CLAY MINERAL QUANTIFICATION USING

GRAVIMETRIC ANALYSIS

by

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ABSTRACT

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The current procedure used by the Texas Department of Transportation (TxDOT) to determine the type of stabilizer is based mainly on the Plasticity Index (PI) and the gradation of the soil. This method of stabilization does not always work because two soils with the same PIs can have very different shrink/swell potential, plastic limits or liquid limits, hence their behavior may be very different. This is mainly due to the fact that two soils that have the same PI can have very different clay mineral composition. Montmorillonite and kaolinite are the clay minerals that cause swelling/shrinking in soils.

Chittoori (2008) had developed three models to quantify the clay minerals using Microsoft Excel Solver, Regression Equations and Artificial Neural networks. The main objective of this research was to validate the recently developed models by Chittoori 2008 for quantifying montmorillonite and kaolinite. It was found that although all the models gave fair predictions, the regression equation accurately quantified high percentages of montmorillonite – the mineral that is the main cause of swelling and water retention in soils.

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CHAPTER 1

INTRODUCTION

<u>1.1 Introduction</u>

Soils are a mixture of mineral and organic constituents that are in solid, gaseous and aqueous states. The physical state and the chemical makeup of the soils contribute to their suitability for engineering and commercial purposes. It is very important to understand the total structure of soils in order to predict how they will behave under natural conditions.

Over the years, soil stabilization has been a topic of great interest and discussion amongst civil engineers. Extensive research was documented with concerning engineering properties, reliability and durability of various types of stabilized materials (Tayabji 1982; Haussman 1989; Moseley and Kirsch, 2004; Puppala et al., 2006). Soil stabilization significantly reduces the construction and maintenance cost associated with building pavements on expansive or poor quality soils as well as increase rider comfort and satisfaction. The stability of the soil beneath the pavement influences the performance of the pavement to a great degree. But in some cases, even after sub grades are stabilized and treated using standard procedures developed by federal agencies, these pavements fail or they have cracks which eventually cause failures. Every year, millions of dollars are spent over maintenance of these pavements. It is not due to poor design that most of these failures occur, as the designs take into consideration all the load factors and water conditions associated with the given area. What they do not take into consideration, or they overlook is the mineral composition of the soils. None of the current design procedures address the affect soil minerals have on the stabilization process used for sub grade improvement.

The current procedure used by the Texas Department of Transportation (TxDOT) to determine the type of stabilizer is based mainly on the Plasticity Index (PI) and the gradation of

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the soil. Figure 1.1 illustrates how the PI of the soil is used to determine the kind of stabilizer to use. This method of stabilization does not always work because two soils with the same PIs can have very different shrink/swell potential, plastic limits or liquid limits, hence their behavior may be very different.

Figure 1-1 Additive Selection Criteria for Subgrade Material Using Soil Classification (Chittoori, 2008)

Most soils are the result of the weathering of rocks. The rocks consist partly of chemically stable and partly of chemically less stable minerals (Terzaghi and Peck, 1960). When the chemical weathering of rocks occur, the stable minerals remain practically unaltered but the less stable minerals transform to very small particles that have a scale-like or flaky crystal form (Terzaghi and Peck, 1960). As further transportation occurs via running water, etc. the aggregates are broken down further and also subjected to grinding and impact. The grinding causes the flaky particles to be broken down into smaller particles. These broken down flakes constitute the very fine fraction of natural soils. There are various kinds of soil minerals, but the

primary minerals that are taken into consideration and contribute to soil behavior are montmorillonite, kaolinite and illite.

1.2 Research Objectives

The main objective of this research is to validate the models developed by Chittoori (2008). Thirty artificial samples have been prepared, each with a different percentage of the minerals. The artificial samples consisted of mixtures of montmorillonite and kaolinite only. The samples were mixed so that each had a different proportion of the minerals. The purpose of this is to figure out the actual behavior of the minerals without the influence of external factors. The goals of this research are listed below.

1. Perform chemical analyses on the samples. The chemical analyses consist of three methods that have been used in the literature. They are – Cation Exchange Capacity (CEC), Specific Surface Area (SSA) and Total Potassium (TP).

2. Use the values obtained from the above mention analyses to determine the percentage of each mineral present in the different samples. These percentages will be obtained using three methods. The first method uses the solver function of Microsoft office Excel, the second method involves regression equations, and the third involves the use of artificial neural network model developed by Chittoori (2008).

3. Compare the predicted percentages to the actual percentage mixed and correlate the accuracy of the prediction.

4. Provide future recommendations as deemed necessary after reviewing the predictions.

1.3 Organization and Summary

This section will provide a brief overview of the contents of the following chapters.

Chapter 2 provides a review of the literature available on clay minerals and the studies conducted by various researchers to better understand and quantify them. It also provides the different methods that are currently in practice for the identification and quantification of clay minerals. It also provides information about the chemical properties that can be used to quantify the clay minerals.

Chapter 3 gives the detailed procedures of the various chemical tests used in this study. Test procedures for the Cation Exchange Capacity (CEC), Specific Surface Area (SSA), and Total Potassium (TP) are explained thoroughly.

Chapter 4 includes all the test results obtained from the samples. These results are used to analyze and quantify the percentage of each mineral present using the models developed by Chittoori 2008. It includes a brief description of the models and the percentage of minerals derived using them. Analysis and comparison of the predicted percentages with the actual mix percentage is also discussed in this chapter.

Chapter 5 provides the summary and conclusions of the research. It addresses the future research needs to improve the predictions and correlation of the data. It also addresses the possible reasons for the errors encountered in the data.

CHAPTER 2

LITERATURE REVIEW

<u>2.1 Introduction</u>

Soil stabilization with the aid of chemical additives has been in practice for many years now. The kinds of chemicals or additives to use for the stabilization have been discussed at length by various researchers and many innovative methods have been discovered (Tayabji et al., 1982). One of the areas where soil stabilization has been used to a great extent is pavements. The stability of the soil beneath the pavement influences the performance of the pave to a great degree. Although many pavements are performing very well after being treated, there are still some cases where the soil stabilization technique did not work like it should have. These failures may be blamed on the kind of stabilizer used, the amount of stabilizer used, or on the properties and mineral content of the soil (Little et al. 2000).

Currently, the Texas Department of Transportation (TxDOT) uses the Plasticity Index (PI) and gradation of the soil to determine the kind of stabilizer to be used. Figure 2.1 illustrates how the PI and gradation are used to determine the type of stabilizer to be used. As mentioned before, this method of stabilization does not always work because two soils with the same PIs can have very different shrink/swell potential, plastic limits or liquid limits, hence their behavior may be very different.
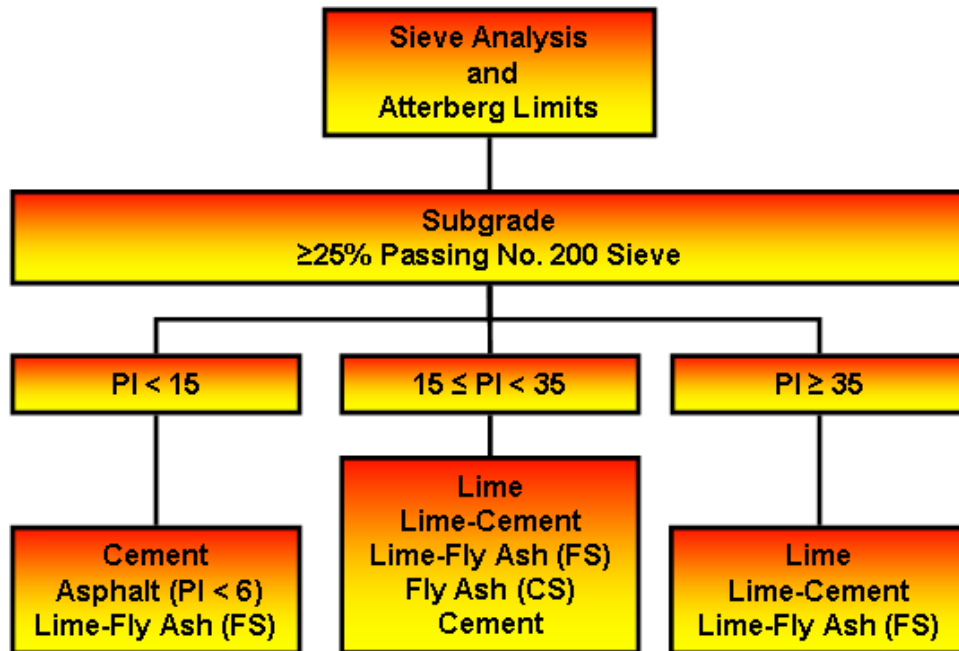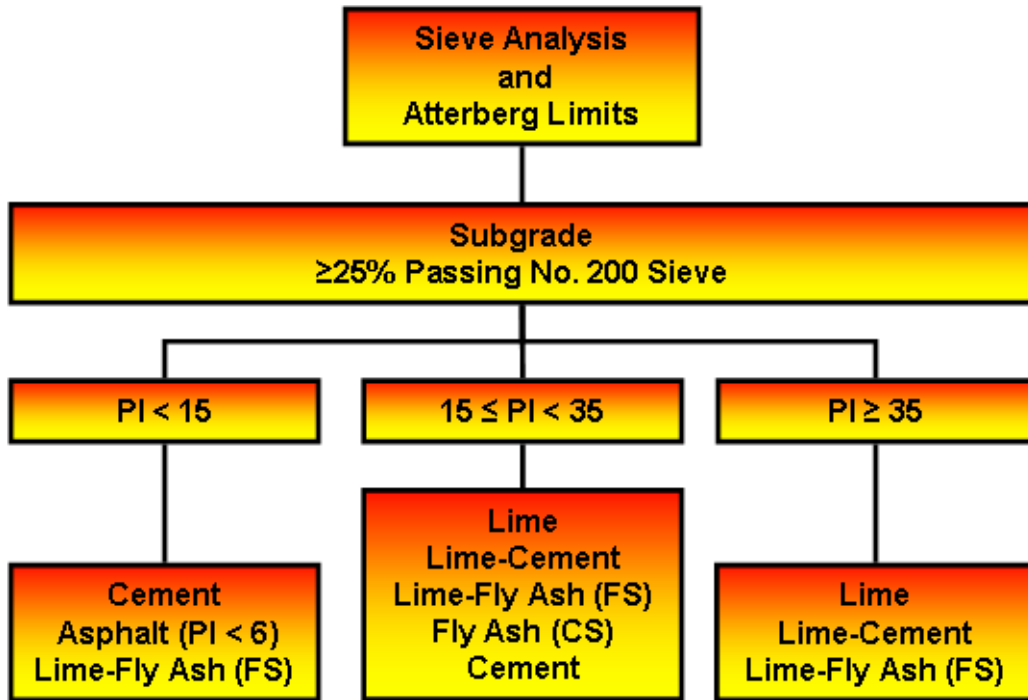
Figure 2-1 TxDOT Additive Selection Criteria for Subgrade Material Using Soil Classification (Chittoori 2008)

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<u>2.2 Clay Minerals</u>

2.2.1 Montmorillonite

Montmorillonite, a clay silicate, is a member of the smectite family. They form by crystallization from solution high in soluble silica and magnesium. Montmorillonite has a 2:1 layer structure. They have an octahedral sheet along with two tetrahedral sheets, in which oxygen atoms are shared (Borchardt, 1977). All tetrahedra in the sheets contain Si^{4+} ions. Aluminum is the normal ion in the central sheet, but about one-eighth of the octahedra contain Mg^{2+} as a substituting ion for $Al^{3+.}$ The negative charge caused by substitution is neutralized by various hydrated cations adsorbed to the surface of sheets. The force of bonding between cations and the sheets is not very strong and depends on the amount of water present. In dry montmorillonites the bonding force is relatively strong. When wet conditions occur, water is drawn into the interlayer space between sheets and causes the clay to swell dramatically (expanding clay) (Borchardt, 1989).

A characteristic feature of montmorillonite is the extensive surface for the adsorption of water and ions, therefore the cation exchange capacity of montmorillonite is very high (Borchardt, 1989). Layers of the smectite group range in thickness from 0.98 to 1.8 nm or more. They are mainly responsible for the shrinking and swelling characteristics of soils and have adhesive properties that help prevent erosion. They absorb large quantities of water, due to their expanded lattice structure, leading to a lower strength, which causes large and destructive landslides as well as creep (Borchardt, 1989). Their negative charge and expansive nature makes them very reactive in soil environments and makes them susceptible to absorb herbicides and pesticides.
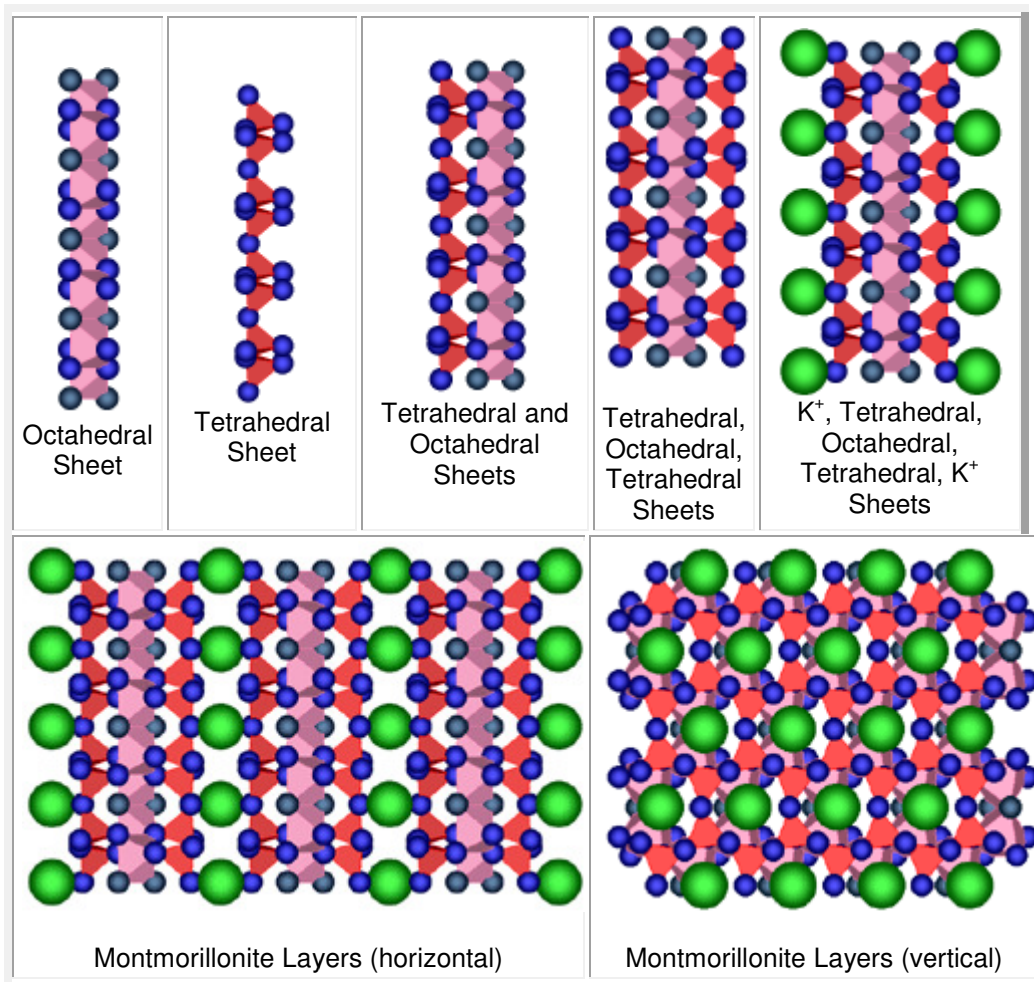
Figure 2-2 Montmorillonite structure
(Source:http://www.wwnorton.com/college/chemistry/chemconnections/Rain/pages/minerals.html)
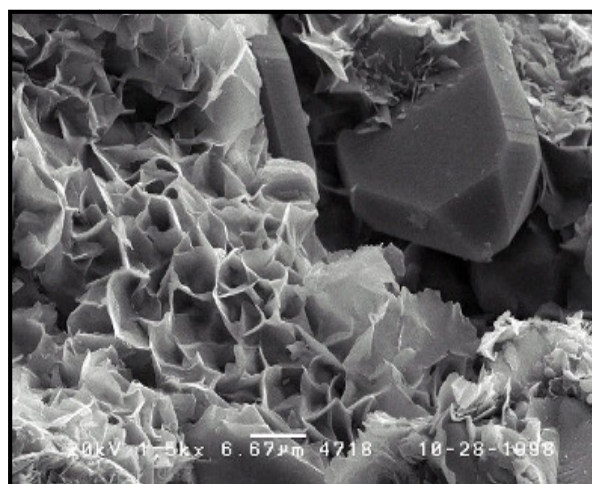
Figure 2-3 Scanning Electron Micrograph of MontmorilloniteSource:
http://www.webmineral.com/specimens/Smectite.jpg

2.2.2 Illites

        Illites are part of the mica family. Micas are 2:1 phyllo-silicates, which mean layered silicates. Each layer is composed of two tetrahedral sheets and one octahedral sheet. They have cations between their interlayer, which balances a high layer charge. The most important and extensive cation is potassium (K). Micas are found in shales, slates, phyllites, schists, gnesses, granites, etc. and in sediments that have been derived from these rocks (Fanning et al., 1977). Illites are the dominant clay minerals in argillaceous rocks and are formed by the weathering of silicates (primarily feldspar), through the alteration of other clay minerals, and during the degradation of muscovite (Fanning et. al., 1977). Formation of illite is generally favored by alkaline conditions and by high concentrations of Al and K. The number of inter particle contacts is less in micas and hence the cohesive forces between the crystallites are weak (Thompson and Ukrainczyk, 2002). The degree to which illite crystals contact adjacent grains is a function of soil water content as well as particle size, shape and flexibility (Fanning et al., 1977)
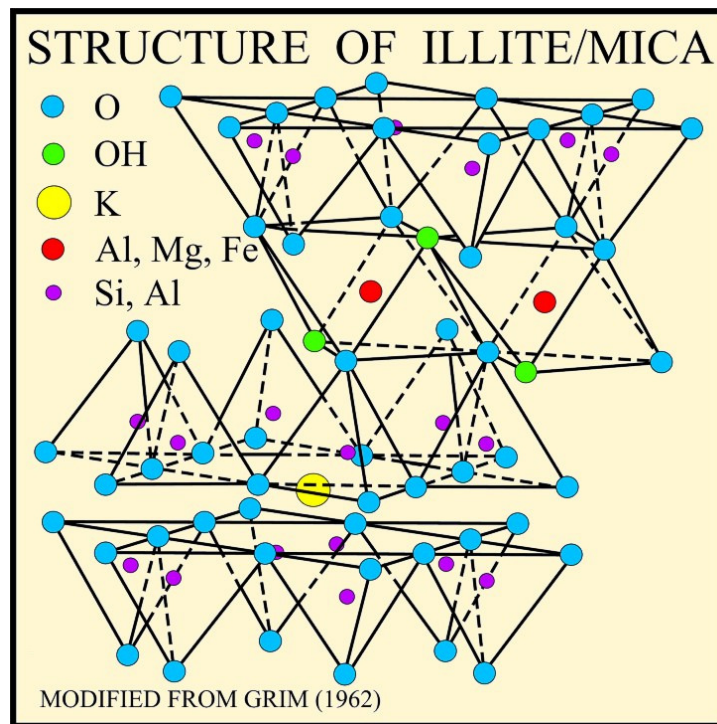
Figure 2-4 Structure of Illite
(Source: http://pubs.usgs.gov/of/2001/of01-041/htmldocs/clays/illite.htm)

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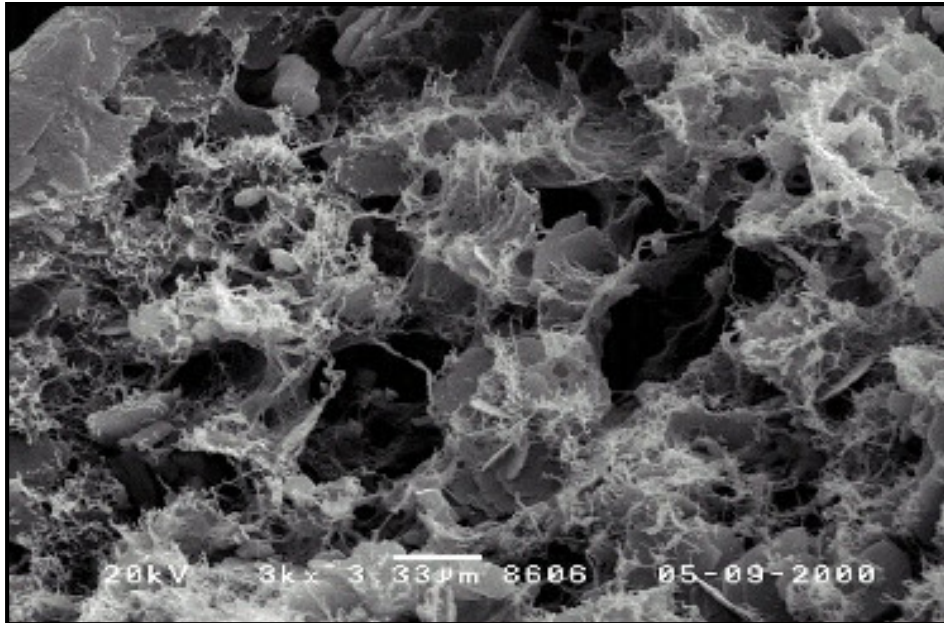
Figure 2-5 Scanning Electron Micrograph of Illite
(Source: http://www.ktgeo.com/tSEM4C.jpg)

2.2.3 Kaolinite

The kaolinite group of minerals includes a lot of different kind of minerals including kaolinite, dickite, nacrite, and halloysite, and the trioctahedral minerals antigorite, chamosite, chrysotile, and cronstedite. Kaolinite is usually abundant in warm and moist climates. Kaolinite's structure is composed of alternate silicate sheets (Si_2O_5) and aluminum oxide/hydroxide sheets ($Al_2(OH)_4$) called gibbsite sheets. The silicate and gibbsite layers are tightly bonded together with only weak bonding existing between these silicate/ gibbsite paired layers (Dixon, 1977). The structure is very similar to the Serpentine Group and at times the two groups are combined into a Kaolinite-serpentine Group It is a 1:1 layer structured alumino silicate, with one tetrahedral sheet linked to one octahedral sheet by oxygen atoms (Dixon, 1977). Aluminum ions occupy two thirds of the octahedral positions and Silicon ions occupy the tetrahedral positions. The aluminum and silicon ions are arranged as shown in Figure 2.6. Every third row in the octahedral sites is vacant and hydroxyl ions, which make up the surface plane of the octahedral anions, bond their hydrogen atoms to the adjacent oxygen sheets (Dixon, 1977).

