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The Role of Marl Components and Ettringite on the Stability of Stabilized Marl

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ABSTRACT

In many sub-tropical and tropical arid regions of the world, marly soils (marls) and lime or cement stabilization of marl soils are used as a convenient and expedient means for development of foundation base courses and inexpensive wearing courses for transport purposes. The failure of many of these natural and stabilized marls to perform their function have been reported. Mechanical factors generally used to explain the causes for the foundation failures have not been satisfactorily accepted. This study uses physico-chemical (reaction) factors to explain the general basic causes for deterioration of the support capability for these types of soil. The presence of *palygorskite* and *sepiolite* in marl soils provides it with some very unique features in its natural state, and particularly when it is stabilized with lime or cement. Formation of an expansive mineral *ettringite* as a transformation product of palygorskite increases the swelling potential of the stabilized soil. The various interactions, reactions and factors contributing to the stability and instability of marl soils, and lime stabilized marls are discussed. Ettringite is a swelling material, which its swelling can be in the order of up to 30 centimetres in road construction. The exact mechanism of these failures is still not well known. Reactions between lime, alumina (released from the clay fraction of soil) and sulfates present in the soil pore fluid can cause the formation of ettringite. These reactions have been responsible for the failure of several soil stabilization projects. In this study, the impact of the structural changes of stabilized marl on its performance are assessed. In this matter, some basic and fundamental aspects and physico-chemical performance of palygorskite and sepiolite as distinguished clay minerals, and ettringite are quantitatively presented. The possible contribution of palygorskite and sepiolite to the post-stabilization failure due to ettringite formation were investigated. By conducting a set of physico-chemical experimental studies, it is shown that the general geotechnical mechanical/physical criteria used to evaluate stabilized soil performance may not be reliable for the evaluation of stabilized marl due to the possible formation of ettringite and its resultant behaviour. A set of physico-chemical studies, which include specific surface area measurements *(SSA)* and *x-ray* diffraction *(XRD)*, are needed for a more complete and realistic evaluation of the long-term stability of stabilized marl. In this study, a soil washing method for extraction of pure palygorskite or clay fraction from the soil mixture is developed and validated by *XRD* analysis. This helped in investigating the role of pure palygorskite on the marl performance. Based on the presented results, the pervious classification of marly soils is developed and a new classification for marly soils is proposed.

Following establishment of the significant role of palygorskite and sepiolite, through the experimental studies, the current *XRD* techniques for quantitative mineral analysis of clay soils are evaluated. The accuracy of these methods are investigated by preparation of a series of artificial soil mixtures. Finally, a quantitative *XRD* method for marly soils and ettringite is presented. By the performance of *XRD* on a series of artificial marly samples having ettringite, a series of practical graphs for *XRD* mineral quantification of marly soils and ettringite is validated.

In the last part of this study, the major difference in the kinetics of ettringite when artificially formed is compared with that of a stabilized soil, and the role of sulfate, alumina, and calcium on the ettringite formation is investigated.

Furthermore, for soil stabilization, the contribution of different clay minerals in ettringite formation is investigated through the experimental study. Among the clay minerals studied, palygorskite was found to be the most rich in alumina, providing the highest source of alumina for ettringite formation.

In the name of God,
the Compassionate, the Merciful

*In memory of my beloved brother **MASOUD**,*
symbol of kindness and humanity

This thesis is dedicated
*to the dear sweet blossom, **ROGHAIEH (S.A)**,*
who passed away when she was so young,
only a few years of age.....

RESUMÉ

Dans plusieurs régions sub-tropicales et tropicales arides du monde, les sols marlés (marls) et les marls stabilisés au ciment et à la chaux sont utilisés comme moyen rapide et pratique pour le développement de fondation de réseaux routiers. L'incapacité de plusieurs de ces marls et marls stabilisés d'effectuer leur fonction a été raportée. Les facteurs mécaniques généralement utilisés pour expliquer l'affaissement des fondations n'ont pas été acceptés de façon satisfaisante. Cette étude utilise des facteurs physico-chimique (réaction) pour expliquer les causes générales de la détérioration de la capacité de support de ces types de sols. La présence de palygorskite et de sepiolite dans les marls leur procurent des caractéristiques uniques (dans leurs états naturels) et particulièrement lorsqu'ils sont stabilisés avec de la chaux ou du ciment. La formation d'un minéral expansif, l'ettringite, issu de la transformation du palygorskite, augmente le potentiel de gonflement du sol stabilisé. Les diverses interactions, réactions et facteurs contribuant à la stabilité ou à l'instabilité des sols marlés et des marls stabilisés à la chaux sont discutés. Le mécanisme exact de ces affaissements n'est pas totalement connu. Les réactions entre la chaux, l'alumina (relâché de la fraction des argiles du sol) et les sulfates présents dans les pores du sols peuvent causer la formation de l'ettringite. Ces réactions sont responsables de la défaillance de plusieurs projets de stabilisation de sols. Cette étude évalue les impacts du changement structurel du marl stabilisé sur ses performances. Les aspects fondamentaux et les performances physico-chimiques du palygorskite et du sepiolite, en tant que minéral d'argile distinct et de l'ettringite sont présentés quantitativement. Nous avons investigué la contribution possible du palygorskite et de la sepiolite sur la défaillance post-stabilisation causée par la formation d'ettringite. En dirigeant une série d'études expérimentales physico-chimiques, on démontre que les critères géotechniques méchaniques/physiques généraux utilisés pour évaluer la performance des sols stabilisés ne paraissent pas être fiables pour l'évaluation du marl stabilisé causé par la formation possible de l'ettringite et son comportement résultant. Une série d'études physico-chimiques, incluant la mesure de la

surface et rayons-x par diffraction, sont requises pour une évaluation plus complète et réaliste de la stabilité à long terme du marl stabilisé. Dans cette étude, nous avons développé une méthode de lavage de sols pour l'extraction du palygorskite pur et de la fraction argileuse de la mixture de sols. Cette méthode est validée par analyses aux rayons-x. Ces expériences ont aidé à investiguer le rôle de la palygorskite pure sur les performances du marl. Basé sur les résultats obtenus, la classification précédente des sols marlés est développée et une nouvelle classification pour les sols marlés est proposée.

Suite à l'établissement du rôle significatif du palygorskite et du sepiolite, nous avons évalué les techniques par rayons-x pour l'analyse minérale quantitative des sols argileux. La précision de ces méthodes est investiguée par la préparation d'une série de mixtures de sols artificiels. Finalement, nous présentons une méthode quantitative pour les sols marlés et pour l'ettringite. Une série de graphiques pratiques pour leur quantification est validée par la performance du rayon-x sur une série d'échantillons de sols marlés artificiels contenant de l'ettringite.

Dans la dernière section de cette étude, nous avons comparé les différences majeures de la cinétique de l'ettringite formée artificillement avec les sols stabilisés. Nous avons investigué le rôle du sulfate, de l'alumina et du calcium sur la formation de l'ettringite.

Au cours de cette étude expérimentale, nous avons investigué la contribution des différents minéraux d'argile sur la formation de l'ettringite. De tous les minéraux d'argile étudiés, le palygorskyte est le plus riche en alumina et fournit la plus grande source d'alumina pour la formation de l'ettringite.

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PUBLICATIONS

(1) Yong, R.N., Ouhadi, V.R., 1997, "The Role of Palygorskite and Sepiolite on the Stability of Marly Soils", Paper Submitted to the Journal of Engineering Geology.

(2) Yong, R.N., Ouhadi, V.R., 1997, "Reaction Factors Impacting on Instability of Bases on Natural and Lime-Stabilized Marls", Special Lecture, Keynote Paper, International Conference on Foundation Failures, Singapore.

(3) Ouhadi, V.R. and Yong, R.N., 1997, "Role of Marl Compositions on Its Behaviour and A new Classification for Marly Soils", Paper Accepted for the Graduate Student Research In-Progress Session, CSCE Annual Conference, Sherbrooke, Quebec.

(4) Yong, R.N., Ouhadi, V.R., and Mohamed, A.M.O.,1996, "Physico-Chemical Evaluation of Failure of Stabilized Marl Soil", 49th Canadian Geotehnical Conference Frontiers of Geotechnology, St. John's Newfoundland, Volume 2, pp. 769-776.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
ASIS	Soil as it is, without any treatment
CEC	Cation Exchange Capacity
CAH	Calcium Aluminate Hydrate
C_3A	Tricalcium Aluminate
CBR	California Bearing Ratio
CEC	Cation Exchange Capacity
COV	Coefficient of Variation
CSH	Calcium Silicate Hydrate
DDL	Diffuse Double Layer
DH	Double Hydrometer Test
DTA	Differential Thermal Analysis
EDL	Electric Double Layer
EGME	Ethylene Glycol Mono-ethyl Ether
ES	Exchangeable Sodium
ESP	Exchangeable Sodium Percentage
ESR	Exchange Sodium Ratio
IR	Infrared Spectral Analysis
JCPDS	Joint Committee on Powder Diffraction Standards
LL	Liquid Limit
meq/l	Milli-equivalent per litre
mtM3	Moderately weathered marl
PDI	Potential Determining Ions
PI	Plasticity Index
PL	Plastic Limit
ppm	Part Per Million
psi (lb/square inch)	Equals to 0.07 kg/square cm
SAR	Sodium Adsorption Ratio, $Na^+/[0.5(Ca^{2+}+Mg^{2+})]^{0.5}$ meq/l
SEM	Scanning Electron Microscope
SSA	Specific Surface Area
TDS	Total Dissolved Salts
tM2	Unweathered tough marl
W.F.	Weighting Factor
WM	Weathered marl
XRD	X-ray Diffraction

LIST OF SYMBOLS

A	Angstrom
α	Reaction ratio (Jander equation)
c	Plowman & Cabrera Constant
C	Equilibrium Solution Concentration
C	Degrees Centigrade
C_{-}	Concentration of the species of ion in the bulk solution(normalityx10^{-3} x avogadro)
C_o	Initial concentration
$\mathrm{C_c}$	Coefficient of curvature($\mathrm{D^2_{30}/D_{10}.D_{60}}$)
$\mathrm{C_u}$	Uniformity coefficient($\mathrm{D_{60}/D_{10}}$)
$\mathrm{D_{10}}$, $\mathrm{D_{30}}$, $\mathrm{D_{60}}$	Diameter at 10%, 30% and 60% respectively
d	Distance between two planes of atoms
e	Elementary charge (4.77 x 10^{-10} esu)
$\mathrm{E_j}$, $\mathrm{B_j}$ and $\mathrm{A_j}$	Constants (adsorption equation)
ϵ	Dielectric constant of pore fluid
hkl	Miller Indices
I	Intensity of the radiation after passing through the layer
$\mathrm{I_o}$	Intensity of the radiation incident on a layer of test sample
$\mathrm{I_A}$, $\mathrm{I_B}$	Intensities of two selected diffractions of two elements present in the mixture
$\mathrm{I_{awi}}$	Average weighted intensity
$\mathrm{I_C}$	Intensity of the strongest peaks of Al_2O_3
$\mathrm{I_c}$	Intensity of the *x-ray* reflected by a component *C*
$\mathrm{I_i}$, $\mathrm{I_{ci}}$, $\mathrm{I_{di}}$	Intensity of the reflection line having a weighting factor equal or more than 30
$\mathrm{I_X}$	Intensity of mineral where its quantity is unknown
$\mathrm{I_S}$	Intensity of the internal standard component
K	Proportionality sign
1/k	Thickness of diffuse ion-layer (angstrom)
$\mathrm{K_c}$, $\mathrm{k_c}$, $\mathrm{k_d}$	Constant for the existing reflection from the component *C* and *D*
KT=0.4x10^{-13} ergs	Product of Boltzman constant and absolute temperature
λ	Wave length of incident rays
M	Mass of soil
n	Order of reflection
n	Porosity
N	Jander constant
P	Rate constant (Jander equation)
$\mathrm{P_c}$	A constant for any certain reflection from the component *C*
pH	$-\log_{10} [H^+]$
q	Concentration of Adsorbed Species

$Q_{Ave.}$	Average of the real quantity of a certain mineral in artificial samples
Q_{Eqg}	Estimated quantity of mineral using established graphs
Q_{Rqm}	Real quantity of mineral present in the artificial multi-phase sample
R	Retardation Factor
r	Coefficient of correlation
S, S_j	Concentration of Adsorbed Species
S, s	Standard Deviation
t	Time
θ	Reflection Angle
V	Volume of liquid added to the soil mass in batch equilibrium testing
V_c	Volume proportion of a component *C* in a mixture
w%	Water content
w_A, w_B	Weight percentage of two elements present in the mixture
W_c	Weight proportion of component *C*
W_i, W_{ci}, W_{di}	Standard weighting factor (W.F.) of the reflection line having a W.F. ≥30
x	Thickness of the layer (test sample in *XRD*)
z	Valence of the species
μ	Mass absorption coefficient
μ_l	Linear absorption coefficient
μ_{lm}	Mixture's mass absorption coefficient
ρ_m	Mass absorption coefficient of a mixture
ρ	Density of the absorbing material
ρ_c	Density of component *C*
ρ_d	Dry mass density of the test specimen
ρ_m	Average density of the mixture

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CHAPTER 1
INTRODUCTION

1.1 STATEMENT OF THE PROBLEM

Soil stabilization is usually accomplished by mechanical or chemical means. Among soil stabilization methods, the use of lime and cement are the most common. Soil stabilization should not be considered just in terms of strength, in fact, to do so could cause serious structural failures. Soil stabilization is any process by which some undesirable properties of a soil are overcome *(Lee 1974)*. Considering marl stabilization solely in terms of its mechanical aspects has resulted in severe problems, and there presently exists no complete definitive interpretation for these failures.

In its "natural state", marl has been reported to be unique because of the radical changes in its resistance to deforming loads or stress under dry or wet conditions, which are principally governed by the presence of *palygorskite* and/or *sepiolite* in its clay fraction. Usually, as it is shown in Figure 1.1, in clay minerals there is a relation between soil cation exchange capacity *(CEC)*, specific surface area *(SSA)* and water sorption capacity. As an example, as the *CEC* and *SSA* increase, the water sorption capacity of soil increases. These clay minerals retain water between their layers. Among the clay minerals, palygorskite and sepiolite's behaviour differs from others. Although they have relatively low *CEC*, they show very high *SSA* and sorption capacity and in some cases their water holding capacity is even greater than montmorilonite. This high sorption capacity is attributed to their chain-like structure (Figure 1.2). Water in their structure is called zeolitic water.

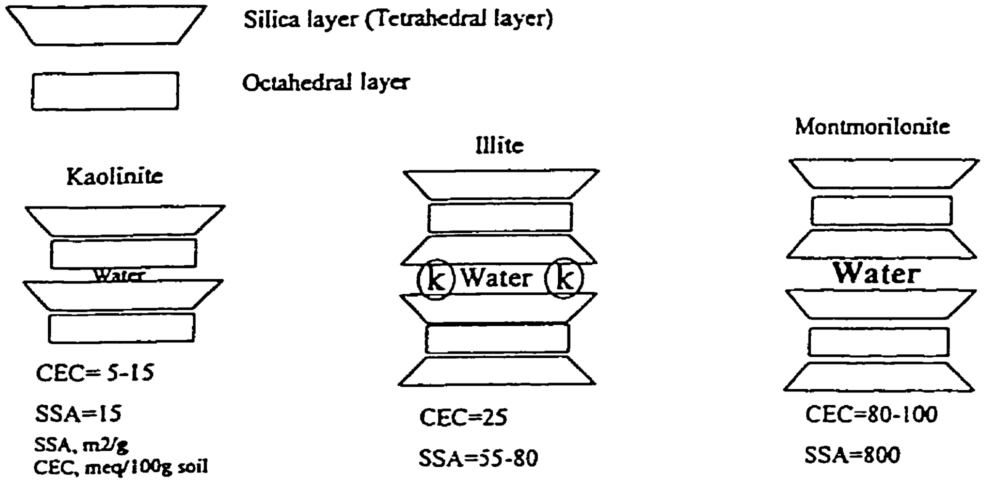


Figure 1.1: Schematic diagrams of the layer structure in clay soils.

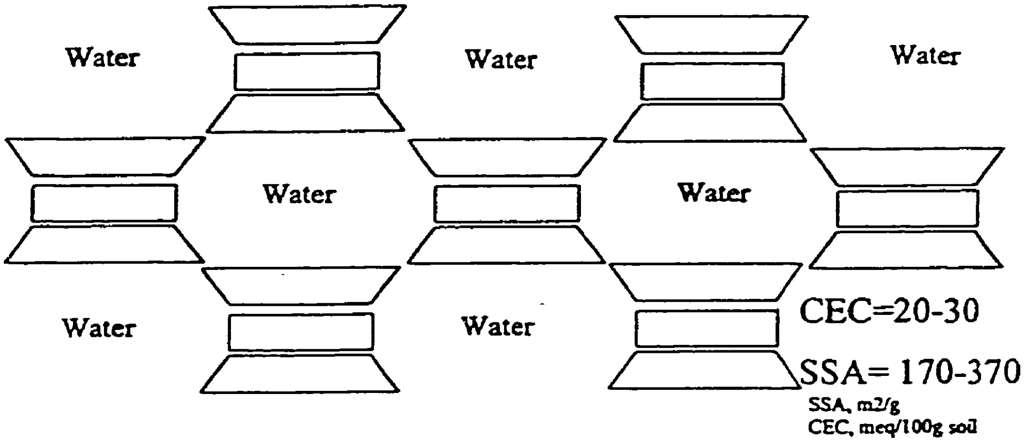


Figure 1.2: Schematic diagram of the palygorskite and sepiolite chain-like structure.

Palygorskite and sepiolite are known to be the major fraction of marly soils *(Yong et al. 1996)*. On the whole, there is noticeable lack of research on the physico-chemical performance of these clay minerals. The literature shows several different structural formula for both palygorskite and sepiolite, to a very large extent because of the many possibilities for the distribution of *Al*, *Mg*, and *Si*, and by and large a considerable range in the relative amounts of *Al* and *Mg*. However, in spite of these variations in compositional features, the palygorskite-sepiolite minerals appear to have the same general *XRD* and dehydration characteristics.

In many parts of the world where the climate is mainly "dry", it is not uncommon to use the soils in their in-situ state or as compacted marl for load supporting capability, particularly as compacted subbase, foundation support, or even as a wearing course for secondary road systems. However, under long exposure to water, the high *CBR* resistance values obtained in the compacted "dried" state could be significantly reduced, particularly when the exposure to water leads to saturation of the soil and a longterm condition of "wet marl". Under such circumstances, the *CBR* resistance values have been reported to drop considerably, thereby undermining support capability and causing foundation failures.

It is useful to note that the existence of palygorskite and sepiolite in marls is due to the chemical precipitation and crystallization of these minerals in what is essentially an alkaline sediment. Significant quantities of *Si* and *Mg* are associated with this type of soil, and the minerals should remain stable so long as the alkaline environment is maintained. However, should leaching of the salts in the soil occur to the extent that the alkaline environment is considerably reduced, decomposition occurs and transformed products would be likely obtained.

Because of the presence of palygorskite and/or sepiolite, marly soils possesses swelling characteristics, and because the soils are generally obtained as a result of deposition in marine environments, high salt contents are not unusual in the soil. However, it is this high salt content that will produce the potential for slaking of the soil in the presence of water, to the point where the difference in *CBR* resistance between dry and saturated states has been reported to drop by about 85% *(Ouhadi et al. 1993)*. When exposed to continuous heavy rain, it is not uncommon for marl soils to be eroded, thereby resulting in failure in overlying structures, buildings and roads.

Similar to other problematic soils, stabilization with cement and lime has often been used to overcome marl related problems. Unfortunately, in the majority of cases, after a period of time, disastrous failure in stabilized marl may still occur. The failure is attributed to the formation of *ettringite* $\{Ca_6Al_2(SO_4)_3(OH)_{12},26H_2O\}$, an expansive mineral which develops in the presence of sulfate, lime, and alumina ions which is released from the clay fraction in high pH reactions. Ettringite (Figure 1.3) produces high swelling in the order of up to 30 centimetres in road construction *(Hunter 1988)*.

To evaluate properly the marl stabilization process, when present, the significant effects of sea-water should be considered. Within fine-grained soils, the use of sea-water for stabilization purposes will cause a two-fold effect. First by decreasing the thickness of the diffuse ion-layer due to the presence of cations in sea-water, followed by the generation of a different expansive mineral resulting from the presence of sulfate, causing soil instability. Other significant properties, such as fluid retention and leaching behaviour, are important in characterizing stabilized marl. Evaluating stabilized marl from a physico-chemical standpoint as opposed to a mechanical perspective, will help in investigating post-stabilization failures which result from the transformation of the clay fraction into a different expansive mineral called *ettringite*.

Figure 1.3: Electron microscopic picture of Ettringite, magnification 20000.

1.2 DEFINITION OF MARL

The term marl has been assigned various meanings. It has been defined *(Pettijohn 1975)* as a rock with 35-65% carbonate and a complementary content of clay. Usually the clay fraction of marl is dominated by the presence of palygorskite or sepiolite which control marls performance *(Davis 1967, Kassler 1973, Yong et al. 1993, Ouhadi et al. 1966)*. Palygorskite and sepiolite have a chain-like structure as opposed to that of other clay minerals which have a mainly layered structure (Figure 1.2). Palygorskite and sepiolite are usually known to be associated with other non-silicates such as carbonates and sulfates *(Velde 1992)*. Tropical environments provide highly favourable conditions for marl deposition *(Ovcharenko 1969)*. Marl may be produced by purely chemical precipitation. Its carbonate fraction may come from percolation of groundwater through carbonate bedrocks and precipitating on reaching the lake, or may be produced by algae in the process of their growth by photosynthesis *(Guillet 1969)*. In the main, palygorskite is an alimino-Mg-silicate generally with equal proportions of *Al* and *Mg*. If the proportions of *Al* were considerably reduced, we would obtain sepiolite. Hence, depending on the origin (parent rock), we can expect to obtain either or both of these chain-like structures as one of the dominant minerals in marls. When they form in a sedimentary environment, a basic evaporitic environment is a favourable condition for their formation. In such a case the nearshore sedimentary mineral is palygorskite, the more aluminous of the sepiolite-palygorskite pair. Towards the centre of the basin one finds more and more sepiolite until it becomes the only clay present *(Velde 1992)*.

1.3 CASE HISTORIES, PROBLEM OF MARLY SOIL

In many sub-tropical and tropical arid regions of the world, marly soils (marls) and lime or cement stabilization of marl soils is used as a convenient and expedient means for development of foundation base courses and inexpensive wearing courses for transport purposes. The failure of many of these natural and stabilized marls to perform their function have been reported as follows:

Failure is reported on a sub-grade of Keuper marl in Britain, where strength was found to be very sensitive to moisture content *(Turner and Seago 1985)*. In the Persian Gulf region the widespread occurrence of failures, in many geotechnical situations, has been reported in situations involving the soil, e.g. erosion, failure in foundations and slopes, tension cracks in roads, widespread instability on natural and manmade slopes and soil washing *(Akili and Torrance 1981, Trenter 1989, Jones 1989, Sanad and Bader 1990)*. Figure 1.4 shows some undesirable behaviours of marl in road construction in this region where the soil obtained for this study was procured. As can be seen, collapsible, dispersive, and swelling behaviours occur, resulting in road failures.

One of the largest recorded landslides on earth occurred in the marly soils in Iran, where the volume of landslide was estimated at nearly 20 cubic kilometres *(Voight 1981)*. In the areas where these failures happened it is reported that since little vegetation is present, the ground surface is totally unprotected from rain action. In some cases the presence of numerous sinkholes 10 to 20 m in diameter and several tens of m in depth is reported *(Rantucci 1987)*. In road construction projects, the instability of some slopes and the swelling of marl on the floor of tunnels were major problems *(Rantucci 1987)*. Marly soils cover large areas of southeastern France. These marls are very susceptible to weathering and are particularly prone to erosion, resulting in high solid transport *(Antoine et al. 1995)*. Disintegration of marl slopes is reported in the west regions of Asia *(Yaacov 1988)*.

On the other hand, the production of low cost roads using lime or cement stabilized marl, whilst offering an apparently simple remedy for good and cheap transportation infrastructure, has created several problems because of seemingly "peculiar" swelling and the resulting instability in post stabilization periods.

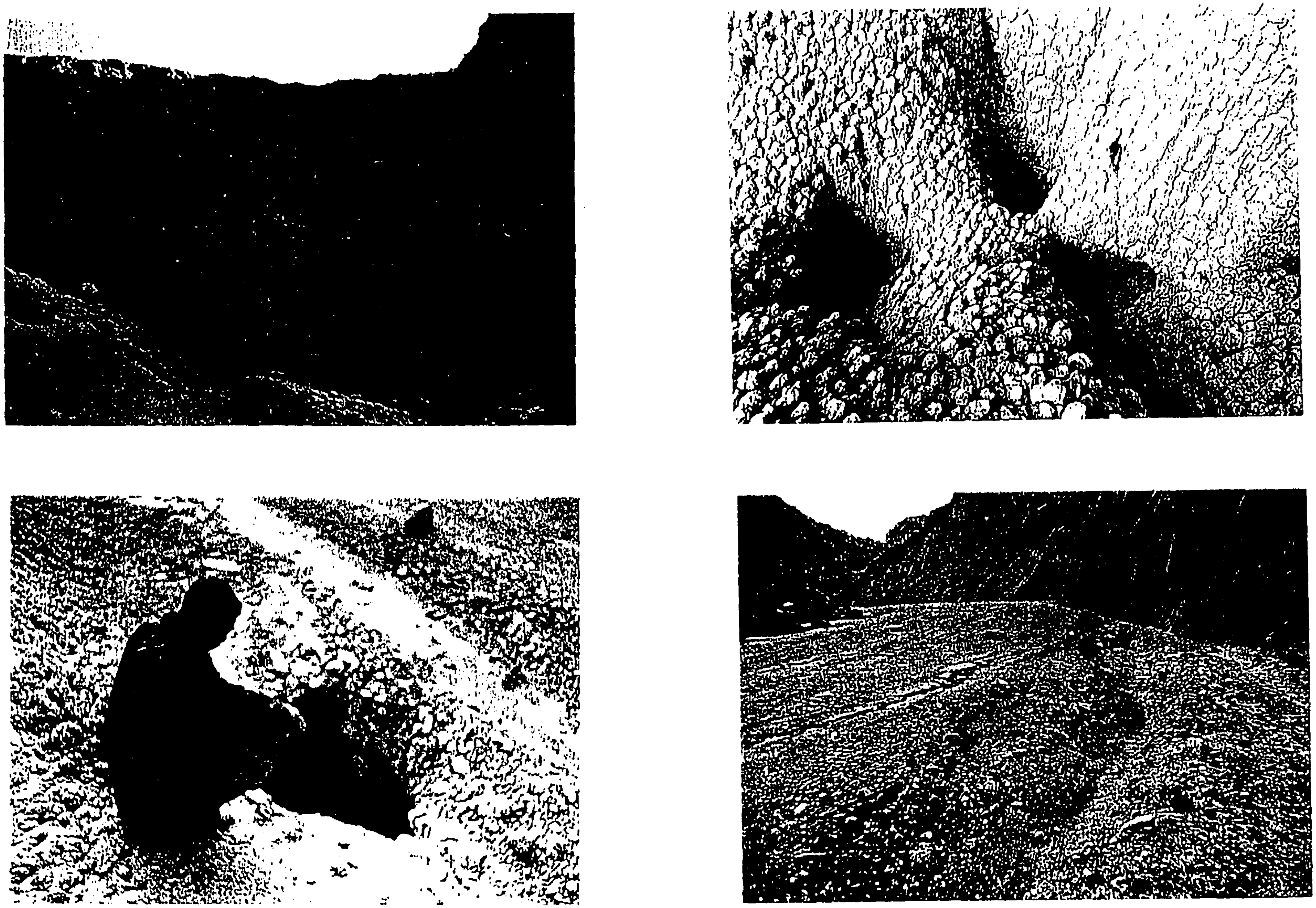


Figure 1.4: Some undesirable behaviours of Marl in road construction.

The destructive effects of high sulfate concentration on cement and lime stabilized soils was presented by *Mehra et al. (1955)* and *Sherwood (1958, 1962)*. It is reported that within a period of two years following lime stabilization in roadway, in Las Vegas, U.S., in spite of acceptable preliminary geotechnical investigations and excellent initial performance, distress began to appear in the form of surface heaving and cracking *(Mitchell 1986)*. Heaves amounting to several centimetres and in some case as much as 30 centimetres above the adjacent pavement were observed and ranged from 30-60 centimetre width *(Hunter 1988)*. Representative samples of damaged subbase analyzed by *XRD* indicted the presence of ettringite minerals *(Mitchell and Dirmatas 1992)*. Other major occurrences of lime-induced heave have been documented. Problem areas have included Southern California, and Texas, U.S., in the highway construction *(California Department of Transportation 1974)* and even in foundation and slab in Paris, France *(Hunter 1989)*. The induced heave is attributed to growth of ettringite. However, the exact mechanism of these failures is still not well known *(Mitchell 1986)*.

