layer governs the engineering properties of montmorillonitic soils. Increase in valence results more compression of diffuse double layer and that leads lower liquid limit values. On the other hand, particle arrangement governs the engineering behavior of kaolinitic soils. The clay taken from Canakkale was mixed-mineral clay (i.e. montmorillonite, illite, and kaolin are found in the structure) and almost 50% of clay is montmorillonite and rest is illite and kaolin. Herein, it can be said that kaolin minerals may govern the consistency behaviour of clay while treating with DDI water. This is because, increase in valence results more flocculated particles and hence greater amount of water entrapment within the large void spaces between the particles; thus, increasing the liquid limit and plastic limit. In addition to this, shrinkage limit test results support this conclusion: more flocculated particles have higher shrinkage limit values than dispersed particles.

The results are in aggrement with the other researchers who conducted the tests on kaolinitic soils. Table 4.2 presents the reported liquid limit of kaolinitic soils.

**Table 4.2 The liquid limit results in the literature conducted with kaolinitic soils (Sridharan, 1988)**

| Cations saturated kaolinite | White (1949) | Lambe & Whitman (1969) | Havlicek & Kazda (1961) |
|---|---|---|---|
| | LL (%) | LL (%) | LL (%) |
| Sodium ($Na^{+}$) | 52 | 53 | 56 |
| Calcium ($Ca^{+2}$) | 73 | - | 70 |
| Iron ($Fe^{+3}$) | - | 59 | 80 |

In addition to these, Sridharan (1988) conducted consistency limit tests with many of the Indian local soils, consisted of several mineral types. In Table 4.3 kao., mus., mont., qua., feld., hem., indicate kaolin, muscovite, montmorillonite, quartz, feldspar, hematite respectively. The liquid, plastic and shrinkage limit data are also in accordance with this study and given in Table 4.4.

**Table 4.3 Mineralogical composition and CEC values of local soils (Sridharan et al., 1988)**

| Soil Specimen | Exchangeable cation content (meq/100 g) | | | | | X-ray diffraction minerology |
|---|---|---|---|---|---|---|
| | Ca | Mg | Na | k | Total CEC | |
| 1 | - | - | 1.8 | - | 1.8 | Kao., mus., qua. |
| 2 | 2.31 | 0.7 | 1.7 | 0.2 | 4.9 | Kao., qua. |
| 3 | 9.00 | 5.5 | 1.0 | - | 15.5 | Kao., mont., mus., qua. |
| 4 | 9.30 | 1.8 | 0.7 | 0.4 | 12.2 | Kao., mont., mus., qua. |
| 5* | - | - | 1.2 | - | 33.5 | Kao., feld., hem., mont., mus. |
| 6 | 10.80 | 4.0 | 2.6 | 1.0 | 18.4 | Kao., mont., mus., qua |
| 7 | 13.90 | 2.7 | 1.0 | 0.6 | 18.2 | As for soil 4 |
| 8 | 12.90 | 2.0 | 1.3 | 0.6 | 16.8 | As for Soil 3 |
| 9 | 15.80 | 3.1 | 1.6 | 1.5 | 22.0 | As for Soil 3 |

* Includes 12.0 meq/100 g of exchangeable $Al^{+3}$ and 20.3 meq/100 g of exchangeable $H^{+}$ ions

**Table 4.4 Index properties of kaolinitic soils (Sridharan et al., 1988)**

| Soil Specimen | Particle size distribution | | | Liquid limit: % | Plastic limit: % | Shrinkage limit: % | Sediment volume in water: $cm^3/g$ |
|---|---|---|---|---|---|---|---|
| | Sand: % | Silt: % | Clay: % | | | | |
| 1 | 36 | 39 | 25 | 25 | 13.8 | 10.8 | 1.00 |
| 2 | 34 | 39 | 27 | 38 | 15.3 | 11.5 | 1.25 |
| 3 | 59 | 16 | 25 | 47 | 21.5 | 16.4 | 1.30 |
| 4 | 40 | 36 | 24 | 47 | 25.4 | 16.8 | 1.40 |
| 5 | 13 | 66 | 21 | 73 | 40.4 | 18.5 | 1.75 |
| 6 | 12 | 58 | 30 | 74 | 25.0 | 15.7 | 1.85 |
| 7 | 11 | 53 | 36 | 75 | 33.8 | 20.1 | 1.85 |
| 8 | 22 | 32 | 46 | 75 | 36.3 | 19.8 | 1.90 |
| 9 | 10 | 39 | 51 | 100 | 35.8 | 27.3 | 2.40 |

FromTable 4.3 and 4.4, it can be easily seen that liquid, plastic and shrinkage limits of soils increase with increasing in the cation valence or cation amount in the exchangeable sites.

However, Anson & Hawkins (1998) investigated the Atterberg limits of kaolinite and montmorillonite while treating with the solutions of calcium at the various concentrations, which are presented in Table 4.5.

**Table 4.5 Atterberg limit results for kaolinite and montmorillonite treated with solution of calcium at various concentrations (Anson & Hawkins, 1998)**

| $Ca^{+2}$: mg/l | Kaolinite | | Montmorillonite | |
|---|---|---|---|---|
| | LL (%) | PL (%) | LL (%) | PL (%) |
| 0 | 57 | 31 | 740 | 44 |
| 80 | 65 | 30 | 330 | 53 |
| 160 | 61 | 29 | 280 | 54 |
| 240 | 62 | 26 | 270 | 50 |
| 320 | 61 | 27 | 225 | 50 |
| 400 | 58 | 30 | 245 | 55 |

From Table 4.5, liquid limit of kaolinite, at all of the concentration level, greater than that of untreated samples, however there is slight changes in the plastic limit of kaolinite between the concentration levels. As can be seen from this table, the highest plastic limit value belongs to the untreated sample. The liquid limit results are consistent with the study conducted with mixed mineral clay; however, plastic limit results increasing with increas in the cation valence for the mixed mineral clay. On the other hand, the liquid limit of montmorillonite decreases with calcium concentrations; however, plastic limit increases with the concentration. In addition to these, Sridharan et al. (1986) also presented similar results. They showed that the liquid limit of bentonite decreased with increasing in the valence; however, the plastic limit of that soil increased while treating with higher cation valence. Table 4.6 shows the results of bentonite and a marine clay when exposured to different valence cations.