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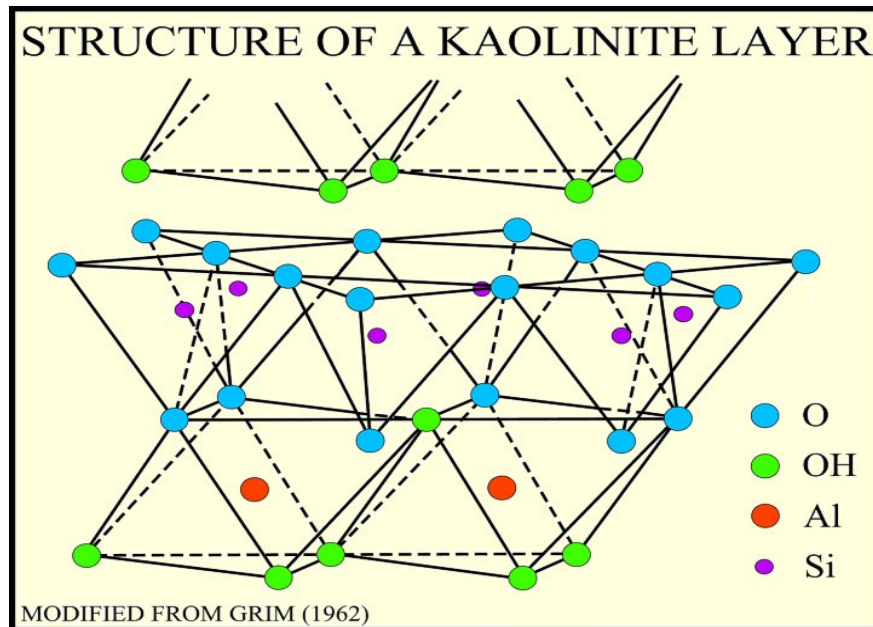
Figure 2-6 Kaolinite Structure
Source: http://pubs.usgs.gov/of/2001/of01-041/htmldocs/clays/kaogr.htm
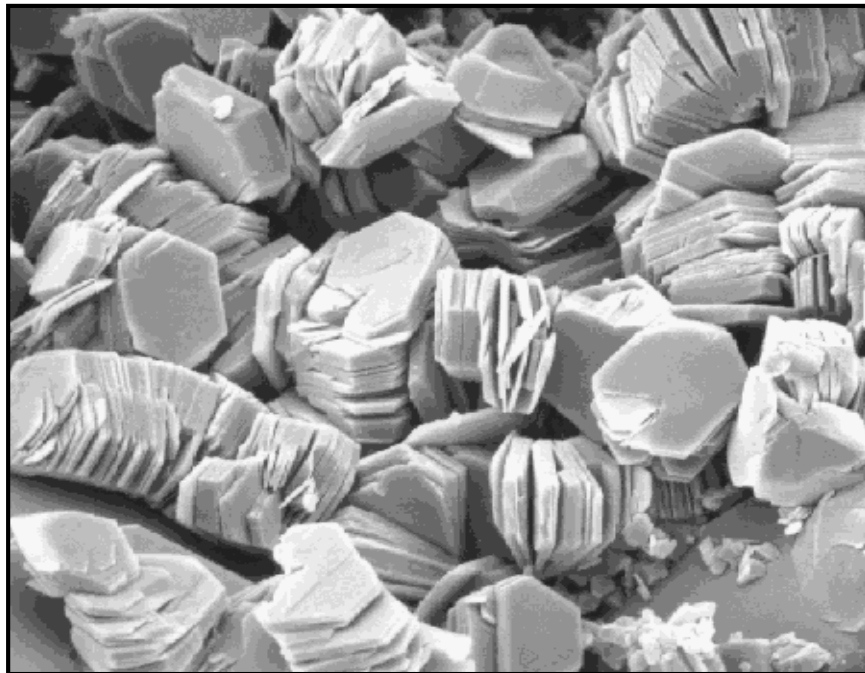
Figure 2-7 Scanning Electron Micrograph of Kaolinite
http://www.webmineral.com/specimens/Kaolinite.jpg

When viewed with an electron scanning microscope, kaolinites usually appear as hexagonal structures. Other minerals like vermiculite also display this characteristic but kaolinites

retain their structure even when heated to 1000^0C (1273K) (Dixon, 1977). However, kaolinites are altered by dry grinding for even a short period of time (Dixon, 1977).

<div align="center">2.3 Identification of Clay Minerals</div>

Soil minerals are identified primarily by their elemental composition and structure. This section is aimed to provide an overview of the different methods that are currently available to identify clay minerals. X-ray diffraction is the most widely used method of identification of the amount of information that can be gathered from x-ray diffraction results, but sometimes other methods like chemical analyses in conjunction with x-ray diffraction are also used (Dixon, 1977).

2.3.1 X-Ray Diffraction

Clay minerals are characterized to be crystalline in nature, i.e. they have long range structure that repeats itself for hundreds of nanometers to millimeters. These kinds of minerals can be identified by X-ray diffraction studies because each crystal contains planes of atoms separated by constant distance which is due to the periodic nature of the standard spacing of the atoms (Whittig & Allardice, 1986). But there are minerals that have a short range structure which extends only to a few nanometers; they are referred to as amorphous or non-crystalline. Identifying these kinds of minerals is a challenge. But, procedures like vibrational spectroscopy or X-ray absorption have been developed to identify these kinds of minerals.

When an X-ray beam falls on equally spaced atoms of a crystalline mineral they are transmitted, absorbed or scattered (Cullity, 1978). When scattering they can be scattered coherently (without loss of energy) or incoherently (with loss of energy). The coherently scattered light will form an interference pattern when the scattering centers are arranged in a regular array and the distance between scattering centers is comparable to the wavelength of the light and this phenomenon is called *diffraction* (Amonette, 2002). When the incident beams of X-rays are diffracted a detector captures the beam and converts the analog signal into digital data which can be plotted. Using Bragg's law the data is the distances between the planes of the atoms are measured. The basis for the identification of crystals using X-ray diffractions is that, no two minerals have same inter atomic distances similar in three dimensions and so have different

intensities. This intensity pattern is compared with standard patterns for known materials. Extensive X-ray diffraction data for clay minerals and other soil minerals are given by Grim (1953), Whittig and Allardice (1986), and Moore and Reynolds (1989). A detailed analysis of X-ray patterns is given by Mitchell and Soga (2005).

As the size of the clay particles is small it is difficult to study single crystals, hence p*owder diffraction* method is generally used for soils. In this method small sample of particles, containing all possible orientations is kept under the X-ray beam. This method works because of the large number of particles that insure that some will be oriented in the right way to produce the desired reflection (Whittig & Allardice, 1986).

Principles

Constructive interference of coherently scattered X-rays produces diffraction peaks related to spacing of atomic planes in sample (i.e., *d*-spacing) and wavelength of X-rays (λ).

Bragg's Law

$$n\lambda = 2d\sin(\theta)$$

Experimental Setup

X-ray Tube or Synchrotron Source   θ   Sample   θ   Detector

Typical Output

Intensities of peaks plotted vs. angle in degrees 2θ, or vs. *d*.

Intensity

Degrees 2θ (Co-K$_a$ X-rays)

Advantages	Disadvantages
Minimal sample prep	Not good for poorly ordered
Well-established database	materials
Microanalysis possible (SXRD)	Quantification difficult

Figure 2-8 Principles, Setup and Typical Output for X-ray Diffraction Pattern

Narasimha Rao (1993) has used XRD and SEM techniques to successfully identify the formation of the compounds such as Calcium Aluminate Hydrate and Calcium Silicate Hydrate

when the soil is treated with lime. In the study conducted by Yan and Jin (2004), clay mineral composition and smectite contents were measured using XRD and dye absorption methods. They have concluded that the laboratory spectral measurement and analysis techniques to the dried and homogenous swelling soils can be productively used for quickly, economically, and conveniently identifying swelling soils, estimating the contents of smectite, colloid, and clay in fields.

2.3.2 Thermal Analysis (TA) Methods

In this technique mineral identification is achieved by evaluating the weight loss and enthalpy changes in the soil sample with temperature. Thermal analysis has been used by many researchers (Norton, 1939; Benham, 1990; Karathanasis and Harris, 1994; Wunderlich, 1990) to identify clay minerals in soils. The most common methods used in TA are thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Beck, 2004). A detailed explanation of these methods can be found in Karathanasis and Harris (1994).

In TGA the weight of the soil sample is monitored by changing the temperature at constant rate. Many researchers (Barshad, 1965; Dish and Duffy, 1990) had used the TGA method to identify and quantify soil minerals. In DSC method the energy required to maintain the soil sample and the reference material at same temperature during heating is measured and evaluated. A detailed explanation of this technique is given by Karathanasis and Harris (1994) and Beck (2004). Figure 2-9 describes in detail the process of thermal analysis which can be used for the identification of minerals.

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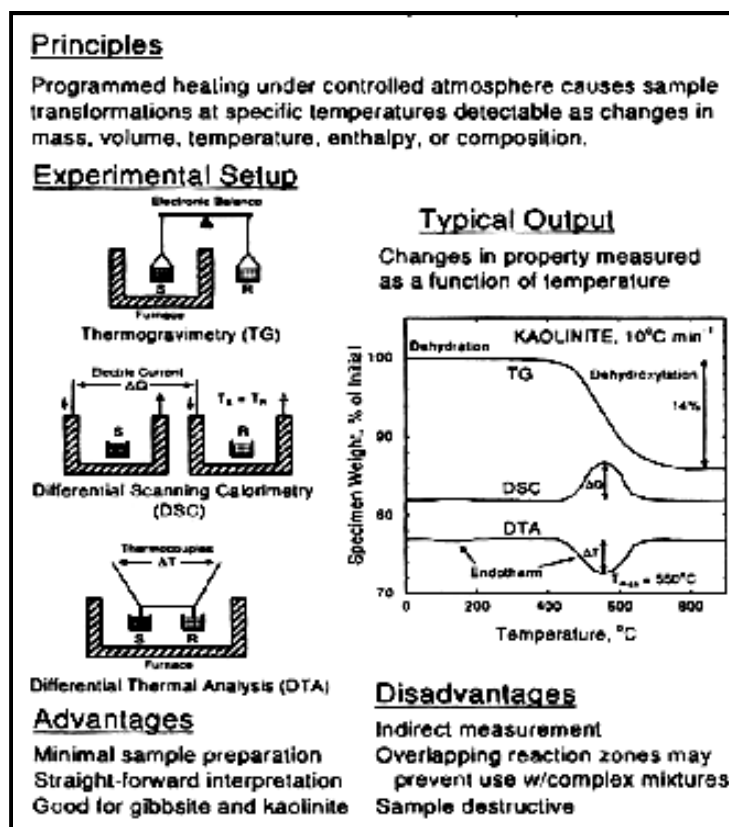
Figure 2-9 Principles, Setup, and Output for Common Thermal Analysis (from Amonette, 2002)

2.3.3 Atomic Absorption Spectrometry (AAS)

Atomic Absorption Spectrometry (AAS) has been used for the identification of elements from quite long time. Atomic absorption as the name implies, depends on the measurement of atomic species. The whole technique depends on the ability to consistently atomize the element of interest in a reproducible manner in both samples and standards. Baker and Suhr (1982) give the principles involved and the different literatures available.

When an atom is excited by thermal energy or other energy sources they emit radiation by dropping down to less energetic states or to the ground states as atoms always try to be in ground state at all times. This can be given by the following equation (Baker and Suhr, 1982):

$$M + h\nu \rightarrow M^* \rightarrow M + h\nu$$

Where M = Neutral atom, h = Planks constant, and v = Frequency of the irradiating light.

AAS relies on the absorption of a photon having the exact energy needed to convert an atom or ion in the ground state to an excited state. For each element to be to be determined, a lamp

producing light of appropriate energy irradiates the atomized sample, and the loss of intensity in this light is used to determine the amount of element present (Amonette, 2002).

The only difference between Atomic Absorption Spectrometry and Atomic Emission Spectrometry (AES) is that in the later the intensity of the light that is emitted is measured and in the earlier case absorbed light intensity i.e. the loss in the intensity is measured. Figure Figure 2-10 gives a pictorial representation of different methods for elemental analysis in which the sample is completely destructed.
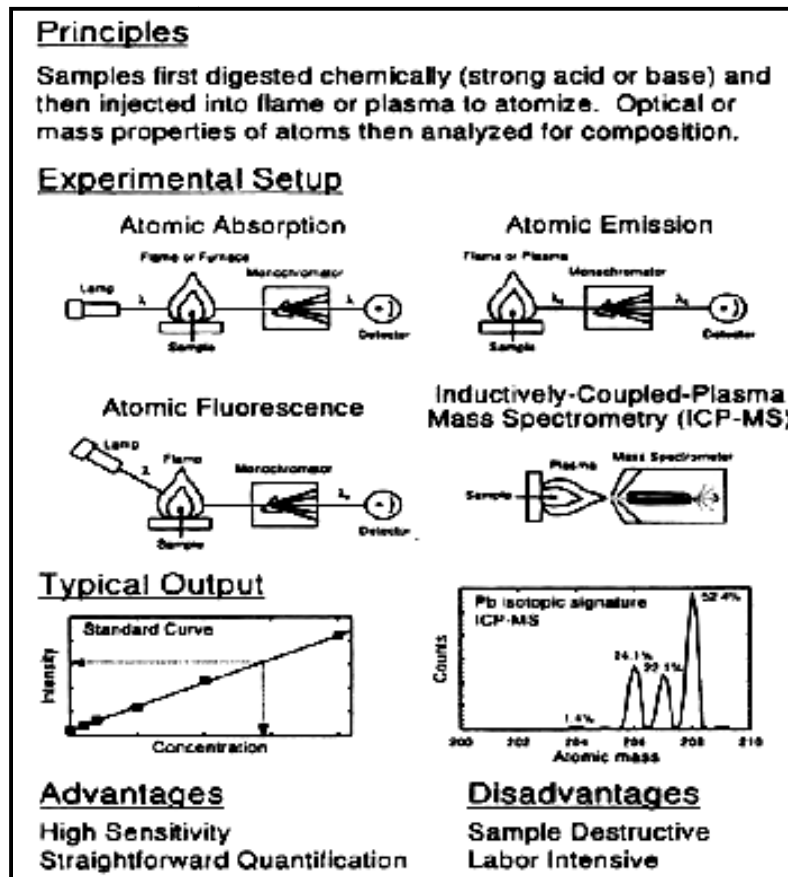
Figure 2-10 Different Methods for Elemental Analysis in Which the Sample is
Completely Destructed (from Amonette, 2002)

Majority of non-destructive soil/clay testing depend on the excitation of atoms in the specimen to produce X-ray characteristics of each element present based on the energies and the intensities of the X-ray produce elements are identified and quantified. X-rays are produced

in two stages. In the first stage a vacancy is created in the inner shell of an electron and then in the second stage that vacancy is filled by a higher energy electron coincident with the release of an X-ray photon. The vacancy is created when the atom absorbs the energy from an energy source in the form of a photon or a charged particle. X-rays produced by absorbing the energy from photons are called X-ray fluorescence (XRF) and that by charged particles are called X-ray emission (XRE). The energy source for XRF can be X-rays from an X-ray tube or gamma rays from nuclear decay. For the XRE a variety of high energy charged particles can be used, although electrons and protons are the most common. (Amonette, 2002)

2.3.4 Vibrational Spectroscopy (VS)

Vibrational spectroscopy provides the most definitive means of identifying the surface species generated upon molecular absorption and the species generated by surface reactions. In principle, any technique that can be used to obtain vibrational data from solid state or gas phase samples including infrared spectroscopy and Raman spectroscopy methods can be applied to study soil surfaces.

Figure 2-11 gives a pictorial representation of the experimental setup of vibrational spectroscopy along with its advantages and disadvantages.

There are, however, only two techniques that are commonly used for vibrational studies of molecules on surfaces. These are Infrared (IR) Spectroscopy and RAMAN Spectroscopy Infrared spectroscopy involves the direct measurement of infrared light absorbed or emitted by a specimen. Raman spectroscopy on the other hand, is an incoherent-scattering technique in which the loss or gain in energy by the interaction of light with the atoms in a bond is measured (Amonette, 2002). A detailed review of the vibrational spectroscopy is given in VS. Vibrational spectroscopy is particularly well suited for characterization of minerals containing hydroxyl, carbonate or sulfate groups and for studies of organic molecules associated with minerals surfaces.

Linker et.al (2005) studied that the use of mid-infrared attenuated total reflectance (ATR) spectroscopy enables direct measurement of nitrate concentration in soil pastes. But their

accuracy depends on the soil type which again depends on the varying contents of carbonate, whose absorbance band overlaps the nitrate band.

Kariuki et al. (2003) has investigated the effectiveness of spectroscopy in identifying the swelling indicator in soils. They used coefficient of linear extensibility (COLE) and the linear extensibility (LErod), as the controlling methods to classify the soils into swelling potential groups and to assign them to dominant clay mineral types. The study indicated that spectroscopy can be used in classifying soils however; high organic matter and the presence of moisture were found to affect area and depth intensities and would require consideration in such applications.