1.4 REACTION FACTORS IMPACTING ON MARL INSTABILITY

By and large, it seems that in terms of marl, the common geotechnical methods for the evaluation of unstabilized/stabilized soil do not work well. These evaluation methods consider stabilized soil only in terms of mechanical properties *(Gillott 1968, Bells 1988, Wild & Arabi 1989, Rao et al. 1993, Amoudi 1994A)*. A physico-chemical (reaction factors) study of the behaviour of unstabilized/stabilized marl must be carried out to answer questions regarding the instability performance of marl. A comprehensive study should consider the behaviour of marl before and after stabilization with significant attention to the role of marl composition upon those failures.

1.4.1 Palygorskite/Sepiolite and Pore Fluid's Role on Marl Behaviour

Since it is believed that palygorskite/sepiolite controls marl behaviour, the significance role of palygorskite, sepiolite, zeolitic water and pore fluid chemistry upon marl performance must be identified as factors contributing to system failures. Questions which arise include: What is the role of palygorskite and sepiolite structures on marl behaviour? How can they be quantified in marly soils? What is the role of carbonate and pore fluid of marl upon its dispersive performance? Since ettringite formation requires sulfate, what is the role of the soil open structure of palygorskite and sepiolite on the pore fluid holding capacity of soil? How does a stabilizer affect the role of zeolitic water?

During ettringite development, due to the mineral transformation, a significant change in the structure of stabilized soil occurs. This will produce clay loss due to the transformation of clay to ettringite. Changes in the structure of stabilized soil, or clay loss, must be considered from at least three perspectives:

-Mineralogical aspect.
-Geoenvironmental aspect (soil ion movement).
-Soil behaviour and geotechnical aspects caused by mineral transformation.

1.4.2 Mineral Identification, Marl Components and Ettringite

To identify the rate of change in the clay fraction of soil, mineral quantification is mandatory. This will help to quantify the presence of each mineral and the magnitude of mineral transformation. *X-ray* diffraction seems to be one of the most common tools used in this aspect. However, the simplicity and accuracy behind such a quantitative analysis are important. Questions which might be asked include, to what extent are common *x-ray* quantification techniques for clay soils accurate? How can we quantify the extent and magnitude of ettringite formation? What are the main factors governing such a quantification analysis in terms of major elements of marl and ettringite mineral?

1.4.3 Geoenvironmental Aspect of Ettringite Formation

Since ettringite formation is associated with a noticeable change in soil structure, it will significantly alter the leachability performance of soil. In particular, the leachability of chloride is of interest, since its presence might affect the extent and rate of ettringite formation *(Lorcher 1968)*. In other words, one might question; How does anion repulsion affect the possibility of ettringite formation? How will the stabilizer affect the chloride movement as a factor contributing to the extent of ettringite development?

To compound the problem of evaluation of soil performance and failures, it is often noted that because of the shortage of fresh water in sub-tropical and tropical arid regions, it is not uncommon for saltwater to be used as a wetting agent in many geotechnical projects. This contributes further to the presence of salts in the soil, and is a factor that has yet to be fully appreciated in the evaluation of the stability of marl in any physical or chemical stabilization process.

1.4.4 Effect of Ettringite upon Soil Behaviour

To find out the rate of ettringite formation and its impact upon stability of stabilized marl, mineral transformation of the clay fraction to ettringite under curing conditions has to be evaluated.

From a geotechnical perspective, questions which arise include: Does the needle-like structure of ettringite contribute positively or negatively to the geotechnical properties of the stabilized soil? What is the rate of ettringite formation and the role of different soil fractions upon ettringite growth? What are the appropriate conditions for ettringite development?

1.5 RESEARCH OBJECTIVES

As was briefly addressed before, the nature of soil stabilization failures and the conditions, both compositional and environmental, that may lead to deterioration are not well known. Knowing these conditions will allow for a better comprehension of the failure mechanism and hopefully help in the prevention of these failures. Prior research has revolved around the stabilization of soil from a mechanical viewpoint and has generally neglected ettringite development, which is intrinsic to the cement hydration process. Furthermore, the vast majority of previous research did not consider the effect of the soil fraction on ettringite formation, or its effect upon soil behaviour. The influence of marl minerals (such as palygorskite and sepiolite) are not considered and in most cases the role of ettringite, as a new mineral which replaces the clay fraction of stabilized soil, is not taken into account. It seems that the main reason for being unable to prevent these failures, results from a lack of a physico-chemical understanding of soil stability *(Yong et al. 1996, Yong and Ouhadi 1997A)*. As such, the main objectives of this research will be as follows:

1- To determine the role of palygorskite, sepiolite and pore fluid chemistry on stability of natural and stabilized marls.

2- To determine the rate at which ettringite is formed after lime treatment.

3- To assess the role of ettringite on the stability of stabilized marl.

The soil to be used in this research is samples from the southern part of Iran. This region is highly prone to both natural and artificial slope instability problems. Large marl deposits exist within the Persian Gulf and in the area of the Sea of Oman. Pure palygorskite, and sepiolite are used in this research as will be addressed in Chapter 3. Control samples of illitic soil (Domtar sealbond) and kaolinite are used in this study.

1.6 TASKS

The aforementioned objectives are accomplished through experimental studies. The details involved in the experimental studies will be given in Chapter 3. The laboratory experimental studies consist of the following:

(1) Physical and chemical tests to determine the composition and properties of the tested soil and sea-water samples (e.g. *x-ray* diffraction, surface activity of soil, amorphous material measurement, and pore fluid chemistry analysis). These analyses will be used to give a general picture of marl components and their role on behaviour. The pore fluid analyses were performed mainly by application of atomic absorption spectroscopy (AAS), turbidimeter and chemical titration, as will be discussed in detail in Chapter 3.

(2) Soil suction testing was used to study the effect of ettringite, palygorskite, and sepiolite on marl behaviour, the role of stabilizers on zeolitic water, and to obtain the energy state of the soil pore fluids. The zeta meter was used to measure the zeta potential of pure ettringite.

(3) *X-ray* diffraction testing was used to establish some basic criteria for quantitative evaluation purposes of palygorskite, sepiolite and ettringite. The performance of this test was also aimed at determining the extent and rate of mineral transformation and to evaluate how environmental conditions impact upon this mineral transformation.

(4) The soil leaching test, was used to examine the leaching and migration behaviour of chloride ion during and after mineral transformation which may affect the quantity of ettringite development.

(5) A series of geotechnical tests were used, including, California Bearing Ratio *(CBR)* and Atterberg limits to determine the role of palygorskite/sepiolite on the geotechnical response of soils and to investigate the effect of ettringite formation upon geotechnical aspects of soil performance.

Figure 1.5 gives the research protocol for achieving the aforementioned objectives.

RESEARCH PROTOCOL

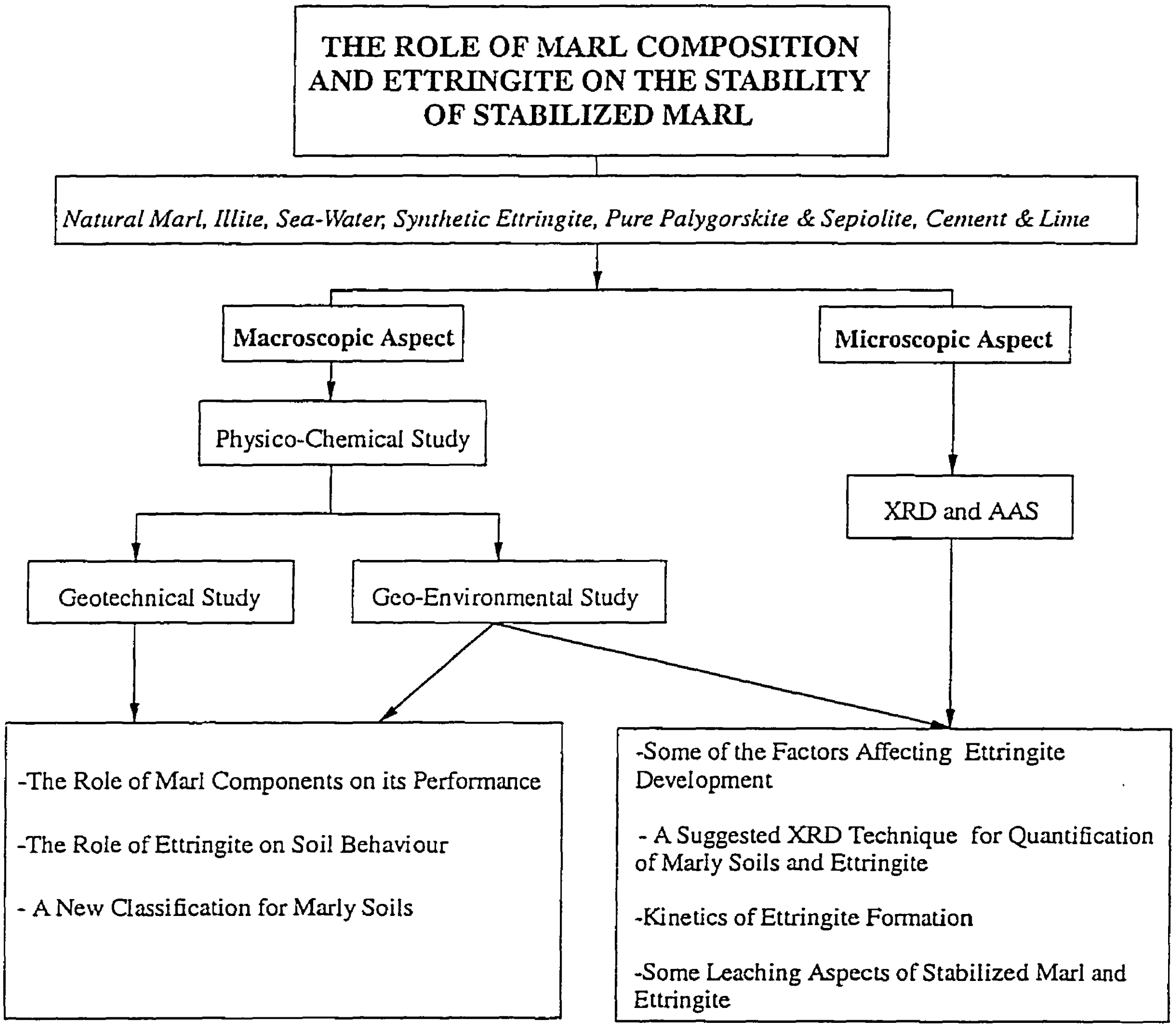


Figure 1.5: Thesis structure

1.7 ORGANIZATION OF THE THESIS

The thesis consists of eight Chapters, the contents of which are as follows:

Chapter 1: an introductory Chapter presenting the problem, objectives and the scope of this study.

Chapter 2: provides a literature review concerning the role of pore fluid chemistry upon soil behaviour. It also includes talks about mineral identification methods, and a review relating to marly soils. Collapsible and dispersive behaviour are discussed and stabilization with cement and lime as a method to overcome those marl related problems are presented. The latter consists of reviews concerning major minerals which form in the stabilization process with emphasis on ettringite.

Chapter 3: presents a description of the experimental methods, materials and techniques as well as testing procedures employed in this research.

Chapter 4: evaluates the accuracy and simplicity of some of the common quantitative *x-ray* methods and includes a suggested *XRD* technique for quantitative interpretation of mineralogical composition of marly soils and ettringite.

Chapter 5: describes the role of marl composition and reaction factors on instability and behaviour of marly soils. It emphasizes the behaviour of palygorskite-sepiolite as the major fraction of marl and provides a suggested soil classification for marly soils.

Chapter 6: summarizes the mineralogy and interaction aspects of stabilized marl and the mineral transformation of palygorskite. It also includes the identification of ettringite in marl stabilization by the *XRD* technique, as well as the role of ettringite on the stability of stabilized marl.

Chapter 7: presents the kinetics of ettringite formation and evaluates some different factors affecting the rate of ettringite development. It also discusses the experimental study on the leaching behaviour of marl. Furthermore, it differentiates between different aspects of soil stabilization using cement and lime in conjunction with the role of stabilizer agents on zeolitic water performance. The possible contribution of different clay soils for ettringite formation is discussed.

Chapter 8: contains a presentation of conclusive statements, contribution of the thesis to original knowledge, together with some suggestions for further studies.

References: presents a listing of the references cited in this thesis.

Appendix I: provides a brief application of the formulation used for error analysis in the evaluation of experimental results of this research.

Appendix II: gives a detailed description of some of the experiments performed in this study.

Appendix III: includes some of the *XRD* patterns of soil samples and ettringite which were resulted from the current research.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION

Water has a high tendency to attach to soil minerals, in particular, to clay. Many clay soils swell when exposed to water. The surface potential at the interface between soil and water is governed by the presence of cations which occur between soil particles within the soil solution. Clay particles are particularly sensitive to these forces due to their inherently large specific surface area. This tends to give a dispersive or flocculated structure which affects soil properties and performance *(Yong et al. 1969, 1992)*. The presence and type of cations and anions in the soil pore fluid, in conjunction with soil mineralogy, grain size distribution, and the history of the soil, govern the soil performance in terms of the presence and extent of swelling, dispersivity and collapsible behaviour. Studies from the geotechnical, geoenvironmental, mineralogical and physico-chemical points of view are among the available tools to study soil behaviour.

Since the problem of marly soils, including their instability in natural and stabilized states was explained in Chapter 1, this Chapter focuses attention mainly on some fundamental aspects of soil behaviour which are used later in this study and will be referred to, in the rest of the thesis.

2.2 DIFFUSE ION-LAYER AND ZETA POTENTIAL

Since soil-water contains dissolved solutes, the interaction between a negatively charged soil particle surface and the cations in the soil-water will generate an electric double layer (EDL), resulting in a pattern of negative and positive charges near the soil particles. The diffuse double layer (DDL) theory, which was independently developed by Gouy and Chapman, provides the recognition necessary to account for the mobility of the ions in solution *(Yong et al. 1992)*. The interaction of the diffuse ion-layer of adjacent particles provides an explanation of the swelling, plasticity, and water retention properties of clays *(Yong and Warkentin 1975)*. *Stern (1924)* proposed a model in which the diffuse ion-layer is divided into two parts. These two parts are assumed to be separated by a plane, called the Stern plane, located at approximately a hydrated ion radius from the surface of particle (Figure 2.1). The potential changes from Ψ_o (the surface or wall potential) to Ψ_δ (the Stern potential) in the Stern layer, and decays from Ψ_δ to zero in the diffuse ion-layer. The details of potential and charge distribution according, to the Stern model, is reviewed by *Olphen (1977)*. The decay of the potential with distance from the surface of the particle has a exponential pattern. The centre of gravity of the space charge corresponds with the plane $\kappa x=1$ or $x=1/\kappa$. According to Gouy-Chapman theory, $1/\kappa$ is called the thickness of diffuse ion-layer which is equal to:

$$\frac{1}{k}=\left(\frac{\epsilon KT}{8\pi C_{o} e^{2} z^{2}}\right)^{1/2} \tag{2:1}$$

where $1/\kappa$ is the representative thickness of diffuse ion-layer (angstrom), ϵ is the dielectric constant of pore fluid, KT is the product of Boltzman constant and absolute temperature (which is equal to 0.4×10^{-13} ergs at room temperature), C_o represents the concentration of the species of ion in the bulk solution (normality $\times$ 10^{-3} $\times$ avogadro's number, ion/cm^3), e is called elementary charge which is equal to 4.77×10^{-10} esu, and z is the valence of the species.

In other words, potential distributions around charged surfaces are a function of the parameters indicated in the above equation. For example, the thickness of diffuse ion-layer will decrease if the concentration of cations increases.

The cations can be arranged in a series which portrays their replacing power. Although the type of clay mineral and ion which is being replaced governs the position of ions in this series, the arrangement of cations in the order of increasing replacing power will appear as follows:

$$Li^+ < Na^+ < H^+ < K^+ < NH^{4+} \leq Mg^{2+} < Ca^{2+} \leq Al^{3+}$$

in which, for a given valence, the cations with a smaller hydrated radius will replace cations with the same valence having a larger hydrated radius and, therefore, will move closest to the clay particle surface and be more strongly adsorbed. As such, the potassium ion with the same valence as the sodium ion has the ability to replace the sodium ion simply because its radius 3.8-5.3 angstrom is smaller than that of the sodium ion which is 5.6-7.9 angstrom. The number of exchangeable cations replaced depends upon the concentration of ions in the replacing solution *(Yong et al. 1992)*.

The significant properties of the diffuse double layer that are experimentally available are, the zeta potential and the thickness of the diffuse ion-layer. Neither of these properties can be measured directly. The zeta potential is computed from measurements of the electrokinetic phenomena at an infinite dilution of particles, while the thickness of the diffuse ion-layer (as was addressed before) is computed from the ionic strength of the medium. The zeta potential is the electric potential in the diffuse ion-layer at the interface between a particle which moves in an electric field and the surrounding liquid. The zeta potential is computed from the electrophoretic mobility of the soil particle. Its magnitude is considered a measure of the particle repulsion *(Yong et al. 1992)*. A colloidal system such as clays due to their microscopic size have a very large surface area to weight ratio. As a result, gravity is insignificant and surface forces control their behaviour. The zeta-meter measures the effect of the electrostatic charge, basic repulsive surface force; which is always opposed by Van der Waals attractive forces. The net result (attraction or repulsion) depends on the relative magnitude of both.

2.3 MINERAL IDENTIFICATION METHODS

The methods used to identify and characterize clay minerals, as well as their chief chemical and fabric characteristics mainly include *X-ray* diffraction *(XRD)*, specific surface area *(SSA)*, infrared spectral analysis *(IR)*, scanning electron microscopy *(SEM)* and differential thermal analysis *(DTA)* *(Yong 1976, Velde 1992)*. An atomic absorption spectrophotometer *(AAS)* has often been used to evaluate the chemistry of pore fluids. *XRD*, *SSA*, and *AAS* have been employed in the current research process. *XRD* is based upon *Bragg's law* *(Bragg 1912)* which is defined as :

$$2d\sin\theta = n\lambda \tag{2.2}$$

in which, d is the distance between two planes of atoms, θ is the reflection angle, λ is the wave length of incident rays, and n is often called the order of reflection. In fact, in *XRD*, each mineral shows a series of peaks which are specific to each individual mineral. ASTM and ICDD (International Centre for Diffraction Data) classified the data for each mineral on the basis of the most intense diffraction lines which are usually called the weighting factor. The data also contain the d spacing for every line and the relative intensities of the line which are presented on the basis of the strongest line is assumed to be 100.

In order to investigate the presence of different minerals in soils, *XRD* quantification methods are often used. However, the use of these methods in soils involves a set of restrictions which causes either time-consuming analysis or fast evaluation with low accuracy. The limitations associated with application of *XRD* for soil quantification will be addressed in Chapter 4.

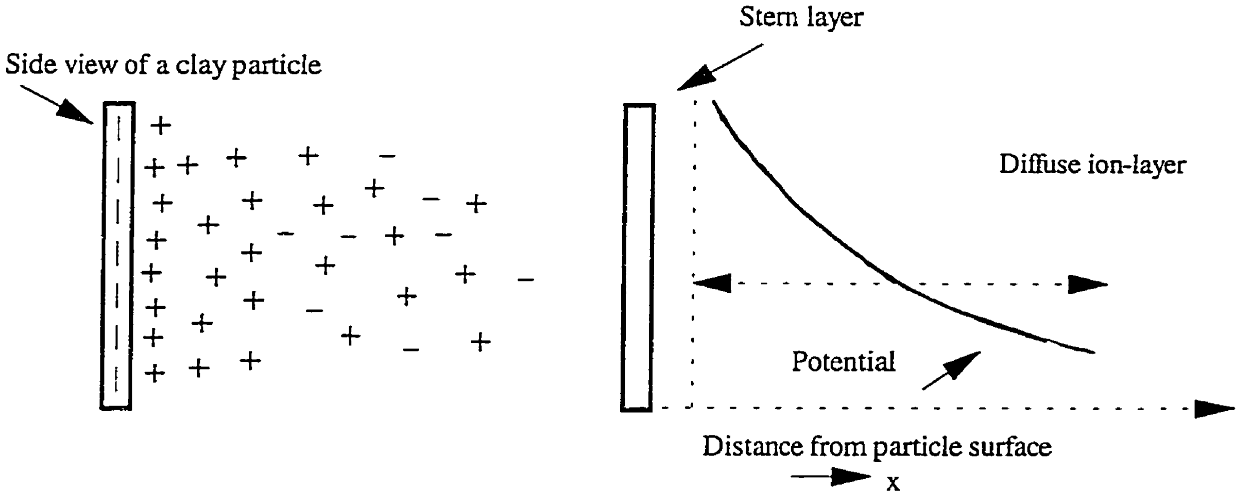


Figure 2.1: Schematic diagram of the diffuse ion-layer (Yong et al. 1992).

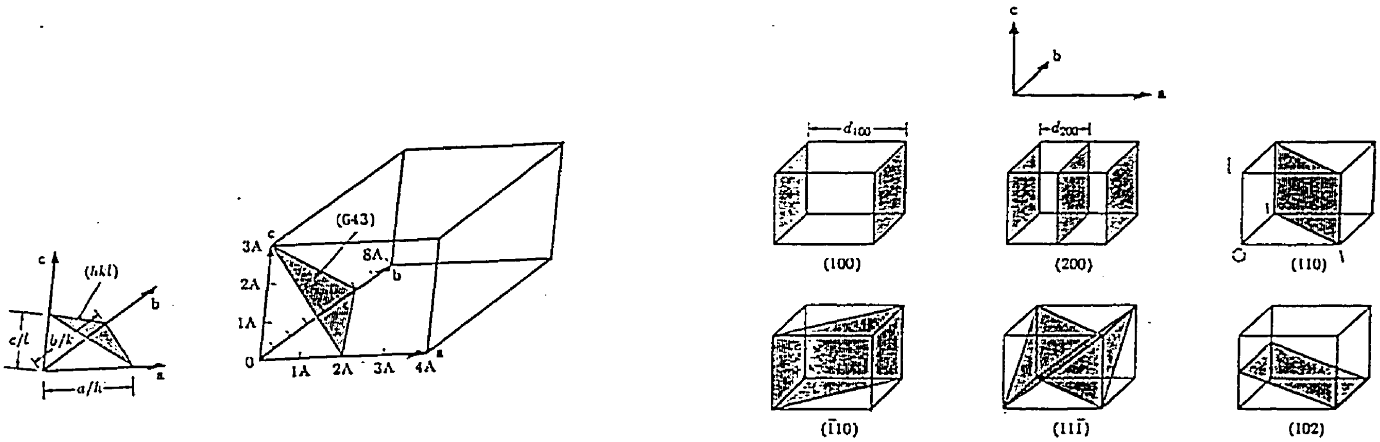


Figure 2.2: Miller indices (Cullity 1967).

Table 2.1 presents the *XRD* reflection lines related to palygorskite mineral. In this Table, *d* and W.F. are the distance between two planes of atoms and the weighting factor, respectively, as introduced before. The letters *h*, *k*, and *l* are called *Miller* indices. Miller indices (Figure 2.2) are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes. They are indications of the orientation of planes in a lattice. The indices are zero when the plane and axis are parallel and are negative if the plane cuts a negative axis *(Cullity 1967)*.

TABLE 2.1: *d* Spacing, weighting factor and Miller indices of palygorskite.

d	W.F.	hkl	d	W.F.	hkl
10.40	100	-110	3.220	16	-311
6.330	20	200	3.170	25	400
5.380	14	130	3.090	12	-321
4.460	30	040	2.885	4	-151
4.260	12	-121	2.673	6	-341
4.130	16	-310	2.605	10	-421
3.990	4	201	2.585	16	341
3.650	10	-221	2.536	18	440
3.440	4	-150	2.507	12	161
3.350	8	-231			

2.4 MARLY SOILS

Clays can occur as sedimentary deposits in fresh- and salt-water environments. These environments affect the structure of the clay. Generally, clay deposited in fresh-water has small relatively porous aggregates and small voids, whereas, marine salt-water clays have large dense aggregates separated by large voids *(Yong and Warkentin 1975, Madedor 1989)*. Marl, although encountered in many different parts of the world, has received little attention in international soil literature. Keuper marl, and its use as a foundation material, has been reviewed by *Meigh (1976)*. Marl in Quebec has been reviewed by *Waddington (1950)*. *Guillet (1969)* reported upon the presence of marl in Ontario and upon its industrial usage. *Kerr et al. (1950)* reviewed microscopic aspects of the clay fraction of U.S. Georgian and Floridian marl. *Ovcharenko (1960)* described mineralogical aspects of palygorskite in Russian marl. Some aspects of leaching behaviour of marl were explored by *Sanad et al. (1990)*. Geological aspects of sedimentation in the Persian Gulf are discussed in articles *(Kassler et al. 1973)* contained within a publication on the subject edited by *Purser (1973)*. *Fookes et al. (1975)* provides a general classification and description of marl soil. Some characteristics of Persian Gulf marl have recently been presented by several authors *(Rantucci (1987), Sanad and Bader (1990), Ismael (1993), Yong et al. (1993), Ouhadi et al. (1993))*.

In spite of many reports expressing instability of marly soils *(Voight 1981, Akili & Torrance 1981, Turner and Seago 1985, Rantuncci 1987, Jones 1989, Antoine et al. 1995)* some of which were addressed in Chapter 1, in almost all previous research work, there has been no serious attention given to the effect of the clay fraction (such as palygorskite and sepiolite) upon marl performance, and its contribution to the formation of ettringite in post stabilization failures. Since almost all those previously mentioned failures (section 1.3) happened in the presence of water, the general recommendation of avoiding the contact of marly soils with water is very common in the literature. However, since mechanical factors generally used to explain the causes for the foundation failures have not been satisfactorily accepted, performing a study which uses physico-chemical (reaction) factors to explain the general basic causes for deterioration of support capability for these types of soils seems quite necessary. In other words, conducting a research work to deal mainly with the various interactions, reactions and factors contributing to the stability and instability of marl soils, and lime or cement treated marls. In particular, as mentioned previously, the presence of swelling-type clay minerals, in combination with the high carbonate, sulfate (gypsum) and salt content are all a recipe for a very interesting and challenging suite of reactions which could prove to be adverse to the longterm stability of the soil. Significant attention should be given to investigating the role of palygorskite and sepiolite on instability of marly soils in such a physico-chemical study.

2.5 COLLAPSIBLE BEHAVIOUR

Collapsible soils exhibit considerable strength and stiffness in their dry and natural state but lose strength and settle upon wetting *(Rollins et al. 1994)*. Collapse is the result of a sudden closure of soil voids. Collapsible soils undergo a sudden decrease in volume when internal structural support is lost. Internal soil support is considered to provide temporary strength, and is derived from a number of sources including, capillary tension and cementing agents. The cementing agents may include amorphous material and calcium carbonate. Other bonding agents include silt, clay and clay bridges. Wetting destroys and leaches out these cementing agents *(Hunt 1983)*. Soils which have a substantial clay content are capable of collapsing or swelling under certain circumstances. Based upon the magnitude of the applied vertical load as a function of the clay content, swelling or collapse could occur *(Alonso 1993)*. It is found that the percentage of clay is the main parameter controlling the behaviour of these soils *(Jimenez et al. 1973)*. There is a limiting value of clay content which marks the transition from collapse to swelling state for a given applied pressure *(Sohby 1984)*. Double oedometer testing has been used to evaluate the collapsible potential of soils *(Jennings et al. 1957, 1973)*. Marly soils are also known to show different performance including collapsible *(Yong et al. 1993, Mohammed 1995)* swelling *(Ouhadi et al. 1993)* and dispersive behaviour *(Yong* *et al. 1996)*.

2.6 DISPERSIVITY AND POTENTIAL DETERMINING IONS

Dispersive soils refer to clayey silty soils in which the physico-chemical state of the clay fraction of the soil mass is such as to cause individual colloidal clay particles to go into suspension when submerged. These soils have a higher dissolved sodium content in their pore water than in ordinary clay soils *(Sherard et al., 1976A)*. Ordinary clay has a predominance of Ca^{++}, Mg^{++}, and K^+ cations in the pore water of its mass *(Haroon et al. 1993)*.

Identification involves both physical and chemical testing. Physical tests include, crumb test *(Holmgren and Flanagan 1977)*, double hydrometer test *(Decker and Dunnigan 1977)* and the pinhole test *(Sherard et al., 1976B)*. Chemical testing methods include, saturation extract to obtain the sodium adsorption ratio *(SAR)* and exchangeable sodium percent *(ESR)* factor *(Sherard et al. 1976A, Mitchell 1993)*. The sodium adsorption ratio *(SAR)* describes the content of the soil solution and is given as follows:

$$SAR=\frac{[Na^+]}{([Mg^{2+}]+[Ca^{2+}])^{\frac{1}{2}}} \tag{2.3}$$

where the concentration of solution is described in meq/L.