**Table 4.6 Valence effect on index properties of montmorillonite**

| Bentonite type | Sridharan et al. (1986) | | Mathew & Rao (1997) | |
|---|---|---|---|---|
| | LL: (%) | PL: (%) | LL: (%) | PL: (%) |
| Lithium | 675 | 49.1 | - | - |
| Sodium | 495 | 49.2 | 65 | 16 |
| Ammonium | 223 | 55.8 | 57 | 21 |
| Potassium | 233 | 57.8 | 59 | 22 |
| Magnesium | 129 | 49.9 | 49 | 23 |
| Calcium | 125 | 40.6 | 48 | 23 |
| Barium | 108 | 45.8 | - | - |
| Aluminum | 108 | 60.5 | 45 | 24 |
| Iron | 120 | 63.5 | - | - |

As can be seen from Table 4.6, liquid and plastic limit of bentonite is influenced from the cation valence. The decrement in the liquid limit and the increment in the plastic limit of bentonite are very pronounced with increasing in the cation valence. Mathew & Rao (1997) obtained the similar results; however, increase in valence lead lower liquid limit value, but higher plastic limit value. On the other hand, the

mineralogical composition was consisted of swelling chlorite, kaolinite, and illite and associated minerals quartz and feldspar. If it is compared with the findings of mixed mineral clay, there is an opposite behaviour can be seen between the index properties of homoionized clays. In fact, the mineralogical analysis almost similar to both soils. However, there is not sufficient information about the percentage of minerals presented in the structure of marine clay. Swelling chlorite may be dominant in the structure and it governs the soil as a montmorillonitic soil.

Computations of ionic distributions adjacent to charged surfaces show that the thickness of the double layer is sensitive to variations in surface charge density $\sigma$ or surface potential $\psi_0$, electrolyte concentration $n_0$, cation valence $v$, dielectric constant of the medium $D$, and temperature $T$. The thickness of the double layer is given by this formula:

$$\frac{1}{K} = \left( \frac{DkT}{8\pi n_0 e^2 v^2} \right)^{1/2} \qquad (4.1)$$

As can be seen from this formula, the thickness of the double layer is inversely proportional to the valence and the square root of the concentration, and directly proportional to the square root of dielectric constant and temperature (Mitchell, 1993). Washing the clays with different valence cations allow particles to be flocculated. That is, increase in cation valence results, decreasing the double layer thickness and, thus, particles tend to approach each other and results particle flocculation.

### 4.1.3 Consistency Limits in Non-Polar Liquids

In order to see the effect of dielectric constant of pore medium on the consistency limit of homoionized clay; various organic liquids such as n-hexane, ethanol and methanol were conducted as pore fluids during the experiments. Table 4.7 shows the dielectric constant values of those liquids and liquid limit and plastic limit values of homoionized samples. The liquid limit values of homoionized clay specimens using

organic liquid, as a pore fluid were determined at once, because of insufficient sample to try for a second trial. However, some of the liquid limit values were repeated to compare with the previous data. It is seen that there was no considerable change between two trials.

**Table 4.7 Consistency limit results at different pore medium (weight basis)**

| Pore Fluid | Dielectric Constant | Na-clay | | | Ca-clay | | | Al-clay | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | LL (%) | PL (%) | PI (%) | LL (%) | PL (%) | PI (%) | LL (%) | PL (%) | PI (%) |
| n-hexane | 1.89 | 38.4 | - | NP | 40.8 | - | NP | 43.6 | - | NP |
| Ethanol | 24.30 | 49.7 | 35.9 | 13.8 | 57.6 | 36.5 | 21.1 | 52.5 | 38.4 | 14.1 |
| Methanol | 32.63 | 46.8 | 31.1 | 15.7 | 52.4 | 36.1 | 16.3 | 50.5 | 36.8 | 13.7 |
| DDI Water | 80.40 | 60.8 | 30.1 | 30.7 | 64.2 | 31.0 | 33.2 | 69.5 | 32.7 | 36.8 |

* PI: Plasticity index (PI = LL – PL)

In Table 4.7, liquid limit and plastic limit values of homoionized samples were obtained by the weight basis. In fact, densities of those liquids are different and hence, should be used volume basis in order to obtain real liquid limit values. Table 4.8 presents, only, the weight basis and the volume basis liquid limit values of homoionized specimens. Figure 4.4 and Figure 4.5 show the weight basis and the volume basis liquid limit values of homoionized samples vs. dielectric constant of the pore medium, respectively.

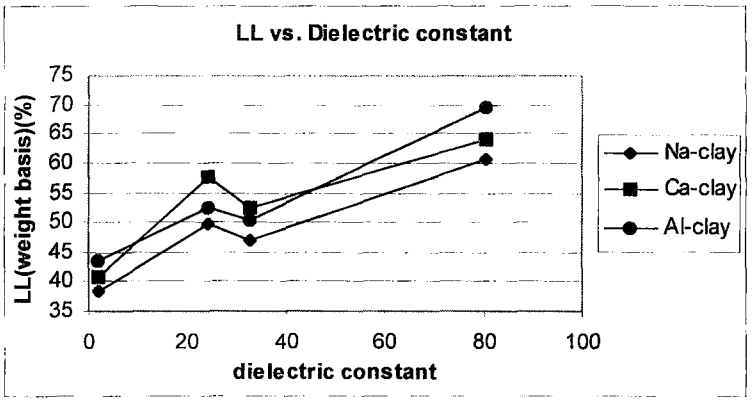


**Figure 4.4 Weight basis liquid limit values of homoionized samples vs. dielectric constant of pore medium.**

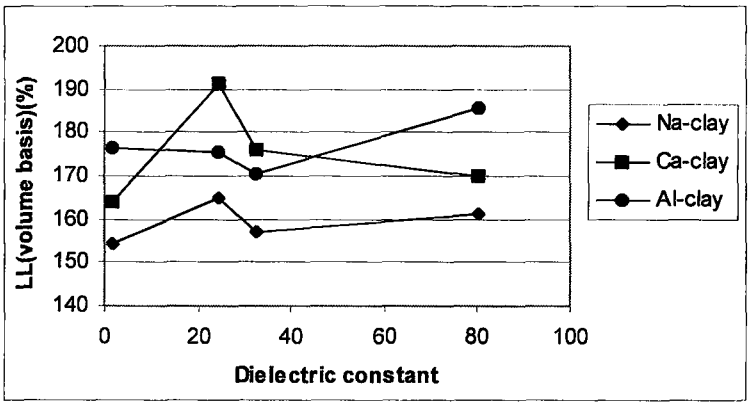


**Figure 4.5 Volume basis liquid limit values of homoionized samples vs. dielectric constant of pore medium.**

**Table 4.8 Weight basis and volume basis liquid limit results at different pore medium**

| Pore Fluid | D.C.* | Density ($g/cm^3$) | Na-clay | | Ca-clay | | Al-clay | |
|---|---|---|---|---|---|---|---|---|
| | | | Wt. basis LL (%) | Volume basis LL (%) | Wt. basis LL (%) | Volume basis LL (%) | Wt. basis LL (%) | Volume basis LL (%) |
| n-hexane | 1.89 | 0.659 | 38.4 | 154.4 | 40.8 | 164.1 | 43.6 | 176.6 |
| Ethanol | 24.30 | 0.798 | 49.7 | 165.0 | 57.6 | 192.3 | 52.5 | 175.7 |
| Methanol | 32.63 | 0.790 | 46.8 | 157 | 52.4 | 175.8 | 50.5 | 170.7 |
| DDI Water | 80.40 | 0.999 | 60.8 | 161.1 | 64.2 | 170.1 | 69.5 | 185.6 |

* Dielectric Constant

The liquid limit values of homoionized clays in distilled water have been given in Table 4.7 and Table 4.8. Weight basis and volume basis liquid limit values of Al-clay in DDI water are higher than those of Ca-clay and Na-clay. However, Ca-clay stands between Na-clay and Al-clay and it is discussed above.