According to Blake and Gassmann (2001) bench-top Fourier transform infrared spectrometer and specular reflection accessory can be used to detect soil surface contaminants. They found that the volume scattering features showed a significant depolarization of the light, the degree of polarization after reflection is less than or equal 20%, and the surface scattering features retained a much higher degree of polarization upon reflection, >75%.
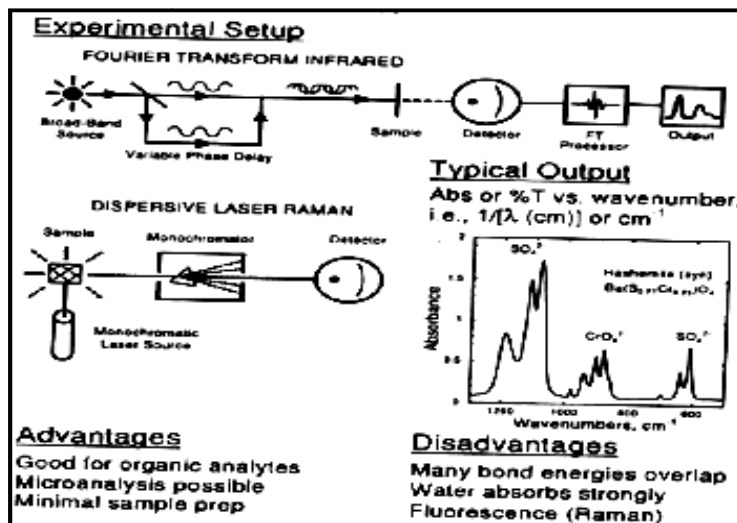
Figure 2-11 Experimental Setup of Vibrational Spectroscopy (from Amonette, 2002)

2.3.5 X-ray Absorbance Spectroscopy (XAS)

X-ray absorption spectroscopy is an element-specific probe of the local structure (short range) of elements in a sample (XAS). Interpretation of XAS spectra commonly uses standards with known structures, but can also be accomplished using theory to derive the structure of a

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material. In either case, the species of the material is determined based on its unique local structure. An important advantage of this technique is its utility for heterogeneous sample, a wide variety of solid and liquids, including whole soils and liquids, can all be examined directly and nondestructively. Additionally, since the local structure does not depend on long-range crystalline order, the structure of amorphous phases (and that of dissolved species) is easily achieved (XAS).

X-ray absorption spectroscopy is commonly divided into two spectral regions; the first is the X-ray absorption near edge structure (XANES) spectral region and the second is termed the extended X-ray absorption fine structure (EXAFS) region (Amonette, 2002). XANES spectra are unique to the oxidation state and speciation of the element of interest, and consequently are often used as a method to determine the oxidation state and coordination environment of materials. EXAFS spectra are best described as a series of periodic sine waves that decay in intensity as the incident energy increases from the absorption edge (Amonette, 2002). These sine waves result from the interaction of the elected photoelectron with the surrounding atomic environment. As such, their amplitude and phase depend on the local structure of excited atom. Since this interaction is well understood, theory is sufficiently advanced that the local structure of the excited atom can be determined by matching a theoretical spectrum to the experimental spectrum. This fitting yields many types of information, including the identity of neighboring atoms, their distance from the excited atom, the number of atoms in the shell, and the degree of disorder in the particular atomic shell (as expressed by the Debye-Waller factor) (XAS). These distances and coordination numbers are diagnostic of a specific mineral or adsorbate-mineral interaction; consequently, the data are useful to identify and quantify major mineral phases, adsorption complexes, and crystallinity.

<u>2.4 Clay Mineral Quantification</u>

Clay minerals can be quantified in two ways. One is using x-ray diffraction results and the other is chemical mass balance equations. Clay mineral content may also be determined by using a combination of the two methods mentioned above. Kaufhold et al. (2002) discusses and

compares three methods for the quantification of montmorillonite. Ten bentonite samples were tested by each method and the results correlated to check whether the methods gave an accurate estimation or not. Method A uses quantitative separation of the < 2-Am fraction in combination with XRD-analysis. Method B utilizes cation exchange capacity (CEC), layer charge (LC) and variable charge. Method C, a new method, uses the comparison of the

CEC of a bentonite with the CEC of the respective pure montmorillonite fraction is proposed. This new method provides accurate values for montmorillonite contents, but is restricted to bentonites, which are free of X-ray amorphous fine-grained constituents. By combining the results of all methods, the layer charge (charges/half unit cell (HUC)) was calculated.

The results obtained by the three methods for quantifying the amount of montmorillonite are given below. It can be seen that the results from the three methods correlate well. It is observed in the paper that the range of values gotten from the three methods is within a range of $\pm$ 2.5% of one another. Only two samples do not correlate well and the paper discusses the factors on why that is the case.

Sample	Method A				Method B				Method C		
	Semiqu. XRD of <2 μm fraction				CEC and layer charge (LC)				Cylinder enrichment		
	<2 μm [% w/w]	Ill [% w/w]	Kln [% w/w]	Mnt [% w/w]	LC [C/HUC]	$CEC_{(pH\ 4)}$ [meq/100 g]	M_{HUC} [g/mol]	Mnt [% w/w]	CEC [meq/100 g]	$CEC_{(100\%)}$ [meq/100 g]	Mnt [% w/w]
BK	69			69	0.31	63	366	75	70	100	70
FE	72		2	70	0.35	43	366	45	51	68	74
GOG	85			85	0.32	77	364	87	86	101	85
M	82	1		82	0.33	79	362	86	87	104	83
OG	76	1		75	0.29	62	363	79	70	88	80
OP	82			82	0.32	83	364	94	89	103	87
RAB	80	1		78	0.32	68	364	77	74	94	79
RAN	84	2		82	0.32	70	366	80	79	100	79
RB	78			77	0.33	66	364	73	73	99	74
UA	80			80	0.35	78	370	82	83	99	84
mean				78	mean			78	mean		79

Figure 2-12 Comparison of Results for montmorillonite quantification (Kaufhold et al., 2002)

The paper concludes that all three methods presented are suitable for determining montmorillonite quantity. The limitation of Methods A and C is that they cannot be used if fine grained poorly crystallized phases are present. Method A can be used if the phases are ferrihydrite, carbonates, and organic matter. No limitations were identified for Method B and

Method C can be used if fine grained XRD amorphous phases are absent. It is also indicated that Method C is the most economical method and can be used in most cases. Finally, it is mentioned that montmorillonite content can be predicted using the methods described with an accuracy of $\pm$ 5%.

XRD alone can also be used to quantify clay minerals. There are several different types of XRD tests and some of them have been briefly discussed in the following section.

Theoretically the diffraction peaks are related to the diffraction planes present in the sample, hence using the relative intensities of the peaks the concentration of the mineral species present in the test specimen can be estimated (Whittig & Allardice, 1986). However, there are other factors such as crystal perfection, chemical composition, variation in sample packing, crystal orientation and presence of amorphous substance that influence the diffraction peaks (Jackson, 1969). A detailed explanation of the influence of these factors on the diffraction maxima can be found in Whittig and Allardice (1986). The influence of these factors in the process of mineral quantification can be overcome by the use of standard mineral. There are two different methods to quantify minerals using standards are a) Internal standards b) External standards. In the internal standards method known amounts of a mineral not already present in the sample is added and the sample is analyzed under the X-ray machine and the diffraction peaks are recorded. These peaks are compared with the standard sample (without the addition of internal standard) to obtain the percentage of the minerals present. A more detailed explanation can be obtained in Whittig and Allardice (1986).

Due to the unavailability of the complete diffraction data and the draw backs of the above methods innovative methods involving full pattern modeling have been developed. One such method is the Rietveld method, which yields a calculated pattern that can be described as the sum of all the patterns for each phase in the sample (Kahle et al., 2002). In this method, differences between the calculated and the observed patterns are minimized by a refinement procedure that uses a least square algorithm. The final quantifications are obtained from the final values of the refined scale factor of each phase. There is another full pattern modeling method

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known as the Arquant model developed by Blanc et al. (2006) which has been successfully applied for clay mineral quantification in soils and rocks.

Other methods such as Absorption-diffraction method and the methods based on mineral intensity factors are also developed and a brief explanation of these methods can be found in Kahle et at. (2002).

Figure 2.13 gives a flowchart of the protocols for the above referred methods.

Known Addition	Absorption-Diffraction	Full-pattern-fitting	Mineral Intensity Factors (MIFs)
phase identification in mixture with unknown composition (soil sample)			
↓	↓	↓	↓
add known amount of a mineral present within the mixture to the mixture	determine peak intensity I_α of the phase α in the mixture	Select method (for example Rietveld) and software (for example Siroquant, Autoquan)	determine MIFs for the phases in the mixture by for example 1:1 mixture with suitable reference phase
↓	↓	↓	↓
measure intensity[a] of suitable peak(s)	prepare sample containing only phase α	fit observed diffraction pattern with synthetic/calculated pattern	determine peak intensities in the mixture (as desired: add internal standard (IS) as reference phase)
↓	↓	↓	↓
repeat several times, increase/decrease amount of selected mineral with every addition	determine peak intensity $I_{\alpha p}$ of pure phase α	check goodness of fit (statistical parameters, difference curve), if necessary continue refinement	determine mineral weight fractions (a): with IS: $W_\alpha = (I_\alpha/MIF_\alpha)(W_{IS}/I_{IS})$ (b): 100% approach: $W_\alpha = (I_\alpha/MIF_\alpha) / \Sigma(I_n/MIF_n)$
↓	↓	↓	
plot peak intensity versus amount added	determine mass absorption coefficients μ for pure phase α and for mixture	software calculates weight fractions (with crystallographic phase parameters refined)	
↓	↓		
extrapolate to zero amount to obtain mineral weight fraction in the sample	calculate weight of fraction $W_\alpha = (I_\alpha /I_{\alpha p}) (\mu_m/\mu_{\alpha p})$		

Figure 2-13 Protocols for XRD-based quantification of clay minerals in soil clay samples
(From Kahle et al., 2002)

Smith et.al., (1986) have developed a different scheme using XRD data which is based on the analysis of the whole diffraction pattern from 2°- 50° 2θ through comparisons with a reference database of diffraction traces obtained from a set of carefully purified reference clay samples run under the same conditions.

Quantitative determinations of the amount of clay minerals based on simple comparison of the diffraction peak heights or areas are not very accurate due to many factors like differences

in absorption coefficients, particle orientations, crystallinity and other factors (Mitchell & Soga, 2005). As a result other techniques have been developed that accounts for the above mentioned differences and are currently being used for the clay mineral quantification (Alexaides & Jackson, 1966; Hodgson & Dudeney, 1984; Johnson et.al., 1985; Randall et.al., 1994).

Hodgson and Dudney (1984) have developed an analysis procedure which uses both XRD data and chemical mass balance concepts to estimate the percentage of each mineral in a soil. Johnson et al. (1985) developed a program of simultaneous linear equations to develop the component proportions of minerals in soils and sediments. This method also uses both XRD data and the chemical data to quantify the clay minerals in the soil. Both these methods require a detailed chemical analysis data.

Chemical mass balance alone can also be used to quantify clay minerals in soils. Many researchers (Alexaides and Jackson, 1966; Hodgson and Dudeney, 1984; Johnson et.al., 1985) have already used elemental mass balance techniques to asses each mineral percentage in the soil samples. In these methods amount of each element is measured with the help of laboratory chemical analysis of the soil sample and this information is used to formulate simultaneous equations which can be solved to obtain the percentage of the minerals in soils.

Randall et al. (1994) compared four such methods of clay mineral quantification using elemental mass balance methods and highlighted their corresponding strengths and weaknesses. A brief description of those methods is given here. These methods primarily are solving a system of simultaneous linear equations which are formulated using the elemental information of the soil specimen and the minerals for which they are being analyzed. A detailed explanation of how these methods work can be found in Randall et al. (1994).

Various indirect methods involving the use of chemical species measurements and physical characteristic measurements can be used to identify the dominating clay minerals in the soils and even approximate quantification of dominating clay minerals. Currently clay mineral quantification using elemental information has only been explored. However, there are other properties of soils that can be used to approximate the clay mineral information.

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In this research a new model was developed using few such properties. Those chemical properties of the soils which can be used to assess the dominating clay mineral are described in the following sections.

2.4.1 Cation Exchange Capacity (CEC)

The cation exchange capacity (CEC) of a soil is simply a measure of the quantity of readily exchangeable cations neutralizing negative charge in the soil. According to Camberato (2001), CEC refers to the quantity of negative charges in soil existing on the surfaces of clay and organic matter. The positively charged ions or cations are attracted by negative charges, hence the name 'cation exchange capacity'. Soil CEC is normally expressed in units of charge per weight of soil. Two different, but numerically equivalent sets of units are used: meq/100 g (milliequivalents of charge per 100 g of dry soil) or $cmol_c$/kg (centimoles of charge per kilogram of dry soil). CEC is a good indicator of soil reactivity with the chemical species.

The negative charges in the soil are obtained from the following sources and reactions (Rhoades, 1982):

(a)   Isomorphous substitution within the structures of layer silicate minerals

(b)   Broken bonds at mineral edges and external surfaces

(c)   Dissociation of acidic functional groups in organic compounds

(d)   The preferential adsorption of certain ions on the particle surfaces.

The first of these charges is permanent and is independent of pH and the rest are dependent on pH. CEC is not independent of the conditions under which it is measured hence it is necessary to measure the soils capacity to adsorb cations from an aqueous solution of the same pH, ionic strength, dielectric constant and composition as that encountered in field.

There are numerous methods for determining CEC and many will give quite different results. As given by Rhoades (1982), the following four methods can be used for CEC determination. Summation method: The exchangeable cations are displaced with a saturating salt solution and the CEC is taken as an equivalent sum of exchangeable cations present in the reacted "leachate". Direct Displacement method: In this method the soil is saturated with an index

cation and the adsorbed cation and the small amount of solution entrained by soil after centrifuging are displaced directly with another salt solution without further treat of the soil. The saturating cation and anion are then determined in the resulting extract, and their difference is taken as equal to the CEC of the soil.

Displacement after washing method: After the exchange sites have been saturated with an index cation in the above type of process, the soil can be washed free of excess saturating salt. The amount of index cation adsorbed by the soil can then be displaced and determined.

Radioactive tracer method: In this method, after saturating the soil CEC with a known index cation, the saturating solution can be diluted and labeled with a radioactive isotope of the saturating cation. The concentration of the index cation in the solution is then determined, and the distribution of the isotope (and hence of the total cation) between the two phases is given by measuring the radiation in the solution and the soil plus solution. There is a significant variation in the results obtained by the above four methods as there are many complicating interactions between saturating, washing, and extracting solutions. Also, CEC is not an independent and a single valued soil property (Rhoades, 1982).

Camberato (2001) says the primary factor determining CEC is the clay and organic matter content of the soil. Higher quantities of clay and organic matter beget higher CEC. Different types of clays have different CECs. Stewart and Hossner (2001) reported unusually high cation exchange capacity (CEC) values relative to clay content for lignite overburden and mine soils. On an average, the CEC values are found to be greater than 100meq/gm. A comparison of methods for particle-size distribution suggests that the major reason lignite overburden samples have CEC to percent clay ratios greater than one is due to incomplete dispersion of aggregates of clay minerals or shale fragments. Another important factor influencing the CEC to percent clay ratio was the presence of organic materials in the samples. Lignite may make a significant contribution to CEC in overburden materials.

2.4.2 Specific Surface Area (SSA)

The specific surface area of a soil sample is the total surface area contained in a unit mass of soil. Soils with high specific surface areas have high water holding capacities, more adsorption of contaminants, and greater swell potentials. Specific surface is therefore an important parameter. Specific surface is closely tied to particle size distribution. This phenomenon is explained by Campbell (2005) with a simple thought experiment in which a 1 cm^3 cube with a density 1 gm/cm^3 is considered. This cube has a specific surface area of 6 cm^2/g. Now, if this cube is divided into smaller cubes of 1 mm on the side, the resulting 1000 cubes would have the same mass of material, but its specific surface area will be 60 cm^2/g, similarly if the cube were to be divided into 10^{12} cubes of 1 um on a side, the surface area would be 6 x 10^4cm^2/g hence it could be understood that within the same mass, presence of smaller particles will result in higher specific surface area. It should be noted here that a soil with high specific surface area has high water holding capacity and greater swell potential.

Various approaches have been used to measure specific surface area, including adsorption of nitrogen and other gases on the soil (Yukselen and Kaya, 2006). The most commonly used method uses the adsorption of ethylene glycol monoethyl ether (EGME) (Carter et al. 1986). This involves saturating prepared soil samples, equilibrating them in a vacuum over a CaCl$_2$-EGME solvate, and weighing to find the point when equilibrium is reached. The specific surface is then determined from the mass of retained EGME in comparison to the amount retained by pure montmorillonite clay, which is assumed to have a surface area of 810 m^2/gm (Carter et al. 1986). The measurement typically takes around two days to complete. Soil is typically in a hydrated state, and surface area measurements should apply to that state. It would therefore be ideal if water could be used as the probe to determine the specific surface area.

Quirk (1955) reviewed such measurements and concluded that water clusters around cation sites, and can therefore lead to errors in the measurements. Recent work which uses more modern methods for measuring the energy state of the water in the soil, have shown promise as simple methods for determining specific surface of soil samples. A comprehensive

evaluation of the EGME method for geotechnical usage was done by Cerato and Lutenegger (2002). They concluded that the method is applicable to a wide range of mineralogies and is capable of determining specific surface area ranging from 15 to 800 m^2/g. They also indicated that the procedure is repeatable and gives reliable results.

2.4.3 Total Potassium

Potassium is an element which can be used to detect the presence of the mineral illite. Potassium belongs to the alkali metals in the periodic table that are characterized by a single electron in the outer most shell. This electron is easily lost and they readily form stable monovalent ions (Knudsen et al., 1982). There are many methods available for the determination of potassium in soils but the one proposed by Knudsen et al. (1982) is widely used. Potassium is the inter layer cation in the clay mineral illite and illite is the only clay mineral to have potassium in its structure (Mitchell and Soga, 2003). Hence measuring the amount of potassium ion in the soil gives a direct indication of the presence of the mineral illite. The test procedure formulated by Knudsen et al. (1984) was followed to obtain the amount of total potassium present in the soil. The method involves a double acid digestion technique developed by Jackson (1958) which uses two acids (Hydrofluoric acid and Perchloric acid) to break the mineral structure of the soil and extract the potassium ions from the structure. Once the potassium is extracted, its concentration in the solution can be obtained with the help of a spectrophotometer or any other suitable device. It should be noted here that the potassium measurement directly provides the percent Illite clay mineral in a given soil since illite is the only clay mineral to have potassium as an interlayer cation.

<u>2.5 Case Studies</u>

Different quantification methods can be used in combination to get accurate results about the amount of mineral present in the soil sample. Islam et al. (1986) discusses XRD and identifies it as the best quantification method available, but also acknowledges that most of the time major difficulties are encountered in the determination of the true relationship between XRD intensities and weight proportions of the minerals in soils and sediments. He goes on to discuss the process

used to derive the correct values of the constant $K_{p,q}$. This constant is used to correlate the peak intensity, obtained from XRD, to the mineral content of the soil.