The exchange sodium ratio *(ESR)* describes the ratio of the exchangeable sodium with regard to cation exchange capacity and is given as follows:

$$ESR=\frac{ES}{CEC-ES} \tag{2.4}$$

where *ES* is the exchangeable Na in meq/100 g of soil and the *CEC* is the cation exchange capacity in the same unit.

In terms of dispersive behaviour, anionic species must be taken into consideration to describe the interparticle forces in the system in addition to the *SAR* and *ESR*, and in evaluating the dispersivity of a soil *(Yong et al. 1979)*. The main factors which may cause the dispersive phenomena are: mineralogy of the clay particles, chemical properties of dissolved salts in the pore water, types of adsorbed cations on the surface of clay particles and chemical properties of flowing water in contact with the soil *(Rahimi 1993)*. *Sherard et al. (1972-1976)* conducted an extensive laboratory program and introduced an evaluation method based on chemical properties of dissolved salts in pore water. Many contradictory results were observed in the application of this method *(Yong et al. 1977, Coumoulos 1977, Villegas 1977, Craft 1984, Rahimi 1993)*. The role of potential determining ions *(PDI)* upon dispersive behaviour is one of the important factors which has generally been neglected in the majority of research to date. Potential determining ions can be specifically adsorbed by the clay particle. In other words, their adsorption onto the clay particle surface is not through electrostatic interaction but rather through chemical adsorption. Chemical or specific adsorption of PDIs refers to strong affinity of ions to the soil particle surface, which generally occurs in the stern layer through covalent bonding. They also do not behave as exchangeable ions *(Yong 1977, 1992, Sparks 1986)*. In addition to the crystal structure of the solid, and chemical composition, potential determining ions are also known to play an essential role in the development of electric charges on clay particles *(Yong et al. 1992)*. In fact PDIs not only influence the surface charge, but also affect the soil surface potential. As an example, H^+ and OH^- ions adsorbed onto particle surfaces not only affect the surface charge, but also affect the surface potential *(Yong et al. 1992)*. The contribution of potential determining ions to the formation of the surface charge of soils causes an increase in their dispersive potential. In circumstances where minerals containing carbonate are present, the significant role of bicarbonate as a potential determining ion has to be strongly considered *(Yong et al.*

1977). Chloride (Cl^-) and sulfate (SO^{2-}_4) ions are known to be among the non-potential ions. In fact, their adsorption will be through electrostatic interaction.

2.7 ANION REPULSION

Once an anion approaches a charged surface, it can be subjected to attractive and/or repulsive forces. Attraction is caused by positively charged sites, while negatively charged surfaces are responsible for repulsion.

Factors affecting repulsion include, 1) anion charge and concentration, 2) species of exchangeable cation, 3) pH, 4) the presence of other anions, and 5) the nature and charge of colloid surfaces. For example, if the negative charge on a soil colloid surface remains constant, anions of a higher charge are repelled more than anions of a lower charge. Similarly, increasing the anion concentration increases anion repulsion *(Bohn et al 1979)*. Ions which commonly exhibit anion repulsion include Cl^- and SO_4^{2-}. In marly soils depending on the environmental condition, both chloride and sulfate anions might be present in the pore fluid *(Hunter 1988, Yong et al. 1966)*. Their competition with the soil surface (as will be discussed in section 2.8.3), may directly affect the possibility of ettringite formation.

2.8 SOIL STABILIZATION AND FAILURE

Soil improvement techniques can be classified from different aspects. A general classification includes mechanical and chemical methods.

Mechanical techniques ensure soil stability mainly through density efforts, providing an appropriate drainage system and the maintenance of the water content at a constant level without the addition of any supplementary material. Chemical approaches concern the improvement of soil properties through the use of additives. This includes the use of cement, lime, bitumen, organic compounds, fly ashes and salt. While the use of cement and lime traditionally are very common as a stabilizers, the use of bitumen is restricted to mainly sandy and silty soils. Bitumen, asphalt and tar as stabilizers are not recommended for soils with medium to high plasticity *(Kezdi 1979)*. Fly ash can be used in conjunction with cement, lime and bitumen. The use of organic compounds as stabilizers is restricted due to their cost and toxicity *(Nelson and Miller 1992)*. The significance of the use of salt as a stabilizer is still debatable.

However, the failure of many of lime- and cement-stabilized soils have been reported which is attributed to the swelling arising from ettringite formation.

2.8.1 Soil Stabilization with Lime

In lime stabilization, hydrate lime $\{Ca(OH)_2\}$, quicklime $\{CaO\}$, or dolomitic quicklime $\{CaO.MgO\}$, can be used. For pavement work, about 1% by weight for each 10% of clay content in the soil is recommended. These amounts are not to be exceeded without careful consideration *(Ingles 1972)*. A small additional amount (1/2 - 1%) should be allowed for inefficient mixing of machinery *(Lee 1974)*.

Four mechanisms can be observed in the lime stabilization process. These include as follows: 1)cation exchange, 2)flocculation/agglomeration, 3)carbonation reactions and 4)pozzolanic reactions *(Thompson 1966-68)*. These processes are affected by an ion exchange in clay minerals and a cementing reaction which cause an increase in the strength of the soil being stabilized. The dissociation of the $Ca(OH)_2$ into Ca^{2+} and OH^- ions, will cause a decrease in the thickness of the diffuse ion-layer of the clay fraction due to the ion exchange. This in turn, will be responsible for producing a flocculated structure. An increase in concentration of OH^- ions will increase the pH, leading to dissolved alumina and silica in the clay fraction. These released alumina and silica will interact with calcium ions to produce two cementing agents of pozzolanic reaction. Those cementing agents are called *CSH* $\{3CaO.2SiO_2.3H_2O\}$ and *CAH*

{$3CaO.Al_2O_3.Ca(OH)_2).12H_2O$}, respectively. The carbonation reaction is caused by the formation of $CaCO_3$, after carbonic acid is produced from the carbon dioxide content of the air in the soil, and free water. This reaction will be as follows:

$$Ca(OH)_2+H_2CO_3+2H_2O \rightarrow CaCO_3+4H_2O \tag{2.5}$$

These four mechanisms, during the application of lime in soil stabilization, cause cohesive soils to become more workable and less plastic. Lime usually reacts most readily with clay soils where the plasticity index exceeds at least 10 *(Gillott 1968)*. The selection of the percentage of lime as an additive is usually based on three tests: consistency limits, pH, and strength tests, where the latter one includes unconfined compression and *CBR* testing *(Kezdi 1979)*. It has been reported that larger strengths are developed in soils treated with quicklime rather than slaked lime *(U.S. Waterways Experiment Station, 1962)*.

While the presence of sulfate in lime stabilized soil is known to adversely affect the stability of the soils *(Sherwood 1962)*, in some circumstances sulfate is known to have a safe effect on lime stabilization *(Holm 1983)*. *Mohamed et al. (1991)* on the evaluation of the performance of different types of additives for soil stabilization purposes, demonstrate the benefits of the addition of cement and lime to improve soil properties and performance. As such, it may be difficult to predict the condition under which lime-induced heave may occur *(Sivapullaiah et al. 1993)*.

Reactions between lime, alumina (released from the clay fraction of soil) and sulfates present in some soils cause the formation of an expansive crystalline mineral called ettringite. These reactions have been responsible for the failure of several soil stabilization projects (section 1.3). Whenever insufficient clay minerals were present, lime induced heave did not occur in these projects. Recently reported failures in the U.S. involving lime stabilization, indicate that the soil before treatment, contained significant amounts of soluble sodium sulfate, up to 1.5 percent by weight *(Mitchell and Dermatas*

1992).

While a small number of studies have been carried out on soil stabilization in presence of sulfate, no actual comprehensive study has been performed to physico-chemically evaluate the reaction of different fractions of stabilized soil and sulfate. As such, the effect of soil composition, the variation of pH and the type of clay fraction present, are almost unknown.

2.8.2 Soil Stabilization with Cement

It is believed that the base exchange and cementing action of Portland cement with clay is similar to that of lime *(Chen 1975, Kezdi 1979)*.

The hydration process of cement and the effects of sulfate solutions on long-term behaviour of cement have been reviewed by *Lea (1970)* and *Neville (1983)*.

Cement in soil stabilization increases the strength of the mixture. The action of cement on clay minerals is to reduce the plasticity index, to prevent potential volume change and to increase the shear strength *(Croft 1967)*. Some aspects of leaching effects upon soil-cement have been presented by *Jackson (1974)*. He shows that the leaching action tends to increase the tendency of soil-cement to form wider and/or new micro-cracks with time.

Timusk and Sheikh (1977) used a mixture of high alumina cement, gypsum and lime to produce very high expansive pressure in drilled piles. The mixture was used to enhance the skin friction between the pile and the surrounding soil. While in granular soils the cementation action of hydrated cement is similar to that of concrete, in clay soils the chemical reaction of cement and soil is responsible for soil improvement. A dry Portland cement consists of four basic elements, as follows: C_3S (tricalcium silicate), C_4S (tetracalcium silicate), C_3A (tricalcium aluminate) and C_4AF (tetracalcium aluminoferrite), as their chemical formulations are presented in the Table 2.2. The hydration products of these elements are described by *Brunauer and Copeland (1964)* and are shown in the Table 2.2. *CSH* which forms from hydration of C_3S and C_2S is the most important product in terms of strength achievement. As Table 2.2 indicates, the hydration process of two major elements of cement produces *CSH* and lime which are two new products in this process. Therefore, the interaction between this lime and clay minerals may also play an essential role in terms of the soil cement interaction process. The mechanism of the latter will be the same as that of a lime-clay interaction, as previously addressed. The produced calcium hydroxide will increase the pH of the solution leading it to dissolve more alumina and silica of the clay fraction. The dissolved ions, in turn, will interact with calcium ions and produce more *CSH* and *CAH* leading to the achievement of more strength.

However, the failure of some of the cement-stabilized soils to perform their function have been reported. The failure is attributed to the formation of ettringite (Mehra 1955, Sherwood 1958, 1962).

Table 2.2: Hydration process of Portland cement.

$2(3CaO.SiO_2)$ + $6H_2O$	=	$3CaO.2SiO_2.3H_2O$ + $3Ca(OH)_2$
(tricalcium silicate) (water)		(CSH) (lime)
$2(2CaO.SiO_2)$ + $4H_2O$	=	$3CaO.2SiO_2.3H_2O$ + $3Ca(OH)_2$
(bicalcium silicate) (water)		(CSH) (lime)
$4CaO.Al_2O_3.Fe_2O_3$ + $10H_2O$ + $2Ca(OH)_2$	=	$6CaO.Al_2O_3.Fe_2O_3.12H_2O$
(tetracalcium aluminoferrite)		(calcium aluminoferrite hydrate)
$3CaO.Al_2O_3$ + $12H_2O$ + $Ca(OH)_2$	=	$3CaO.Al_2O_3.Ca(OH)_2.12H_2O$
(tricalcium aluminate)		(tetracalcium aluminate hydrate)
$3CaO.Al_2O_3$ + $10H_2O$ + $CaSO_4.2H_2O$	=	$3CaO.Al_2O_3.CaSO_4.12H_2O$
(tricalcium aluminate) (gypsum)		(calcium monosulfoaluminate)

2.8.3 Ettringite and Major Minerals Formed in the Stabilization Process

CSH {$3CaO.2SiO_2.3H_2O$} and *CAH* {$3CaO.Al_2O_3.Ca(OH)_2).12H_2O$} are two major cementing agents which form in the stabilization process. These cementing agents are responsible for the improved soil strength. With regard to the major minerals which form during the hydration process of lime and cement, the majority of research to date has solely studied the hydration of Portland cement concrete. *Copeland et al. (1967)* reported that sulfate could be adsorbed by *CSH* gel at early hydration ages and released at later ages. *Fu et al. (1994)* studied the effect of temperature on sulfate adsorption by *CSH* and reported that *CSH* gel will adsorb sulfate faster at high temperatures and desorb the sulfate more slowly than gel that has adsorbed sulfate at normal temperatures. This may be critical for delayed ettringite formation in high temperature cured samples. *Fu et al. (1995)* also reported that an increase in temperature apparently accelerates the sulfate absorption rate by *CSH*. There are few studies on the effects of ettringite on the formation and growth of these cementing agents.

Ettringite {$Ca_6Al_2(SO_4)_3(OH)_{12},26H_2O$} was first discovered as a natural mineral in Ettringite and Mayen at Rhineland in 1847 *(Dana 1898)*. It might form during the hydration of cement. Its formation in Portland cement concrete can be responsible for deleterious phenomena *(Neville 1983)*. In concrete, ettringite formation can cause cracking due to the development of tensile stress, which is frequently strong enough to overcome the tensile strength of concrete *(Mehta 1973)*. It is indicated that the size of the ettringite mineral is dependent on the condition in which it forms and the amount of lime available *(Mehta 1969, 1982)*. These studies reported that the ettringite crystals formed from saturated lime and sulfate solutions were approximately 1 μm in length and 1/4 μm thick. Both the rate of ettringite formation and the size of the crystals produced are greatly reduced when the solution is saturated with $Ca(OH)_2$ *(Mehta 1976)*. In hydration of cement paste, ettringite peak intensity values generally increase with temperature and hydration time *(Fu et al. 1995)*. Assuming a hexagonal layer structure lattice, the unit cell dimensions and the *d*-spacing for ettringite were calculated by *Mehta (1966)*.

Among several calcium-aluminum-sulfate hydrates which exist during calcium alumina sulfate reactions, only monosulfate hydrate $\{Ca_4(Al_2O_6)(SO_4).12H_2O\}$ and ettringite remain stable in aqueous phase solutions *(Lerch et al. 1929)*.

The chemical interactions leading to ettringite formation in soil stabilization can be summarized as follows *(Hunter 1986)*:

$CaO + H_2O \rightarrow Ca(OH)_2$ *(Hydration of lime)*

$Ca(OH)_2 \rightarrow Ca^{2+} + 2(OH)^-$ *(Ionization of calcium hydroxide; pH rises to 12.3)*

$Al_4Si_4O_{10}(OH)_2.\ nH_2O + 2(OH)^- + 10H_2O \rightarrow 2\{2Al(OH)_4^- + 4H_4SiO_4\} + nH_2O$ (dissolution of clay mineral, at $pH > 10.5$)

$2H_4SiO_4 \rightarrow 2H_3SiO_4^- + 2H^+ \rightarrow 2H_2SiO_4^{2-} + 2H^+$ (dissociation of silicic acid)

$M_XSO_4.\ nH_2O \rightarrow XM^{Y+} + SO_4^{2-} + nH_2O$ dissolution of sulfate minerals; $x=1$, $y=2$ or $x=2$, $y=1$)

Sulfate*(from soil or groundwater)* + Alumina*(released from the clay)* + Calcium*(from lime)* → calcium-aluminum-sulfate*(Ettringite)*

$6Ca^{2+} + 2Al(OH)_4^- + 4OH^- + 3(SO_4)^{2-} + 26H_2O \rightarrow Ca_6\ Al_2\ (SO_4)_3\ (OH)_{12},\ 26H_2O$ *(Formation of Ettringite)*

$CO_2 + H_2O \rightarrow H_2CO_3$ (formation of carbonic acid)

$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2H^+ + 2CO_3^{2-}$ (dissolution of calcite in carbonic acid)

$Ca_6[Al(OH)_6]_2\ .\ (SO_4)_3\ .\ 26H_2O + 2H_2SiO_4^{2-} + 2CO_3^{2-} + O_2 \rightarrow Ca_6[Si(OH)_6]_2\ .\ (SO_4)_2\ .\ (CO_3)_2\ .\ 24H_2O + 2Al(OH)_4^- + SO_4^{2-} + 4OH^- + 2H_2O$ (isostructural substitution as ettringite changes to thaumasite)

$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4.2H_2O$ (formation of secondary gypsum)

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ (formation of secondary calcite)

Mehta and Klein(1966) established that the formation of monosulfate hydrate is favoured in a relatively high alumina content environment, whereas ettringite formation is favoured in a lower alumina content environment. In terms of stability of ettringite and monosulfate, *Gabrisova et al. (1991)* demonstrated that ettringite is stable above $pH=10.5$, and monosulfate disappeared from system below $pH=11.6$. At lower values of pH, only gypsum was present in the system studied. Monosulfate hydrate is stable in moist conditions only, whereas ettringite is stable in wet or dry conditions. Furthermore, formation of monosulfate hydrate does not lead to expansion when exposed to water, while the formation of ettringite leads to substantial increases in volume upon wetting. The swelling arising from ettringite formation is reported to be responsible for many failures of soil stabilization projects. Damage in soil-cement is reported by *Sherwood (1962)* where ettringite was responsible for observed swelling. Formation of ettringite is also known to be responsible for severe damage which has happened in roadway in U.S., where the total cost of rehabilitation exceeded $2,700,000 more than the initial cost of improvements *(Hunter 1988)*. Little attention has been given to the physico-chemical factors involved in these failures, as explained in Chapter 1.

Thaumasite also is known to contribute to the deterioration of soil-cement *(Gouda et al. 1975)*. Thaumasite, $\{Ca_6[Si(OH)_6]_2.(CO_3)_2.(SO_4)_2.24H_2O\}$ is a rare calcium-silicate-hydroxide-sulfate-carbonate-hydrate, not present in the native soils, and not occurring naturally in sedimentary environments *(Edge et al. 1971)*. Other secondary minerals, including calcite $\{CaCO_3\}$ and gypsum $\{CaSO_4.2H_2O\}$, are also produced by the hydration process of cement and lime. Without an abundance of water, they cannot form *(Mitchell 1986)*.

The formation of trichloride alumina hydrate in the cement hydration process $\{3CaO.Al_2O_3.3CaCl_2.32H_2O\}$, which affects the sulfate resistance and as such the durability of cement, was reported to be favourable at high chloride concentrations. In summary, the effect of the joint presence of chlorides and sulfates and whether the resistance of hydrated Portland cements are affected, is debatable. *Kind (1953)* through his research on chloride-sulfate interaction in water retaining structures, reported a noticeable increase in sulfate resistance in cements containing high sulfate and chloride concentration. On the other hand, *Lorcher (1968)* concluded that sulfate attack was generally increased by the addition of chloride to sulfate solutions. Recently, *Amoudi (1994B)* through his research on chloride-sulfate interactions indicated that sulfate deterioration in plain cement was mitigated by the presence of chloride ions. The significance of the effect of the chloride ion content upon the performance of stabilized soil has, in the past, been entirely ignored in the evaluation of soil stabilization failures. Furthermore, stabilized soil is directly associated with the migration of pore fluid in soil over a period of time. This in turn will affect the availability of ions, specifically chloride, to interact with soil components. This discussion indicates the significant of the necessity to study the migration of chloride in stabilized soil, with regard to the above mentioned points.

2.9 SUMMARY

The literature review carried out in this research indicates a strong need to conduct a physico-chemical study of soil stabilization. Most of the previous research has focused on soil stabilization only from the mechanical/physical point of view. In terms of marly soils, in spite of the presence of palygorskite and sepiolite as a dominant clay fraction of marl, there has been no serious attention paid to the role of these minerals on marl behaviour and to their contribution to the formation of ettringite. A comprehensive study of soil stabilization including physical, chemical, mineralogical and geotechnical evaluation as opposed to only a mechanical study is necessary to overcome the secondary failure which is the result of post stabilization circumstances. In those failures the presence of sulfate, clay fraction and lime or cement as a stabilizing agent is known as a major element. Based on the governing roles of sepiolite, palygorskite and ettringite upon soil performance, their quantification by *x-ray* diffraction analysis will help to figure out to what extent they might affect soil behaviour. Although the degree of accuracy of such an evaluation method in clay soils is still debatable.

CHAPTER 3
MATERIALS AND METHODS

3.1 INTRODUCTION

This Chapter focuses attention on the laboratory testing program which was carried out in this research. This includes an explanation of testing procedures, soil sample preparation and material, in conjunction with a brief explanation of the testing apparatus.

3.2 MATERIAL PROPERTIES AND CHARACTERISTICS

Three types of soil and two solutions were used in this research. Cement and lime were applied as stabilizer agents. These are explained as follows:

(1) Natural marly soil, representing the marly soils of the southern area of Iran and the northern sector of the Persian Gulf.

(2) Pure palygorskite and sepiolite as a major fraction of marl. The pure palygorskite is extracted from the natural marl, as will be pointed out later, and the pure sepiolite was obtained from Vallecas Spain.

(3) Illite (Domtar sealbond) was obtained from Domtar Construction Materials, Ltd., and comes from pulverizing Canadian old marine shale and is known as a major source material of the Champlain Sea clay *(Quigley 1984)*. This illitic soil was used as a control laboratory soil for comparative points.

(4) Two solutions were used including distilled and sea-water. Sea-water samples were taken from the same area as the marl.

(5) Portland cement (Type 10 as specified by CSA and Type I as specified by ASTM) and hydrated lime, for which the constituents will be presented later in this Chapter.

Marl samples are hereinafter called:

tM2: Unweathered tough marl
mtM3: Moderately weathered marl
WM: Weathered marl

In all these cases, the marl samples were collected from the surface to a depth of about 2 *m*. These samples are known to be representative of the most critical behaviours in terms of geotechnical aspects in the aforementioned area *(Ouhadi et al. 1993)*. Due to the similarities of their textures and mineralogical aspects and the abundance of "Unweathered marl" (tM2), these soil samples were used as a representative marl sample in this study. However, the main part of this research focuses attention on the role of the palygorskite and sepiolite on marl stability and ettringite development. The properties and composition of unweathered marl samples are given in Table 3.1. The experiments and evaluations were performed following procedures and methods illustrated by ASTM standards and several techniques suggested by different investigators as follows:

Evaluation of compaction characteristics was performed following ASTM D698. Determination of specific gravity and consistency limits were carried out following ASTM D854 and ASTM D4318, respectively. Particle size analysis was evaluated using the method described in ASTM D422. The measurements of pH of 1:10 soil-water or soil-additives-water were conducted following ASTM D1293 using a pH meter called Beckman Century TM SS-1.

Preparation of samples for *x-ray* diffraction *(XRD)* was carried out according to the procedure described by Moore and Reynolds *(Moore and Reynolds 1989)*. Cation exchange capacity (CEC) determination of soil samples was measured according to different methods. These include: the barium chloride method *(Hendershot and Duquette 1986)*, the ammonium acetate method *(Lavkulich 1981)*, and the homoionic method *(Polemio and Rhoades 1977)*. Determination of carbonate and bicarbonate was achieved using the acid titration method following ASTM D3875 and the rapid titration method with hydrochloric acid *(Hesse 1971)*. Organic content measurement was done following the wet oxidation technique *(Nelson and Sommers 1986)*.

The specific surface area (SSA) was measured using the ethylene glycol-monoethyl ether (EGME) method with and without sample pretreatment *(Eltantawy and Arnold 1973, Carter et al. 1986)*. A good agreement was observed between the results of these techniques. The method described by *Segalen (1986)* was used for determination of amorphous material.

Some of the physico-chemical properties of illite sample will be addressed in this Chapter and a part of them will be mentioned in following Chapters. The physico-chemical characterization of sepiolite samples will be addressed in Chapter 4 and Chapter 7 of this research.

Table 3.1: Some geotechnical properties of marl (sample tM2).

Geotechnical Properties	*Value*	*Geotechnical Properties*	*Value*
Maximum dry density(Mg/m^3)	1.97	*Chemical*	
Opt. Moisture Content(w%)	14	Soil pH(1:10)	8.7
γ_d (Mg/m^3)Marl+10%Cement	1.87	pH of Distilled Water	6.3
ω_{opt} (w%)Marl+10%Cement	16.8	Surface Area (m^2/kg)	74
γ_d (Mg/m^3)Marl+4%Lime	1.93	Organic Content (w%)	0.6
ω_{opt} (w%)Marl+4%Lime	15	Carbonate Content (w%)	25.7
Specific Gravity	2.7	Amorphous content (w%)	0.8
Soil texture	CL/CH	*Mineralogical Composition*	
C_u, using dispersion agent	116	(by *X-ray* analysis, in decreasing order of abundance)	
C_c, using dispersion agent	1.15		
$C_u = D_{60}/D_{10}$	1.85		
$C_c = D^2_{30}/(D_{60} \times D_{10})$	1.15	Palygorskite, Calcite, Quartz, Chlorite, Kaolinite, Dolomite, Illite, Feldspars, Montmorilonite, Gypsum, Arcanite, Thendernite	
Soil Gradation			
Sand (w%)	<4		
Silt (w%)	41		
Clay (w%)	55		
Percent Dispersion	74%		

3.2.1 The Application of Sea-Water and Distilled-Water

Two solutions are used in this research. While sea-water is used as an indicator to evaluate the effect of ground water rising on the stabilized soil behaviour, distilled-water was implemented to simulate the role of rainfall penetration on the stabilized soil behaviour. As is presented in Table 3.1, the pH of distilled-water is equal to 6.3 which lies within the pH range of rainwater for the area from which soil samples were taken *(Doornkamp et al. 1980)*.

Abry et al. (1982) presents a procedure for the preparation of a standard Canadian shield saline solution. This can be used to produce synthetic sea-water based on sea-water chemical analysis *(Mohammed 1995)*. In this research, adequate sea-water samples were obtained directly from the same area as the marl and were used for these research activities.

3.2.2 Chemical Analysis of Soil Pore Fluid and Sea-Water

To complete the chemical characterization of soil samples, pore fluid analysis was performed. Sea-water analysis was also conducted. To do this, the concentration of different ions existing in soil and sea-water samples was determined.

The soil pore fluid analysis was conducted by preparing a 1:10 suspension of soil in water *(Hesse 1971)*. After shaking the suspension for 24 hours, the sample was centrifuged to obtain a clear supernatant. The supernatant was analyzed using atomic absorption spectrophotometry (AAS). Double hydrometer testing (ASTM 4221-83a) and the saturation extract method *(Hesse 1971, Sherard 1976A)* were also used to determine the dispersivity behaviour of soil samples. In the saturation extract method, the soil sample should be mixed with distilled-water to reach the saturation point. This is assumed to be just above the liquid limit condition. The suspension is then left to equilibrate overnight and is eventually filtered to obtain the pore fluid called the saturation extract. The result of this test will determine the sodium adsorption ratio (SAR), as was defined in Chapter 2.

The double hydrometer test consists of the determination of the percent of soil particles smaller than 5 micron diameter in a soil-water suspension. This measurement is done in two steps. First, the performance of common hydrometer testing in which mechanical agitation and a dispersing agent are used. Secondly, performing the same experiment while no mechanical agitation and a dispersing agent are used. The dispersing agent used was a solution of sodium hexa-metaphosphate (sometimes called sodium metaphosphate) at the rate of 40 *g* of chemical per a litre of solution. In the case of clay and silty soils the use of 50 *g* soil and 125 *mL* of sodium hexa-metaphosphate is suggested (ASTM D 422). According to ASTM (D4221- 90), the percent of dispersion is defined as the ratio of percent of soil particles smaller than 5 microns while no dispersion agent is used, over the percent of soil particles passing 5 microns in the common hydrometer experiment. Soil having a dispersion ratio of more than 35% are considered as dispersive soil. As can be seen in Table 3.2, the percentage of soil dispersion for marl samples was above 74%.

Soil pore fluids and sea-water samples were subjected to different experimental analyses. These analyses included the following:

- Determination of soluble and exchangeable cations for determination of CEC. These cations consist of Na, K, Mg, and Ca. Soluble sodium and potassium were determined following the ASTM D4191, and ASTM D4192 test method for sodium and potassium in water by atomic absorption spectroscopy, respectively. Soluble magnesium and calcium were determined according to the ASTM D511, test method for calcium and magnesium in the water. These results were used to determine cation exchange capacity of soil samples based on the aforementioned methods (section 3.2) in conjunction with determination of *ESR* ratio as was defined in Chapter 2 and will be discussed further in Chapter 5.
- Chloride was determined following the titration method presented in ASTM D4458 and the determination of sulfate was performed in accordance to the turbidimetric method presented in ASTM D4130. Sulfate measurement included

the addition of distilled-water at the ratio of 1:10, shaking in the end-over-end shaker for 24 hours, and analysing the supernatant for sulfate. By the addition of a certain amount of barium chloride to the supernatant, $BaSO_4$ will precipitate. This precipitation, which is representative of sulfate concentration of supernatant, can be monitored by the use of turbidimetric apparatus and preparation of calibration graphs.

Figures 3.1 through 3.7 represent the results of the chemical analyses of soil pore fluid of three marl samples in comparison to illite. The specific surface area measurement of these samples is also illustrated in Figure 3.8. Table 3.2 indicates the results of the saturation extract method of marl (tM2) and illite samples. More explanation of these figures will be given in Chapter 4. The results of sea-water analysis are presented in Table 3.3.