On the other hand, the order of liquid limit with cations changes with different pore fluid. Na-clay keeps itself the lowest value at all steps during testing by pore

fluids. But, Ca-clay moves above Al-clay in the methanol and ethanol in both figures (i.e. Fig. 4.4 & Fig 4.5). The position of homoionized clays in n-hexane is similar to that of DDI water. In Figure 4.4, the weight basis liquid limit of all three homoionized clays decreased with methanol, then increased with ethanol and again decreased with n-hexane. In Figure 4.5, the volume basis liquid limit of Na-clay decreased with methanol. The similar behaviour is also seen in Al-clay, but the drop is very pronounced when comparing with Na-clay. However, volume basis liquid limit of Ca-clay increased with decreasing in the dielectric constant of the pore medium (i.e. methanol). Then, all three homoionized samples increased with ethanol and at n-hexane, rapid drop can be seen for Ca-clay and Na-clay; however, a slight increase was noted for Al-clay.

The pH measurements were conducted to all homoionized samples after determining the sediment volumes. The measured pHs of homoionized samples is given in Table 4.9. On account of harmful characteristics of n-hexane to the plastic, pH probe did not dip into this solution, thus no reading was taken.

**Table 4.9 pHs of homoionized samples in different pore medium**

| Clay Type | pH | | | |
|---|---|---|---|---|
| | n-hexane | Ethanol | Methanol | DDI water |
| Na-clay | - | 4.86 | 5.44 | 5.88 |
| Ca-clay | - | 4.54 | 5.64 | 4.54 |
| Al-clay | - | 2.86 | 1.9 | 3.75 |

As can be seen from Table 4.9, the lowest pH values belong to Al treated clay while conducting with either organic or inorganic liquids. This is because, during washing the purified clay with 1N aluminum chloride ($AlCl_3$), the reaction of $AlCl_3$ and DDI forms HCl (hydrochloric acid) resulting a decrease in the pH of the medium. The reaction can be summarized as following:

The reaction was: $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$

The pH of Al-clay in DDI water is higher than those in methanol and ethanol. The reduction in pH is more pronounced in methanol for Al-clay. On the other hand, an increase in the pH can be seen in methanol for Ca-clay. The acid (HCl) may attack the clay mineral edges and dissolve the aluminum ions (Anson & Hawkins, 1998). Some of the aluminum sites in the octahedral structure may be deformed because of decreasing pH and that may explain the reduction in volume basis liquid limit of Al-clay in the methanol comparing with the Ca-clay. Increase in pH for Ca-clay during methanol treatment may also affect the liquid limit behaviour. As a result, volume basis liquid limit of Ca-clay may be greater than that of Al-clay.

Treating the soil with ethanol, volume basis liquid limit of all samples tend to increase. There is still considerable difference between the pH values of Al-clay and Ca-clay and that may not permit Al-clay to be higher liquid limit than that of Ca-clay.

The behaviour in n-hexane is similar to that of in DDI water. However, it should be noted that during conducting the tests with n-hexane, rapid evaporation was observed. Hence, it was very temperature dependent. Higher volume basis liquid limit values were expected in n-hexane for all homoionized samples comparing with those in ethanol. This kind of increase was noted only for Al-clay in n-hexane. The expected behaviour is shown with the dashed lines between n-hexane and ethanol for all three homoionized specimens in Figure 4.6.

Kaya & Fang (2000) investigated the index properties of kaolinitic, montmorillonitic, and a local soil in Bethlehem, PA in various pore fluids. The liquid limit of kaolinite increased with decreasing in the dielectric constant of pore fluid. That result is consistent with the data obtained by Sridharan et al. (1991). However, liquid limit of montmorillonite decreased with decreasing in the dielectric constant of the pore medium. That result is also in agreement with the results of Sridharan et al. (1991). On the other hand, the local soil used by Kaya & Fang (2000) showed the similar trend with the mixed mineral clay used in this study. However, the values obtained from homoionized clays are in agreement with the results of previous

researchers (Kaya & Fang (2000), Sridharan et al. (1991)). Figure 4.7 shows the comparison of the data obtained in this study with the ones published in the literature.