The study considered four soils obtained from different regions of Bangladesh and used a combination of XRD, CEC and selective dissolution techniques to obtain the mineral content of the soils. The different regions studies are shown in Figure 2.14.
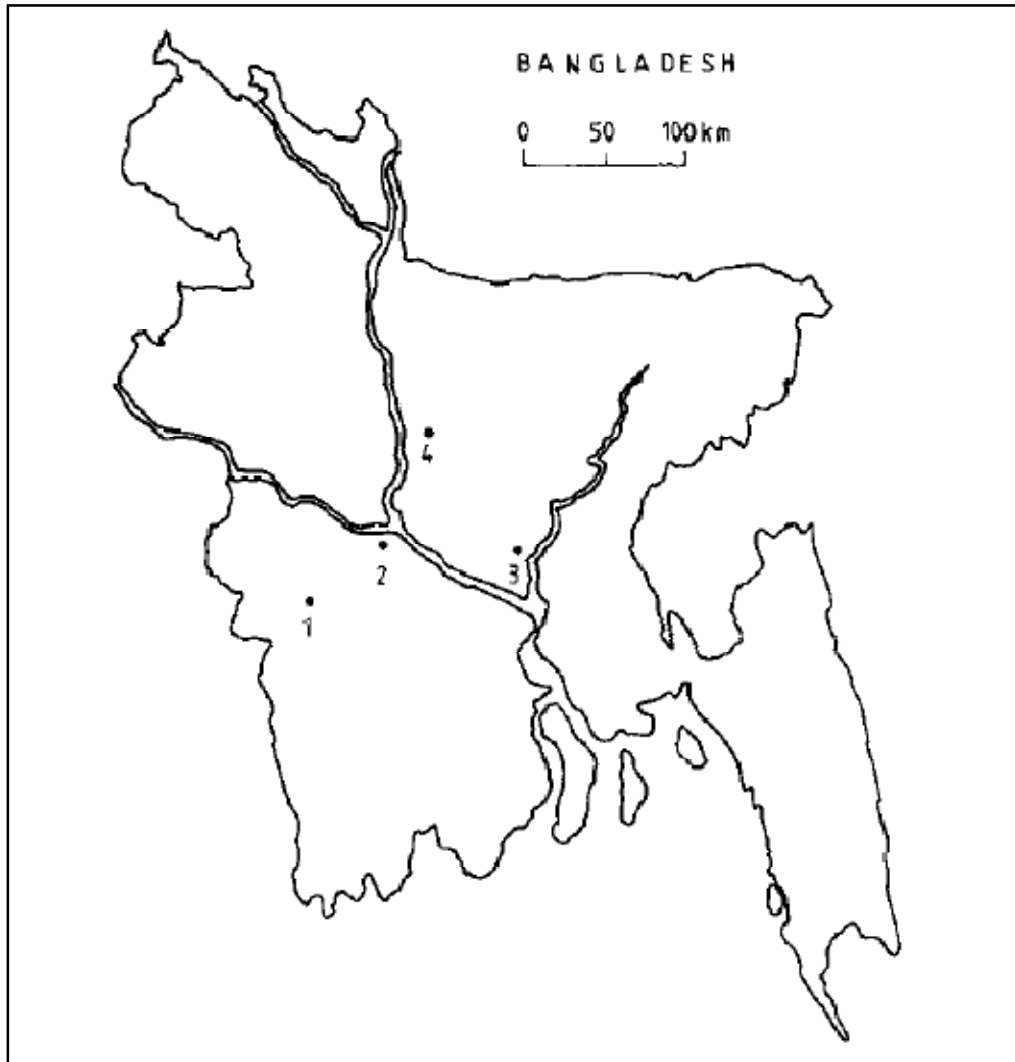
Figure 2-14 Map of Bangladesh showing approximate locations of the sampling sites. 1.Batra; 2. Ghior 3. Naraibag; 4. Ghatail. (Islam et al, 1986)

The mineral contents of the soils were found by using a combination of XRD and chemical analyses methods, namely Cation Exchange Capacity and Selective Dissolution

methods. The details of the test and the chemical analyses used are described very briefly in the following section. A more detailed description can be found in the original paper.

The soils were treated with 1N NaOAc (pH 5) and H_2O_2, and then treated with 1N NaOAc (pH7) and Ni-dithionite. After complete dispersion in distilled water, the samples were centrifuged to obtain three different size fractions. These size fractions were saturated with Mg^{2+}, K^+. The Mg^{2+} saturated fractions were x-rayed in the air dried and glycol solvated states and the K^+ saturated ones were X-rayed after air drying and heating to 300 and 550^0C for 2 h (Islam et al, 1986)

Alexiades and Jacksons' technique of selective dissolution was used to quantify mica, quartz and feldspar and ion exchange analyses were used to quantify vermiculites and smectites. For the determination of mica, quartz and feldspars, the samples were treated with $Na_2S_2O_7$ to decompose mica and other layer-silicates (smectite, vermiculite, kaolinite, and chlorite). The layer-silicate relics were dissolved by washing with 3 N HCl and then boiled with 0.5 N NaOH for 2.5 min, leaving quartz and feldspar in the residue. The residue was further treated with $HF-HClO_4$ and 6 N HCl to determine K, Na and Ca of feldspars. It was concluded that mica was the dominant mineral in 10 out of the 12 samples. In addition, Batra and Ghior soils have smectite as the dominant mineral. It was observed that for some samples, mineral contents predicted using XRD gave a lower number when compared to the amount predicted using chemical analyses. This was thought to be caused by the treatment used for the XRD preparation.

From this paper, it can be concluded that although X-ray diffraction can be used for quantification, results are more accurate when chemical analyses are used in addition to XRD. The mineral contents obtained by using a combination of XRD, CEC and SDA are summarized in Figure 2-15.

Soil series	Depth cm	Size fraction μm	Methods applied	Mi	Sm	V	V-H	K	Ch	Mi-Ch	F	Q	Amor	Sum
													%	
Batra	0–15	<0·2	CEC/SDA	24	42	10	n.d.	7	n.d.	n.d.	0	0	7	107
			X-ray	24	48	8	6	2	3	8	0	0	n.d.	
		2–0·2	CEC/SDA	46	2	5	n.d.	11	n.d.	n.d.	10	14	4	110
			X-ray	40	1	6	5	12	6	7	11	12	n.d.	
		20–2	CEC/SDA	37	0	1	n.d.	4	n.d.	n.d.	21	35	2	110
			X-ray	38	0	2	4	3	5	1	15	33	n.d.	
Naraibag	15–24	<0·2	CEC/SDA	34	11	6	n.d.	33	n.d.	n.d.	0	0	10	108
			X-ray	34	9	5	7	37	2	5	0	0	n.d.	
		2–0·2	CEC/SDA	37	0	9	n.d.	10	n.d.	n.d.	14	11	5	101
			X-ray	37	0	7	5	9	5	5	19	12	n.d.	
		20–2	CEC/SDA	32	0	3	n.d.	9	n.d.	n.d.	19	37	3	117
			X-ray	30	0	2	5	9	5	4	16	30	n.d.	
Ghior	0–8	<0·2	CEC/SDA	26	38	15	n.d.	7	n.d.	n.d.	0	0	8	111
			X-ray	26	41	15	7	3	3	7	0	0	n.d.	
		2–0·2	CEC/SDA	49	3	12	n.d.	9	n.d.	n.d.	11	12	3	108
			X-ray	42	0	11	2	10	5	2	13	15	n.d.	
		20–2	CEC/SDA	38	0	3	n.d.	6	n.d.	n.d.	18	40	1	115
			X-ray	35	0	3	3	7	3	3	12	35	n.d.	
Ghatail	12–30	<0·2	CEC/SDA	35	7	10	n.d.	18	n.d.	n.d.	0	0	11	108
			X-ray	35	7	6	19	26	2	6	0	0	n.d.	
		2–0·2	CEC/SDA	38	0	11	n.d.	21	n.d.	n.d.	7	9	4	105
			X-ray	41	0	9	7	25	3	5	6	4	n.d.	
		20–2	CEC/SDA	31	0	4	n.d.	6	n.d.	n.d.	22	35	2	117
			X-ray	25	0	5	6	6	5	6	17	31	n.d.	

n.d. = not determined

Figure 2-15 Mineral content of the four soils (Islam et al., 1986)

Many researchers (Engler et al., 1987; Ouhadi et al 2003) have discussed the benefits of using chemical analyses in addition to XRD to quantify clay minerals. A lot of problems can arise if the mineral content of the soil is not carefully identified and quantified. Wang et al. (2004) discusses the benefits of knowing the mineral content of the soil before designing a stabilization process.

Etringite, or calcium sulfoaluminate, formation in sulphate rich soils leads to swelling of the soil. Wang et al., (2004) discusses the minerals that promote etringite formation. When soils containing kaolinite and montmorillonite are stabilized with lime, etringite forms due to the presence of aluminum in the mineral structures. The paper discusses a case where a road heaved in just a few days after being stabilized with type I cement. Upon investigation, it was

found that the heaving was caused by the minerals in the soil which caused etringite to form. Different techniques including x-ray diffraction, thermal analysis, differential scanning colorimetry, infrared spectroscopy, scanning electron microscopy and x-ray absorption near edge structure (XANES) were used to identify and quantify the sulphate and clay mineral content. Using thermogravimetric analyses it was found that there was about 7.8% gypsum in the soil, but for the same soil x-ray quantification indicated a value of about 12.9% (Wang et. al, 2004). After the gypsum was removed from the soil using acid dissolution, it was found that kaolinite was the dominant mineral when compared to illite and montmorillonite, and montmorillonite was found to have the lowest concentration in the soil.

Wand et al, (2004) recommends that better quantification methods be used to properly quantify the clay minerals. Multiple analytical techniques are needed for detailed and quantitative analyses of the sulfate and clay minerals in soils susceptible to sulfate attack (Wang et al, 2004). The issue of cost is also important because as the number of techniques needed to come up with an accurate quantification increases so does the cost.

<u>2.6 Summary</u>

This chapter serves as a review of the available literature on clay mineralogy, their identification and quantification. The different types of clay minerals usually found have been described briefly and several methods of identification have also been discussed. Some of the cost effective chemical analyses methods have also been explained. Furthermore two case studies have been discussed to provide perspective on the importance of clay mineral quantification.

CHAPTER 3

EXPERIMENT METHODOLOGY

3.1 Introduction

The dominant clay minerals that are found most frequently in expansive soils are montmorillonite and illite. Different methods have been discussed in the literature to quantify the amount of minerals present. These methods, although adequately accurate, require expensive equipments and trained analysts. Also, just using PI to determine the type of stabilizer required is not a reliable method because PI does not truly represent the behavior of the soil.

Three chemical properties of soil namely cation exchange capacity (CEC), specific surface area and total potassium are used for the determination of the dominating clay mineral (Chittori, 2008). The test procedures that can be used to determine these properties will be discussed and outlined in this chapter.

For this research 40 artificial samples and 4 natural soil samples were used to validate the authenticity of the test methods developed. The artificial samples consisted of mixtures of montmorillonite, illite and kaolinite only. The samples were mixed so that each had a different proportion of the minerals. The purpose of this is to figure out the actual behavior of the minerals without the influence of external factors. A detailed description of each method is given in this chapter along with how the results can be used to determine the mineral content of the sample.

3.2 Test Methods

The three chemical properties that are used to determine the mineral content are:

1. Cation Exchange Capacity (CEC)

2. Specific Surface Area (SSA)

3. Total Potassium (TP)

3.2.1 Cation Exchange Capacity (CEC)

The Cation Exchange Capacity (CEC) of a soil can be defined as the capacity or the ability of the soil to exchange free cations that are available in the exchange locations. Montmorillonite is the most problematic mineral present in soils, from a geotechnical engineering perspective, since the presence of this mineral leads to water retention and hence expansive soils. If the results from a CEC test have a high value, it is an indication of a high amount of montmorillonite and therefore suggests that the soil is an expansive soil. Likewise, a low CEC value indicates the presence of kaolinite or illite, both of which are not expansive in nature.

One of the earliest methods and the most commonly used method, for determining the CEC of a soil was proposed by Chapman in 1965 and this is the method that is used for CEC determination. A saturating solution is added to the sample and then an extracting solution is used to remove the adsorbed cations. The saturating solution used for this research is ammonium acetate (NH_4OAc) at pH 7 and the extracting solution used is potassium chloride (KCl). When using natural soil samples, the soil has to be treated for organics using 30% Hydrogen Peroxide (H_2O_2).

After the treatment, 125 ml of ammonium acetate (NH_4OAc) is added to a 25g sample, shaken for half an hour and set aside for 16 hours. This is done to ensure that all the exchange locations are occupied by ammonium ions (NH_4^+). The solution is filtered using a Buchner Funnel, while applying a light vacuum, and washed with 5 separate 25ml additions of NH_4OAc. This is done to filter out all the cations replaced by the NH_4^+. Any excess NH_4OAc is washed out by 8 separate 10ml additions of 2-propanol. This step ensures that any excess ammonium ion is washed out. The leachate is discarded. Now the sample is washed with 8 separate 25ml additions of 1 molar potassium chloride solution. The potassium ions substitute the ammonium ions and these are leached out into the solution. The amount of ammonium ions can be determined by using a spectrophotometer. Therefore, the concentration of ammonium ions in the KCl extract gives the CEC of the sample. The steps followed to determine the CEC are given in figures 3.1 and 3.2.

33

```
                    ┌──────────────┐
                    │    Start     │
                    └──────┬───────┘
                           │
                           ▼
              ┌──────────────────────────┐
              │ Take 25.0 g of soil in a 500 │
              │         mL flask          │
              └────────────┬─────────────┘
                           │
                           ▼
              ┌──────────────────────────┐
              │ Add 125 mL of the 1 M NH4OAc │
              │   (shake thoroughly, and allow to │
              │   stand 16 hours (or overnight)) │
              └────────────┬─────────────┘
                           │
                           ▼
              ┌──────────────────────────┐
              │ Transfer the soil into another beaker using a 5.5 │
              │ cm Buchner funnel with retentive filter paper │
              │ applying light suction. If the filtrate is not clear, │
              │        refilter through the soil │
              └────────────┬─────────────┘
                           │
                           ▼
              ┌──────────────────────────┐
              │ Now, wash the soil four times with 25 mL additions │
              │   of the NH4OAc, allowing each addition to filter │
              │   through, but not allowing the soil to crack or dry. │
              └────────────┬─────────────┘
                           │
                           ▼
              ┌──────────────────────────┐
              │ Wash the soil with eight separate additions of 95% 2- │
              │            Propanol        │
              └────────────┬─────────────┘
                           │
                           ▼
              ┌──────────────────────────┐
              │ Leach the soil with eight separate 25 mL additions of 1 M │
              │ KCl, discard the soil and transfer the leachate to a 250 mL │
              │ volumetric flask. Dilute to volume with additional KCl. │
              └────────────┬─────────────┘
                           │
                           ▼
              ┌──────────────────────────┐
              │ Determine the amount of NH4 in │
              │   the solution by using the │
              │        spectrometer       │
              └──────────────────────────┘
```

Figure 3-1 Flowchart of procedure to determine CEC

Soil sample saturated with NH₄OAc

25 mL 1 M NH₄OAc additions

25 mL Ethanol additions

25mL 1 M KCl additions

Spectrophotometer

Colorimetric determination of ammonia concentration
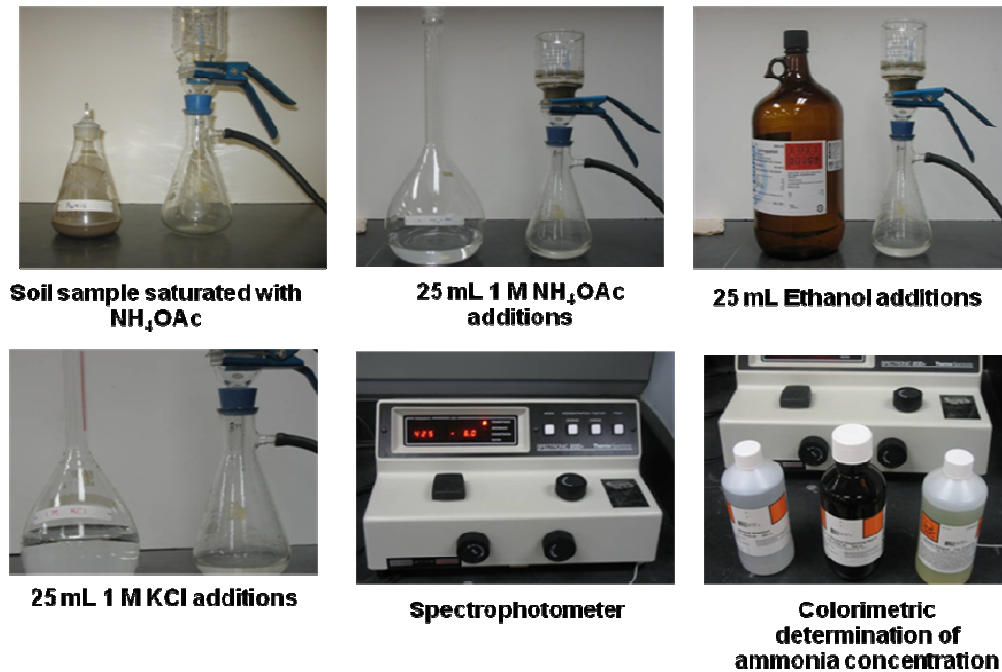
Figure 3-2 Photographs illustrating the various steps to determine CEC

3.2.2 Specific Surface Area (SSA)

The specific surface area of a soil can be defined as the total surface area per unit mass of sample. The SSA is dependent on the particle size of the sample. Smaller particles tend to have a high SSA. This indicates that they have more surface area available for adsorption and hence can retain more moisture. Soils rich in montmorillonite or expansive soils usually have a high SSA.

In agronomy, adsorption of Ethylene Glycol Monoethyl ether (EGME) is the most commonly used procedure. The sample is saturated with 3 ml of EGME and then placed in a dessicator over a $CaCl_2$ – EGME solvate. A vacuum is applied and then the samples are weighed every 2 hours to find the point when equilibrium is reached. Specific surface is then determined from the mass of retained EGME in comparison to the amount retained by pure montmorillonite clay, which is assumed to have a surface area of 810 m^2/g (Carter et al. 1986). It usually takes two to three days for the samples to reach equilibrium. Cerrato and Lutenegger evaluated the method in 2002 and determined it to be viable for use in geotechnical investigations. They determined that the procedure is applicable for a wide variety of soil minerals, since SSA can

measure values ranging from 15 to 800 m^2/g. They also determined that the test procedure is repeatable and gives reliable results. The steps used to determine the SSA by EGME saturation are explained in figures 3.3 and 3.4.

```
                    ┌──────────┐
                    │  Start   │
                    └────┬─────┘
                         ▼
            ┌─────────────────────────────┐
            │   Weigh 1.1 g of treated soil │
            │   into a tared aluminum can   │
            └──────────────┬──────────────┘
                           ▼
            ┌─────────────────────────────┐
            │ Dry the sample in oven at 100 – │
            │      110°C for 24 hrs           │
            └──────────────┬──────────────┘
                           ▼
            ┌─────────────────────────────┐
            │ Weigh the dried sample taking care │
            │ not to adsorb atmospheric water.   │
            └──────────────┬──────────────┘
                           ▼
            ┌─────────────────────────────┐
            │  Add 3 mL of EGME to make slurry  │
            └──────────────┬──────────────┘
                           ▼
            ┌─────────────────────────────┐
            │ Place the can with slurry in the chamber │
            │ containing CaCl₂-EGME solvate over a     │
            │ hardware cloth                           │
            └──────────────┬──────────────┘
                           ▼
            ┌─────────────────────────────┐
            │ Close the lid of the chamber and place it │
            │ in desiccator containing CaCl₂            │
            └──────────────┬──────────────┘
                           ▼
            ┌─────────────────────────────┐
            │ Wait for 30 minutes and evacuate for 45 │
            │ minutes and close the stopcock. After 6 to 7 │
            │ hours, release vacuum                        │
            └──────────────┬──────────────┘
                           ▼
            ┌─────────────────────────────┐
            │ Now weigh the soil sample in the can with the lid of the aluminum │
            │ can. Repeat weight measurements for every 2 to 4 hours of        │
            │ evacuating until there is no further decrease in the weight (Wa)  │
            └─────────────────────────────┘
```

Start

Weigh 1.1 g of treated soil into a tared aluminum can

Dry the sample in oven at 100 – 110°C for 24 hrs

Weigh the dried sample taking care not to adsorb atmospheric water.