Table 3.2: Pore fluid analysis of marl & illite in accordance to saturation extract method.

Soil	Concentration of cations (meq/L)				SAR[1]	TDS[2]	%Na	% Dispersion, DH[3] test
	Na	K	Ca	Mg				
tM2	1882	16.2	125.4	128.2	167.1	2151.8	87.5	74
Illite	16.4	5.1	2.1	1.8	11.7	25.4	64.6	-

SAR[1]: Sodium adsorption ratio, TDS[2]: Total dissolved salts, DH[3]: Double hydrometer

Table 3.3: Sea-Water analysis of sample used in this research.

Element	Mean		Number of tests	Standard deviation ppm	Standard deviation, 90% Confidence level, ppm
	ppm	meq/l			
Na	13858	595.9	18	1332	515
Ca	641	32.1	18	60	23
Mg	1604	133.1	18	105	41
K	355	8.9	18	44	17
HCO_3	92	1.5	12	6	5
SO_4	4180	4.4	30	210	100
CL	25470	718.5	12	1930	914

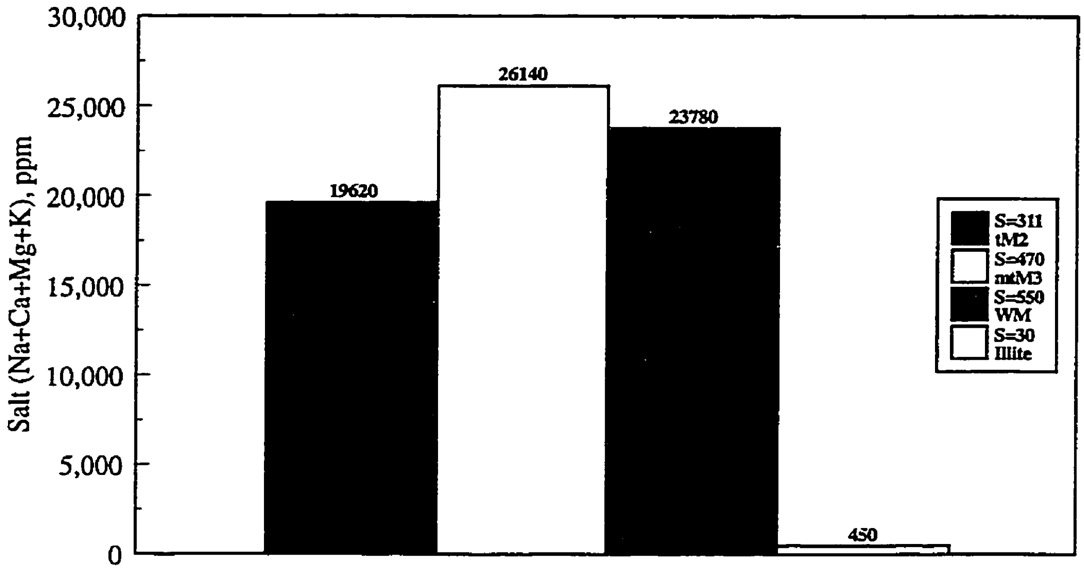


Figure 3.1: Total soluble salt of soil samples.

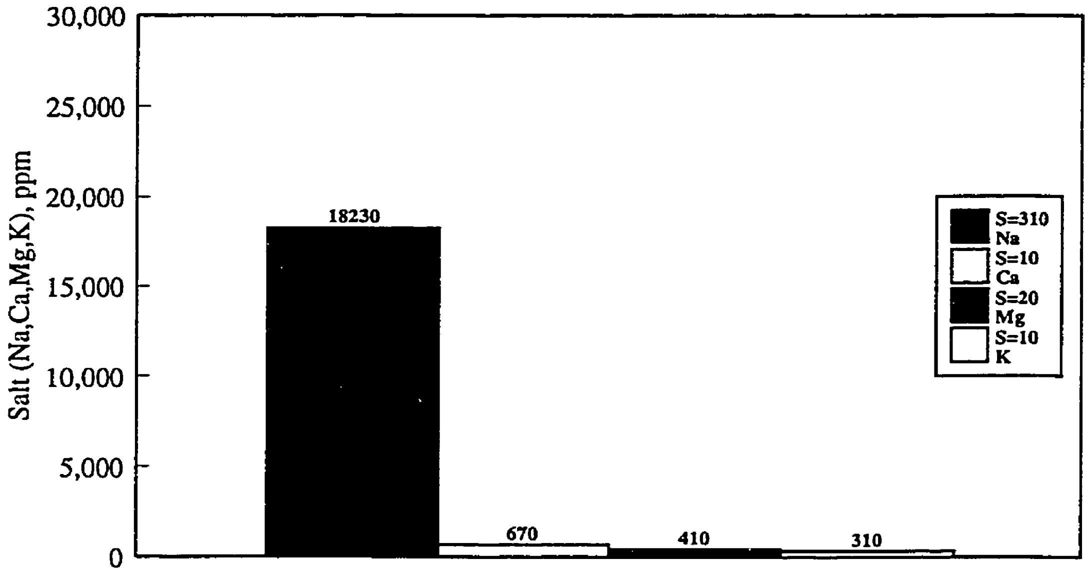


Figure 3.2: Soluble salt of a Marl sample (tM2).

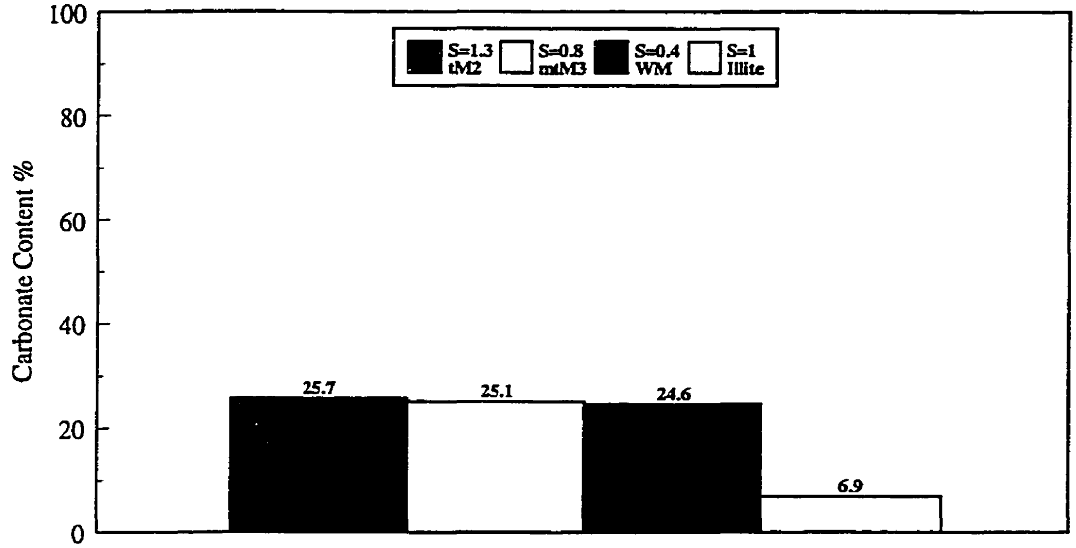


Figure 3.3: Carbonate content of soil samples.

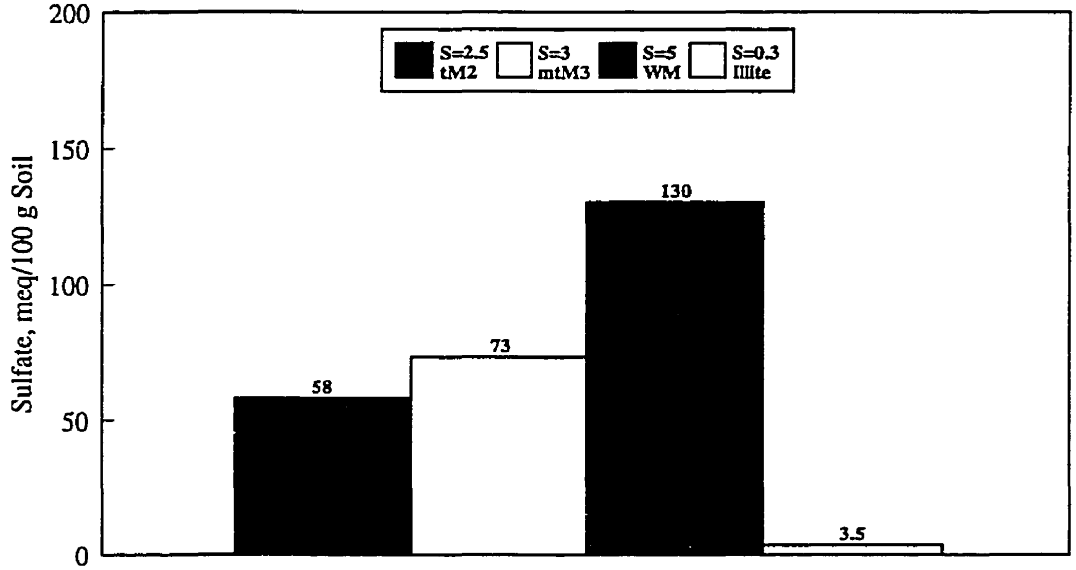


Figure 3.4: Sulfate content of soil samples.

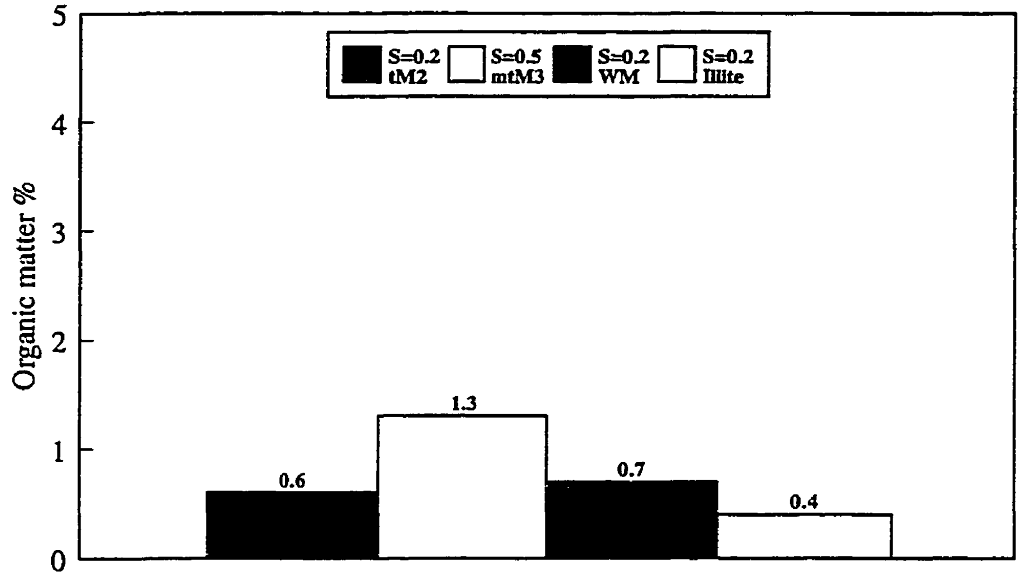


Figure 3.5: Organic content of soil samples.

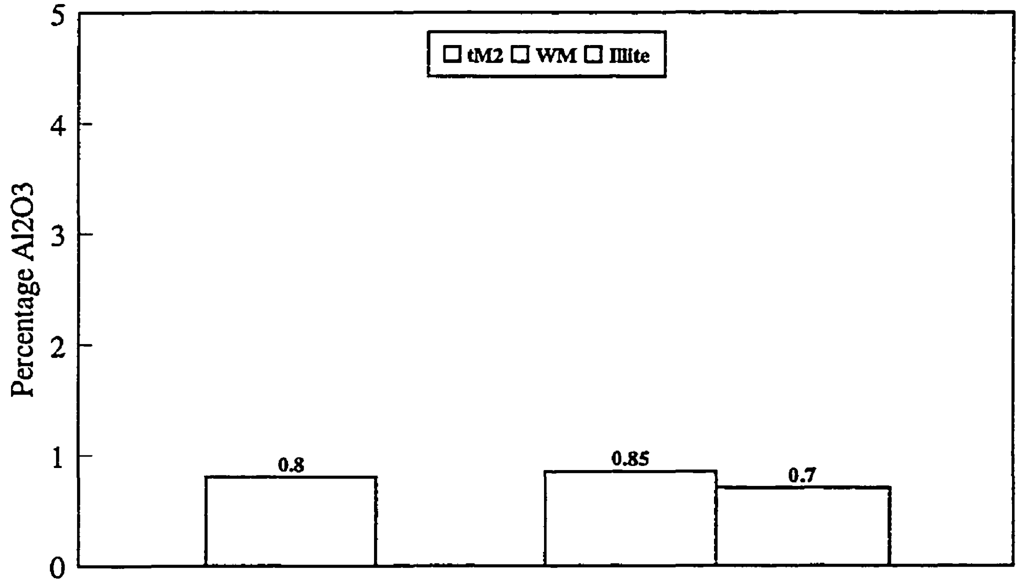


Figure 3.6: Amorphous content of soil samples.

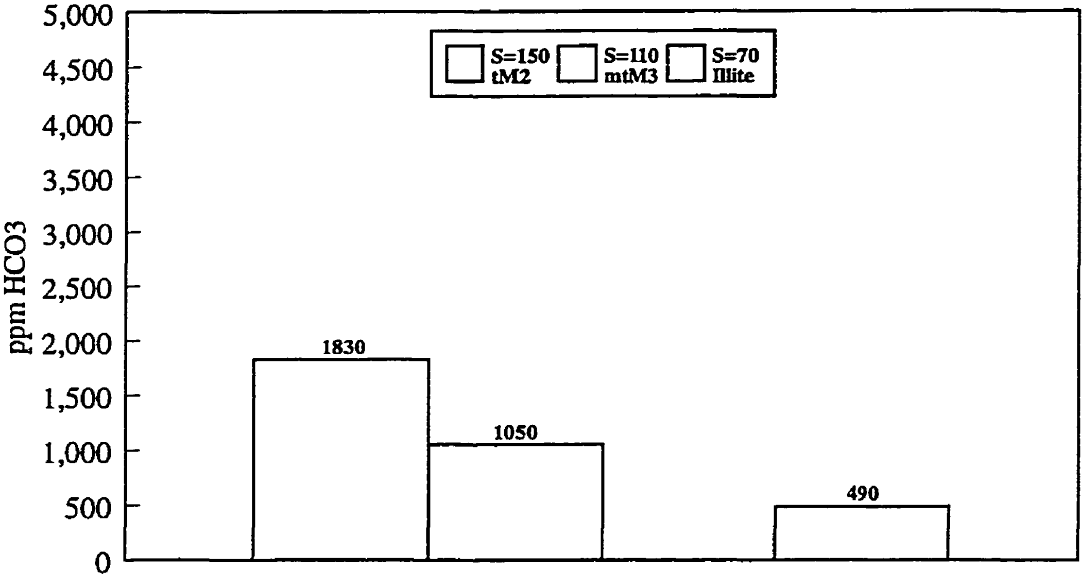


Figure 3.7: Bicarbonate content of soil samples.

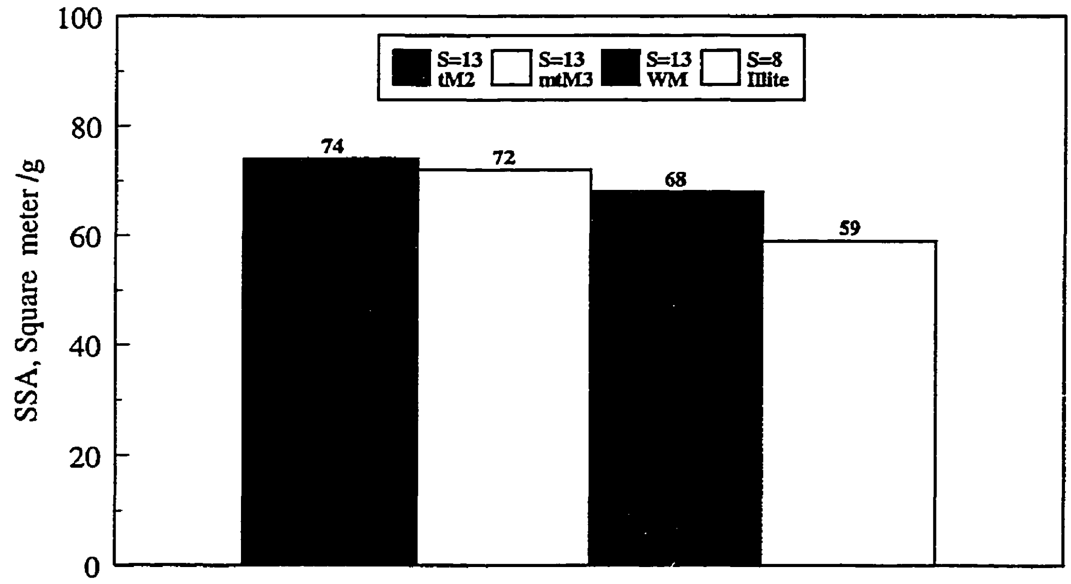


Figure 3.8: Specific surface area of soil samples using the EGME method.

3.2.3 The Composition of Cement and Lime

These investigations involved testing of samples stabilized with cement and lime where some of the samples tested contained sulfate and some were free of sulfate with the aim of differentiating between the behaviour obtained in the different cases. The ordinary Portland cement (Type 10 as specified by CSA and Type I as specified by ASTM) used in the investigation had the chemical and physical properties given in Table 3.4. A commercial hydrated calcium lime, at different concentrations (as will be pointed out later), was added to the natural soil and pure minerals. Table 3.5 summarizes the properties of the commercial lime.

Table 3.4: Composition of cement used.

Composition	% by Weight
Silica, SiO_2	19.78
Aluminum oxide, Al_2O_3	5.54
Ferric oxide, Fe_2O_3	3.44
Calcium oxide, CaO	62.57
Magnesium oxide, MgO	3.91
Sulphuric anhydride, SO_3	2.24
Sodium oxide, Na_2O	0.24
Potassium oxide, K_2O	0.70
Manganese oxide, Mn_2O_3	0.07

Table 3.5: Composition of hydrated lime used.

Composition	% by Weight
Calcium oxide, CaO	72.1
Magnesium oxide, MgO	1.2
Sulphuric anhydride, SO_3	1.1
Hydrated lime	93.5
Unhydrated MgO	1.2
Impurities	5.3

3.3 THE PREPARATION OF SAMPLES

The marl samples used in this study were initially dried. To achieve a uniform sample, all the natural marl soils, including samples in different weathering states, were ground and sieved to finer than 75 micron mesh. These samples were used in the remainder of research activities. The determination of grain size distribution of the soil was performed using a natural sample before grinding.

The soil-additive (cement and lime) mixtures were prepared following ASTM D 588-82 and ASTM D 3551-83, respectively. In accordance with ASTM D3551-8 the standard method for laboratory preparation of soil-lime mixtures using a mechanical mixer, soil for mixture preparation should be in an air-dried or oven-dried condition. Then soil and lime should be mixed in the dry condition for 1 minute, or until the mixture appears uniform in colour. The latter one was followed in sample preparation and sometimes took up to 5 minutes to achieve a homogenous mixture. The required water was added after the mixing period. Following complete mixing, the sample was sieved through a No. 8 sieve to obtain a homogeneous specimen. Samples were compacted according to either their maximum dry density, or in some cases (as will be pointed out later) less than their maximum dry density. Before compaction and after the addition of water, samples were wrapped in a plastic bag and stored overnight for equilibration *(Green et al. 1981)*.

The optimum water and maximum dry density reported in Table 3.1 indicates that while optimum water content increases with the increasing percentage of additives, the maximum dry density decreases within this range of additive variations. The same patterns were observed in prior research *(Kezdi 1979, Mohamed et al. 1991)*. *Kezdi (1979)* shows the effect of soil stabilization upon maximum dry density and optimum water content where different kinds of soil are used. Depending on type of the soil, different patterns are observed in terms of variation of maximum dry density and optimum water content. As the results of this research confirm (Figure 3.9), *Kezdi* reports a decrease in γ_d and increase of ω_{opt} for soils classified as CL/CH and stabilized by cement and lime. On the other hand, the preparation of samples for the leaching column test requires compaction in the wet side of optimum water content to provide enough adhesion between soil and cell. Due to the low difference observed in the variation of γ_d and ω_{opt} at different percentages of additives, with consideration of recommendation suggested by *Kezdi (1979)* and the compaction results illustrated in Table 3.1, the maximum dry density and optimum water content were chosen linearly for different additive percentages, as will be addressed in a particular case in the following related Chapters. In all cases, the addition of additives and water was determined as a percentage of the weight of the dried soil before mixing. In each experiment, after the sample preparation process, the soil was left for equilibrium for 24 hours in the humid room in sealed plastic bags. To assure the repeatability of the results of experiments, sample preparation and testing were rigorously managed and performed. Furthermore, the majority of testing was performed with a 90% confidence level assuming normal and t distributions *(Ang and Tang 1975)*. The selected evaluations were carried out on several samples and the mean values are reported. The calculated standard deviation will be addressed in each related case. Also, to provide similar conditions during experimental performance, all the experiments were conducted at a room temperature of 22±2 degrees centigrade.

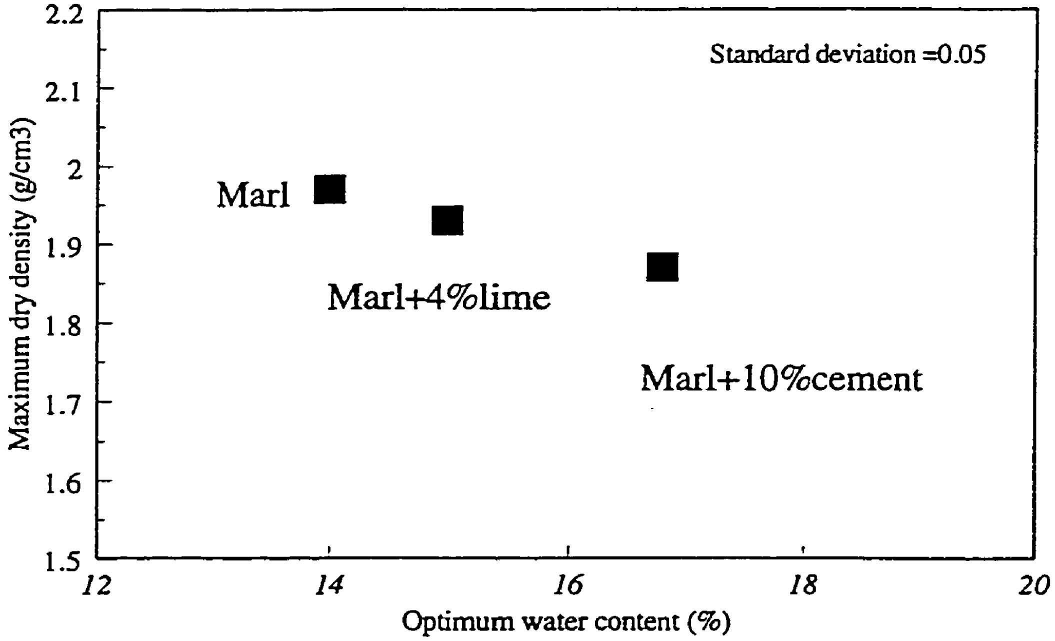


Figure 3.9: Effect of stabilizer agents on compaction characteristics of a Marl sample.

3.3.1 Effect of Curing

Since it is expected that stabilized soils properties alter upon aging, the effects of the curing process on the soil properties and behaviour were selectively studied. In this manner the altered performance characteristics due to the mineral transformation and ettringite development can be monitored.

To evaluate the curing process, freshly-prepared samples were stored in a humid room at 20±2 degrees centigrade and 100% relative humidity. The experimental results for the cured samples are presented in specified sections. For those not specified, fresh soils were usually used.

3.4 *X-RAY* DIFFRACTION TESTING

A Phillips apparatus "PW1710-System 1984" with Cu-Kα radiation was used to obtain the *x-ray* diffraction *(XRD)* patterns of soil samples. The *x-ray* diffraction mineral patterns were identified by comparison with file standard *x-ray* powder diffraction patterns *(International Centre for Diffraction Data (ICDD), Mineral Powder diffraction file Search Manual 1988)* of the most commonly found minerals. The quantitative analysis was carried out with the aid of the developed *XRD* method as will be described later. For sample preparation, in each case 0.2 *g* of air dried soil was mixed with 10 *mL* distilled-water in a small volumetric flask and shaken by hand for 2-3 minutes. Then the volumetric flask was placed on a ultrasound to adequately disperse the soil before *XRD* testing. Finally, using a micro pipette, 4 drops of the prepared solution was positioned on a glass slide. The coatings on glass slides for all samples had similar thicknesses. The *XRD* spectra were obtained by scanning in the 2θ range of 5 to 17 and 5 to 70 degrees. In terms of cured samples, at the end of the required moist-curing periods, the samples were taken from the humid room for immediate processing. Various treatment techniques were used as follows: soil "as it is", acid, heat, magnesium and glycerol treatments. Soil "as it is" refers to an *x-ray* of a sample without any treatment and prepared as previously indicated. Acid treatments cites the performance of an *x-ray* of a sample prepared by heating 0.2 g of soil in an equal volume of concentrated *HCl* for 1/2 *hr*. Following this period the sample was washed three times with water to neutralize the acid. Each time a mixture of sample and distilled-water was shaken for 1/2 *hr* and centrifuged to discard the supernatant. Finally, 4 *mL* of a mixture of sample and distilled-water was placed onto a glass slide and air-dried. This treatment was used to destroy chlorite peaks to distinguish chlorite from kaolinite. Heat treated samples were prepared in a similar manner to the soil "as it is" treatment and heated to 550 degrees centigrade, in the muffle furnace for one hour. The fact that kaolinite will be destroyed and chlorite will not be affected by the heating process is used to differentiate between these clay minerals. To provide an unvarying expansion for all crystals of an individual mineral, the soil sample should be treated to become homoionic. Magnesium and potassium treatments might be used *(Moore and Raynolds 1989)*. To prepare magnesium treated samples, 0.2 g of soil is mixed with $MgCl_2$ and left to equilibrate for 2 hours. It is then centrifuged and the clear supernatant discarded. The sample is then washed once with $MgCl_2$, twice with $MgAc_2$, and once more with $MgCl_2$. In each case, one normal solution was used, then samples were washed with 50/50 water/ethanol. After this stage, the tube is centrifuged and the clear supernatant discarded. The excess Cl^- is removed by washing the sample three times with ethanol and water (80/20). The sample is then oven dried and four drops of the mixture of treated soil and distilled-water are placed on a glass slide. After running this slide a solution of 10% glycerol in ethanol was spread on the magnesium treated slide. These were used to determine presence of montmorilonite.

3.5 GEOTECHNICAL TESTING

Usually geotechnical investigations are performed to evaluate the extent of soil behaviour improvement by the addition of additives such as cement and lime. However, in this research, the geotechnical testing program was based mainly on the following three reasons: First, to investigate the geotechnical performance of stabilized marl over mineral transformation. Secondly, to establish the role of pure palygorskite and sepiolite as a major fraction of marl. And third, to indicate that the current mechanical evaluation of soil stabilization is not capable of surveying the long-term behaviour of stabilized marl when ettringite mineral forms and develops. According to ASTM standards, to evaluate soil stabilization performance three general criteria can be used. These include unconfined compression or *CBR* testing, Atterberg limits evaluation, and pH variation. Therefore, to achieve the aforementioned objectives, *CBR* testing was chosen as the main tool, in terms of soil strength refinement, in the stabilization process. The explanation of geotechnical testing is as follows:

3.5.1 Evaluation of Dispersivity Behaviour

The dispersivity performance of soil samples was determined by the application of two series of experiments:

First, saturation extract and double hydrometer methods in conjunction with exchangeable cations determination. These techniques determine the sodium adsorption ratio (SAR), exchangeable sodium ratio (ESR) and percent of dispersion, as was explained in Chapter 2 and section 3.2.2 and will be addressed in Chapter 5.

The second series of experiments includes the study of the slaking performance, of unstabilized and stabilized marl. This slaking performance (as will be discussed in Chapter 6) is attributed to the dispersing behaviour of marl. In this series of experiments, samples were mixed with different percentages of additives. After storing for equilibrium, they were compacted according to their maximum dry density and optimum water content. After the desired curing period of 30 days, soil samples were kept in water for 24 hours. The ratio of the dry weight of sample after soaking in water to that of the same sample before soaking, is taken as representative of the ability of additives to control slaking behaviour of marl *(Ouhadi et al. 1993)*.