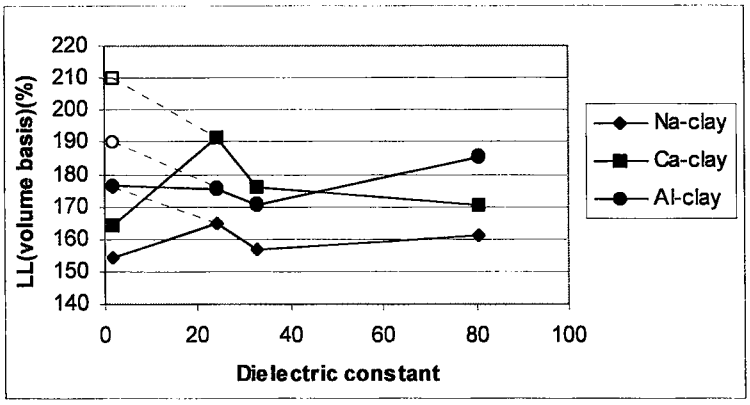


**Figure 4.6 Expected volume basis liquid limit vs. dielectric constant**

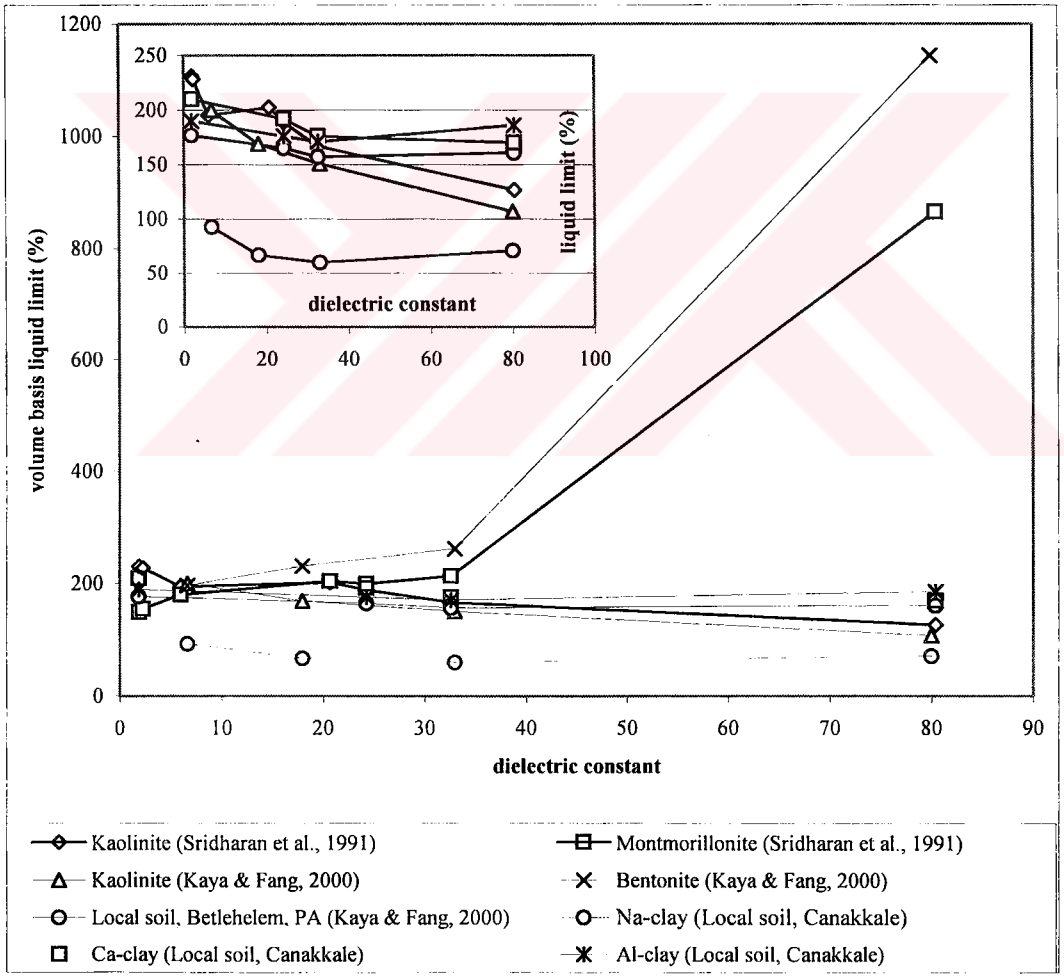


**Figure 4.7 Comparison of several volume basis liquid limit of soils**

Plasticity index of homoionized samples are a little different from each other. During the plastic limit test, treating with n-hexane, samples gave no plasticity. That means homoionized samples act like non-plastic when the dielectric constant of pore medium is low enough such as n-hexane, which is in agreement with the findings of Kaya & Fang, (2000).

Treating the homoionized clays with organic fluids also decreases the double layer thickness (Equation 4.1). This is because, if the dielectric constant decreases, double layer also decreases, and results particle flocculation. As it was mentioned before, water has the highest and n-hexane has the lowest dielectric constants.

As a result, kaolin minerals govern the index properties of homoionized clays in DDI water, however montmorillonite minerals may cause a reduction in the volume basis liquid limit of homoionized clays while treating with methanol. Then, kaolin minerals may be effective on the volume basis liquid limit of homoionized clays in order to increase the values while treating with either ethanol or n-hexane.

### 4.2 Sedimentation Test Results

The sediment volumes of homoionized specimens were determined in different pore fluid. Sediment thickness and sediment volume of those clays are shown in Table 4.10. Figure 4.8 also represents the sediment thickness of homoionized samples in different pore medium. Figure 4.9 shows the sediment volumes of those clays vs. dielectric constant of the pore medium.

**Table 4.10 Sediment thickness and sediment volumes of homoionized samples**

| Clay Type | n-hexane | | Ethanol | | Methanol | | DDI water | |
|---|---|---|---|---|---|---|---|---|
| | Sediment Height (cm) | Sediment Volume ($cm^3/g$) | Sediment Height (cm) | Sediment Volume ($cm^3/g$) | Sediment Height (cm) | Sediment Volume ($cm^3/g$) | Sediment Height (cm) | Sediment Volume ($cm^3/g$) |
| Na | 3.63 | 2.16 | 3.14 | 1.86 | 2.97 | 1.76 | In progr. | In progr. |
| Ca | 3.96 | 2.35 | 3.55 | 2.11 | 3.30 | 1.96 | 4.21 | 2.50 |
| Al | 4.37 | 2.60 | 3.83 | 2.27 | 3.60 | 2.14 | 4.04 | 2.40 |

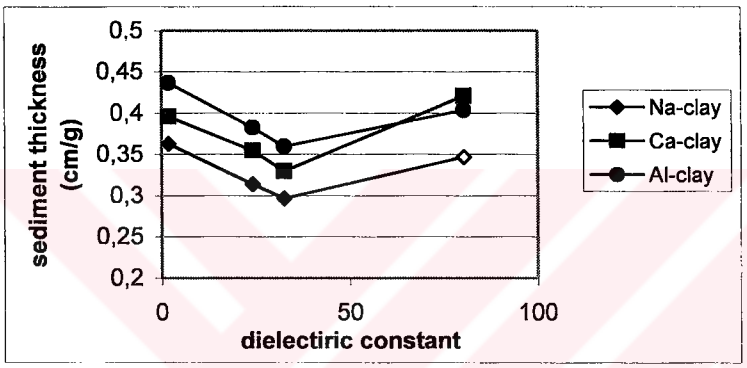


**Figure 4.8 Sediment thickness of homoionized samples in different pore medium**

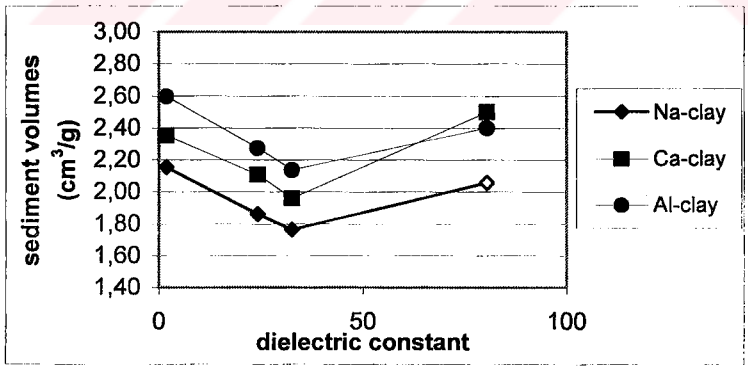


**Figure 4.9 Sediment volumes of homoionized samples vs. dielectric constant of pore medium**

The shape of the figures of sediment thickness and sediment volumes of homoionized samples vs. dielectric constant are consistent with that of the liquid limit test results. Na-clay fell under Al-clay and Ca-clay in all pore fluids, but

sedimentation test in water is still in progress and the expected sediment thickness with DDI water is plotted with non-filled diamond in Figure 4.8 and Figure 4.9.