Add 3 mL of EGME to make slurry

Place the can with slurry in the chamber containing $CaCl_2$-EGME solvate over a hardware cloth

Close the lid of the chamber and place it in desiccator containing $CaCl_2$

Wait for 30 minutes and evacuate for 45 minutes and close the stopcock. After 6 to 7 hours, release vacuum

Now weigh the soil sample in the can with the lid of the aluminum can. Repeat weight measurements for every 2 to 4 hours of evacuating until there is no further decrease in the weight (W_a)

Figure 3-3 Flow chart of SSA procedure

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Dried soil sample	Addition of 3 mL of EGME	Desiccator containing CaCl$_2$
Desiccator containing CaCl$_2$-EGME Solvate over CaCl$_2$	EGME mixed soil sample placed in the desiccator placed	Apply vacuum to the desiccator
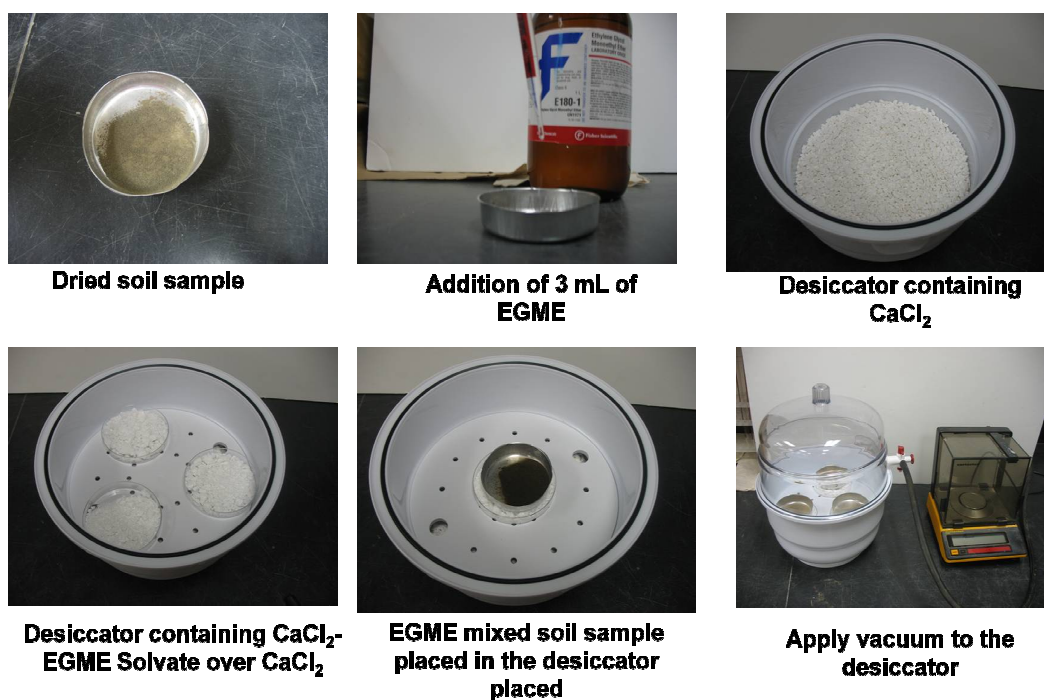
Figure 3-4 Photographs illustrating the various steps of SSA determination

3.2.3 Total Potassium (TP)

Illite is the only clay mineral, among the dominant clay minerals, that has potassium as an interlayer cation. Measuring the potassium content in a soil give a direct indication of how much illite is present in the soil. The procedure developed by Knudsen et al. (1984) has been followed to determine the amount of potassium ion present in the soil. This method utilizes a double acid digestion procedure developed by Jackson 1958. The two acids are hydrofluoric and perchloric acid, which break up the mineral structure and hence extract the potassium ion from the soil. The concentration of the potassium ion can be easily measured by a spectrophotometer.

A 0.1000 g sample of the soil is taken in a Teflon container. The original procedure recommends the use of a platinum vessel for the experiment, since hydrofluoric acid dissolves silica (the main component of glass vessels). Since platinum vessels are very expensive, they are not feasible for the experiment. Teflon vessels, on the other hand, are relatively cheaper, resistant to hydrofluoric acid and can withstand temperatures of about 200^{0}C.

5 ml of hydrofluoric acid and 0.5 ml of perchloric acid are added to the sample. The mixture is placed on a hot plate and heated to 200^{0}C. In this process dissolves the silicate

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mineral structure is dissolved by hydrofluoric acid, releasing the interlayer cations and the organic matter in the sample is oxidized by the perchloric acid. After heating up to 200^0C, the vessel is cooled and another 5 ml of hydrofluoric acid followed by another addition of perchloric acid is added. The solution is now heated until it is dry. This step is done to ensure that all the cations have been released and all the organic matter dissolved. The final step is the addition of 5 ml of 6N Hydrochloric acid and heating up the mixture until it boils. The solution can now be used to determine the amount of potassium ions present, using a spectrophotometer. The steps used to determine total potassium are described and illustrated in figures 3.5 and 3.6.

The results obtained from the above tests are explained in Chap 4

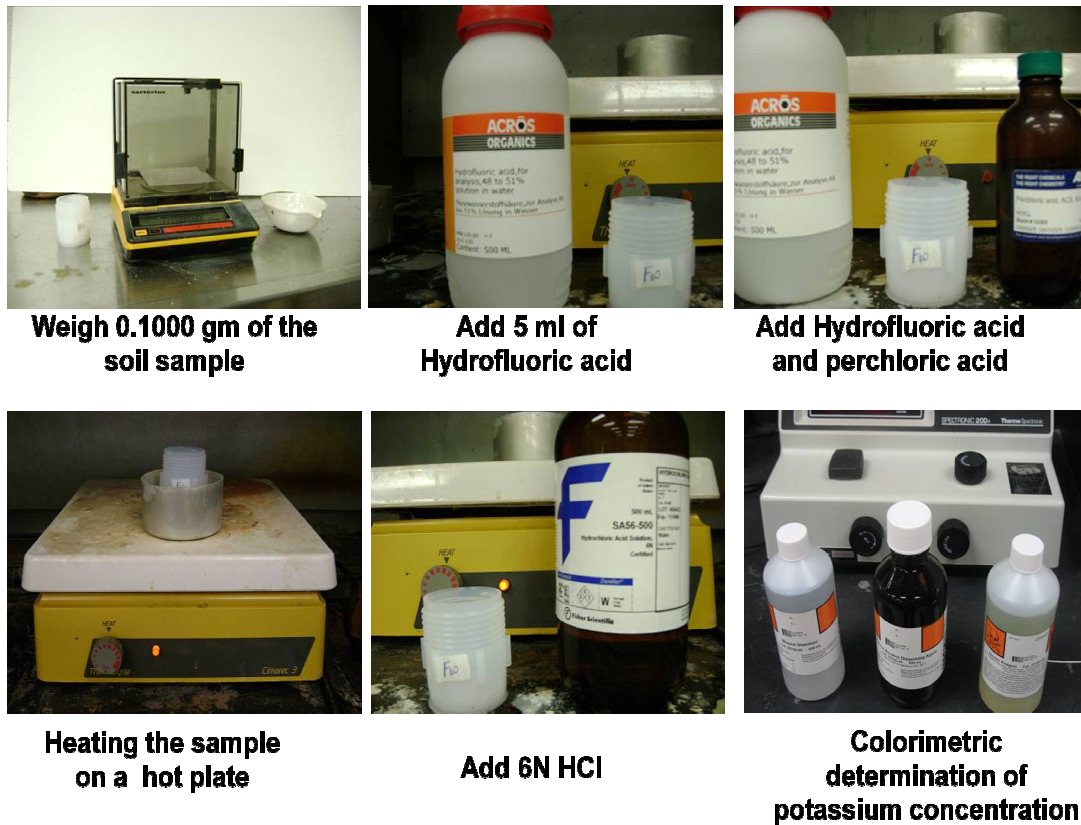| Weigh 0.1000 gm of the soil sample | Add 5 ml of Hydrofluoric acid | Add Hydrofluoric acid and perchloric acid |
| Heating the sample on a hot plate | Add 6N HCl | Colorimetric determination of potassium concentration |

Figure 3-5 Photographs illustrating the various steps of Total Potassium determination

```
                              ┌─────────┐
                              │  Start  │
                              └─────────┘
                                   │
                                   ▼
                    ┌────────────────────────────────┐
                    │ Take 0.1000 g of finely ground │
                    │ soil in a 60 ml Teflon         │
                    │ digestion vessel               │
                    └────────────────────────────────┘
                                   │
                                   ▼
                    ┌────────────────────────────────┐
                    │ Wet the soil with few drops of │
                    │ water and then add 5 ml of HF  │
                    │ and 0.5ml of HClO4 to the      │
                    │ vessel                         │
                    └────────────────────────────────┘
                                   │
                                   ▼
                    ┌────────────────────────────────┐
                    │ Heat the soil-acid mixture on  │
                    │ hot plate until fumes of HCLO4 │
                    │ appear or heat till the        │
                    │ temperature in more than 200°C │
                    └────────────────────────────────┘
                                   │
                                   ▼
                    ┌────────────────────────────────┐
                    │ Cool the vessel and then add   │
                    │ 5 ml of HF. Place the vessel   │
                    │ on a hot plate and cover nine  │
                    │ tenths of the vessel top using │
                    │ the ported closure             │
                    └────────────────────────────────┘
                                   │
                                   ▼
                    ┌────────────────────────────────┐
                    │ Heat the crucible to 200-225°C │
                    │ and evaporate the solution to  │
                    │ dryness                        │
                    └────────────────────────────────┘
                                   │
                                   ▼
                    ┌────────────────────────────────┐
                    │ Again cool the crucible and    │
                    │ add 2 ml of water and few      │
                    │ drops of HClO4                 │
                    └────────────────────────────────┘
                                   │
                                   ▼
                    ┌────────────────────────────────┐
                    │ Replace the vessel on the hot  │
                    │ plate and evaporate to dryness │
                    └────────────────────────────────┘
                                   │
                                   ▼
                    ┌────────────────────────────────┐
                    │ Now remove the crucible from   │
                    │ the hot plate and when it is   │
                    │ cool, add 5 ml of 6N HCl and   │
                    │ 5 ml of water                  │
                    └────────────────────────────────┘
                                   │
                                   ▼
                    ┌────────────────────────────────┐
                    │ Place the vessel back on the   │
                    │ hot plate and boil it slightly.│
                    │ If the sample doesn't dissolve │
                    │ repeat the steps 2 through 9   │
                    └────────────────────────────────┘
```
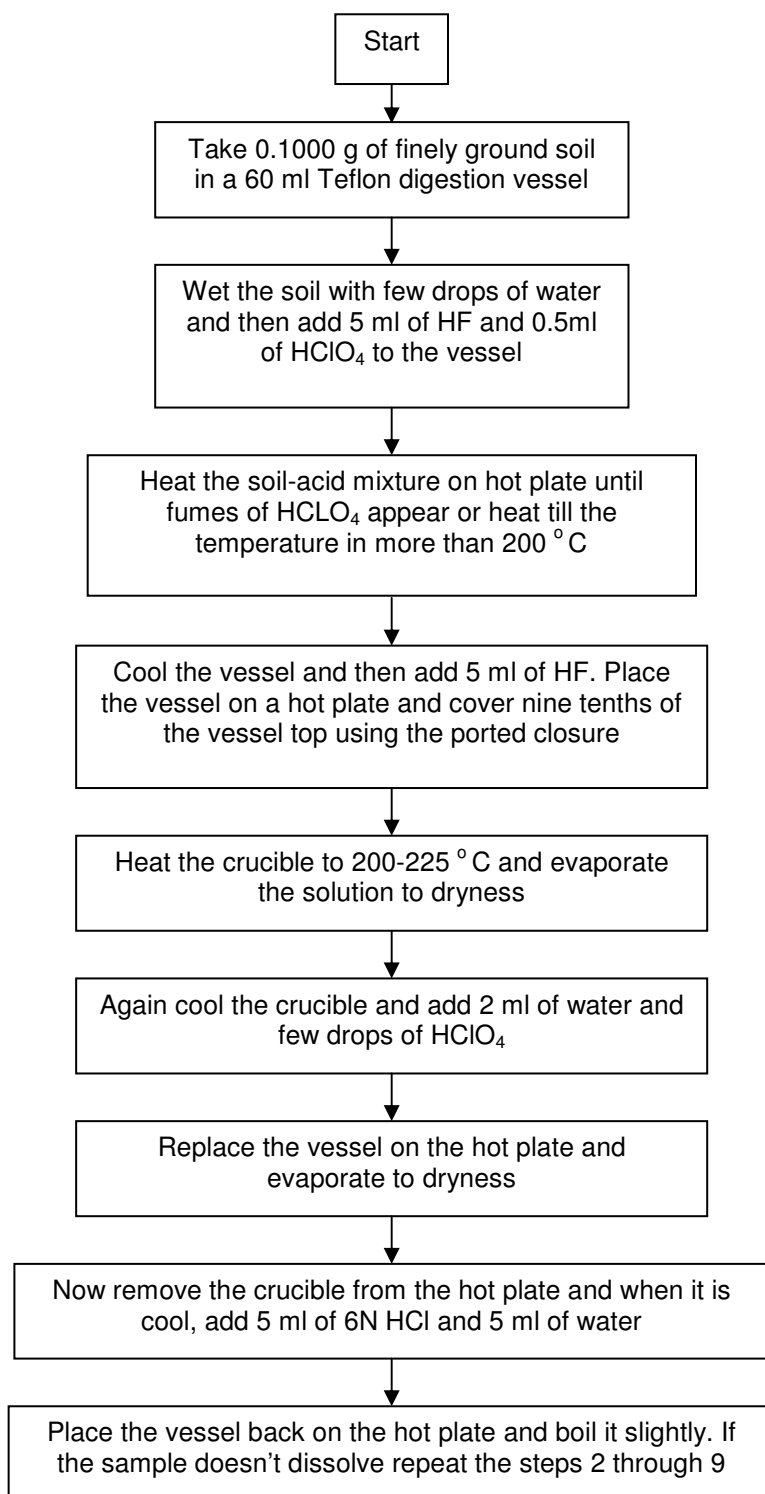
Figure 3-6 Steps to determine Total Potassium (TP)

3.3 Summary

This chapter provides a detailed description of the methodology used to quantify the dominant clay minerals – montmorillonite and illite. The results obtained from the described test have been used in the next chapter to predict the quantity of montmorillonite and illite present in the artificial mixtures.

CHAPTER 4

RESULTS AND ANALYSIS

4.1 Introduction

This chapter provides the results and analysis of the chemical and mineralogical methods that have been explained in the previous chapter. These results serve as a way of validating the methodology developed by Chittoori 2008. A total of 30 artificial mixtures were prepared. Cation Exchange Capacity (CEC), Specific Surface Area (SSA) and Total Potassium (TP) were performed on them to determine the percentage of illite and montmorillonite present in each sample. A statistical model, regression equations and an artificial neural network have been used to determine the percentage of minerals present in each sample. The 30 samples consisted only of the minerals illite and montmorillonite, along with traces of some other 1:1 minerals, mixed at different percentages.

4.2 Repeatability of Tests

As discussed in the previous chapter, several chemical methods – namely cation exchange capacity (CEC), specific surface area (SSA) and total potassium (TP) have been used to determine the mineral percentages of each sample. A very important task is to address the repeatability of the test. To ensure the consistency of the results, each test was performed thrice on three different soil samples. The results are presented in Table 4.1 and it can be observed that the standard deviations between the results are very low. This indicates that the tests have very good repeatability.

The test results obtained for all thirty soil samples are given in Table 4.2. These results have been obtained from the Cation Exchange Capacity (CEC), Total Potassium (TP) and Specific Surface Area (SSA) tests. Once these three properties are obtained, the clay minerals present in the soil can be quantified based on the assumption that each clay mineral in the

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sample contributes linearly to the content present. As mentioned earlier, a major assumption of this research, based on the XRD analysis, is that the fine fractions of the soil specimens contain Montmorillonite and Illite as the dominant minerals. The range of values obtained from the literature for pure minerals are given in Table 4.3

Table 4-1 Test Results to Show Repeatability of the Procedures

Soil Type : El Paso					
	Trial 1	Trial 2	Trial 3	Mean	SD
CEC, meq/ 100 gm	55.2	57.7	53.3	55.40	2.21
SSA, m^2/gm	158	164	161	161.00	3.00
TP, %	3.6	3.6	3.8	3.67	0.12
Soil Type : Paris					
	Trial 1	Trial 2	Trial 3	Mean	SD
CEC, meq/ 100 gm	130.1	133.9	135.4	133.13	2.73
SSA, m^2/gm	431	424	440	431.67	8.02
TP, %	0.77	0.79	0.78	0.78	0.01
Soil Type : Bryan					
	Trial 1	Trial 2	Trial 3	Mean	SD
CEC, meq/ 100 gm	77.4	79.1	75.2	77.23	1.96
SSA, m^2/gm	207	202	204.9	204.63	2.51
TP, %	1.37	1.4	1.32	1.36	0.04

Table 4-2 CEC, SSA and TP values of the soil samples

Soil No.	Sample	CEC meq/100gm	SSA m^2/gm	TP %
1	1	81.3	418	3.000
2	2	50.6	266	2.725
3	4	26.7	248	3.450
4	6	34.9	248	2.250
5	7	41.7	174	3.575
6	8	31.8	132	2.400
7	9	107.9	221	2.950
8	10	43.4	172	2.500
9	12	49.2	194	2.850
10	13	45.8	219	2.500
11	14	120.2	239	2.350
12	15	76.9	133	1.860
13	18	147.4	324	2.425
14	19	91.6	226	**1.950**
15	20	142.8	291	2.625
16	21	89.4	240	**2.200**
17	27	43.5	97	1.900
18	28	178.8	378	**1.275**
19	29	149.8	352	2.000
20	30	152.9	387	**1.350**
21	31	140.5	355	2.100
22	32	171.9	431	**1.350**
23	33	156.1	403	1.675
24	34	179.7	434	**1.650**
25	35	173.6	203	1.450
26	36	171.1	187	**1.325**
27	37	189.5	218	1.150
28	38	188.6	221	**1.275**
29	40	194.0	166	**1.500**
30	43	183.2	208	**1.225**
31	45	129.9	169	**1.650**

Table 4-3 Range values of SSA, CEC and TP for pure clay minerals

Mineral Type	CEC, meq/100 gm	SSA, m^2/gm	% Potassium
Illite	15 to 60	80 to125	6
Kaolinite	1 to 6	5 to 45	0
Montmorillonite	80 to160	850	0

4.3 Quantification Procedure

It can be seen from the literature that several methods are available for the quantification of clay minerals. Some of these methods rely on XRD peaks to quantify the amount of minerals present based on the intensity of the peaks. Other methods rely on the use chemical analyses to predict the quantity of minerals present. For the purpose of this research, the focus was given on chemical analysis to quantify the clay minerals present in the different samples.

The first method, developed by Chittori 2008, utilizes the solver function of Microsoft Excel. Using information from the literature available, the mineralogical compositions of different soils can be estimated using the following set of three simultaneous equations:

$$\%M \times CEC_M + \%K \times CEC_K + \%I \times CEC_I = \qquad CEC_{soil} \qquad (1)$$

$$\%M \times SSA_M + \%K \times SSA_K + \%I \times SSA_I = \qquad SSA_{soil} \qquad (2)$$

$$\%M \times TP_M + \%K \times TP_K + \%I \times TP_I \qquad = \qquad TP_{soil} \qquad (3)$$

Where,

%M, %K, %I are the percentages of the minerals Montmorillonite, Kaolinite, and Illite present in the soil sample;

CEC_M, CEC_K, CEC_I are the CEC values of the pure minerals Montmorillonite, Kaolinite, and Illite present in the soil sample, respectively;

SSA_M, SSA_K, SSA_I are the SSA values of the pure minerals Montmorillonite, Kaolinite, and Illite present in the soil sample, respectively;

TP_M, TP_K, TP_I are the TP values of the pure minerals Montmorillonite, Kaolinite, and Illite present in the soil sample, respectively;

CEC_{soil}, SSA_{soil}, TP_{soil} are the values of the properties CEC, SSA and TP of the soil samples.