3.5.2 Calibrating Coefficients for Compaction Characteristics

Evaluation of compaction characteristics was performed following ASTM D698. This includes the measurement of maximum dry density and optimum water content. Due to the limited amount of soil available for this study and also the considerable time required for measurement of these two factors in regular molds, the measurement of optimum moisture content and maximum dry density of some samples was performed by calibrating a Harvard Miniature apparatus using a small mold (7.1 cm height and 3.3 cm diameter). To do so, specimen preparation was performed according to ASTM D 4609-86, standard guide for screening chemicals for soil stabilization and the suggested method of test for moisture-density relations of soils using a Harvard compaction apparatus. In this test, the selection of the most appropriate number of layers, tamping force, and number of tamps applied per layer is a function of the type of material. Therefore, it is first necessary to calibrate the Harvard apparatus to find out the correct number of tamps per layer and to manage the tamper springs so that the required tamping spring, commonly producing 5 to 20 kg can be employed. Generally, ten or more tamps per layer are required *(ASTM 1990)*. For calibration, sufficient soil-water mixture was prepared. Then the amount of water required for the maximum dry density according to ASTM D698 was evaluated. From the same batch of sample, a series of specimens was prepared using an arbitrary combination of number of tamps per layer (20, 25, 30, 40) and having constant tamper spring (15 lb (6.81 Kg) and 30 lb (13.62 Kg). For each group of samples having the same compacted layers and tamper spring pressure, the maximum dry density and optimum water content was calculated. The standard deviation of maximum dry density and optimum water content are calculated based on the coefficient of variation suggested by *Stamatopoulos (1985)*. As can be seen in Figure 3.10, for a certain tamper spring, with increasing number of tamps per layer, maximum dry density increases and finally reaches an almost constant value where, by increasing the number of tamps per layer, a significant change in dry density cannot be observed. At the same condition, as Figure 3.11 shows, the optimum water content decreases until finally it is inclined to a constant value. In fact, for a 15 lbs (6.81 Kg) tamper spring, after 30 tamps per layer, both optimum water content and maximum dry density go towards a constant value. More or less the same pattern can be seen once the tamper spring is increased to 30 lbs (13.62 Kg). While in the latter case, with a lesser water content, higher density is achieved. The optimum water content for the former condition is almost 1.1 times of the one achieved in standard proctor test while the maximum dry density in this case is almost 74% of proctor test. Therefore, to achieve the optimum water content and maximum dry density for different additive percentages and other cases in the rest of this research, compaction was performed using the Harvard Miniature apparatus with the application of a 15 lbs (6.81 Kg) hammer and 30 tamps per layer. To obtain the best estimation of maximum dry density and optimum water content for different cases, the correction factor of 1/0.90 and 0.74 was used for maximum dry density and optimum water content, respectively. These calibration coefficients were found to be 1/0.93 and 0.93 when the 30 lbs (13.62 Kg) hammer and 40 tamps per layer are used. In this process the best estimation of maximum dry density and optimum water content of the common compaction test will be achieved. Based on the method of error analysis suggested by *Stamatopoulos (1985)*, the standard deviation for estimated optimum water content and maximum dry density lies within the same range as presented in the Figures 3-10 and 3-11.

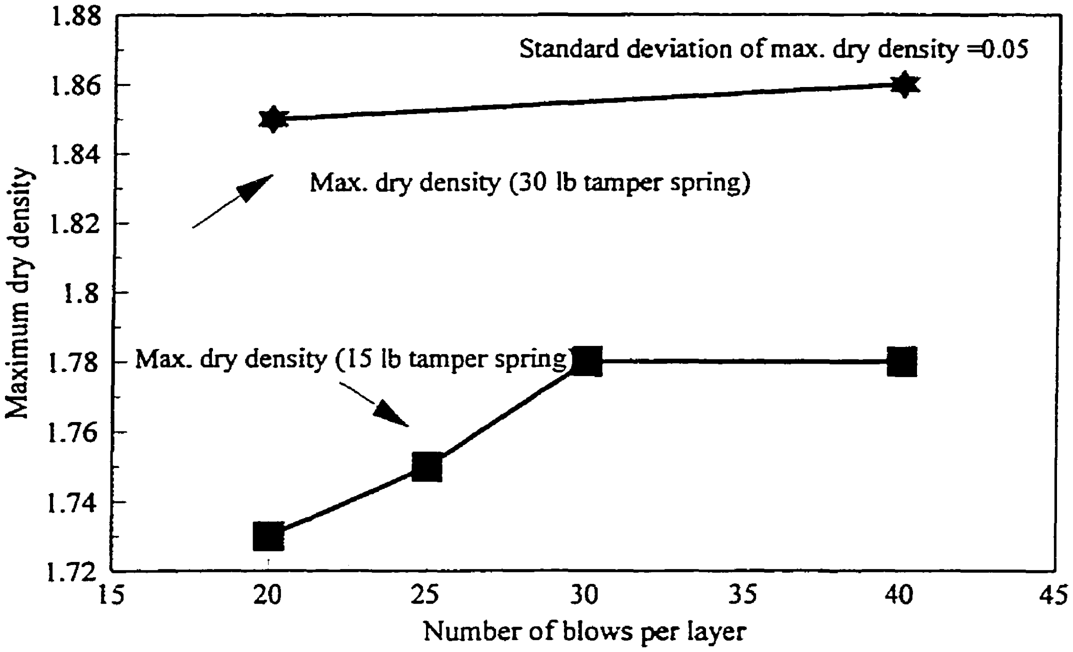


Figure 3.10: Calibrating coefficient for maximum dry density using the Harvard Miniature apparatus.

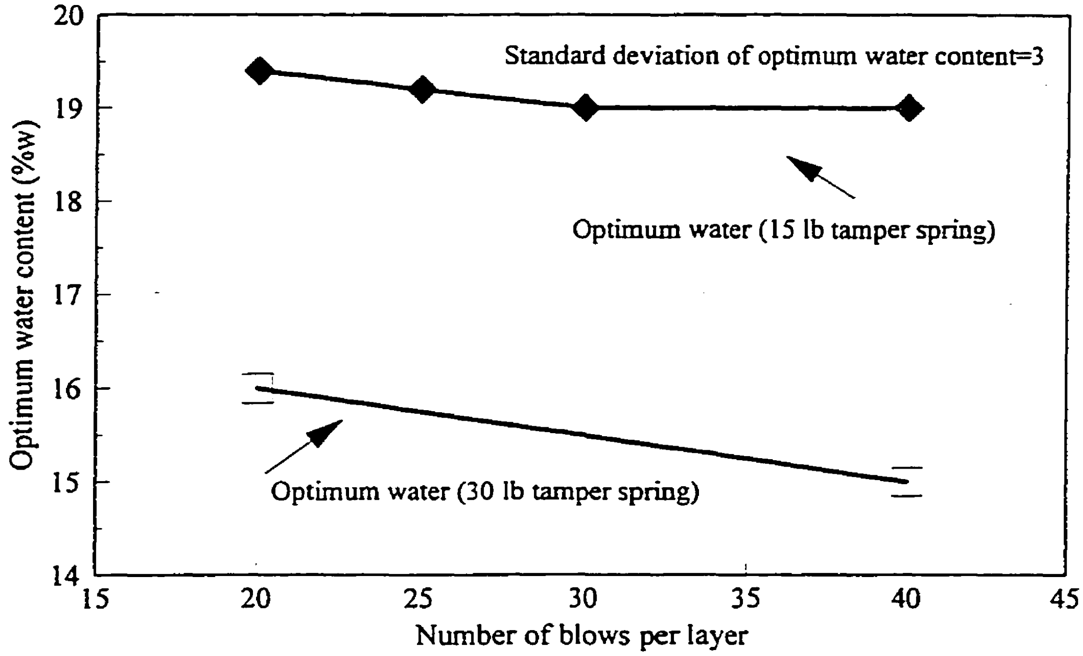


Figure 3.11: Calibrating coefficient for optimum moisture content using the Harvard Miniature apparatus.

3.5.3 *CBR* Testing

CBR testing is suggested as a criterion for the evaluation of strength of soils, in both unstabilized and stabilized conditions *(ASTM 1990)*. Furthermore, it has been used as a design criterion in road construction *(DSIR 1952)*. *CBR* testing was conducted, following ASTM D 1883 on unsoaked and soaked samples, before and after stabilization. In the first step, the marl behaviour before adding additives is evaluated, while the second series of tests covers the mechanical evaluation of soil stabilization during the mineral transformation. In each case, as will be presented later, the curing period is addressed.

3.5.4 Oedometer Mold for Free Swelling Measurement

The oedometer mold is used to measure the free swelling of marl and palygorskite samples and to investigate the role of carbonate upon variation of free swelling of marl. The dimension of the mold was 62 *mm* diameter and 45 *mm* height. By applying a static load, the sample was compacted to the desired density. It had already been mixed with the necessary water content and sieved through No. 8 screen to have a homogeneous sample. In the case of a soil having a different percentage of calcite, the sample was mixed with calcite in dry condition before performing the above process. A light lucite cap (which weights 123.95 *g*) was placed on the top of the sample. By placing a gage on the lucite cap, the monitoring of the free swelling was possible. To have enough space for the cap, each sample was compacted up to approximately 25 *mm* height in the mold. To provide appropriate water distribution across the sample and quick relaxation of pore water pressure induced by compaction force, a porous plate and filter paper were placed on the top and bottom of the soil sample. On the top, they were set between cap and soil sample. On the bottom they were fitted between soil and mold base. A water supply tube was connected to the bottom of the mold. No external load was applied to the top of the sample except the stress caused by the cap, which was calculated to be 0.004 kg/cm^2 .

3.6 SOIL SUCTION TESTING

Pressure plate apparatus were employed to investigate some of the factors influencing the behaviour of soil before and after ettringite development. Those factors are as follows:

1) To evaluate the effect of soil structure on suction behaviour of soils. This includes focusing attention on the suction behaviour of palygorskite and sepiolite with comparison to that of for illite.
2) To determine how stabilizers affect the influence of soil structure in terms of suction performance.
3) To investigate the role of mineral transformation, ettringite development and carbonate on the retention of pore fluids by the soil.

Tests were performed on natural marl soil, pure sepiolite, pure ettringite, illite and stabilized marl. Calcite was added to the soil samples and the role of calcite on soil suction was also investigated in this manner. Sand-box and pressure plate extractors were used as devices for suction measurement.

Sand-box, is a small water tank containing clean, coarse sand (<0.5 *mm* diameter) providing a pF range of 0 to 1, in which suction pF is the logarithm value of the water head in *cm*. The sand sample was compacted to a height of 15 *cm* into a lucite-box. Then it was covered with a sheet of filter paper. A water supply was connected to an outlet at the bottom of the tank. The water level was adjusted to 1 *cm* below for pF 0 and 10 *cm* below for pF 1. The sand-box was finally covered to minimize the evaporation of water.

The test procedure was performed according to the method described by *Yong and Warkentin (1975)*. For preparation purposes, the sample was compacted in a lucite ring of 38.1 *mm* diameter and 15 *mm* height until achieving the desired dry density. Following preparation, to saturate samples, they were placed in the sand-box in which the water level was up to the middle of the height of the lucite rings. After a one week saturation period, the sand-box was used to measure suction of samples in the range of pF 0 to 1. Another sets of saturated samples, were placed in pressure plate extractors, (a closed chamber device) for suction measurement for higher suction ranges. In this apparatus a water-saturated ceramic plate was placed at the bottom of the samples and the bottom of this plate was retained in connection with atmospheric pressure. Following increasing the air pressure in the enclosed chamber, water was caused to move out of the samples through the ceramic plate. This process endured to reach an equilibrium between the applied air pressure and the energy at which pore fluid was retained in the soil. This process were carried out by applying different pressures in each case and following equilibrium the moisture content was measured. Two different cycles called absorption and desorption can be conducted on samples. While in the desorption cycle, water is removed from the sample by increasing the applied pressure, in the absorption cycle water is absorbed by the sample by decreasing the applied pressure. The suction range was adopted between pF 0.0 and pF 3.8. Due to the small height of the sample, as pointed out before, the gravitional effects are negligible. Furthermore the osmotic impacts are assumed to be negligible in samples having pure mineral. Due to the limitation of equipment, the osmotic effects in samples are not taken into account. It was observed that in order for each pF stage to reach an equilibrium, a minimum period of about 5 to 7 days was required. This period of time is mainly a function of grain size distribution and composition of soil samples.

3.7 SOIL LEACHING STUDY

The process of soil leaching may affect the condition of ettringite development. This is particularly important in terms of the ability of ions, especially chloride, and sulfate, in the process of interaction with soil components, as the importance of theoretic aspects was addressed in Chapter 2. In this study, leaching cells were used to study the migration of chloride in unstabilized and stabilized soil. The test plan was carried out in accordance with the methods proposed by *Fuller (1982)* and *Yong et al. (1986)*.

The main objectives of this experimental scheme are to evaluate:

1) the role of soil open structure on leaching potential of soil
2) the effect of mineral transformation, clay loss and presence of ettringite on the leachability behaviour of marl and availability of chloride ions for interaction with additives.

3.7.1 Cell Characteristics

Each cell consists of a cylindrical plexiglass having 50 *mm* diameter, 100 *mm* height and 3 *mm* thickness, as is represented in Figure 3.12. Each dry sample was mixed with the desired amount of water (few percents more than the optimum water content of soil). This will make the samples to be compacted on the wet side of their maximum dry density (in the compaction curve) and will provide enough adhesion between mold and soil. Before compacting the samples, and after the addition of water, samples were thoroughly mixed and sieved through No. 8 sieve to obtain a homogeneous sample, then wrapped in parafilm and stored overnight for equilibration *(Green et al. 1981)*. As is indicated in Figure 3.12, each cell has two connections, one at the top and the other one at the bottom. The top one is connected to a pressure gauge which controls the gradient. The other one acts as an effluent collector during the leaching process. Two porous stones, having a thickness of 3 *mm*, were established on top and bottom of the soil sample to provide uniform distribution of the hydraulic pressure on the soil surface and to collect and lead the effluent to the drainage outlet, respectively. The leaching cells were subjected to a constant gradient under a hydraulic gradient of 17.5 which was applied to the top of the cell and the effluent was drained from the bottom at atmospheric pressure. This hydraulic gradient was provided by the application of 2.5 *psi* (each *psi* or *lb/square inch* equals to 0.07 *Kg/square cm*) pressure applied to a cell of 10 *cm* height. Distilled-water as a leachate solution was allowed to permeate through the soil sample for periods varying to several months. During this period, effluent was collected periodically in a plastic bottle after different pore volumes as will be addressed in Chapter 7.

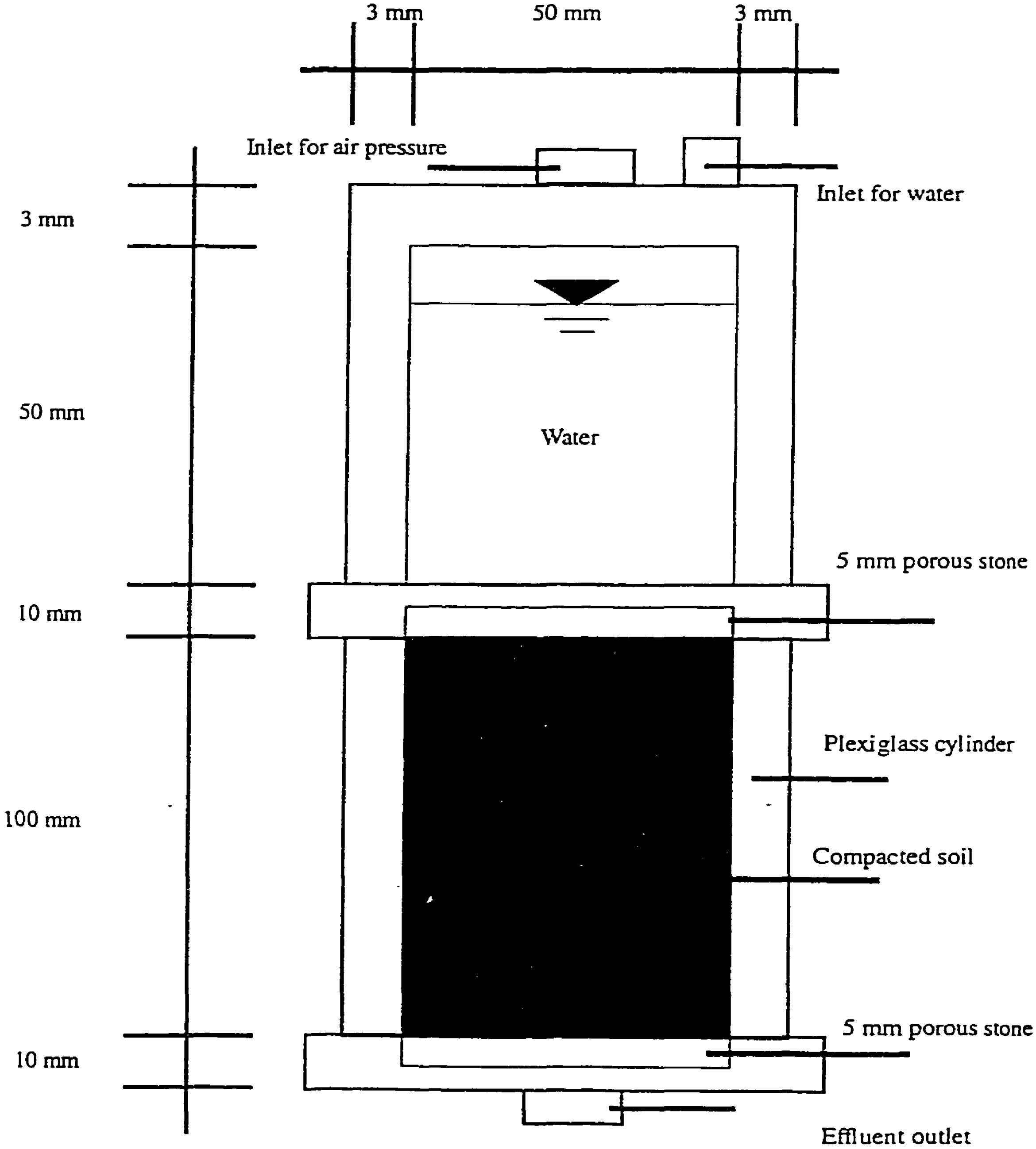


Figure 3.12: Schematic representation of the laboratory leaching cell used in this research.

3.7.2 Leaching Test Procedure

Two series of samples were used in this study, which are as follows:

1) Natural marl when it was mixed with the ratio of 60 percent marl and 40 percent silica sand No. 16.
2) The same marl-sand mixture when stabilized with different percentages of lime and lab produced ettringite.

The effluent from the cells was tested after termination of the passage of different pore volumes (*PV*). The concentration of chloride was determined by chemical analysis of effluent.

3.8 ZETA POTENTIAL STUDY

Electrokinetic phenomena occur when two phases move with respect to each other while the interface is the seat of an electric double layer. In this motion, for example between a solid and a liquid phase, a thin layer of liquid adheres to the solid surface, and the shearing plane between liquid and solid is located in the liquid at some unknown distance from the soil surface. Part of the counter-ion atmosphere therefore moves with the soil, and part moves with the liquid. The electric double-layer potential at the shearing plane is called the electrokinetic or zeta potential. The sign and magnitude of the zeta potential reflect the sign and magnitude of the charge on the particle. Zeta potential measurements are made using a procedure called "micro-electrophoresis".

The sample should be prepared using a minute quantity of specimen (about 0.02% solid concentration). To measure the zeta potential of a colloidal sample, the specimen is placed in an electrophoresis cell and a *DC* voltage is applied to the electrodes which are inserted in either end and are already connected to the power unit. Since the particles are electrically charged, they move toward the opposite electrode. Their velocity in cell is relative to the zeta potential and their velocity is measured by timing individual particles on a microscope grid as they move through the cell. Each traverse takes 3 to 15 seconds. Approximately fifteen colloids are usually tracked and the average time is then reported. The zeta meter is used to measure the zeta potential of artificial ettringite.

3.9 BATCH EQUILIBRIUM TESTING

The soil sample was dried and ground until a uniform powdery specimen was acquired (section 3.3). From this soil sample, 3 grams of soil were taken and placed in a plastic bottle. Different concentrations of sulfate, which is one of the main elements for ettringite formation, were provided. Then, 30 *mL* of these concentrations were added to a bottle and bottles were placed in the end-over-end shaker (40-50 *rpm*) for 24 hours. This period is known to be the optimum time to reach equilibrium *(Mohamed et al. 1994)*. One bottle was considered a "blank sample", filled up solely with solution and where no soil sample was added. Following the shaking period, the bottles were placed in centrifuge to separate soil fraction from liquid part. After filtering the supernatant from the bottle, the concentration of interested constituent of the supernatant was measured using a turbidimeter. This concentration is called C. While C_o is the initial ion concentration and q is defined as a adsorption/desorption mass ratio. q is computed according to the following equation:

$$q=(C_o-C)V/M \qquad (3\text{-}1)$$

where V is the volume of liquid added to the bottle and M represents the mass of soil in a bottle. In the above equation, the numerator indicates the mass of constituent adsorbed onto or desorbed from the solid fraction. To assess the magnitude of the relative mass of the constituent adsorbed onto the solid phase, the nominator of the above expression has to be divided by the mass of the soil. In other words, the unit of q would be gram of constituent adsorbed per gram of dry soil. For soil pore fluid analysis, three gram of soil were mixed with 30 *mL* of distilled-water and after the same procedure of shaking and centrifuging, the clear supernatant was analyzed for different ions determination.

3.10 SUMMARY

A series of physico-chemical experimentations which were carried out in this research are discussed in this Chapter. Experimentation has been addressed through the explanation of materials properties, sample preparation, test procedures and apparatus. Marly soil has been chosen as the natural soil sample of this research in which its clay fraction is dominated by the presence of palygorskite. The other pure clay minerals which are used in this research include, pure palygorskite extracted from marl, pure sepiolite, illitic soil and pure kaolinite. Artificial ettringite was formed and was added to soil samples to investigate its influence on soil behaviour. Some of the general physico-chemical characteristics of these soil samples were addressed in this Chapter.

CHAPTER 4

THE NECESSARY CRITERIA FOR QUANTITATIVE *XRD* ANALYSIS OF MARLY SOILS AND ETTRINGITE

4.1 INTRODUCTION

In order to classify marly soils and to investigate the role of their different minerals on their behaviour, it is necessary to have a quantitative *XRD* evaluation. Current *XRD* techniques for quantitative analysis are based mainly on four methods as follows:

- Mineral quantification based on peak areas.
- Analysing based on the identical mass absorption coefficient method.
- Mineral diagnosing based on using an internal standard.
- Quantitative mineral evaluation based on an external standard.

The intensities of the *XRD* pattern of an individual mineral are known to be proportional to the concentrations of the different minerals present. Therefore, by measuring the intensities of patterns, some idea of the relative amounts of each phase can be achieved. The diffracted intensity of any *hkl* reflection from any crystalline material can be related to its composition, matrix, and to the instrumental characteristics *(Alexander and Klug 1948, Noorish and Taylor 1962)*. Based on different evaluations of achieved densities, a number of quantitative methods have been devised. Among them, the four mentioned methods have received the major attention of researchers. These methods will be reviewed, and examined, as an introduction to the proposed method of this research for quantitative *XRD* analysis of marly soils and ettringite.

In all explained methods, intensities can be measured either based on peak heights or the area under the peaks.

4.2 QUANTITATIVE MINERAL EVALUATION METHODS USING *XRD*

Based on the limitation and difficulties involved in the application of these techniques, it is not as common to use these methods for a fast and accurate quantitative evaluation in clay soils. Specifically, when several minerals are present in the soil. The main aims of this Chapter will be: 1) Investigating the main *XRD* characteristics of sepiolite, palygorskite, and ettringite in order to provide the necessary data for quantitative *XRD* analysis. 2) To review the current quantitative *XRD* methods and to evaluate the accuracy of these methods for their application to marly soils. 3) An attempt to develop a simplified *XRD* analysis to be used for quantitative mineral evaluation of marly soils. To do this, several artificial samples were prepared for *x-ray* diffraction. The *XRD* results on these controlled samples have been examined by the current quantitative *XRD* methods. This will help to achieve the above objectives based on the application of the artificial controlled samples. These artificial samples consist of four different sets of samples including: 1) Several different mixtures of kaolinite and sepiolite. 2) Various mixtures of kaolinite, sepiolite and calcite. 3) Several different mixtures of palygorskite-calcite and sepiolite-calcite. 4) Various mixtures of palygorskite-ettringite and kaolinite-ettringite. 5) A mixture of kaolinite, palygorskite, calcite and ettringite. 6) Pure samples of the major elements.

4.2.1 Intensity of the Radiation

It is known that families of planes of atoms in a given crystal will reflect an *x-ray* beam when *Bragg*'s law is fulfilled *(Bragg 1912)*. *Bragg*'s law is as follows:

$$2d\sin\theta = n\lambda \tag{4.1}$$

in which d is the distance between two planes of atoms, θ is the angle between the planes and the *x-ray* beam, λ is the wave length of incident rays, and n is often called the order of reflection. Based on *Bragg*'s law, if a single crystal is located in an *x-ray* beam, then there would be a minor possibility for *Bragg*'s law being satisfied. This is because there will be no guarantee that a particular family of planes are placed in the correct position to fulfil the *Bragg*'s law. On the other hand, if the crystal is powdered, without destroying the crystal structure it produces plenty of very small crystals in all directions. Therefore, there would be at least enough crystals having planes to satisfy *Bragg*'s law.

The general equation evaluating the *x-ray* radiation absorption, while it goes through a test sample, is expressed by *Lambert*'s law. *Lambert*'s law is generally accepted to govern the absorption of radiation as it passes through matter. This law is based on the assumption that the amplitude of absorbed radiate while it passes through a layer of matter is proportional to two factors. First, the thickness of the layer and secondly, the nature of absorbing matter and wave length of radiation. The role of absorbing matter and wave length of radiation are included through a factor called "the absorption coefficient". If I_o is the intensity of the radiation incident on a layer of test sample *(AB)* and I is the intensity of the radiation after passing through the layer, according to the *Lambert*'s law the governing equation will be:

$$\frac{I_o - I}{I_o} = \frac{\Delta I}{I_o} = -\mu_l \Delta x \qquad (4.2)$$

where Δx is the thickness of the layer and μ_l is an indication of the linear absorption coefficient. This equation is true only when Δx becomes infinitesimal, therefore, assuming I_o equal to I in this limiting case in the denominator, the equation will become:

$$\frac{dI}{I} = -\mu_l dx \qquad (4.3)$$

the integration of the above equation over the thickness of sample will be:

$$\log I - \log I_{\circ} = \log\frac{I}{I_{\circ}} = -\mu_l x \tag{4.4}$$

and the final form of *Lambert*'s law can be written as follows:

$$I = I_{\circ} e^{-\mu_l x} \tag{4.5}$$

The value of μ_l for a certain material depends on the material status in terms of being solid, liquid or gas. For a particular material, absorption increases and μ_l decreases when going from the solid to the gas. In fact μ_l is a direct function of the number of atoms traversed by the incident rays. Therefore, for a particular material, as is confirmed by observation, the ratio of μ_l over density *(ρ)* will be constant. In the latter case, the material status does not affect the amplitude absorption of the material since it is already included in the new defined parameter *(μ_l/ρ)* called the mass absorption coefficient. Therefore, *Lambert*'s law as applied to *x-rays* is usually written as follows *(Sproull 1946)*:

$$I = I_{\circ} e^{-\mu x \rho} \tag{4.6}$$

in which:

$$\mu = \frac{\mu_l}{\rho} \tag{4.7}$$

where ρ is the density of the absorbing material and μ is called the mass absorption coefficient.

Based on the above explanation, the concept of a mass absorption coefficient seems to be an essential factor governing quantitative mineral evaluation.

4.2.2 Instrument and Sample Preparation Error in *XRD* Testing

Two major sources of error in quantitative *XRD* analysis include, the error resulting from sample preparation and an instrument error. Due to the sample preparation process (Chapter 3) the quantity of sample being deposited on the glass slide will not have the same mineral concentrations when different slides for a single mineral are prepared. This will cause a different *XRD* intensity for a single mineral in these slides since the intensity of reflection lines is a function of mineral concentration on the glass slides. At the same time, this difference in concentration will affect the degree of mineral orientation on the glass slide which in turn, will influence the quantity of reflection lines.

On the other hand, instrumental effect will cause fluctuations in the quantity of intensity and reflection lines of mineral, even if a single sample is analyzed by *XRD* several times. To take into consideration these sources of error, 19 *XRD* tests were performed in an attempt to establish some basic quantity as the coefficient of variation (*COV*) for *XRD* experiment.