The sedimentation test explains why the liquid limit value of Na-clay was lower than those of Al-clay and Ca-clay in different pore medium. This is because, particles of Na-clay are more dispersed than other homoionized clays. In addition to this, sedimentation test for Na-clay in DDI water has been going on for five weeks. Al-clay and Ca-clay completed their settlement in a few hours this is because the cations depress the diffuse double layer, in turn causing the flocculation of the soil particles. The flocculated particles settle faster than dispersed particles. Thus, the more flocculated particles, the more sediment thickness and sediment volumes.

On the other hand, the volume basis liquid limit and sedimentation test results for Ca-clay and Al-clay are opposite of each other. With DDI water, volume basis liquid limit of Al-clay is higher than that of Ca-clay. However, as it was mentioned before, Ca-clay stands in volume basis liquid limit over the Al-clay in the rest of the pore fluids (Fig. 4.6). It should be noted that the expected behaviour of volume basis liquid limit in n-hexane was pointed on the Figure 4.6. The trend of sediment thickness and sediment volumes of homoionized samples in those pore fluids are consistent with the trend for expected volume basis liquid limit. This is because flocculation increases with decrease in the dielectric constant of the pore medium. Edge to face flocculation governs higher sediment thickness and sediment volumes than dispersed ones. Therefore, entrapped void spaces for liquid also increases and that should lead higher liquid limit in n-hexane than in either ethanol or methanol.

Sridharan & Prakash (1999) conducted the sedimentation tests on homoionized kaolinitic local Indian soil by using DDI water. Sediment volume of sodium treated kaolinitic soil was lower than calcium and iron treated soil. However, sediment volume of calcium treated kaolinitic soil was higher than those of iron treated clay and that result is in agreement with the above result, which is found the sediment volume of calcium treated clay was higher than that of aluminum treated clay.

The sediment thickness and sediment volumes of Al-clay are lower than Ca-clay in DDI water, but higher than Ca-clay in the rest of the pore fluids. That result is interesting because not only particle flocculation govern the liquid limit of soils but also some other reasons may have a role on this behaviour. As it is mentioned before, entrapped water in void spaces due to particle flocculation leads the consistency limit behaviour. However, there is an opposite behaviour was observed between the Ca-clay and Al-clay for their sediment volumes and volume basis liquid limit values. That may be attributed to the differences in pH and further investigation is necessary to evaluate this behaviour.

### 4.3 One-dimensional Consolidation Test Results

One-dimensional consolidation tests were conducted on Na-clay, Ca-clay and Al-clay. The average of two tests was presented for Na-clay, three for Ca-clay and only one for Al-clay.

Figure 4.10 presents the typical compression versus time curves for the different valence cations for a pressure increment of 1-2 $kg/cm^2$. The results indicates that aluminum saturated soil consolidates faster than Ca-clay and Na-clay and Ca-clay consolidate faster than Na-clay. This is because; the flow area in Al-clay is higher than that of Ca-clay and the flow area in Ca-clay is also higher than that of Na-clay. The same figure also shows that Na-clay compress less than Ca-clay and Al-clay. It may be attributed to the soil fabric: more flocculated particles may compress higher than dispersed particles.

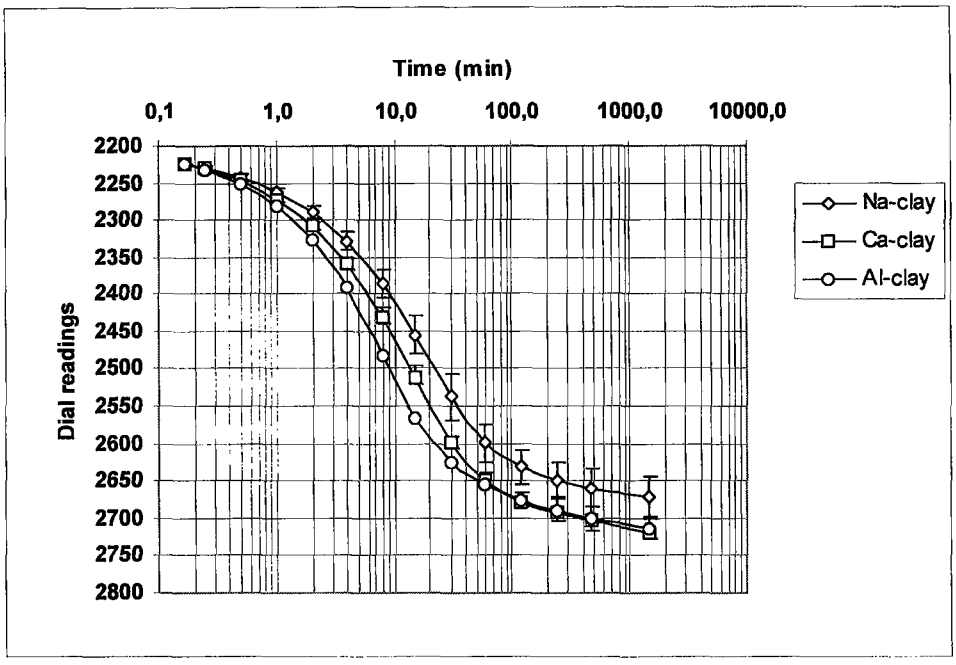


**Figure 4.10 Compression vs. time curve for a pressure increment of 1-2 kg/cm$^2$**

Knowing that the variations in the initial remolding water contents of the different homoionized specimens result in different origins for their e-log *p* curves, the procedure presented by Sridharan et al (1986) was followed to obtain compressibility curves starting from the same locus, the total compression undergone by the homoionized specimen at the end of each load increment ($\Delta H_i$), divided by the height of the soil solids ($H_s$), is plotted as a function of applied pressure. Figure 4.11 presents the $\Delta H_i / H_s$ versus pressure plots for the different valence cations. The order of the cations is different from the consolidation test results. Na-clay placed between the Ca-clay and Al-clay. This is because; the flocculated or dispersed particles may have different compressibility behaviour in different pressure increments. In fact, all three homoionized specimens have similar compressibility characteristics. However, the change in the height (i.e. compression) during loading is smaller in Na-clay as can be seen in this figure. Thus, the result is consistent with Figure 4.10, this is because dispersed particles may compress less than flocculated particles.