4.3.1 Microsoft Solver Function

Solving the simultaneous equations is a very tedious task and the measured CEC and SSA values for the pure minerals do not remain constant, as only a range of values can be obtained from the literature. To solve this problem, a solution was developed by Chittoori 2008, using the *Solver* function of Microsoft Excel® program. *Solver* is part of a suite of commands sometimes called "what-if" analysis tools. Using this function an optimal value can be obtained for a formula in one cell, called the target cell in a worksheet, by adjusting the values in the cells, called changing cells, which can be specified to produce the result that is specified from the target cell formula. Constraints can be applied to the changing cells to restrict the values that *Solver* can use in the model to obtain the specified value for the target cell. A more detailed explanation on how the solver function works can be obtained in the help manual of MS Excel (2007).

The target cell is the absolute error defined as the difference between the measured CEC and SSA and the calculated CEC and SSA. Calculated CEC and SSA are defined as the CEC and SSA values that are obtained after substituting the acquired mineral percentages back in equations (1), (2) and (3). The changing cells are the CEC and SSA values of the pure minerals along with the percentages of the minerals illite, kaolinite and montmorillonite. Figure 4.1 shows a snapshot of the program.

Table 4.4 shows the original percentages of each mineral in the soil samples. Table 4.5 gives the predicted mineral percentages of all the twenty four soils obtained by solving the equations using the Microsoft Solver Function explained above. Since the procedure is iterative, it is important to check the values for the specific surface and cation exchange capacity by comparing with the original mineral percentages mixed in the artificial sample.

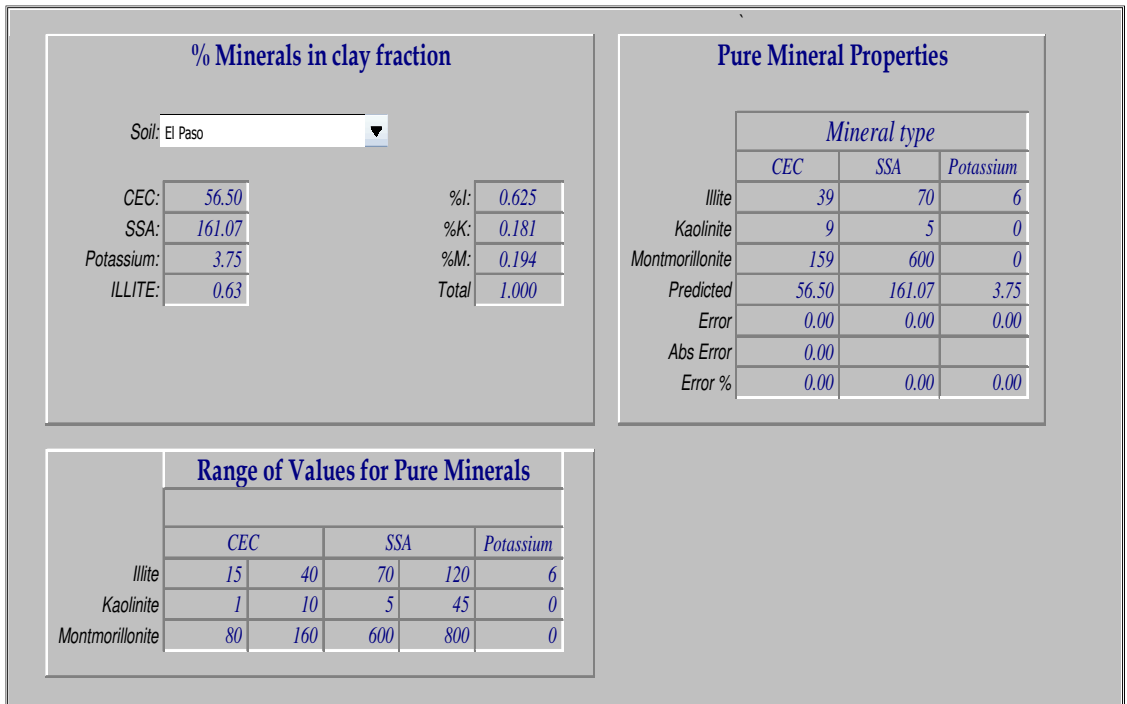Figures 4.2 and 4.3 show the comparison between the predicted values and the original values for each mineral.

% Minerals in clay fraction

Soil: El Paso ▼

CEC:	56.50	%I:	0.625
SSA:	161.07	%K:	0.181
Potassium:	3.75	%M:	0.194
ILLITE:	0.63	Total	1.000

Pure Mineral Properties

Mineral type			
	CEC	SSA	Potassium
Illite	39	70	6
Kaolinite	9	5	0
Montmorillonite	159	600	0
Predicted	56.50	161.07	3.75
Error	0.00	0.00	0.00
Abs Error	0.00		
Error %	0.00	0.00	0.00

Range of Values for Pure Minerals

	CEC		SSA		Potassium
Illite	15	40	70	120	6
Kaolinite	1	10	5	45	0
Montmorillonite	80	160	600	800	0

Figure 4-1 Snapshot of the Microsoft Excel® program used for the quantification of clay minerals.

Table 4-4 Original Percentages of Mineral in the Samples

Soil No.	Sample #	% Illite	% Montmorllonite
1	2	52.20	11.98
2	27	59.59	12.73
3	4	53.21	15.17
4	45	52.80	17.78
5	8	54.23	18.35
6	15	47.84	20.78
7	6	55.24	21.53
8	10	48.86	23.97
9	12	49.87	27.15
10	7	57.27	27.90
11	19	43.49	29.58
12	21	44.50	32.77
13	13	51.90	33.51
14	1	59.29	34.26
15	9	52.91	36.70
16	14	53.93	39.88
17	20	47.54	42.31
18	18	48.56	45.50
19	31	34.78	47.18
20	29	35.80	50.37
21	28	36.81	53.55
22	33	30.43	55.98
23	30	37.82	56.73
24	32	31.44	59.17
25	34	32.46	62.35
26	36	26.08	64.78
27	40	33.47	65.53
28	35	27.09	67.97
29	43	20.71	70.40
30	37	21.72	73.58

Table 4-5 Predicted Percentage of Minerals obtained Using Microsoft Excel® Solver

Soil No.	Sample	% Illite	% Montmorillonite
1	1	50	50
2	2	45.4	38.1
3	4	57.5	33.6
4	6	37.5	36.1
5	7	59.6	20.9
6	8	40	16.3
7	9	49.2	30.1
8	10	41.7	22.8
9	12	47.5	25.8
10	13	41.7	30.7
11	14	39.2	34.4
12	15	31	17.6
13	18	43.8	48.1
14	19	32.5	33
15	20	43.8	39.2
16	21	36.7	34.9
17	27	31.7	11.5
18	28	21.3	60
19	29	33.3	54.1
20	30	22.5	61.4
21	31	35	54.4
22	32	22.5	68.8
23	33	27.9	63.4
24	34	27.5	68.6
25	35	24.2	30.2
26	36	22.1	27.8
27	37	19.2	33.4
28	38	21.3	33.6
29	40	25	23.9
30	43	20.4	30
31	45	27.5	24.1
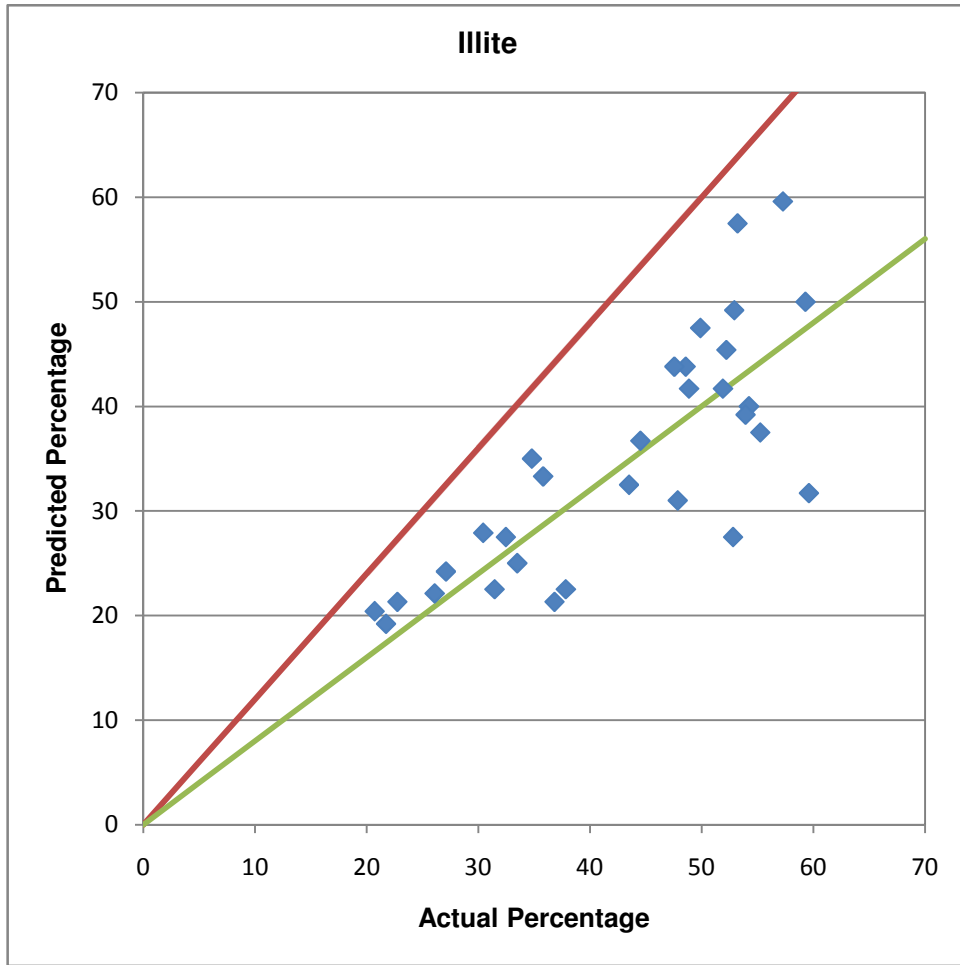
Figure 4-2 Comparison of Predicted Percentage Illite with Original Percentage
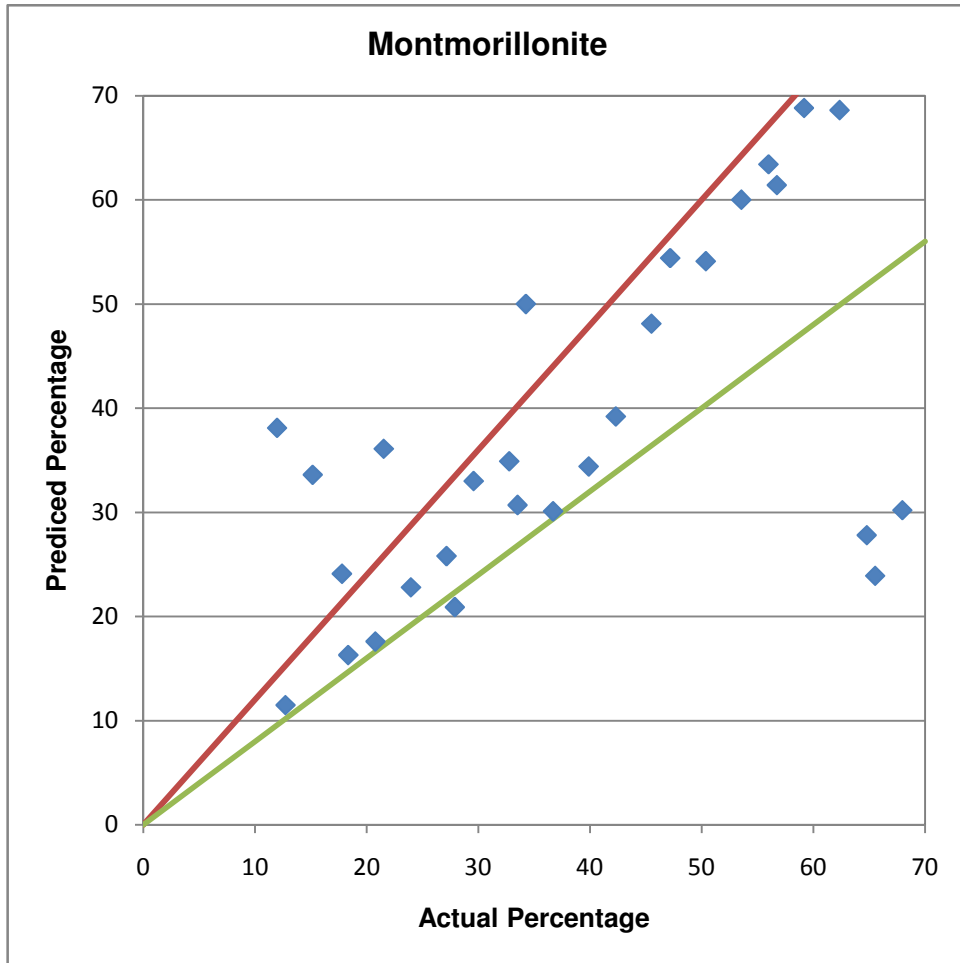
Figure 4-3 Comparison of Predicted Percentage Montmorillonite with Original Percentage

It can be observed from the graphs that the Microsoft Excel Solver program developed by Chittoori (2008) has yielded close predictions for both montmorillonite and illite contents. Most of the data for both minerals are within the $\pm$ 20 % range of the true percents. It can be observed that for high percentages of montmorillonite, the model was not accurate as three samples were under predicted by about 40% of the actual percentage. For illite percentage, the prediction was fair and most of the predicted data are again within the $\pm$20% range. It can be observed that only for a handful of artificial clay specimens, this method did not give a good correlation.

4.3.2 Regression Equations

As mentioned earlier, solving the simultaneous equations is a very tedious process and involves numerous iterations. In order to provide a simpler way to calculate the mineral percentages from the CEC, SSA, and TP values obtained, Chittoori 2008 developed a methodology to determine mineral quantity using regression equations. The following equations were recommended by Chittoori 2008.

$$\%I = \left[\frac{TP}{6} \right] \times 100$$

(4)

$$\%M = -2.87 + 0.08 \times SSA + 0.26 \times CEC$$

(5)

where,

%I = Percentage of the mineral illite

%M = Percentage of the mineral montmorillonite

TP = Total potassium

CEC = Cation exchange capacity

SSA = Specific surface area

Equation 4 can be used to determine the percentage of illite present in the soil based on the Total Potassium values of the soil. Equation 5 is the regression model developed by Chittoori 2008 to obtain the percentage montmorillonite in the soil and this equation considers two independent measurements, namely Specific Surface Area and Cation Exchange Capacity. The predictive performance of the multiple regression models is measured through the coefficient of determination (R^2). The coefficient of determination (R^2) for equation 2 was found to be 0.95, which indicated that the model can be used to give accurate predictions.

Table 4.6 gives the approximate mineral percentages of all the thirty soils obtained by solving the regression equations presented in this section.

Table 4-6 Percentage of Minerals obtained Using Regression Equations

Soil No.	Sample	% Illite	% Montmorillonite
1	1	50.00	51.70
2	2	45.42	31.53
3	4	57.50	23.88
4	6	37.50	26.02
5	7	59.58	21.87
6	8	40.00	15.96
7	9	49.17	42.86
8	10	41.67	22.18
9	12	47.50	25.45
10	13	41.67	26.59
11	14	39.17	47.49
12	15	31.00	27.78
13	18	40.42	61.35
14	19	32.50	39.05
15	20	43.75	57.55
16	21	36.67	39.55
17	27	31.67	16.17
18	28	21.25	73.86
19	29	33.33	64.20
20	30	22.50	67.85
21	31	35.00	62.08
22	32	22.50	76.27
23	33	27.92	69.98
24	34	27.50	78.60
25	35	24.17	58.51
26	36	22.08	56.53
27	37	19.17	63.86
28	38	21.25	63.81
29	40	25.00	60.83
30	43	20.42	61.37
31	45	27.50	44.45
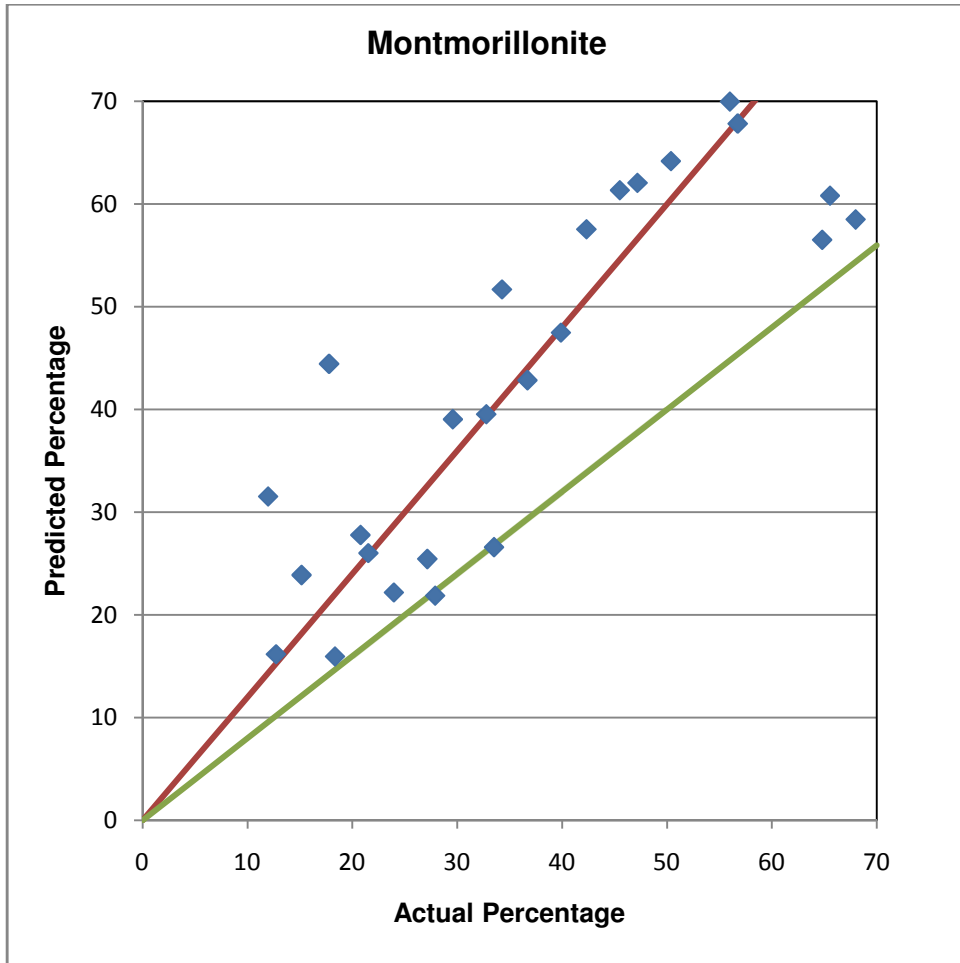
Figure 4-4 Comparison of Calculated Percentage Montmorillonite with Original Percentage
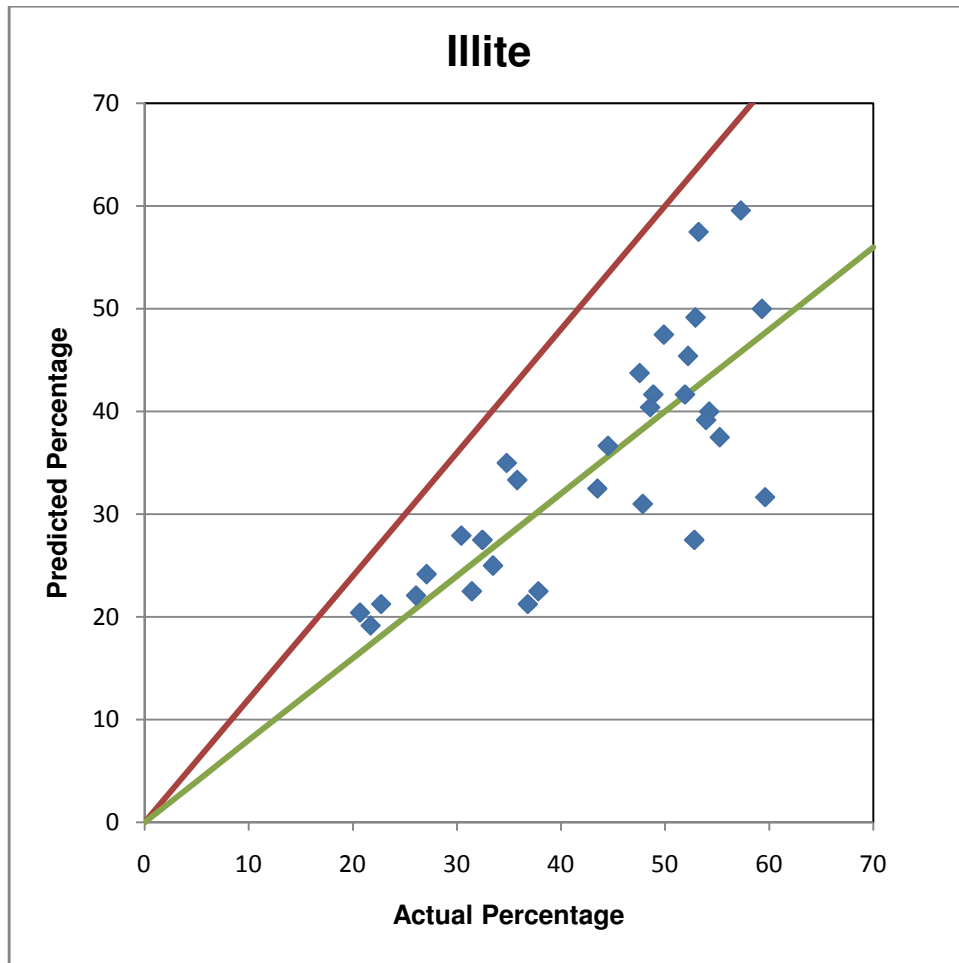
Figure 4-5 Comparison of Calculated Percentage Illite with Original Percentage

It can be observed from the graphs that the regression model equations, developed by Chittoori (2008) successfully predict most of the montmorillonite percentage, within a range of about ± 20%. This model also successfully predicts the high mineral percentages that the Microsoft Excel Solver model failed to predict accurately. That accurate prediction of high montmorillonite content is a very crucial part of the research, since montmorillonite is the mineral that causes the most drastic swelling and shrinking behavior in clays.