To figure out the error arising from an instrument source, a single sample of sepiolite was prepared on a glass slide (Chapter 3) and run by *XRD* 10 times. Only one sample was used to identify the instrumental error. Then the quantity variation of the sepiolite major reflection line and its intensity were monitored. The results of these experiments are presented in Figures 4.1 and 4.2 in which, to show the scattering of data in each Figure, the vertical and horizontal axis are representative of a similar quantity. The very low coefficient of variation presented in these two graphs indicates the negligible error which comes from instrumental effects. On the other hand, to find the sample preparation effect on *XRD* test results, another series of samples (including 9 different slides prepared using artificial ettringite) were run by *XRD*. The results of these experiments are shown in Figures 4.3 and 4.4 for the major reflection line of ettringite and its peak intensity, respectively. While the coefficient of variation for the reflection line is the same as in the previous series of experiment, the *COV* for ettringite peak

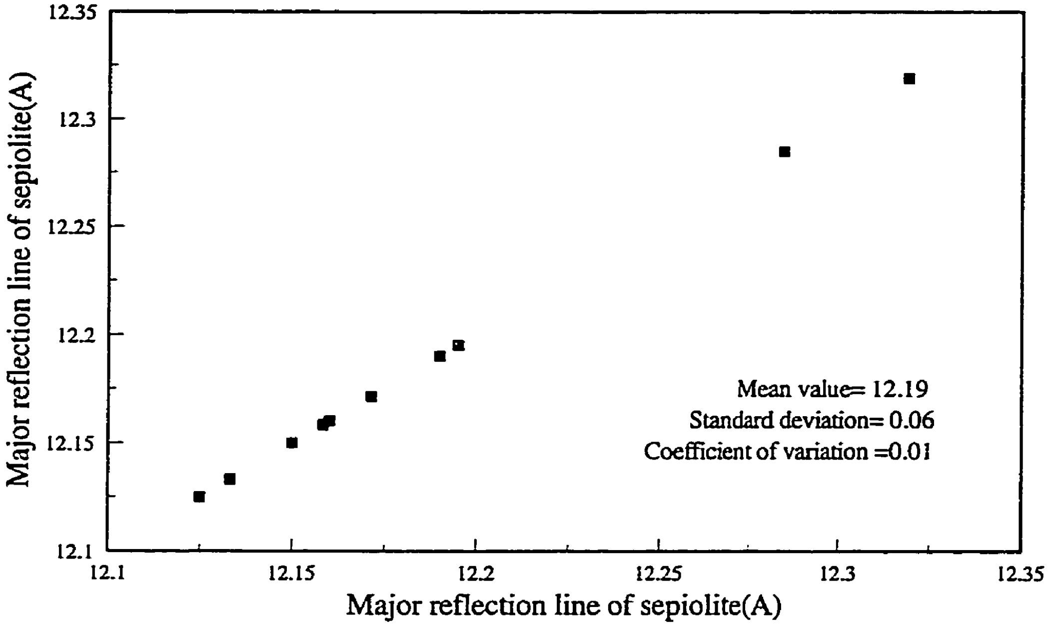


Figure 4.1: Instrument source of error of reflection line's quantity in *XRD* analysis, single Sepiolite sample run 10 times for its major reflection line.

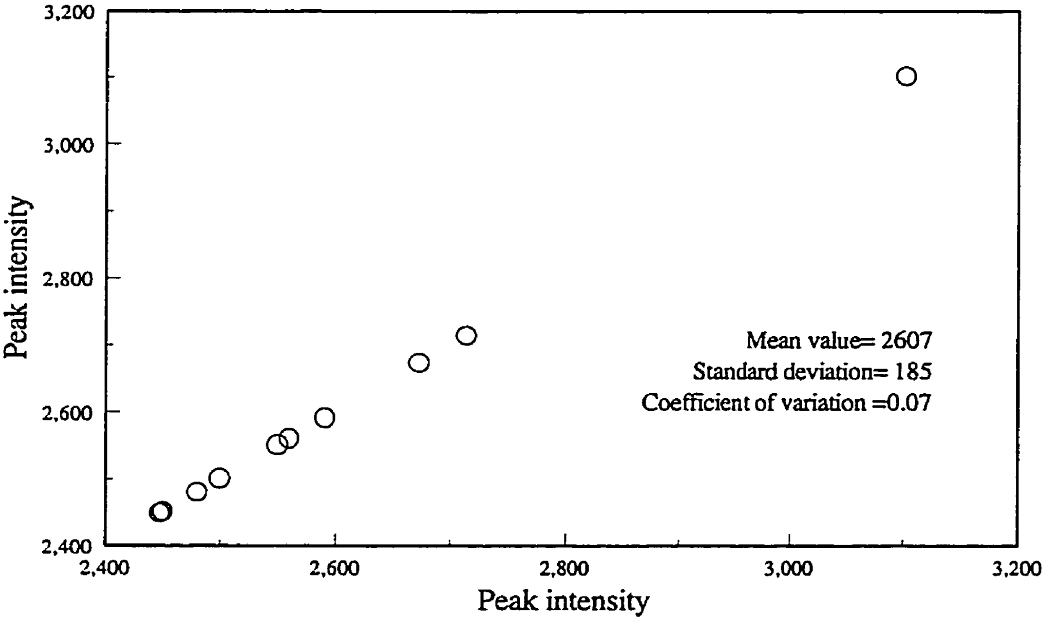


Figure 4.2: Instrument source of error of peaks' intensity in *XRD* analysis, single Sepiolite sample run 10 times for its major reflection line.

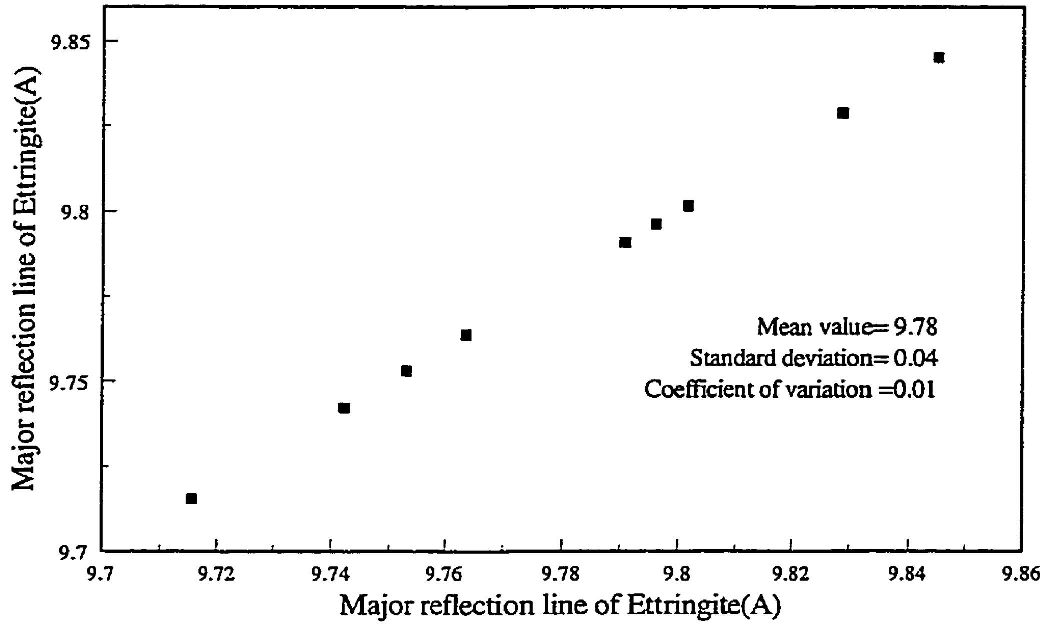


Figure 4.3: Sample preparation error in *XRD*, scattering of reflection line's quantity for 9 Ettringite samples.

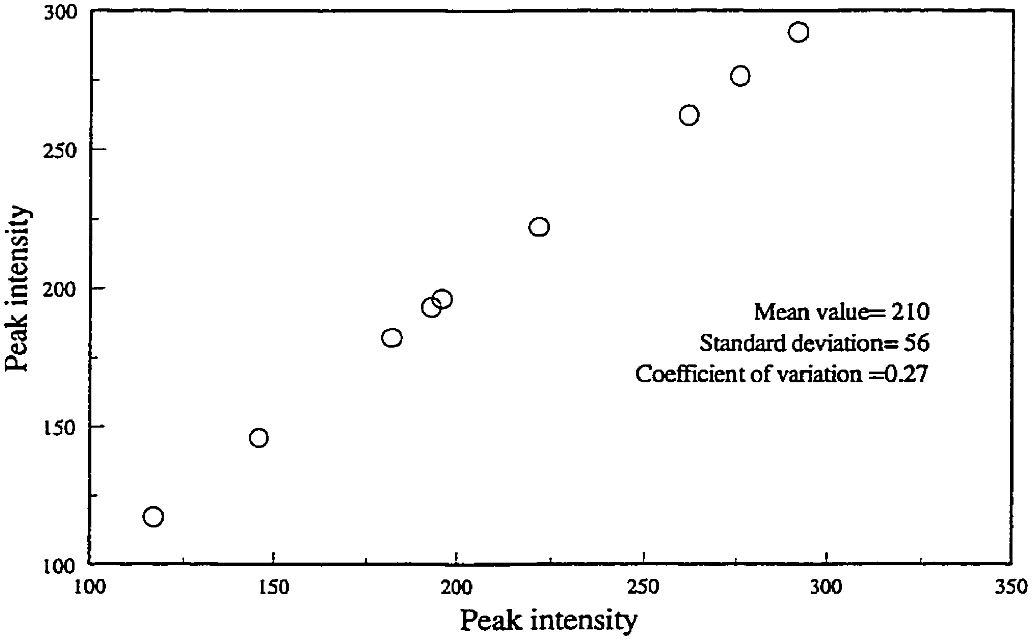


Figure 4.4: Sample preparation error in *XRD*, scattering of peak intensity's quantity for 9 Ettringite samples.

intensity is much higher in comparison to the previous series of tests, where it increased from 0.07 to 0.27. It can be concluded that as opposed to the instrumental effect, the error arising from sample preparation, should be taken into consideration as a source of error in the intensity evaluation of *XRD* testing. In this research, the quantity of coefficient of variation arising from sample preparation is considered as the population's coefficient of variation for *XRD* testing.

4.2.3 Standard Deviation and Relative Deviation of *XRD* Analysis

The accuracy of some common quantitative *XRD* techniques and the suggested method are examined through the calculation of the correlation coefficient and computing the "relative deviation of estimation" where these parameters are defined as follows:

The coefficient of correlation, r, indicates the correlation between the quantity of mineral estimated from established graphs of any certain method and the real quantity of mineral present in the artificial control samples based on the relationship shown in equation 4.8 *(Samani 1987)*.

$$r=\sqrt{1-\frac{\sum_{i=1}^{M}[Q_{Rqm}-Q_{Eqg}]^2}{\sum_{i=1}^{M}[Q_{Rqm}-Q_{Ave.}]^2}} \qquad (4.8)$$

in which Q_{Rqm} is the real quantity of mineral present in the artificial multi-phase sample, Q_{Eqg} is the estimated quantity of mineral using the established graphs, and $Q_{Ave.}$ is the average of the real quantity of a certain mineral which we are looking for, in the series of artificial samples being tested.

Another criterion to evaluate the accuracy of mineral estimation by the use of quantitative *XRD* methods, is the calculation of "relative deviation of estimation from real quantity present in the artificial multi-phase sample". This is calculated based on equation 4.9.

$$r_{ed}=\sqrt{[\frac{(Q_{Rqm}-Q_{Eqg})}{Q_{Rqm}}]^2} \qquad (4.9)$$

in which the Q_{Rqm} and Q_{Eqg} are the same as the quantity defined in equation 4.8.

4.3 DEFICIENCY OF *XRD* ANALYSIS USING AREAS UNDER PEAKS

This method is based on the direct comparison of intensities or peak areas of minerals identified by *XRD* testing. Due to the simplicity of mineral evaluation of soils, this method is very common among researchers. Even though this technique can give an estimation of the quantities of the individual minerals, due to the difference mass absorption coefficients of minerals, as will be extensively discussed later, this method might lead to a wrong quantitative mineral estimation *(Carroll 1970)*. To evaluate the accuracy of this method, the peak intensity of several artificial mixtures of palygorskite and calcite are analyzed by *XRD*. Samples were prepared as previously outlined in Chapter 3. Figure 4.5 indicates the variation of peak intensity of the major reflection line of palygorskite and calcite in these samples. Under similar conditions, calcite indicates a higher reflection line intensity in comparison to palygorskite. In other words, as can be seen from Figure 4.5, quantitative analysis based on peak area or peak height of the mineral present in the mixture, might strongly lead to an underestimation of the quantity of palygorskite. This is shown in Figure 4.6, which illustrates how extensively the mineral evaluation based on peak height might underestimate the presence of palygorskite and overestimate the presence of calcite in a two phase system. As an example, in the artificial mixture of 50% calcite and 50% palygorskite, this method illustrates the percentage of palygorskite as only 16%. The correlation factor between the predicted quantity based on areas under the peak and the real quantity present in the sample (Equation 4.8) for palygorskite is 0.22. The same deficiency was observed in the two phase system of sepiolite and kaolinite. While in the latter case, analysis based on peak height or areas will lead to an overestimation of the presence of sepiolite. This can be observed by simply comparing the peak intensity of sepiolite and kaolinite in Figures 4.7 and 4.8, in which the different percentages of artificial samples of mixtures, in a two phase system, are analyzed. Figure 4.7 indicates the variation of the percentage of mineral versus the intensity of the major reflection lines for mixtures of kaolinite and sepiolite. These reflection lines are chosen as 12.1 and 7.2 angstrom for sepiolite and kaolinite, respectively. Figure 4.7 shows that sepiolite in these mixtures has a higher relative intensity in comparison to kaolinite, where similar concentrations in different mixtures is monitored. This is well illustrated in Figure 4.8 where it can be easily seen that estimation based on peak height or areas of minerals in these conditions might strongly lead to an overestimate of the presence of sepiolite, especially in its low concentration. The correlation factor between the real quantity present in the artificial sample and the magnitude predicted using height of the peak is 0.78.

Therefore, it seems that analysis based on only peak's area or height, will not be reliable in terms of quantitative evaluation. Furthermore, although it may give an overall estimation of the presence of minerals in the soil mixture, still in terms of mineral identification based on descending or ascending order of existing minerals in the soil this method will not be reliable.

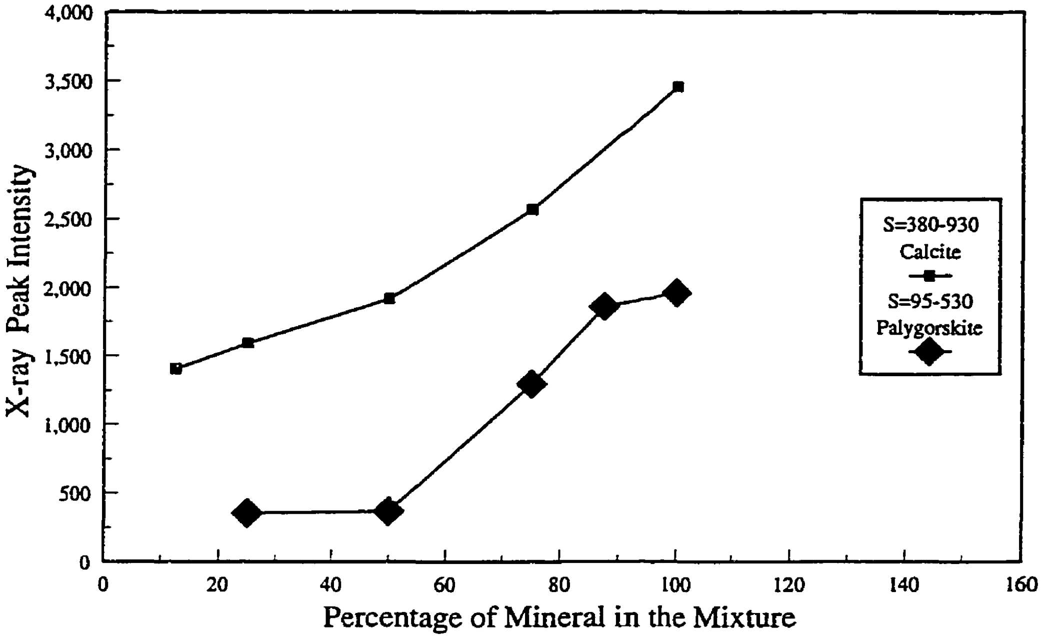


Figure 4.5: Variation of peak intensity of major reflection lines of Palygorskite and Calcite in their different artificial mixtures.

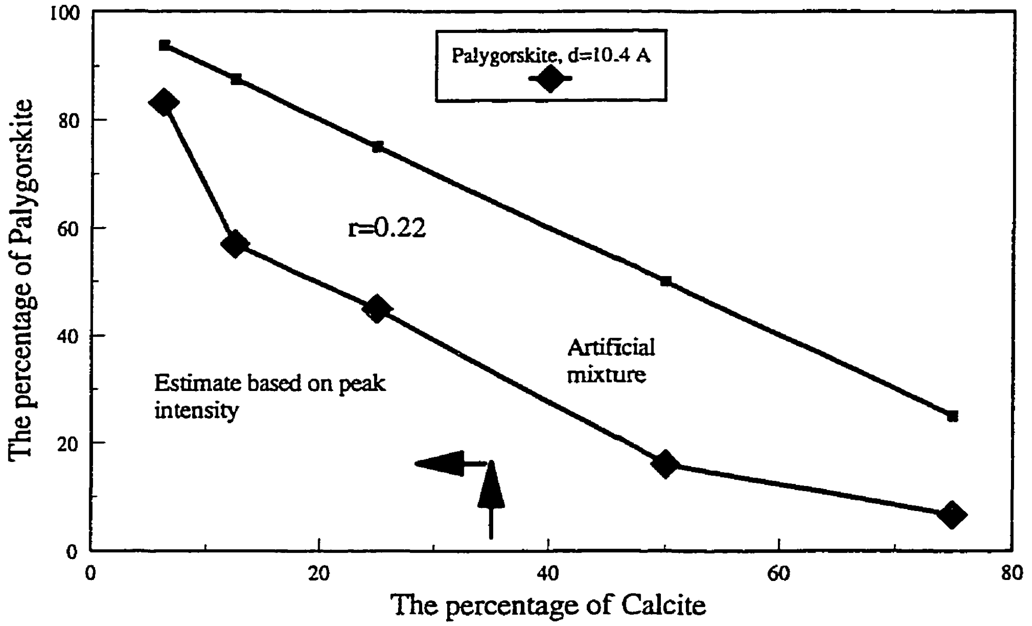


Figure 4.6: Correlation between quantity of Palygorskite based on its peak's height and the real quantity present in the different artificial soil mixture of Palygorskite and Calcite.

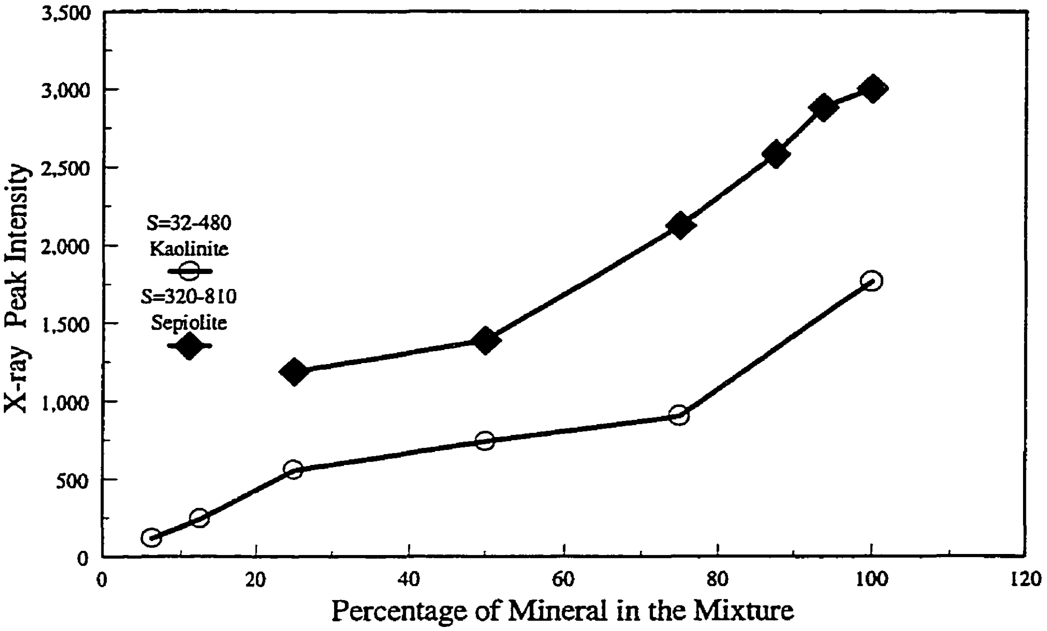


Figure 4.7: Variation of peak intensity of major reflection lines of Sepiolite and Kaolinite in the different artificial mixtures.

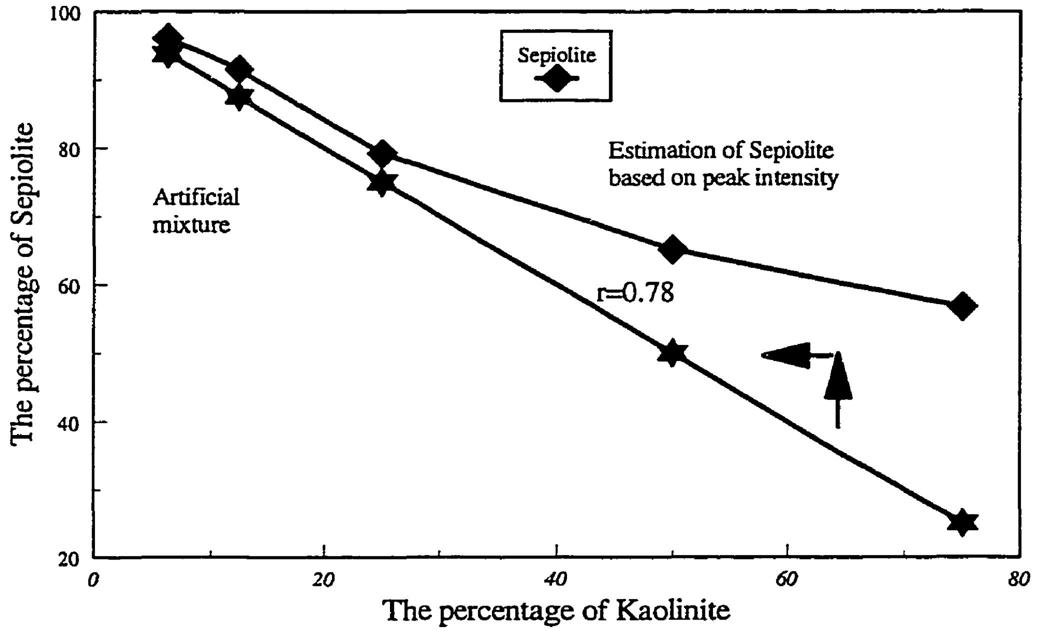


Figure 4.8: Correlation between quantity of Sepiolite based on its peak height and the real quantity present in the artificial mixtures of Sepiolite/Calcite.

4.4 *XRD* ANALYSIS USING IDENTICAL MASS ABSORPTION

Since intensity is proportional to concentration, then for a mixture of two elements the following proportion can be written *(Whiston 1987)*:

$$\frac{w_A}{w_B} \propto \frac{I_A}{I_B} \tag{4.10}$$

in which A and B are representative of two elements present in the mixtures, w_A and w_B are the weight percentages of the two elements, and I_A and I_B are the intensities of two selected diffractions of these two elements, respectively.

The proportionality sign can be replaced by proportionality coefficient, K, as follows:

$$\frac{w_A}{w_B} = K\frac{I_A}{I_B} \tag{4.11}$$

Assuming a two-component mixtures, we would have:

$$w_A + w_B = 100 \tag{4.12}$$

Solving these latter equations for w_B will give:

$$w_B = \frac{100}{1 + K(I_A/I_B)} \tag{4.13}$$

Based upon the latter equation, to determine K, it is required to prepare a mixture of these mentioned minerals (i.e. A and B) of known weight percentages. Having the intensities of the two selected minerals is sufficient to solve the latter equation for K. The main problem involved with this method includes the limitation of derivation equations when more than two minerals are used. On the other hand, in this method the relationship between intensity and concentration is assumed to be constant.

4.4.1 Palygorskite and Sepiolite Quantification

To investigate the accuracy of this assumption for sepiolite and palygorskite, a series of mixtures of palygorskite and sepiolite at different concentrations was prepared and run by *XRD*. The quantity of sample deposited on all slides was carefully prepared to be the same. Figure 4.9 indicates the variation of *XRD* peak intensity of sepiolite versus its percentage in a series of artificial samples. As can be seen in this Figure, in a two-phase system of sepiolite and kaolinite, by increasing the percentage of sepiolite, the intensity of sepiolite's major peak increases. Three samples in a multiple-phase system having a controlled amount of sepiolite were analyzed for the intensity of sepiolite's major peak. These are presented on the same graph. This, in fact, shows the effect of mineral interference on the *x-ray* diffraction intensities of sepiolite's major peak. The relative deviation from the real quantity present in the artificial sample (Equation 4.9) for sepiolite determination in a multi-phase system in comparison to the standard graph will be 45%, 3% and 4%. Where 25%, 50% and 100% sepiolite are present in the tested mixtures, respectively. In fact, these interference effects are concentrate dependent, as will also be confirmed later, at a low concentration of mineral, intensity shows a higher deviation from the multi-phase system. Figure 4.10 compares the variation of proportionality coefficient of sepiolite and palygorskite versus the concentration of these minerals. Two different sets of experiments using different mixtures of sepiolite-kaolinite, and palygorskite-calcite have been used. This Figure illustrates the concentrate dependency of proportionality coefficients of the tested minerals. A high proportionality coefficient of sepiolite in its low concentration indicates that even in low concentrations, sepiolite might show a high diffraction intensity. The average of the proportionality coefficient was found to be 2.05 with a standard deviation of 0.96 and coefficient of variation of 0.47. Samples having above 25% sepiolite gives the average proportionality coefficient of 1.58 with a standard deviation of 0.2 and coefficient of variation of 0.12. This again indicates the significant effect of scattered data in the low concentration of sepiolite on the calculated proportionality coefficient.

This suggests that up to around 25 percent sepiolite will be hard to quantitively identify by this method. This lowest identifiable percentage seems to be even more than those reported for the other clay minerals *(Carroll et al. 1963)*. This finding is in good agreement with the data presented in Figure 4.9, in which there is a relatively high scattering of data in the low concentrations of sepiolite when two and multiple-phase mixtures are compared. For palygorskite, the average value of the proportionality coefficient for these two phase samples was found to be 0.24 with a standard deviation of 0.05.

In addition to the above discussion, as is illustrated in Table 4.1, the proportionality coefficient obtained for these mixtures is not consistent when different reflection lines for K measurement are used. Table 4.1 indicates the variation of proportionality coefficient , K, for different mixtures of the two phase system of kaolinite and sepiolite according to their three different reflection lines. In this Table the calculated K, is based on the use of the different reflection lines of these minerals which have a similar weighting factor. Even though for evaluation of the proportionality coefficient, this method suggests the use of the peak intensity related to the major reflection line, there is no explanation why the other peak intensities of a certain mineral rather than the highest one, should not be used. Moreover, some minerals such as a palygorskite, sodium chlorite and calcium chlorite hydrate are known to have more than one peak having possible highest intensity. For some kinds of illite, even four different lines are known to have the highest reflection intensity *(ICDD 1988)*. These factors also make questionable the use of only major reflected lines in the quantitative mineral evaluation of clays by this method.

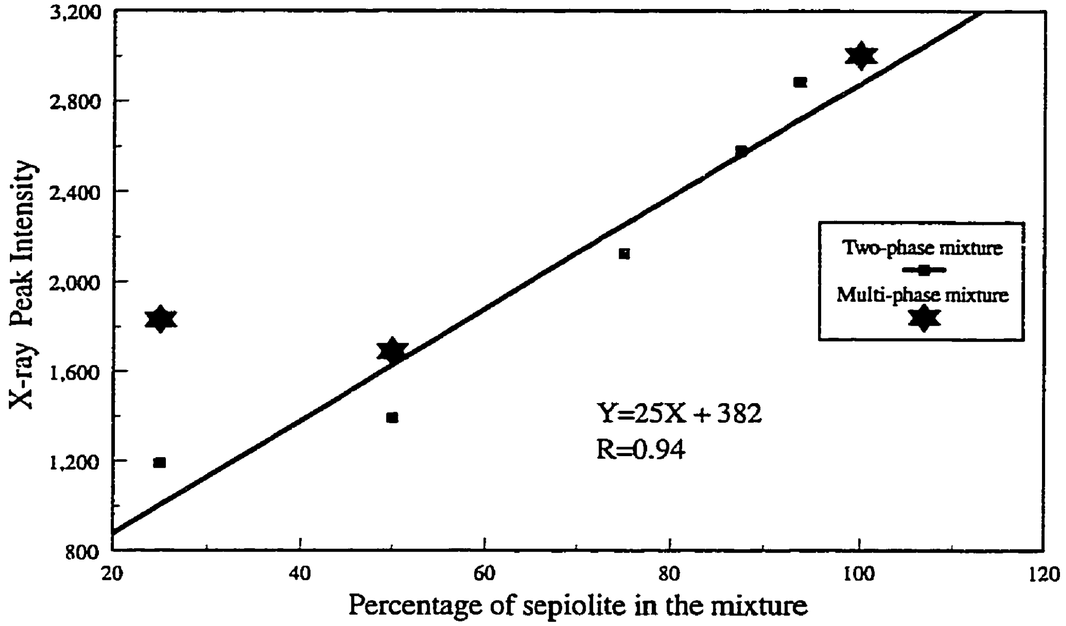


Figure 4.9: Relationship between intensity and concentration for two- and multi- phase mixture of Sepiolite.