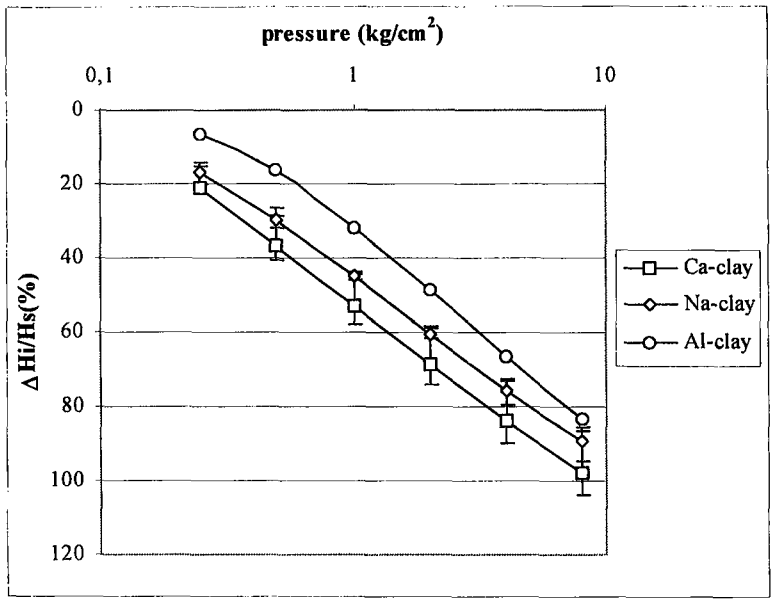


**Figure 4.11 The $\Delta H_i / H_s$ versus pressure plots for the different valence cations**

The void ratio-hydraulic conductivity and pressure-hydraulic conductivity relationships are shown in Figure 4.12 and 4.13, respectively. The HC (Hydraulic Conductivity) is calculated from the expression

$$k_p = \frac{c_v a_v \gamma_p}{1+e} \qquad (4.2)$$

where $k_p$ is the hydraulic conductivity (cm/sec), $c_v$ is the coefficient of consolidation ($cm^2$/sec), $a_v$ is the coefficient of compressibility ($cm^2$/kg), $\gamma_p$ is the unit weight of the pore fluid ($kg/cm^3$) and $e$ is the void ratio (Terzaghi, 1925).

The results are in aggrement with the findings of Rao & Mathew, (1995). They found an increasing order of hydraulic conductivity with increasing in the cation valence. In another words, increase in cation valence results higher hydraulic conductivities. In figure, bars show the upper and lower limits of variations.

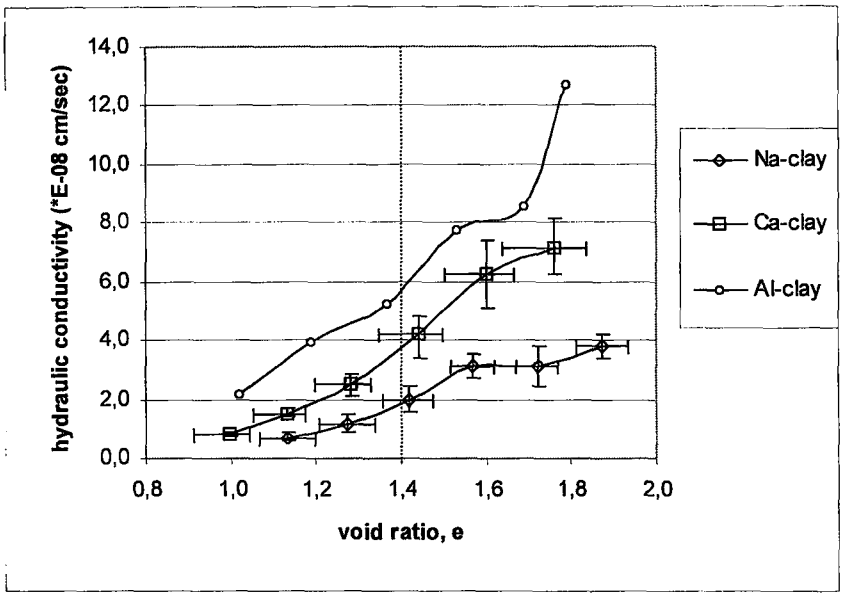


**Figure 4.12 void ratio-hydraulic conductivity relationships between homoionized clays**

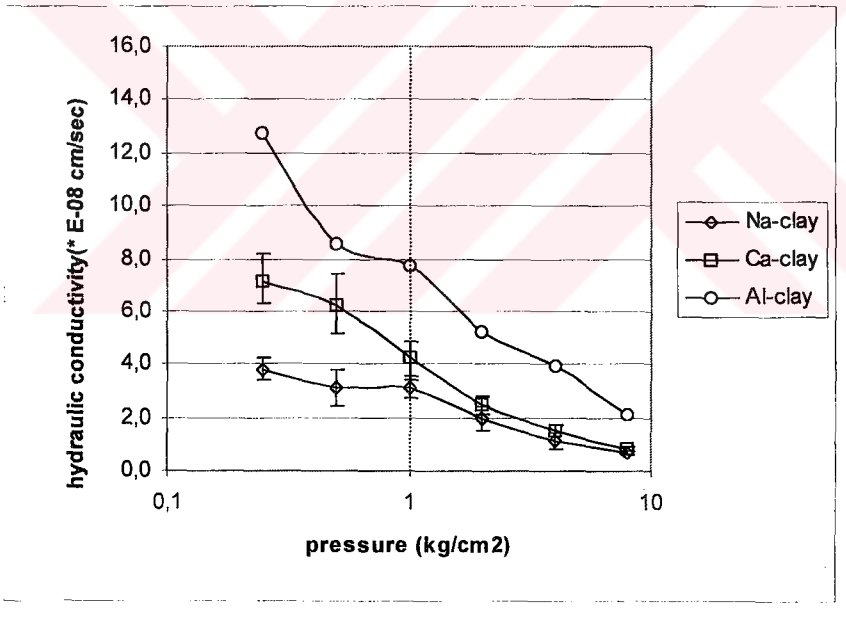


**Figure 4.13 Pressure-hydraulic conductivity relationship between homoionized clays**

As can be seen from Figure 4.12, hydraulic conductivity increases with increasing in the cation valence in a constant void ratio (for example void ratio, e = 1.4). In Figure 4.13, hydraulic conductivity decreases with decreasing in pressure, as

expected, and for the constant pressure (for example pressure = 1 kg/cm$^2$), increase in cation valence results increasing hydraulic conductivity.