For illite, again most of the predictions are again within the ± 20% range with only a handful below the -20% range. Even though these are below the lower range, they are still close to it and not too scattered. The prediction of illite percentage, by both the Microsoft Solver Model and Regression Equation model, follow the same pattern since the equation used to calculate the

percentage is the same. Hence, it can be said that the regression model gives a fair prediction of montmorillonite and illite.

4.3.2 *Artificial Neural Network Model*

An **artificial neural network (ANN)**, also called a "neural network" (NN), is a mathematical model or computational model that is based on biological neural networks that exist in the structure of the human brain. It consists of an interconnected group of artificial neurons and processes information using a connectionist approach to the computation. ANN is an adaptive system that changes its structure based on external or internal information that flows through the network during the learning phase.

It is an emerging technique that has been applied to many geotechnical engineering applications successfully by many researchers (Shahin et al., 2001). Transportation Research Board (TRB) has summarized the state-of-the-art ANN applications in geotechnical engineering (E-C012, 1999). As stated earlier, neural networks aim to predict the relationship between the inputs and outputs. This can be achieved by repeatedly feeding the known examples of input/output relationships to the model and minimizing the error function defined between the measured and predicted outputs by the model. A more detailed explanation of the model used to quantify clay minerals has been developed by Chittoori 2008. The network architecture developed by Chittoori 2008 is shown in figure 4.6

The model that is used was trained by the data obtained by Chittoori 2008. The predicted mineral percentages using this model are given in Table 4.7
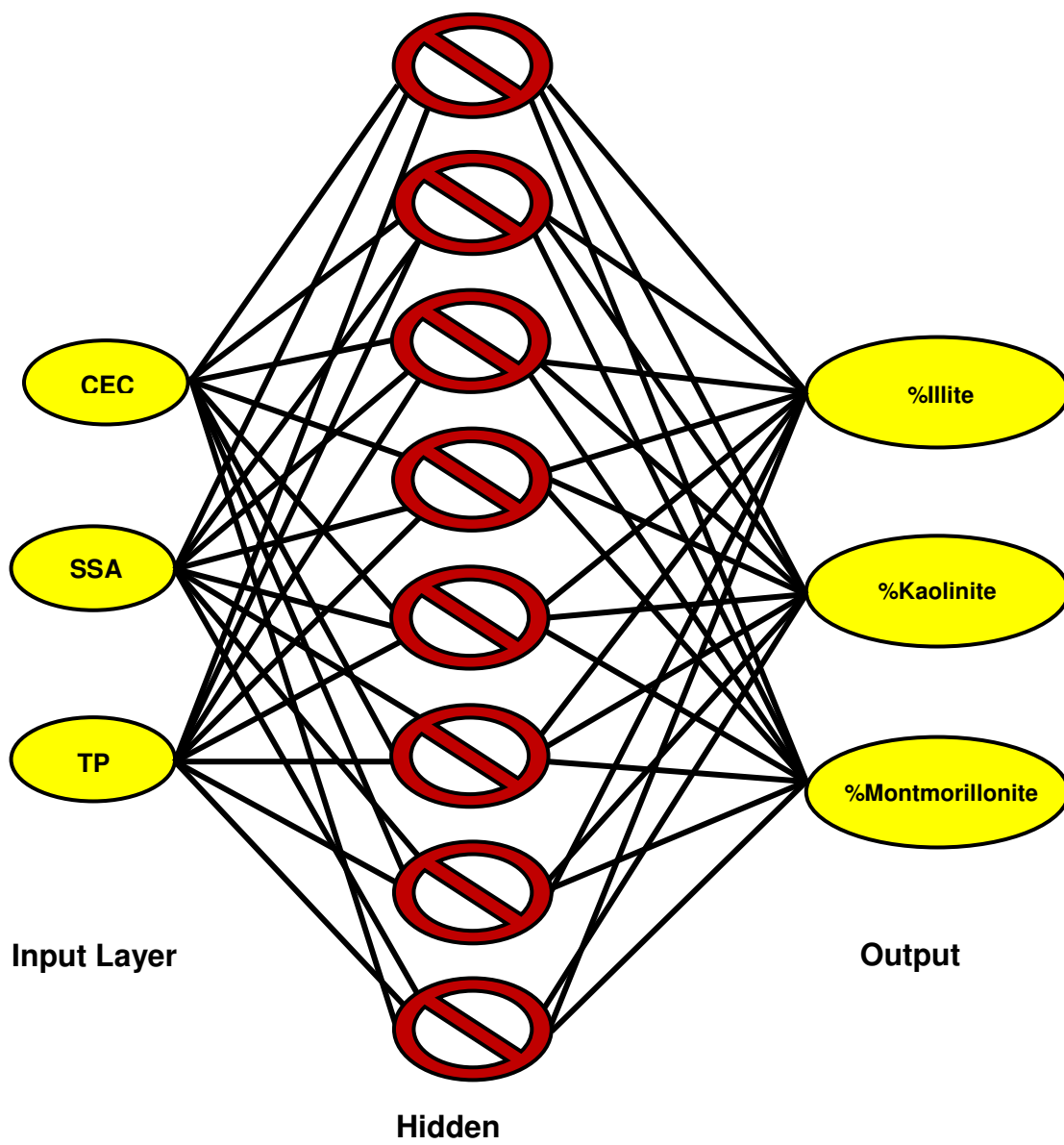
Figure 4-6 Neural Network Architecture (Chittoori 2008)

Table 4-7 Percentage of Minerals obtained Using Neural Network Analysis

Soil No.	Sample	% Illite	% Montmorillonite
1	1	61.35	68.92
2	2	58.37	41.66
3	4	65.18	36.90
4	6	49.62	41.98
5	7	65.65	24.51
6	8	51.27	24.94
7	9	59.13	28.13
8	10	53.58	27.88
9	12	59.65	28.88
10	13	54.17	34.40
11	14	45.29	32.90
12	15	32.61	23.56
13	18	46.39	47.28
14	19	35.93	34.33
15	20	51.42	39.99
16	21	43.81	35.76
17	27	35.68	22.57
18	28	18.13	59.42
19	29	34.44	54.52
20	30	20.07	62.95
21	31	38.27	55.51
22	32	19.89	66.86
23	33	26.45	63.73
24	34	25.03	65.41
25	35	19.57	30.31
26	36	18.05	28.90
27	37	16.10	34.26
28	38	17.26	33.87
29	40	19.53	25.17
30	43	16.84	32.34
31	45	24.45	25.79
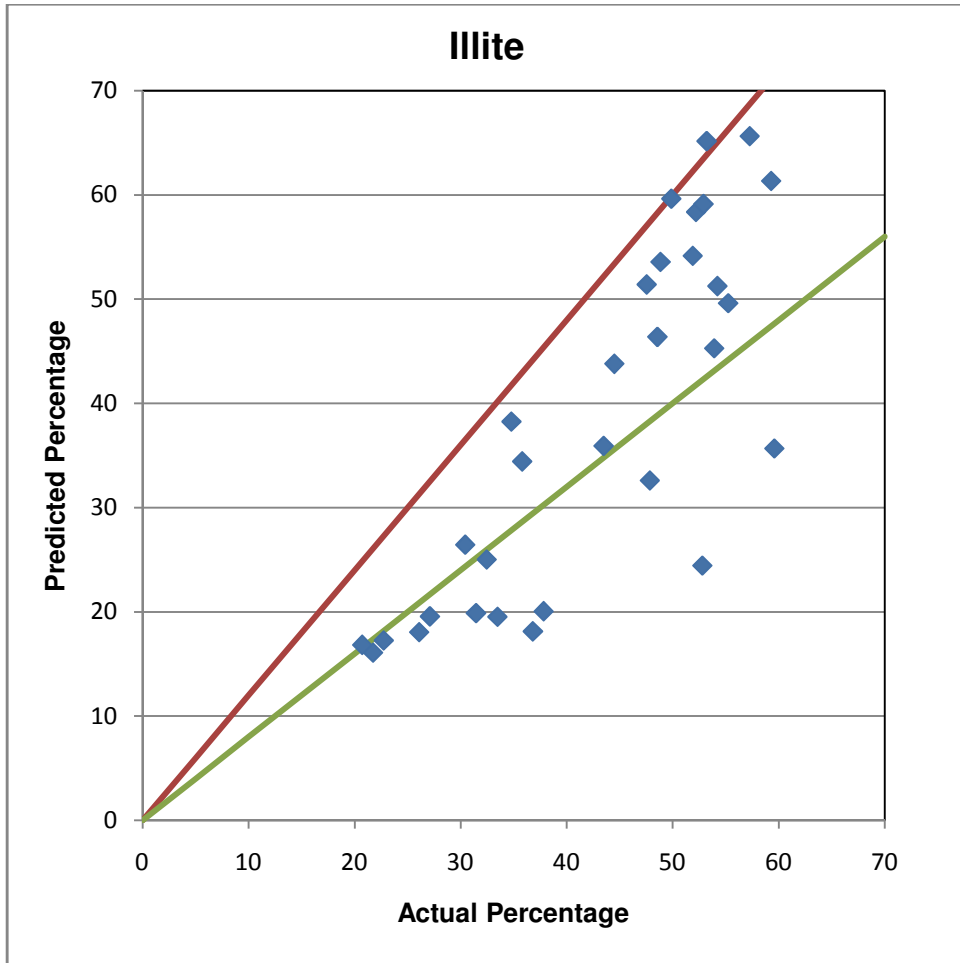
Figure 4-7 Comparison of Predicted Percentage Illite with Actual Percentage
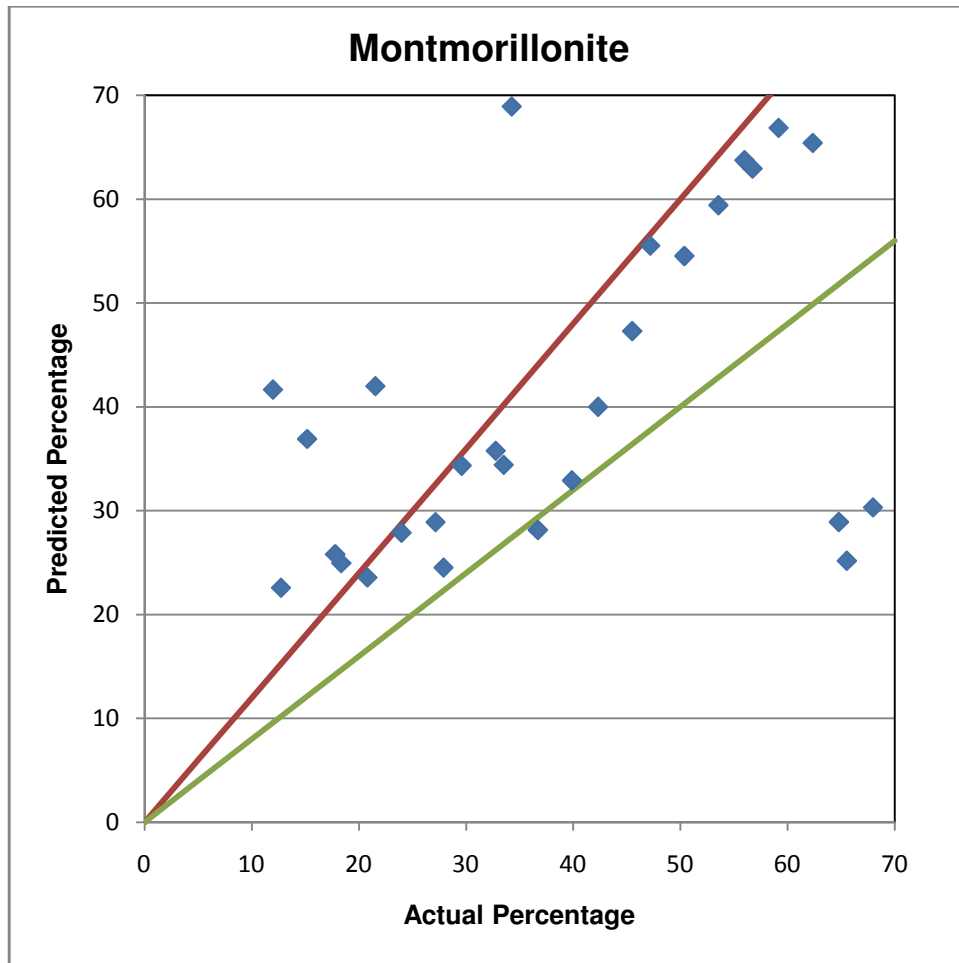
Figure 4-8 Comparison of Predicted Percentage Montmorillonite with Actual Percentage

From Figure 4.7, it can be observed that the most of the data fall within the range of $\pm$ 20%. The artificial neural network gives a fair correlation between the actual and predicted illite percentages. As observed with the previous methods, some percentages were under predicted

For the correlation between the predicted and actual percentages of montmorillonite, it can be observed that although most of the data fall within the $\pm$20% ranges, three samples with high percentages of montmorillonite are not getting predicted accurately. The data for these three samples are being under predicted by about 40%, which is not acceptable.

<u>4.4 Interpretation of Results</u>

To prevent the predictions of the percentages of minerals from being biased, the samples were prepared beforehand, by a different person, and the percentages of minerals in the mixtures were not revealed. In order to get better interpretations of the percentages from the results, the artificial samples have been divided into two groups based on the original mixture percentages. Group A consists of the samples that have montmorillonite as the dominant mineral and Group B consists of those that have Illite as the dominant mineral. Table 4.8 and Table 4.9 show a breakdown of the samples according to their mineral dominance.

Table 4-8 Samples Dominant in Montmorillonite

Soil No.	Sample #	Actual	Predicted Using Microsoft Excel Solver
1	31	47.18	54.4
2	29	50.37	54.1
3	28	53.55	60
4	33	55.98	63.4
5	30	56.73	61.4
6	32	59.17	68.8
7	34	62.35	68.6
8	36	64.78	27.8
9	40	65.53	23.9
10	35	67.97	30.2
11	43	70.40	30
12	37	73.58	33.4
13	38	76.77	33.6

Table 4-9 Samples Dominant in Illite

Soil No.	Sample #	% Illite	% Montmorllonite
1	2	52.20	11.98
2	27	59.59	12.73
3	4	53.21	15.17
4	45	52.80	17.78
5	8	54.23	18.35
6	15	47.84	20.78
7	6	55.24	21.53
8	10	48.86	23.97
9	12	49.87	27.15
10	7	57.27	27.90
11	19	43.49	29.58
12	21	44.50	32.77
13	13	51.90	33.51
14	1	59.29	34.26
15	9	52.91	36.70
16	14	53.93	39.88
17	20	47.54	42.31
18	18	48.56	45.50

(b)

Group A
(Montmorillonite Dominant)

Artificial Samples

Group B

(Illite Dominant)

Figure 4-9 shows a flowchart to better illustrate the soil groups.

The results for group A soils are summarized in Table 4.10.

Table 4-10 Predicted versus Actual Montmorillonite Percentages for Group A

Soil No.	Sample #	Actual	% Montmorillonite		
			Predicted Using Microsoft Excel Solver	Predicted with Regression Equations	Predicted with Artificial Neural Network
1	31	47.18	54.4	62.08	55.51
2	29	50.37	54.1	64.2	54.52
3	28	53.55	60	73.86	59.42
4	33	55.98	63.4	69.98	63.73
5	30	56.73	61.4	67.85	62.95
6	32	59.17	68.8	76.27	66.86
7	34	62.35	68.6	78.6	65.41
8	36	64.78	27.8	56.53	28.9
9	40	65.53	23.9	60.83	25.17
10	35	67.97	30.2	58.51	30.31
11	43	70.40	30	61.37	32.34
12	37	73.58	33.4	63.86	34.26
13	38	76.77	33.6	63.81	33.87
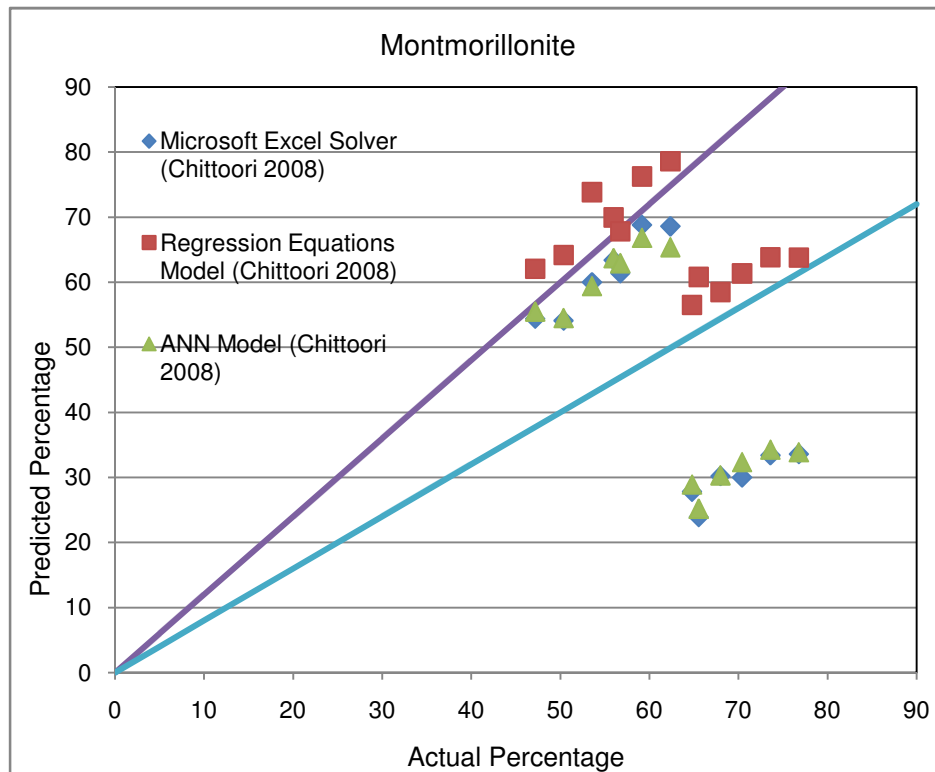
Figure 4-10 Comparisons of Actual Percentages of Montmorillonite with Predicted Ones

It can be observed from figure 4.11 that the percentage of montmorillonite predicted using the regression equations gave the most accurate predictions, especially in the cases where the percentage of montmorillonite is greater than 50%. The other models give good predictions when the percentage is less than 60% but for percentages greater than that, the results are underestimated. It can be deduced that the montmorillonite content of soils can be accurately predicted using the regression equations, within a 20% margin of error.