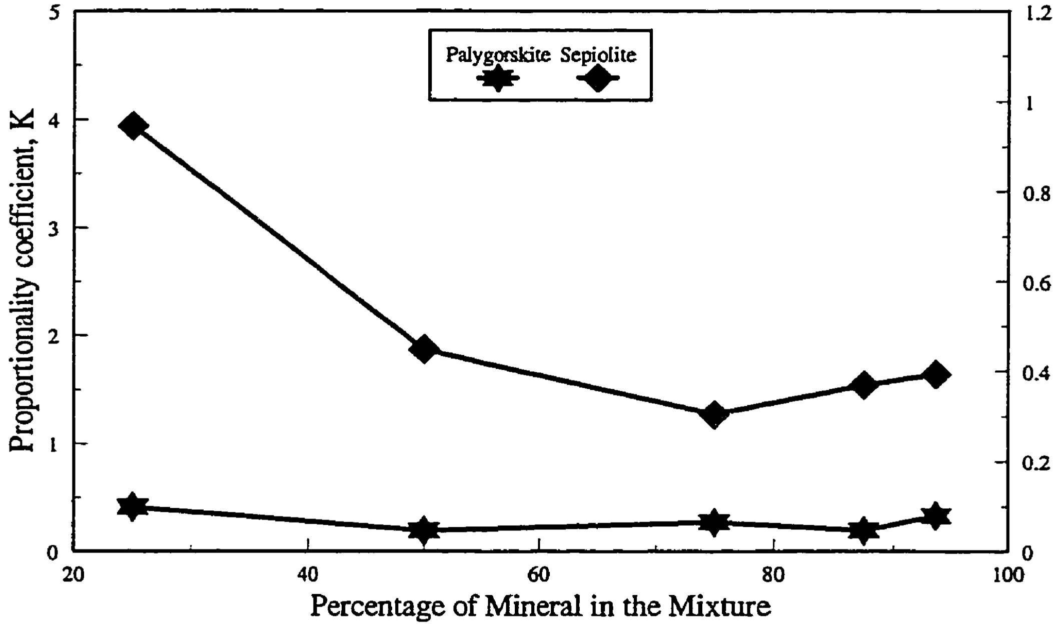


Figure 4.10: The variation of proportionality coefficient of Sepiolite and Palygorskite versus the concentration of those minerals in a series of artificial mixtures of Palygorskite/Calcite and Sepiolite/Kaolinite.

Table 4.1: The calculation of proportionality coefficient for different mixtures under different reflection angles.

Weighting Factor of Reflection Lines	Proportionality Coefficient		
	50% Kaolinite 50% Sepiolite	**25% Kaolinite 75% Sepiolite**	**12.5% Kaolinite 87.5% Sepiolite**
100	1.87	1.27	1.54
40	1.19	0.42	0.11
35	2.6	0.82	0.29

4.5 MINERAL DIAGNOSING USING INTERNAL STANDARDS

This method is based on the use of an internal standard to calculate how peak intensities vary with variation of concentration. By adding a certain amount of a particular component, as a standard, to the tested sample and using different artificial samples, having different concentrations of the desired mineral, the establishment of a calibration graph is possible. This particular component should not necessarily be one of the elements present in the soil sample. A calibration graph presents the different percentages of mineral, which we are looking for (i.e. $X\%$), versus the ratio of intensity of this mineral on that of the internal standard component (i.e. I_X/I_S, while I_S is the intensity of the internal standard component). Then, having the latter ratio from the unknown sample, the amount of desired mineral (i.e. X) can be calculated. With the establishment of different calibration graphs, the investigation for different minerals will be possible. This method, in spite of its advantage of not assuming a linear relationship between the intensity of a certain diffraction peak and concentration during the addition of standard to the unknown sample, assumes a linear relation between the intensity of consumed standard and mineral concentration. Therefore, it finally ignores the interference effects of different minerals in making and using the calibration graphs. Furthermore, in this method, for establishment of different calibration graphs, only the intensity of one peak (usually the peak with the highest intensity) will be used. In other words, as was previously addressed, despite of problems involved with use of only the major reflection line, in this method the role of other peaks of a certain mineral will not be considered. Therefore, there is a significant possibility of mistakingly defining the presence of a mineral, since for each mineral only one peak will be used. For instance, as will be addressed in Chapter 5, the reflection angle of palygorskite's major peaks in soils rich in salt, is of the same order of magnitude as those of illite peaks and will be mistaken with illite.

Different internal standards have been proposed including aluminum powder *(Burtner 1974)*, zinc hydroxide *(Mossman et al. 1967)*, and molybdenum sulfids (MoS_2) *(Quakernaat 1970, Gody and Thompson 1976)*. Al_2O_3 is usually used as an internal standard. The Joint Committee on Powder Diffraction Standards *(JCPDS)* publishes ratios of I/I_C, the ratio of peak heights of the major strongest reflection of minerals to the strongest peaks of Al_2O_3 for a 1:1 mixture by weight of the two phases. Thus, if one takes a 1:1 mixture of Al_2O_3 and a sample to be tested for a certain mineral (i.e. *X*), then the amount of this particular mineral in the original sample will be as follows:

1/2 (I/I_C for mixture of Al_2O_3 and sample in terms of a particular mineral divided by I/I_C for *JCPDS* value)

By and large, since the reflection lines of minerals in clay soils have been shown to be very sensitive to the soil fabric, it seems that in *XRD* analysis of clay soils, focusing only on a major reflection angle of mineral is questionable. This fact has already been addressed in section 4.4.1 and will be addressed in the evaluation of the role of salt in diffraction peaks of soils in section 5.4.1, which shows that the soil fabric plays an essential role in changing not only intensity of reflection lines *(Gillott 1960, Yoshinaka and Kazama 1973)*, but also the quantity of reflection lines in clay soils. Furthermore, while it is feasible to make a set of binary mixtures for the principal associated minerals, the method becomes less practicable for systems with three or more components *(Brindley 1961)*. Due to the similarity of the principals associated with the internal and external methods and the above explanations, only the external method, as will be discussed in the following, has been examined in this research.

4.6 ANALYSIS BASED ON THE EXTERNAL STANDARD

This method is based on the use of pure minerals, as a standard, when they are known to be present in the testing sample. By making artificial samples having different percentages of a known pure mineral (i.e. *Y*), the peak intensity of the major reflecting line of this added pure mineral will be monitored in all artificial samples, pure mineral and unknown sample as well. With the calculation of the ratio of peak intensity of *Y* in all samples over its intensity in the pure mineral, the preparation of a calibration graph will be possible. This calibration graph will have the percentage of known mineral in one axis and the ratio of peak intensity of added mineral over peak intensity of pure mineral in the artificial sample, on the another axis. Therefore, having the ratio of peak intensity of this mineral in the unknown sample over the peak intensity of pure mineral and using calibration graph, it is possible to determine the estimated percentage of mineral in the unknown sample.

Although this method might lead to a good estimation of existing minerals in the sample, it requires many sample preparations as well as *XRD* analysis to make calibration graphs of different minerals present in the natural soils. Furthermore, since for some minerals, different major peak intensities might be possible due to the presence of different structures of a certain mineral, it will be very hard to say that the added pure mineral is exactly the same as the one which exists in the soil. For instance, while the major reflection line of illite appears at 10 angstrom, some illites are known to have the major reflection line at 4.43 or 2.58 angstrom *(ICDD 1988)*. The use of just the major reflection line in this method enhances the above mentioned problem.

4.6.1 Multi-Phase System of Marly Soils

Figure 4.11 indicates the use of different mixtures of kaolinite and sepiolite as an external standard for quantitative mineral analysis in a series of artificial samples. In this Figure, the horizontal axis is representative of the percentage of sepiolite in the mixtures. The vertical axis indicates the intensity ratio of the major basal spacing of sepiolite in the mixture over that of pure sepiolite. For instance, applying linear regression for data presented for mixtures of sepiolite and kaolinite in Figure 4.11, gives the correlation factor of 0.94. Following the establishment of a standard graph, sepiolite quantification of five artificial multi-phase mixtures was examined by the external method where, the percentage of sepiolite was fixed at 25, 50, and 75 percent. As can be seen, at a low percentage of sepiolite, there is noticeable deviation among the achieved data with respect to the calibration graph. For instance, for multi-phase samples having 75, 50, and 25 percent sepiolite, the use of these established standard graphs gives the relative deviation of estimation (Equation 4.9) equal to 4%, 6%, and 52%, respectively. As is illustrated in the graph, the low amount of sepiolite can indicate a very high intensity. In other words, as was addressed in this research and by previous researchers (i.e. *Carroll et al. 1963)*, in the use of these quantitative analyses methods, one should always notice that low concentrations of mineral can lead to a wrong quantitative evaluation. This in turn shows the importance of parallel physico-chemical methods with quantitative *XRD* evaluation of soils. Problems addressed in the use of the internal method, exist in the application of the external method. For instance, the ignorance of the absorption coefficient of the multi-phase, the difficulty of making several artificial samples and the ignorance of other reflection lines of minerals can be counted. One advantage of the application of the external method will be the possibility of differentiating between the magnitude of the mass absorption coefficient of minerals. Figure 4.12 differentiates between the variations of intensity of palygorskite and sepiolite in the controlled two phases samples. The data of the several artificial two phases mixtures, including mixtures of sepiolite/kaolinite, sepiolite/palygorskite, and calcite/palygorskite, are plotted based on data evaluation by the external standard method. This in turn indicates that for a similar mineral concentration in the mixture, palygorskite has the lower peak intensity in its major basal spacing when compared to sepiolite. The data presented in this Figure again illustrates the important consideration of different mass absorption coefficients of minerals in quantitative mineral evaluation.

4.7 PROPOSED *XRD* ANALYSIS FOR MARLY SOILS & ETTRINGITE

Based on the above evaluation of the most common quantitative *XRD* methods, the following results are summarized and may be used for a more practical and accurate quantitative *XRD* evaluation of clay soils:

a) The direct analysis based on peak intensity or areas under the peaks might strongly cause an overestimation or underestimation of the quantity of clay minerals.

b) Quantitative evaluation based on only the major reflection line might strongly induce the following mistakes in mineral identification of clays: Providing the wrong evaluation of the presence of clay minerals due to similar or very close major reflection lines of some clay minerals. This includes achievement of wrong results in mineral recognition due to the fabric effect on fluctuation of the reflection lines's quantity or intensity variation of certain reflection lines. More explanation of this will be addressed in Chapter 5.

The above mentioned two points can be attributed to the role of mass absorption

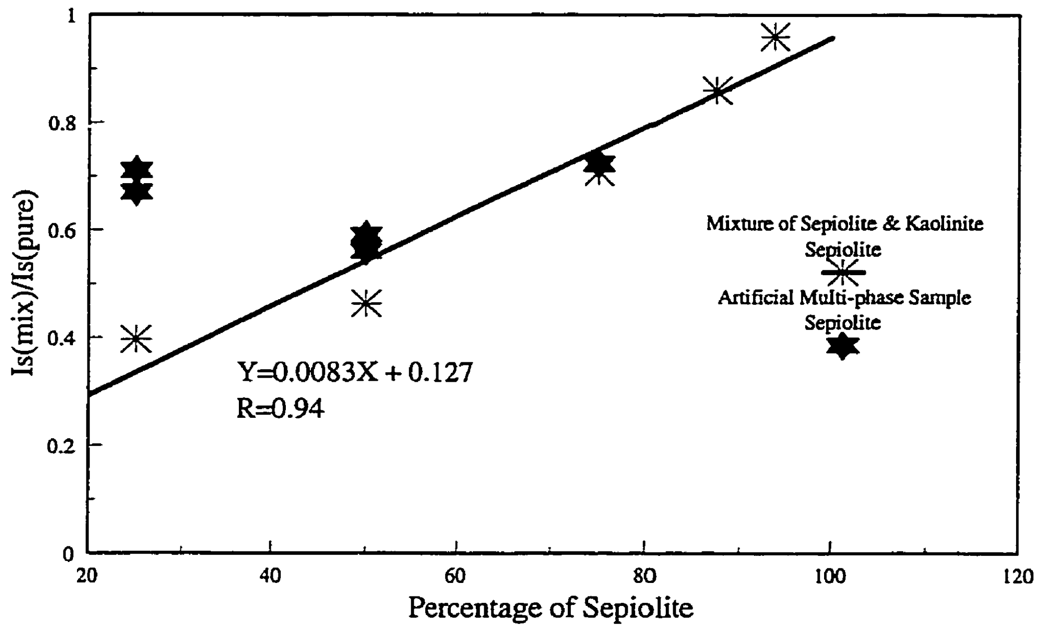


Figure 4.11: Application of external standard method for *XRD* quantification of Sepiolite.

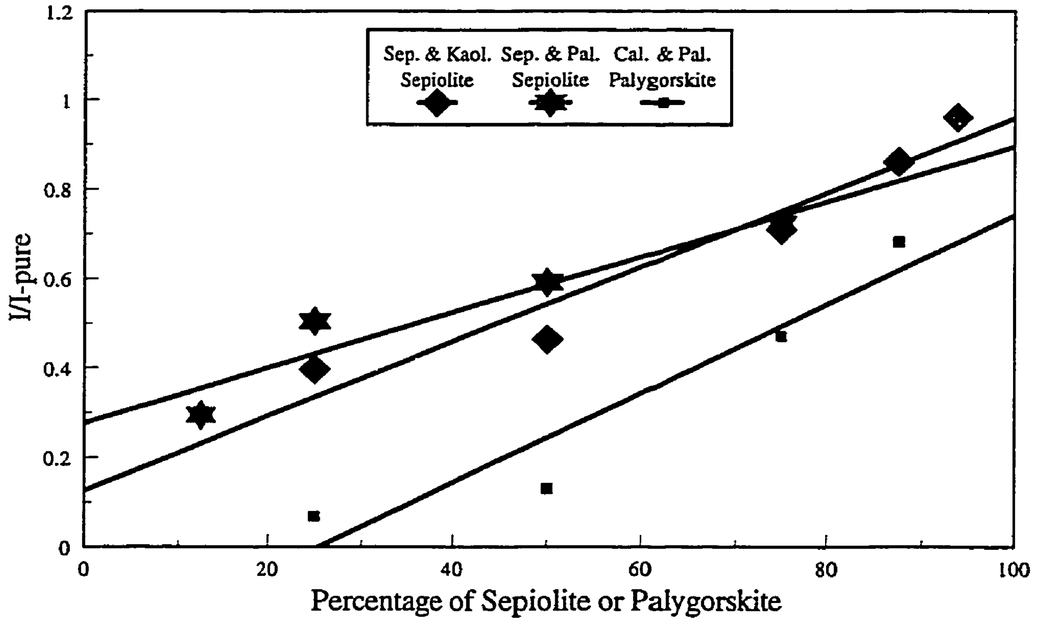


Figure 4.12: Variation of major reflection line peak's intensity of Palygorskite and Sepiolite in different two-phase artificial mixtures.

coefficients of clay particles which arise from the different crystallization degree, orientation and chemical composition of minerals, the different particle size of soil fraction, and the different microscopic structure of clay soils. The ignorance of the different crystallization degrees of similar minerals will be involved only if the major reflection line is used.

c) Even though the absorption coefficient plays an essential role in clay identification, the interference effect makes it necessary to take into account a border as an identifiable quantity for evaluation of clay minerals by *XRD*. This detection limit might be different for different clay soils due to the difference in their mass absorption as confirmed in this research and as addressed before *(Carroll 1970)*.

The theoretical basis of the proposed quantitative *XRD* analysis is based on the relationship established between the intensity and the absorption coefficient of the soil sample as suggested by *Klug and Alexander (1954), and Brindley (1961)*. According to them, the intensity of the *x-ray* reflected by a component *C* in a mixture is known to be related to the volume proportion V_c as follows:

$$I_c = \frac{P_c V_c}{\mu_{lm}} \tag{4.14}$$

in which μ_{lm} is the mixture's mass absorption coefficient and P_c is a constant for any certain reflection from the component *C*. To avoid the previously addressed difficulties involved with the use of just major reflection lines for quantitative analysis, the other reflection lines, especially those which have a relatively high intensity weighting factor, should be taken into consideration. This will have the following advantage in clay identification: First, the possibility of any mistake of clay identification when considering only the major reflection line will be eliminated. Secondly, the concept of the crystallization degree which causes the disappearance of some reflection lines will be taken into account. Thirdly, all the reflection lines of clay minerals having more than one major line will be considered. Therefore, the proportionality coefficient which is usually calculated based on the major reflection lines *(Cullity 1967)*, can be estimated based on at least those reflection lines with a relatively high intensity weighting factor. The reflection lines with an intensity weighting factor of equal to or more than 30, are used in this research to determine the proportionality coefficients of sepiolite, palygorskite, and ettringite. To do so, for proportionality coefficient measurement, the average weighted intensity is calculated as follows:

$$I_{awi} = \frac{\sum_i^n I_i \times W_i}{\sum_i^n W_i} \tag{4.15}$$

in which I_i is the intensity of the reflection line having a weighting factor equal to or more than 30, W_i is the standard weighting factor of that reflection line, *n* is the number of reflection lines having weighting factors equal to or more than 30, and I_{awi} is the average weighted intensity for proportionality coefficient measurement purposes. Replacing the latter equation in the former equation, one will get:

$$\frac{\sum_i^n I_i \times W_i}{\sum_i^n W_i} = \frac{K_c V_c}{\mu_{tm}} \tag{4.16}$$

in which K_c is a constant for the existing reflections from the component *C*. On the other hand, volume proportion V_c can be defined as follows *(Brindley 1961)*:

$$V_c = W_c \frac{\rho_m}{\rho_c} \tag{4.17}$$

in which ρ_m is the average density of the mixture, ρ_c and W_c are the weight proportion and density of component *C*, respectively. Replacing V_c in the former equation will result in:

$$\frac{\sum_i^n I_i \times W_i}{\sum_i^n W_i} = K_c \frac{W_c \rho_m}{\rho_c \mu_{lm}} \tag{4.18}$$

Based on Equation 4.7, the mass absorption coefficient of a mixture can be defined as follows:

$$\mu_m = \frac{\mu_{lm}}{\rho_m} \tag{4.19}$$

in which μ_{lm} is the absorption ratio and ρ_m is the average density of the "mixture", respectively. By replacing the mixture's mass absorption ratio in the previous equation the following can be written:

$$\frac{\sum_i^n I_i \times W_i}{\sum_i^n W_i} = k_c \frac{W_c}{\mu_m} \tag{4.20}$$

In any multi-component mixture, the latter equation can be written for two component to eliminate the mass absorption coefficient of the mixture as follows:

$$\frac{\dfrac{\sum_i^n I_{ci} \times W_{ci}}{\sum_i^n W_{ci}}}{\dfrac{\sum_i^n I_{di} \times W_{di}}{\sum_i^n W_{di}}} = \frac{k_c \times W_c}{k_d \times W_d} \tag{4.21}$$

The latter equation in turn indicates that the intensity ratio is directly proportional to the weight ratio of components. The application of this latter equation will be applicable to quantify the percent of minerals in the unknown sample. In fact, once again similar to the external and the internal standard methods, one can use pure minerals and make calibration graphs for the binary mixtures of minerals present in the unknown samples. These calibration graphs, which show the variation of the intensity ratio versus the weight ratio of minerals for standard mixtures, can be used to estimate the ratio of the binary minerals in the unknown sample. By applying this process to all components in pairs, the quantification of minerals in the mixture can be provided.

4.7.1 Practical Graphs for *XRD* Mineral Quantification of Marly Soils

To include these important factors, the above mentioned considerations are used in mineral identification and quantitative mineral evaluation of artificial marly soils in a set of controlled samples. Very good correspondence was observed as described in the following. As was presented before, the main elements of marly soils consist of palygorskite/sepiolite, calcite and quartz. Among other clay minerals, kaolinite and illite are known to be possibly present in marly soils *(Davis 1967, Purser 1973, Yong et al.1996)*. Since the behaviour of marl is controlled by a combination of these major elements, the quick quantitative analysis to quantify the magnitude of each fraction is of interest. As will be mentioned in Chapter 5, the quartz fraction can be easily separated by the different soil washing steps. This, in fact, will eliminate the interference effect of quartz and clays in the quantitative analysis. Therefore, the major elements to be quantified will include, sepiolite or palygorskite, calcite, kaolinite and illite. Based on the suggested quantitative evaluation technique, a series of binary mixtures of standard minerals were prepared in different concentrations. Figures 4.13, 4.14, 4.15, and 4.16 show the results obtained for palygorskite-calcite, sepiolite-kaolinite, palygorskite-sepiolite, and kaolinite-illite in the binary mixtures. In these graphs, the horizontal axis indicates the weight ratio of two minerals and the vertical axis represents the ratio of the average weighted intensity of two minerals in the mixture as was defined in Equation 4.15. The linear pattern is chosen for regression analysis purposes based on the prior assumption of a relationship between intensity and concentration *(Alexander and Klug 1948, Noorish and Taylor 1962)*. As is shown in these graphs the correlation factor for each series of data is more than 0.93 which indicates the acceptable linear fitting of the relationship between weight ratio of minerals and the average weighted intensity.

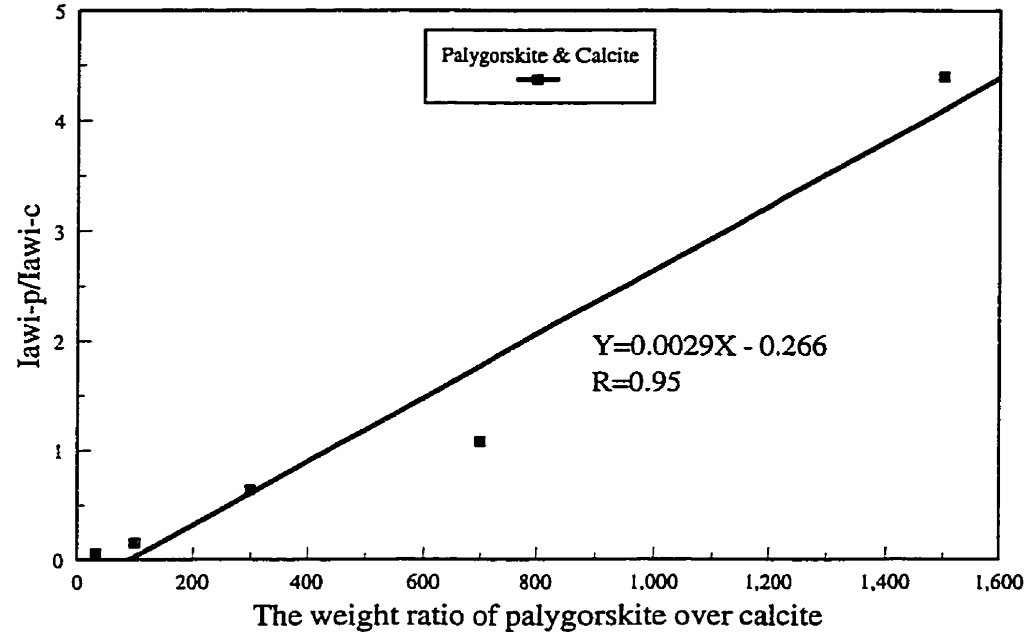


Figure 4.13: Relationship between weight ratio of minerals and ratio of average weighted intensity for reflection lines having weighting factor equal or more than 30, Palygorskite/Calcite artificial mixtures.

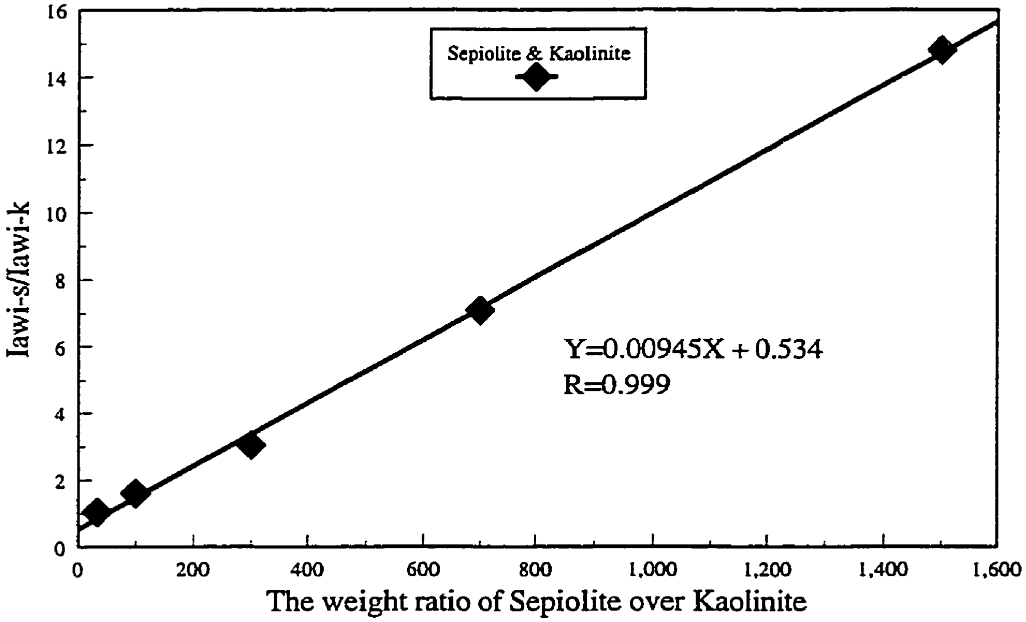


Figure 4.14: Relationship between weight ratio of minerals and ratio of average weighted intensity for reflection lines having weighting factor equal or more than 30, Sepiolite/Kaolinite artificial mixtures.

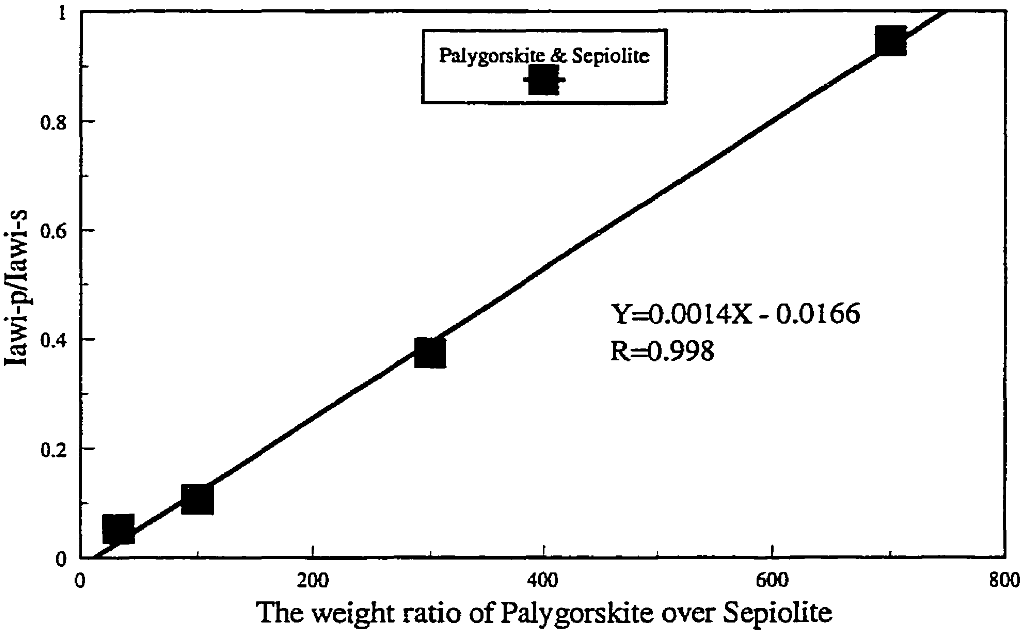


Figure 4.15: Relationship between weight ratio of minerals and ratio of average weighted intensity for reflection lines having weighting factor equal or more than 30, Palygorskite/Sepiolite artificial mixtures.