Increase in cation valence results particle flocculation and flow area is higher in Al-clay than those of Ca-clay and Na-clay. The obtained results are in agreement with the findings of Kaya & Fang (2000), which is an increase in the diameter of the pores causes significant changes in the pore-size distribution, resulting higher hydraulic conductivity of fine-grained soils. Fig. 4.14 illustrates the changes in the pore size distributions due to changes in the double layer thickness.

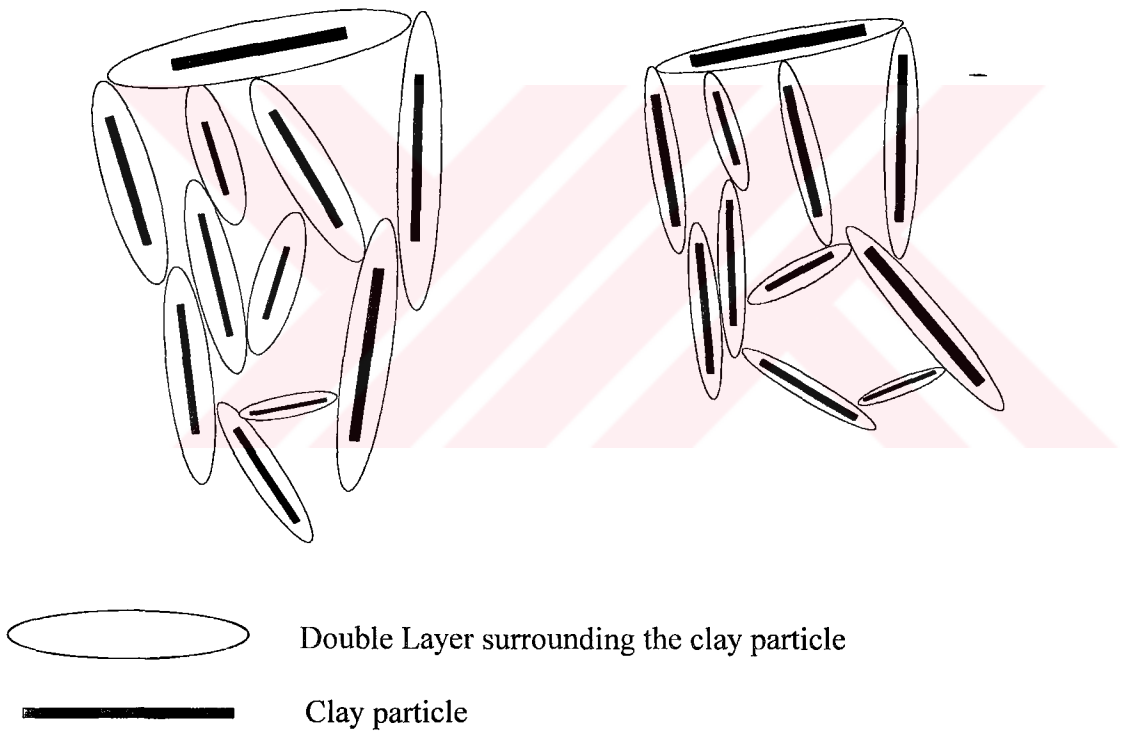


**Figure 4.14 Changes in pore-size distribution due to changes in double layer thickness**

### 4.4 Practical Applications of the Results

Results showed that engineering properties of fine-grained soils (especially clays) are very sensitive to the changes in the environment chemistry. Environmental changes (for example pore fluid contamination) in the particulate level of clays influence the engineering properties of clay significantly. Increasing or decreasing the thickness of the double layer allow particles to be either flocculated or dispersed. Flocculated particles settle faster than dispersed particles under gravitational force.

Changes in the double layer thickness results immediate settlement of soils under pressure. Higher valence cations settle faster than lower ones, and influence the compressibility of fine-grained soils significantly. This effect is more pronounced for the montmorillonitic soils.

Contamination of ground water also effects the hydraulic conductivity of fine-grained soils. Increase in valence result more flocculated particles, and the pores between these particles also increases with increasing in the cation valence. Also, changes in the dielectric constant of the pore fluid affects the permeability of fine-grained soils.

Changes in the microstructure of clays may influence the strength parameters of the fine-grained soils. The shear strength of fine-grained soils are related with the micro-structural changes of clays. On the other hand, particle orientation changes the thickness of sediments and results higher or lower effective stress due to the flocculation or dispersion.

In addition to these, grain size distribution of fine-grained soils can be affected from the changes in the pore medium. Clay may act as non-plastic due to the changes in the dielectric constant of the pore fluid.

# CHAPTER FIVE
# SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Previous research has shown that the engineering behaviour of either kaolinitic or montmorillonitic soil may change after treating with chemical solutions. The objective of this study was to determine the engineering properties of mixed mineral clay in some organic liquids and in an inorganic liquid. Some of the tests were conducted by organic liquids and observed the changes in the microstructure such as flocculation or dispersion.

## 5.1 Summary

### 5.1.1 Changes in Consistency Limits of Homoionized Clays in Polar and Non-polar Liquids

Consistency limit tests includes liquid limit, plastic limit, and shrinkage limit tests. All of the tests were conducted with DDI water; and only liquid and plastic limit of homoionized clays were conducted with organic liquids such as methanol, ethanol, and n-hexane.

Liquid, plastic and shrinkage limits of homoionized clays treated with DDI water increased with increasing in cation valence; and there were a linear relationship between each other.

Liquid and plastic limit tests were performed with organic liquids showed different behaviour. The liquid limit values of homoionized clays decreased with methanol comparing with that of DDI water. Then, increased with ethanol and it

decreased again with n-hexane. Herein, volume basis liquid limit values were used to compare with each other. However, sedimentation results showed that sediment thickness, thus sediment volumes, of homoionized clays in n-hexane due to flocculation were higher than those of other liquids. Then, a correction were applied to the volume basis liquid limit of homoionized clays in n-hexane.

Volume basis liquid limit of Al-clay was higher than that of Ca-clay. However this order changed in organic liquids. pH results showed that pHs of Al-clay in organic liquids were much lower than that of Ca-clay. However, it must be noted that pH of homoionized clays in n-hexane were not measured because of the harmful effect of this liquid on the plastic probe of pH apparatus.

Sedimentation results between this two homoionized clays showed an opposite behaviour observed in volume basis liquid limit. Herein, sediment height and sediment volumes of Ca-clay in DDI water was higher than those of Al-clay. However, this order changed while treating the clays with organic liquids. Al-clay in organic liquids have higher sediment thickness and sediment volumes than those of Ca-clay.