The results for soils in Group B are summarized in Table 4.11

Table 4-11 Predicted versus Actual Illite Percentages

| Soil No.	Sample #	% Illite		
		Actual	Predicted Using Microsoft Excel Solver	Predicted with Regression Equations	Predicted with Artificial Neural Network
1	19	43.49	32.5	32.50	35.93
2	21	44.50	36.7	36.67	43.81
3	20	47.54	43.8	43.75	51.42
4	15	47.84	31	31.00	32.61
5	18	48.56	43.8	40.42	46.39
6	10	48.86	41.7	41.67	53.58
7	12	49.87	47.5	47.50	59.65
8	13	51.90	41.7	41.67	54.17
9	2	52.20	45.4	45.42	61.35
10	45	52.80	27.5	27.5	24.45
11	9	52.91	49.2	49.17	59.13
12	4	53.21	57.5	57.5	65.18
13	14	53.93	39.2	39.17	45.29
14	8	54.23	40	40.00	51.27
15	6	55.24	37.5	37.50	49.62
16	7	57.27	59.6	59.58	65.65
17	1	59.29	50	50.00	61.35
18	27	59.59	31.7	31.67	22.57
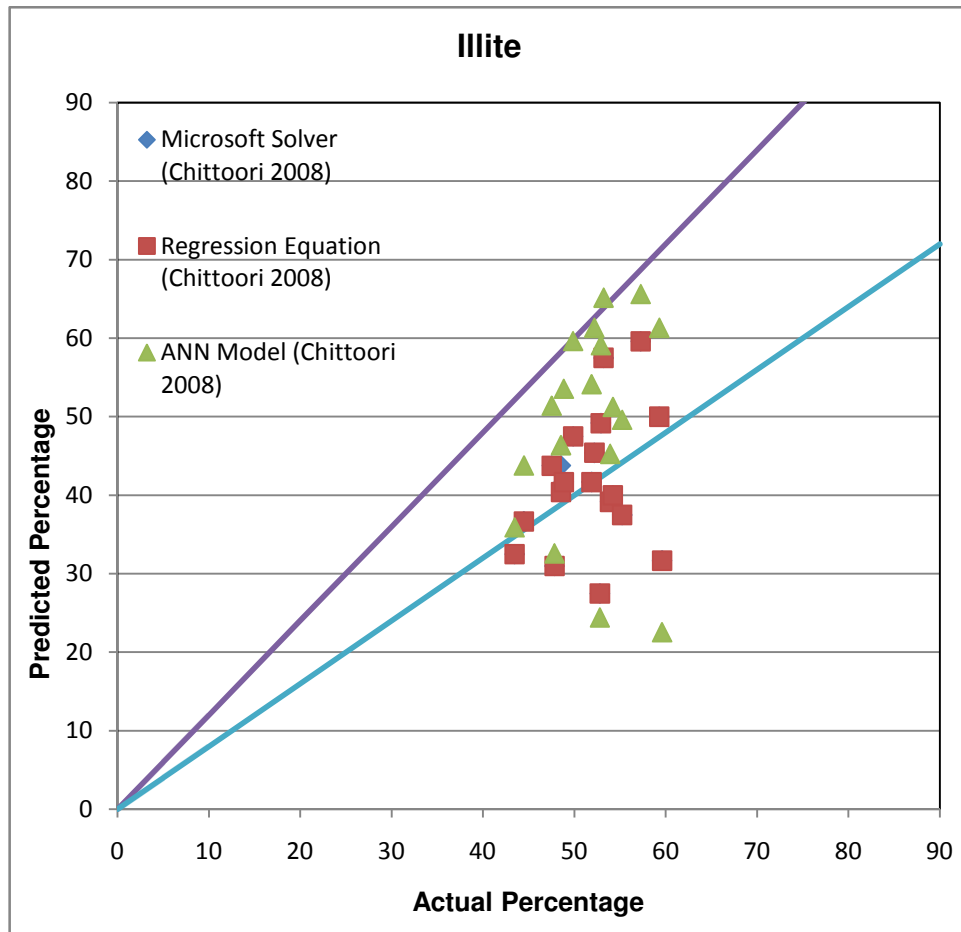
Figure 4-11 Comparisons of Actual Percentage of Illite with Predicted Ones

It can be observed that all the models give a fairly good prediction of the percentage of illite in the sample. It can be further observed that for lower percentages of illite, all the data points are giving good predictions. Therefore it can be said that all the models are equally effective at predicting the percentage illite present.

4.5 Summary

It was observed that, for the quantification of montmorillonite, the model using regression equations predicted the percentages more accurately than either the solver function of Microsoft Excel or the artificial neural network model.

In this chapter the data obtained, from Cation Exchange Capacity (CEC), Total Potassium (TP) and Specific Surface Area (SSA) done on thirty artificially prepared soil samples, to quantify the dominant clay minerals present in soils have been presented and analyzed. The

results were predicted using the solver function of Microsoft Excel, regression and artificial neural network models developed by Chittoori 2008. The repeatability of the test procedures has also been addressed. The next chapter will discuss the conclusions that were arrived at from the results and will provide the recommendations needed to improve the validity of the models.

CHAPTER 5

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary and Conclusion

Over the years, soil stabilization has been a topic of great interest and discussion amongst civil engineers. Soil stabilization significantly reduces the construction and maintenance cost associated with building pavements on expansive or poor quality soils as well as increase rider comfort and satisfaction. The stability of the soil beneath the pavement influences the performance of the pavement to a great degree. But in some cases, even after sub grades are stabilized and treated using standard procedures developed by federal agencies, these pavements fail or they have cracks which eventually cause failures.

The current procedure used by the Texas Department of Transportation (TxDOT) to determine the type of stabilizer is based mainly on the Plasticity Index (PI) and the gradation of the soil. This method of stabilization does not always work because two soils with the same PIs can have very different shrink/swell potential, plastic limits or liquid limits, hence their behavior will be very different.

The main objective of this research was to validate the recently developed models by Chittoori 2008 for quantifying montmorillonite and kaolinite. Thirty artificial samples were prepared, each with a different percentage of the clay minerals. Since the intent is to identify the expansive clay minerals, artificial samples with dominant clay minerals of montmorillonite and illite were only considered. The artificial clay samples consisted of mixtures of montmorillonite, illite and traces of kaolinite and other 1:1 minerals. The samples were mixed such that each had a different proportion of the minerals. To maintain unbiased predictions and reporting, the percentages were mixed by a different person and these percentages were not revealed to the researcher until all the results had been reported. Then, the predicted percentages were

compared to the original mix percentages and the results reported. The following section summarizes the research, conclusion and recommendations. The repeatability of the Cation Exchange Capacity, Specific Surface Area, and Total Potassium methods were verified by performing each test thrice on three samples. The test results obtained indicated a very low standard deviation between the results of each sample. This indicates that the tests have good repeatability.

1. The Microsoft Excel Solver program developed by Chittoori (2008) yielded close predictions for both montmorillonite and illite contents. Most of the data for both minerals are within the $\pm$ 20 % range of the true percents. It was observed that for high percentages of montmorillonite, the model was not accurate as three samples were under predicted by about 40% of the actual percentage. For illite percentage, the prediction was fair and most of the predicted data were again within the $\pm$20% range. It was observed that only for a handful of artificial clay specimens, this method did not give a good correlation.

2. It was observed that the regression model equations, developed by Chittoori (2008) successfully predicted most of the montmorillonite percentages accurately, within a range of about $\pm$ 20%. This model also successfully predicted the high mineral percentages that the Microsoft Excel Solver model failed to predict accurately. That accurate prediction of high montmorillonite content is a very crucial part of the research, since montmorillonite is the mineral that causes the most drastic swelling and shrinking behavior in clays. For illite, again most of the predictions were again within the $\pm$ 20% range with only a handful below the -20% range. Even though these were below the lower range, they were still close to it and not too scattered. The prediction of illite percentage, by both the Microsoft Solver Model and Regression Equation model, follow the same pattern since the equation used to calculate the percentage is the same. Hence, it can be said that the regression equation model gives a fair prediction of montmorillonite and illite.

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3. Using the Neural Network Analysis model developed by Chittoori 2008, it was observed that for illite most of the data fall within the range of $\pm$ 20%. The artificial neural network gives a fair correlation between the actual and predicted illite percentages. As observed with the previous methods, some percentages were under predicted. For the correlation between the predicted and actual percentages of montmorillonite, it was observed that although most of the data fall within the $\pm$20% ranges, three samples with high percentages of montmorillonite are not getting predicted accurately. The data is being under predicted by about 40%, which is not acceptable.

4. For the accurate quantification of high percentages of montmorillonite and illite, the regression equation model developed by Chittoori 2008 was observed as giving the most accurate data. This accurateness is very crucial as montmorillonite content of the soil leads to drastic behavior in terms of swelling and shrinking. Although the other models give fair prediction for low to medium percentages of montmorillonite and illite, they do not give accurate results where high montmorillonite percentages are concerned.

5. For future studies, more soils need to be studied and kaolinite should be included in the prediction analyses. Further research may also be done to include other 1:1 minerals and also soils from different regions that exhibit swelling behavior.

REFERENCES

[1]   Alexiades, C. A., and Jackson, C. A., (1966), "Quantitative clay mineralogical analysis of soils and sediments", Clays and clay minerals, 14, pp 35-42

[2]   Amonette, J. E. 2002. "Methods for Determination of Mineralogy and Environmental Availability." Chapter 5 in J. B. Dixon and D. G. Schulze (eds.) Soil Mineralogy with Environmental Applications, SSSA Book Series, Soil Science Society of America, Madison, WI

[3]   Baker, D.E., and Suhr, N. H., (1982), "Atomic absorption and flame emission spectrometry", In A.L. Page et al. (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. SSSA and ASA, Madison, WI, pp. 13–27.

[4]   Chittoori, B. C. S., (2008), "Clay mineralogy effects on long term performance of chemically treated expansive clays" Dissertation submitted to The University of Texas at Arlington.

[5]   Blanc, Phillippe, Legendre, Olivier and Gaucher, Eric C. (2006). "Estimate of clay minerals amounts from XRD pattern modeling: The Arquant Model", Physics and Chemistry of the Earth, v 32, p 135-144

[6]   Blake, T. A., Gassman, P. L. (2001). "Detection of soil surface contaminants by infrared reflection spectroscopy", Proceedings of SPIE - The International Society for Optical Engineering, v 4577, p 239-261.

[7]   Blum, A. E. and Eberl, D. D. (2004), "Measurement of clay surface areas by polyvinylpyrrolidone (PVP) sorption and its use for quantifying illite and smectite abundance" Clays and Clay Minerals, v 52, no. 5, p 589-602.

[8]   Borchardt, G. (1989), "Smectites", In J.B. Dixon and S.B. Weed, eds., Minerals in Soil Environments, 2nd ed., Madison, WI: Soil Science Society of America.

[9]   Camberato, J.J. (2001) Cation exchange capacity – everything you want to know and so much more. Website address:

http://virtual.clemson.edu/groups/turfornamental/tmi/fertlime/Cation%20exchange%20capacity. PDF

[10]   Campbell, G. S., (2005), "Measuring Specific Surface of Soil with the WP4", Application Note, Source: http://www.decagon.com/appnotes/SpecificSurface.pdf.

[11]   Carter, D. L., Mortland, M. M. and Kemper, W. D., (1986), "Specific Surface" In A. Klute(ed),Methods of Soil Analysis, Part 1, 2nd. Ed. Agronomy 9:413-423.

[12]   Cerato, Amy B., and Lutenegger, Alan J., "Determination of surface area of fine-grained soils by the ethylene glycol monoethyl ether (EGME) method", Geotechnical Testing Journal, v 25, n 3, September, 2002, p 315-321

[13]   Chapman, H. D., (1965), "Cation-exchange capacity" In: C. A. Black (ed.) Methods of soil analysis - Chemical and microbiological properties. Agronomy 9, pp. 891-901

[14]   Cullity, B.D. and Stock, S.R., (2001), "Elements of X-Ray Diffraction", Third Edition, Addison-Wesley.

[15]   Engler, P. and Iyengar, S. S., (1987), "Analysis of mineral samples using combined instrument (XRD, TGA, ICP) procedures for phase quantification", American Mineralogist, v 72, p 832-828

[16]   Grim, R. E., (1953), "Clay Mineralogy", McGraw Hill Book Company, New York.

[17]   Grim, R.E., (1962), "Applied clay mineralogy", McGraw Hill, New York.

[18]   Hodgson, M., and Dudeney, A. W. L., (1984), "Estimation of clay proportions in mixtures by x-ray diffraction and computerized chemical mass balance." Clay and Clay Minerals, v 32, p 19-28.

[19]   Hughes, R. E., Moore, D. M., and Glass, H. D., (1994), "Qualitative and quantitative analysis of clay minerals in soils", In J.E. Ammonette and L.W. (eds.) Quantitative methods in soil mineralogy, SSSA Miscellaneous publication, Soil Sci. Soc. Am., Madison, WI. Soil Science society of America, pp 330-359.

70

[20] Islam, A. K. M. E., and Lotse, E. G., (1986), "Quantitative mineralogical analysis of some Bangladesh soils with x-ray, ion exchange and selective dissolution techniques", Clay Minerals, v 21, p 31-42.

[21] Jackson, M. L., (1958), "Soil chemical analysis", Prentice Hall Inc., Englewood Cliffs, N.J.

[22] Johnson, L, J., Chu, C. H., and Hussey, G, A., (1985), "Quantitative clay mineral analysis using simultaneous linear equations", Clays and Clay minerals, Vol. 33, No. 2, pp. 107-117

[23] Jones, D. E., Holtz, W. G. (1973) "Expansive Soils - the Hidden Disaster", Civil Engineering (ASCE), 43(8), p.49.

[24] Kahle, M., Kleber, M., and Jahn, R., (2002), "Review of XRD- based quantitative analyses of clay minerals in soils: the suitability of mineral intensity factors", Geoderma, v 109, p 191-205.

[25] Karuiki, P. C., Woldai, T., and Van Der Meer, F., "Effectiveness of spectroscopy in identification of swelling indicator clay minerals" Int. J. Remote Sensing, VOL. 25, NO. 2, pp. 455–469.

[26] Kaufhold, S., Dohrmann, R., Ufer, K. and Meyer, F.M. (2002), "Comparison of methods for the quantification of montmorillonite in bentonites" Applied Clay Sciences, v 22, p 145-151.

[27] Knudsen D., Peterson G.A. and Pratt P.F. (1982),"Lithium, sodium and potassium" In: Page A.L. (ed.), Methods of Soil Analysis, Part 2. American Society of Agronomy, Madison, WI, pp. 229–231.

[28] Linker, R, Shmulevich, I, Kenny, A, & Shaviv, A, (2005) "Soil identification and chemometrics for direct determination of nitrate in soils using FTIR-ATR mid-infrared spectroscopy", Chemosphere, v 61, n 5, p 652-658.

[29] Little, D. N., (1995), "Stabilization of pavement sub-grades and base courses with lime", Technical report made for Lime association of Texas.

71

[30] Mitchell, J. K., and Soga, K., (2005), "Fundamentals of soil behavior", 3nd Ed., Wiley, New York

[31] Moore, D. M. and Reynolds, R.C., Jr., (1989), "X-Ray Diffraction and the Identification and Analysis of Clay Minerals", Oxford University Press, New York, pp 332.

[32] Mosley, M. P., (2004), "Ground Improvement", 2nd ed, Spon Press, New York.

[33] Murray, H. H., (1999) "Applied clay mineralogy today and tomorrow", Clay Minerals 34, pp.39-49

[34] Narasimha Rao, S., Subba Rao, K. V., Rajasekaran, G.,(1993) "Microstructure Studies of Lime Treated Marine Clays", Proc. 12th International Conference on Offshore Mechanics and Arctic Engineering, V 1, pp 425-431.

[35] Ouhadi, V. R. and Yong, R. N., (2003), "Impact of clay microstructure and mass adsorption coefficient on the quantitative mineral identification by XRD analysis", Applied Clay Science, v 23, p 141-148.

[36] Puppala, A. J., Punthutaecha, K, Vanapalli, S. K., (2006), "Soil-water characteristic curves of stabilized expansive soils", Journal of Geotechnical and Geoenvironmental Engineering, v 132, n 6, June, 2006, p 736-751

[37] Quirk, J. P., (1955), "Significance of surface areas calculated from water vapor sorption isotherms by use of the B. E. T. equation", Soil Science Journal, 80,pp 423-430.

[38] Randall, K. K., Laird, D. A., and Nater, E. A., (1994), "Comparison of four elemental mass balance methods for clay mineral quantification" Clays and Clay Minerals, v 42, p 437-443.

[39] Rhoades, J.D., (1982), "Cation exchange capacity", A. L. Page et al. (ed.) Methods of soil analysis: Part 2: Chemical and microbiological properties. Soil Science Society of America, Madison, Wisconsin, USA, pp. 149-157.

[40] Smith, Deane K., Johnson, Gerald G. Jr.; Ruud, Clayton O., " Clay mineral analysis by automated powder diffraction analysis using the whole diffraction pattern" , Advances in X-ray Analysis, v.29, 1986, p 217-224

[41]   Sridharan, A., Rao, S. M., Murthy, N. S., (1988), "Liquid limit of Kaolinite soils", Geotechnique 38: 191-198.

[42]   Stewart, W.M., Hossner, L.R., (2001) "Factors affecting the ratio of cation exchange capacity to clay content in lignite overburden, Journal of Environmental Quality, v 30, n 4, p 1143-1149.

[43]   Tayabji, S. D., Nussbaum, P. J., and Ciolko, A. T., (1982). "Evaluation of Heavily Loaded Cement-Stabilized Bases," Transportation Research Record 839, TRB, National Research Council, Washington, D.C., pp. 6-11.

[44]   Thompson, M. L., and Ukrainczyk, L., (2002), "Micas" in J.B. Dixon and D.G. Schulze (ed.) Soil mineralogy with environmental applications, SSSA Book Ser. 7. SSSA, Madison, WI, pp431-466.

[45]   Wang, L., Roy, A., Tittsworth, R., and Seals, R. K., (2004), "Mineralogy of soil susceptible to sulphate attack after stabilization", Journal of Materials in Civil Engineering, ASCE, July/August 2004, p 375-383.

[46]   Whittig, L. D., and Allardice, W. R., (1986), "X-Ray diffraction techniques", In A.Klute, (ed.). Methods of Soil Analysis, Part 1—Physical and Mineralogical Methods, 2nd ed. American Society of Agronomy, Madison, Wisconsin, pp. 331-362.

[47]   Wiseman, G., Komornik, A. and Greenstein, J. (1985) "Experience with Roads and Buildings on Expansive Clays" Transportation Research Record 1032, pp.60-67.

[48]   Wunderlich,1990, http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=6805908

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