### 5.1.2 Changes in Compressibility Behaviour of Homoionized Clays

One-dimensional tests were conducted to all homoionized samples by using DDI water as a pore fluid. The average of two tests for Na-clay, three for Ca-clay and only one for Al-clay were used to explain the compressibility behaviour of homoionized clays. Results showed that Al-clay consolidated faster than Ca-clay, and Ca-clay consolidated faster than Na-clay. However, Na- clay showed lower compressibility than Ca-clay and Al-clay and that of Al-clay was similar to that of Ca-clay.

Hydraulic conductivity values were calculated from the consolidation test results. As expected, hydraulic conductivity of Al-clay for the constant pressure and void ratio was higher than that of Ca-clay and Na-clay and that of Ca-clay was higher than

that of Na-clay. Increase in cation valence results more permeable homoionized clays.

## 5.2 Conclusions

Herein, the engineering behaviour of mixed mineral clay (i.e. 50% montmorillonite, 50% kaolin and illite) was investigated. Treating the clays with different valence cations allows particles to be more flocculated. Flocculation increases with increasing in the cation valence.

During the consistency limit tests, there was a linear relationships between liquid, plastic and shrinkage limits of homoionized clays while treating with a polar liquid (i.e. DDI water). Because of the entrapped water in the void spaces within the particles due to flocculation results higher liquid limit values than dispersed particles. The results are in agreement with the results reported by previous researchers conducted the experiments on kaolinitic soils. In fact, kaolin minerals may govern the engineering properties of mixed-mineral clayey soil, while conducting the experiments by DDI water. Liquid limit value of aluminium treated clay was obtained 13% higher than that of sodium treated clay. Also, flocculation of Al-clay was higher than that of Ca-clay and Na-clay. Sedimentation test in DDI water completed in a few hours for Al-clay and Ca-clay, however, Na-clay has been going on for five weeks.

There were also slight increase for the plastic and shrinkage limits of homoionized clays with increasing in the cation valence.

Liquid limit of homoionized clays while treating with organic liquids was calculated in the volume basis because of the different densities of those liquids. Considering the dielectric constant of the organic liquids, the increasing order in the volume basis liquid limit of homoionized clays in DDI water was, as it is mentioned above, Al-clay > Ca-clay > Na-clay. This order changed to: Ca-clay > Al-clay > Na-clay by decreasing dielectric constant of the pore medium (i.e. methanol, ethanol,

and n-hexane, respectively). In all of the liquids, monovalent sample (i.e. Na-clay) showed the lowest values; however; the order between Ca-clay and Al-clay may exchange. This may be attributed to the changes in the pHs of the Ca-clay and Al-clay. While treating the pure clays with $AlCl_3$, HCI was formed when exposed to DDI water. For this reason, the decrement in the pH of the Al-clay comparing with the other homoionized clays were significant. In a lower pHs, acid (HCI) can dissolve some of the aluminium sites. The decrement in pH was considerable enough for the Al-clay in methanol and ethanol when comparing with the DDI water. On the other hand, there was an increase in the pH of Ca-clay while treating with methanol.

Sedimentation test results showed an opposite behaviour when comparing with the volume basis liquid limit test results. However, the trend in Figures 4.6, 4.7 & 4.8 were the same. For volume basis liquid limit test results and sedimentation test results, it can be noted that there was a transience point in dielectric constant of methanol. Herein, montmorillonite minerals may lead the engineering behaviour of mixed mineral soil. Then, from this point, volume basis liquid limit of homoionized clays increased in ethanol and then decreased in n-hexane. However, the flocculation is higher in n-hexane than that of in other liquids. Therefore a correction was applied for the volume basis liquid limit values of n-hexane because of temperature dependence of this liquid. When the volume basis liquid limit of homoionized clays tend to increase, the soil act again like a kaolinitic soil. Then, kaolin mineral may govern the engineering behaviour while treating with ethanol and n-hexane.

The difference between sediment thickness and sediment volumes of Ca-clay and Al-clay was very low. However, the increasing order in DDI water was obtained as follows: Ca-clay > Al-clay > Na-clay. Sediment thickness and sediment volumes of Ca-clay was higher than that of Al-clay. This order changed as: Al-clay > Ca-clay > Na-clay while treating the clays with methanol, ethanol, and n-hexane. Hence, not only particle flocculation governs the liquid limit of soils but also some other reasons may have a role on this behaviour. This is because Al-clay was expected as the highest sediment volumes in DDI water comparing with the other homoionized

clays; which may be attributed to the differences in pH. However, further investigation is necessary to evaluate this behaviour.

Compressibility of homoionized clays was also different from each other. Al-clay consolidate six times faster than Na-clay, and Ca-clay consolidate two times faster than Na-clay. The change in height during the loading was similar for the three homoionized clays. However, Na-clay compress lower than that of Al-clay and Ca-clay.

Hydraulic conductivity values were determined from the consolidation test data. Hydraulic conductivity of Al-clay was higher than that of Ca-clay and Na-clay, and that of Ca-clay is also higher than that of Na-clay. This is because, increase in cation valence results particle flocculation, thus, increases the flow area between the particles and as a result more permeable soil occurs.

### 5.3 Recommendations

This study can be enlarged by the further investigations and experiments. To obtain the shear strength parameters, direct shear test can be conducted to homoionized samples.

The chemical analysis of the homoionized clays can be determined by ICP analysis. This analysis gives us the chemical composition of homoionized clays after treating with NaCl, $CaCl_2.2H_2O$, and $AlCl_3$. The differences in the cation concentration can give some information and for the Al-clay, the amount of aluminum in the aluminum sites can be controlled by ICP analysis in order to observe the changes before and after the treatment of $AlCl_3$.

Liquid limit tests can be conducted to all homoionized clays by using n-hexane as a pore fluid at a low temperature in order to eliminate the temperature effect. Then, after obtaining the liquid limit value, the data will be evaluated with the data of ethanol and methanol.

Further one-dimensional consolidation test can be applied with Na-clay and Al-clay in order to support the previous data.

Hydrometer test should be conducted on homoionized clays in determine to observe the grain size-distribution of those clays. Flocculated particles should settle faster than dispersed particles and percent finer must be higher in Na-clay than Ca-clay and that of Ca-clay must be greater than Al-clay. This test also explains the flocculation as well.

Viscosity test should be conducted to all homoionized clays with various clay concentrations. The shear stress- shear strain curves can give some relationship between different valence cations.

Zeta potential of homoionized clays in DDI water can also be determined and results give some information about the thickness of the double layer. Further more pH measurements can be adapted to the homoionized clays.

SEM (Scanning Electron Microscopy) can be obtained for all homoionized clays and compared the changes in the particulate level.

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