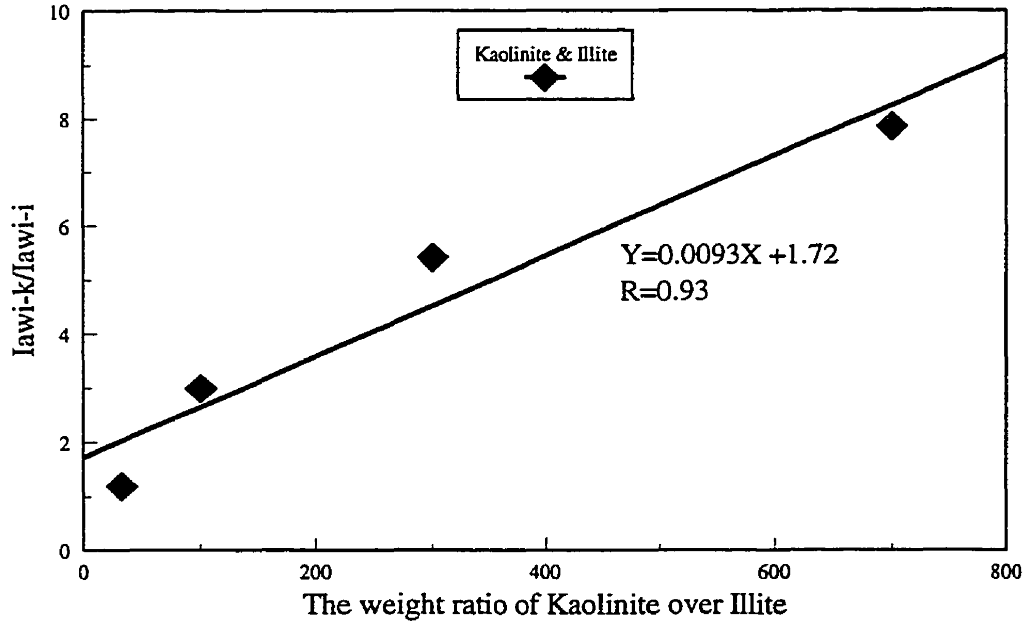


Figure 4.16: Relationship between weight ratio of minerals and ratio of average weighted intensity for reflection lines having weighting factor equal or more than 30, Kaolinite/Illite artificial mixtures.

For each mineral the average weighted intensity is chosen based on reflection lines having a weighting factor equal to or more than 30. The application and validation of the established graphs will be evaluated later in this Chapter.

4.7.2 *XRD* Quantification of Ettringite in Marly Soils

To be able to quantitively monitor the mineral transformation of the clay fraction of marly soils to ettringite, the required graphs, based on the application of average weighed intensity of reflection lines, are established. With the use of prepared artificial ettringite, pure extracted palygorskite, kaolinite and calcite, several artificial mixtures were prepared. Figures 4.17, 4.18, and 4.19 indicate the established graphs for several mixtures of palygorskite/ettringite, ettringite/kaolinite and ettringite/calcite. In all series of samples the linear relationship between the average weighted intensity and mineral concentration seems to be valid where the correlation factor, based on a linear fitting of data, is shown to be more than 0.97. While graphs 4.17 and 4.18 can be used directly to monitor mineral transformation, Figure 4.19 may be used for control purposes, since the quantity of calcite can initially be found by performing chemical analysis.

4.7.3 Validation of Established Graphs for *XRD* Quantification

To validate the extent of accuracy of these graphs for a quantitative analysis of minerals in marly soils, a set of artificial multi-component mixtures was prepared. The artificial mixtures consist of different percentages of palygorskite, sepiolite, calcite, kaolinite, and ettringite. Two different series of artificial samples were used. The first series consists of several different mixtures of calcite, sepiolite, and kaolinite as representative of marl soils. The second series of samples had different percentages of kaolinite, palygorskite, calcite and ettringite (Table 4.2). Chemical analysis was chosen for calcite determination which gave accuracy within 1% *(Hesse 1979)*. For marly samples the quantity of calcite was fixed at 25, 25, and 50 percent. In marly samples having artificial ettringite, the quantity of calcite was fixed to be 12.5, 25, and 37.5

percent. Some of the *XRD* diffraction of these mixtures are presented in Appendix III. Based on the above explanation, by finding the percentage of calcite, the analysis of *XRD* data was completed by analysing the average weighted intensity ratio of sepiolite/kaolinite peaks in marly samples. For artificial samples having ettringite in the components, the ratio was calculated for kaolinite-ettringite and palygorskite-ettringite. The reflection lines having a weighting factor equal to or more than 30 was chosen in this analysis.

The results obtained are plotted in Figure 4.20, in which the real quantity of mineral in the mixture is plotted against the percentage achieved from *XRD* analysis. For comparative purposes, the bisector of the graph is drawn and called the ideal case in which the quantitative *XRD* evaluation gives the same results as in the real case. Having extreme accuracy, means the quantity of all calculated points locate on this bisector. Based on previously presented graphs (4.13 to 4.19), the quantitative mineral evaluation of the artificial samples was achieved. Figure 4.20 shows all the calculated percentages of different minerals in these experiments. The correlation factor between these points and the ideal case (bisector) using Equation 4.8 is found to be 0.90.

Table 4.2: The artificial mixtures prepared for validation of *XRD* quantification method.

Sample Number	**Quantity of Minerals Present in the Artificial Mixtures**				
	Palygorskite	**Sepiolite**	**Calcite**	**Kaolinite**	**Ettringite**
1	-	25%	25%	50%	-
2	-	50%	25%	25%	-
3	-	25%	50%	25%	-
4	25%	-	25%	25%	25%
5	12.5%	-	37.5%	12.5%	37.5%
6	37.5%	-	12.5%	37.5%	12.5%

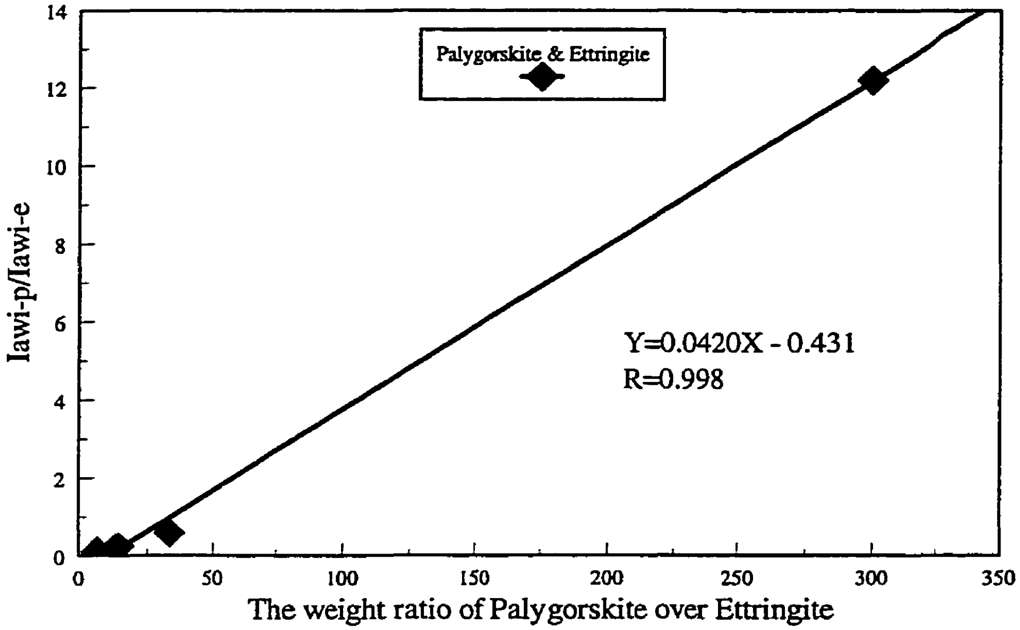


Figure 4.17: Relationship between weight ratio of minerals and ratio of average weighted intensity for reflection lines having weighting factor equal or more than 30, Palygorskite/Ettringite artificial mixtures.

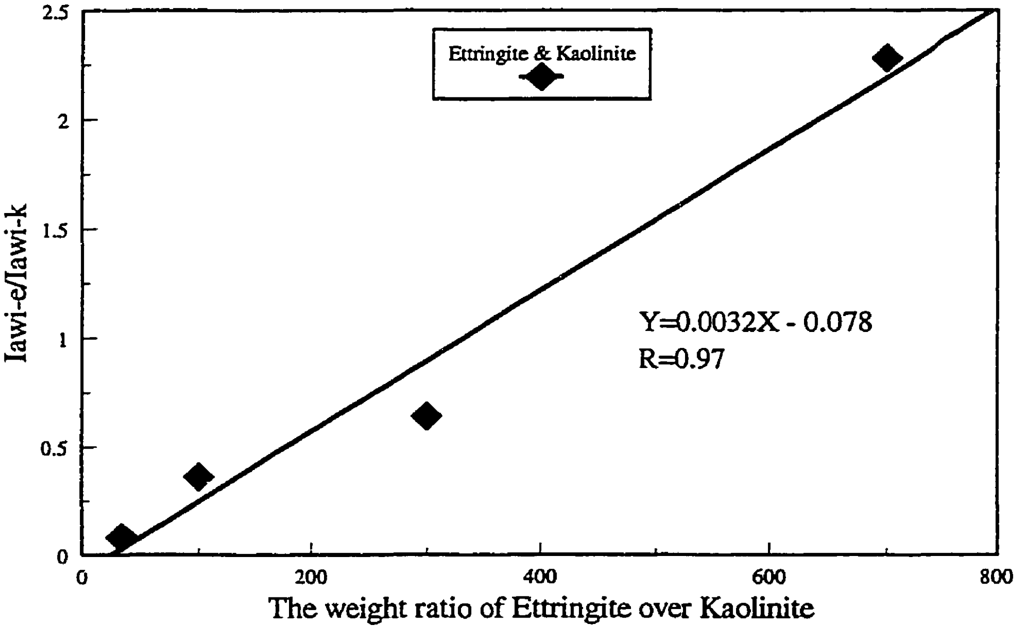


Figure 4.18: Relationship between weight ratio of minerals and ratio of average weighted intensity for reflection lines having weighting factor equal or more than 30, Ettringite/Kaolinite artificial mixtures.

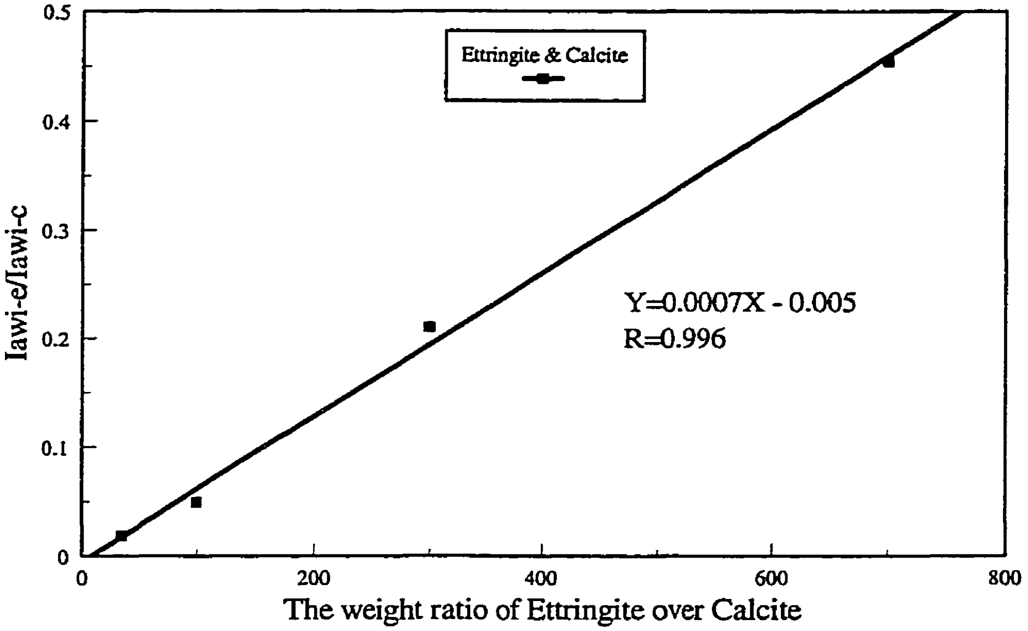


Figure 4.19: Relationship between weight ratio of minerals and ratio of average weighted intensity for reflection lines having weighting factor equal or more than 30, Ettringite/Calcite artificial mixtures.

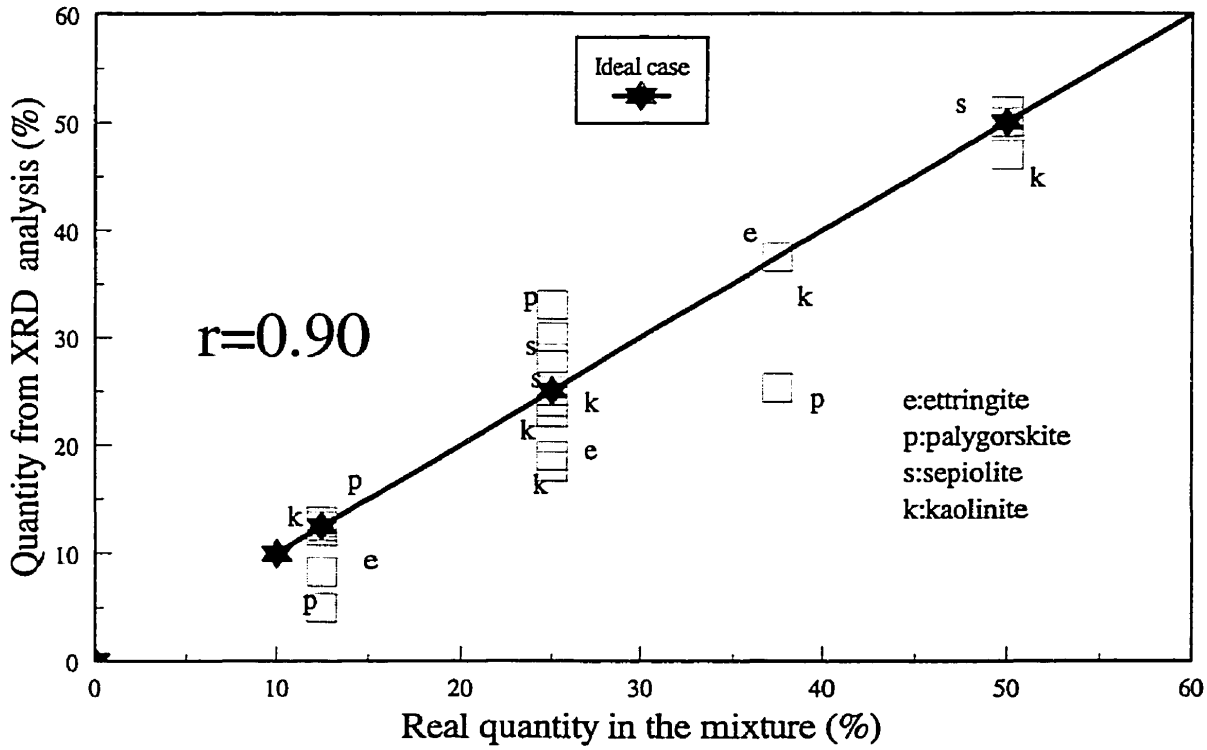


Figure 4.20: Validation of established graphs for *XRD* quantification of Ettringite and marly soils using different multi-phase artificial samples.

4.8 SUMMARY

Quantitative mineral evaluation of marly soils is an essential step to provide the expected behaviour due to the importance of the quantity of each major mineral fraction on the performance. This also helps to have a more accurate classification of soil, as will be presented in Chapter 5. The application of the four current methods for mineral quantification purposes were experimentally reviewed for clayey soils. This lead to a proposed quantitative mineral evaluation for marly soils. The problems involved in clay mineral evaluation based on the direct use of peak intensity or areas under the peak, are addressed. In addition, several mistakes induced by the application of only the major reflection lines of clay minerals for quantitative evaluation purposes have been cited. Using the refinement made to the proposed relationship between the intensity and absorption coefficient in the method suggested by *Klug and Alexander (1954)*, the use of all major reflection lines having a weighting factor equal to or more than 30 was employed. By performing a series of *XRD* tests on artificial samples, a set of practical graphs for binary mixtures of major marl components and ettringite mineral is proposed. The applicability of these graphs for mineral quantification of marly soils and ettringite is examined via preparation of multi-component artificial samples which are quantified by the established graphs. Very good agreement was observed between the computed and the real quantity of each mineral present in the artificial samples.

CHAPTER 5

THE ROLE OF MARL COMPOSITION AND REACTION FACTORS ON INSTABILITY AND BEHAVIOUR OF MARLY SOILS

5.1 INTRODUCTION

The very general definition of marl as a mixture of clay and carbonate *(Barth et al. 1939, Fookes and Higginbottom 1975, Pettijohn 1975)* has failed to differentiate between the noticeable performance of marl and other clay minerals. In other words, the role of marl composition and, in particular, the role of palygorskite and sepiolite as the major fractions of marl *(Yong et a. 1996, Ouhadi et al. 1996)* in conjunction with the presence of calcite as the source providing potential determining ions *(Yong et al. 1978, 1979)* has strongly contributed to the very distinct performance of marl. The so-called open-structure of palygorskite and sepiolite in conjunction with the presence of salt and sulfate in the pore fluid of marl, cause some significant effects in the *CEC* measurement. That has resulted in an important need to make refinements in the current *CEC* methods. In this Chapter a physical technique was developed for extracting pure palygorskite from a marl sample. By application of the *x-ray* diffraction technique, extraction of pure palygorskite was confirmed. A series of physico-chemical tests were performed to establish the role of marl components on its behaviour and to investigate the wetted-state reactions of marly soils. Significant attention was placed on the role of palygorskite and sepiolite on marl performance. Finally, based on the introduced results, a new classification for marly soils is presented.

5.2 MODIFICATION IN THE *CEC* METHOD, SOILS RICH IN SULFATE

The measurement of cation exchange capacity *(CEC)* is important in so many aspects and mainly indicates how reactively soils behave. For *CEC* measurement, different methods are suggested by different investigators. Some of the best known of those methods were run to evaluate the *CEC* of marl. As will be addressed in this section, very conflicting results were observed, which lead us to apply a modification to the current *CEC* methods.

Cation exchange capacity *(CEC)* is a quantitative evaluation of easily exchangeable cations which are balanced by the negative charge of the soil particles. The negative charges in soils arise from different sources including, isomorphous substitution within the structures of minerals, broken bonds at different ages of minerals and adsorption of certain ions on the soil particle surface. While negative charges, which arise from isomorphous substitution, are independent of the pH variation or bulk solution properties, the other sources of charges are highly dependent on the pH value, bulk solution properties and anion nature present in the solution. Therefore, due to the many different parameters affecting the capability of soils for exchanging cations, the *CEC* is not a soil characteristic which can be independently measured without considering the type of mineral, the measurement conditions and limitations. This will also produce different results when different methods of evaluation are used.

Some of the sources of error in conventional *CEC* methods are reviewed by *Rhoades (1982)*. The general principle of *CEC* measurement requires either saturating the soil with a strong cation to measure the amount of replaceable cations of the soil, or replacement of saturating cations. In the saturation step, there is a possibility of not completely saturating the sites of the soil fraction. During the replacement stage, trapped adsorbed cations between inter-layers might prevent replacement during extraction *(Bower 1950)*. Evaluating exchangeable cations and total exchange capacity by the ammonium acetate *(NH_4OAC)* is suggested by *Lavkulich (1981)*. This method is based on measuring the total extractable cations (exchangeable and soluble) by saturating a certain amount of soil with ammonium acetate and analysing the supernatant for Na^+, K^+, Ca^{2+}, and Mg^{2+}. This method is known to have significant errors due to the dissolution of $CaCO_3$ and gypsum which result in an excess of Ca^{2+} being extracted by NH^{4+}. In soils containing these minerals, exchangeable Ca^{2+} will be too high. *Polemio and Rhoades (1977)* suggested a method particularly suited to arid land soils. This method is based on the saturation of cation exchange sites with a sodium acetate *(NaOAc)* solution and extraction with *0.5 N* $MgNO_3$. During this measurement, chloride should be determined so that the soluble sodium carried over from the saturation step to the extraction step can be subtracted from the total sodium in evaluating exchangeable sodium. Exchangeable cations and *CEC* may be measured using barium chloride *(Hendershot and Duquette 1986)*. This method provides a rapid means of determining the exchangeable cations and the *CEC* of a wide range of soil types. The same as the ammonium acetate method, this method is based on saturating the exchangeable sites (here with 0.1 molar barium chloride) and analysing for major cations as addressed in the ammonium acetate method. Problems may arise if this method is used with saline soils containing sulfate, since $BaSO_4$ will precipitate *(Hendershot and Duquette 1986)*.

These three major methods were used in this research to evaluate the *CEC* of marl. Different marl samples having different weathering states were used in this series of experiments. Illite was used as a control sample. Table 5.1 indicates some of the problems involved with the barium chloride method for *CEC* measurement of marly soils.

Table 5.1: Problem involved with the barium chloride method for *CEC* measurement of marly soils.

Soil Sample	**Concentration of Cations (*meq/100 g* soil)**		
	Soluble Cations	**Extractable Cations**	**Exchangeable Cations (*CEC*)**
tM2	90±7	92±7	2±10
mtM3	118±10	110±9	-8±13
WM	96±8	104±9	8±12
Illite	3±0.3	43±3	40±3

As can be seen in Table 5.1, for all different states of weathered marl, the extractable cations, which normally include both soluble and exchangeable cations, show very noticeably low amounts of extractable cations. Even in moderately weathered marl (soil sample mtM3 in Table 5.1), the extractable cations are less than those of soluble cations (i.e. negative *CEC*). In this method, barium is responsible for replacement of other exchangeable cations to represent a measure of available exchange sites. However, as was pointed out before, since marl soil is rich in sulfate, barium sulfate will precipitate and there will be insufficient barium ions to replace all exchangeable sites. The very similar magnitude of soluble and extractable (including exchangeable and soluble) cations for all marl samples, shown in Table 5.1, confirms this conclusion. This will persuade us to extremely underestimate the total extractable cations, leading us to obtain a very low or even negative cation exchange capacity. The very high concentration of calcium cations observed in the extractable measurement, can be related to either the solubility of remaining insoluble gypsum (calcium sulfate) which is available by the formation of barium sulfate or the replacement of a low amount of barium by exchangeable calcium in the clay fraction of marl. Moreover the concentration of soluble sodium was found to be less in the extractable step when compared with that of the soluble step. In Chapter 2, it was discussed that, the hydrated radius of cations plays a significant role in terms of the replaceability of the cations with the same valence. From the particle interaction standpoint, the larger the ion, the thicker the layer required to accommodate the necessary number of cations, and hence, the greater the interparticle repulsion *(Yong 1975, 1992, Mitchell 1993)*. Therefore, barium ions with a hydrated radius of 8.8 angstrom have the ability to replace calcium and magnesium ions with the hydrated radius of 9.6 and 10.8 angstrom, respectively. Furthermore, the replacement of barium cations with a high valence in the exchangeable sites of clay and the availability of a relatively high concentration of calcium, mainly from gypsum, will decrease the repulsion force. This leads to a more flocculated structure. Creating a flocculated structure will, in turn, keep more sodium ions in the pores and trap them in the flocculated structure of soil *(Bower 1950)*, ending up with a lower concentration of sodium ions in the pore fluid of the soil.

Attempts were made to overcome these problems which lead to incorrect results in the *CEC* measurement. Based on the origin of these difficulties in the different methods, as previously addressed, the removal of problems associated with the barium chloride method was studied. To do this, the removal of sulfate from the soil and the possibility of sulfate adsorption by marl were examined. The variations of sulfate removal versus different processes of soil washing for marl and illite samples are shown in Figure 5.1. Sulfate was measured (section 3.2.2) for soil samples and after every soil washing process. Each soil washing process included the addition of distilled-water at the ratio of 1:10, shaking in the end-over-end shaker for 24 hours, and analysing the supernatant for sulfate. After centrifuging and sulfate measurement by turbidimetric method, the supernatant was discarded. Afterwards, by the addition of distilled-water, this process was repeated. As can be seen in Figure 5.1, following three soil washings, the sulfate was removed and the percentage of sulfate decreased to as low as 3% in the weathered marl and 5% in the unweathered marl with relation to the initial conditions.

The higher amount of sulfate after three soil washings in marl samples in comparison to illite can be attributed to the role of the open structure of palygorskite, as will be addressed later, and also the higher amount of sulfate background in marl. In both samples, the final amount of sulfate is less than the amount of sulfate in unwashed illite. According to Table 5.1 and the following discussion, this amount of sulfate in the non-washed illite sample seems to be within the safe range. In other words, sulfate concentration does not have a noticeable effect on the *CEC* result of illite which may occur by the precipitation of barium sulfate. This can be concluded by comparison of the *CEC* for illite using different methods (Table 5.1, 5.2, and 5.3) and different authors *(Warith 1987, Yong et al. 1992)*. In fact, these different methods give more or less the same *CEC* for illite with regards to the calculated standard deviation of measured *CEC*. Therefore, it can be reasonably assumed that the application of the barium chloride method for an illitic sample is not noticeably affected by the quantity of sulfate present in the pore fluid of soil. As can be seen in Figure 5.1, the amount of sulfate, present in the marl sample after three washings, is less than the initial amount of sulfate in illite, the so-called safe range of sulfate. Therefore, it would be an acceptable assumption that this remaining sulfate will not play a significant role in the final result of *CEC* measurements of marl when the barium chloride method is used. Based on the above explanation, *CEC* measurements were performed using the modified barium chloride method. To do this, soil samples were washed with distilled-water three times. Each time the soil sample was mixed with 1 to 10 soil-water ratio and shaken for 24 hours. Supernatant was separated and kept for cation measurement and again distilled-water was added and the process was repeated. After three soil washings, the barium chloride method was performed on the soil samples. The results for marly soils and illite are shown in the Table 5.2. Based on the above discussion, the *CEC* results for marl samples achieved from modifications made in the barium chloride method, seem to lie within the range of their real cation exchange capacity.

Table 5.2: Cation measurement after different soil washings to perform the modified *CEC* measurement.

Soil Sample	Total Soluble Cation Concentration (*meq/100 g* soil)			*CEC* By use of barium chloride method after the third soil washing
	First Washing	Second washing	Third Washing	
tM2	93.4	4.1	1.7	39±3
mtM3	120.4	4.5	1.6	42±3
WM	97.2	3.4	2	42±3
Illite	2.9	0.9	0.6	45±4

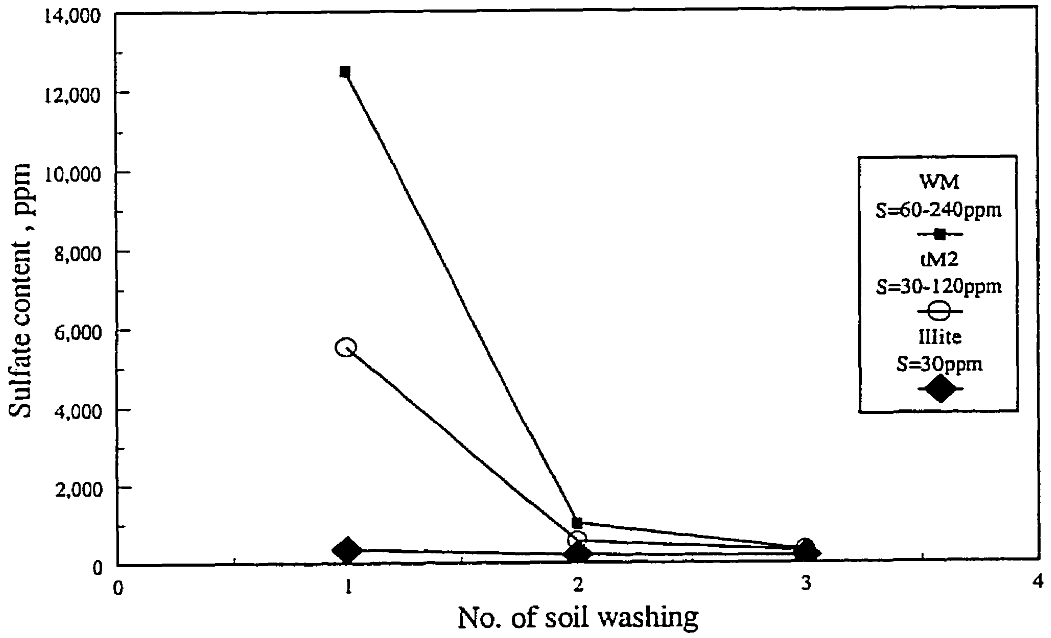


Figure 5.1: Effect of soil washing on sulfate removal of Marl and Illite.

To support these findings, sulfate adsorption by palygorskite was investigated. To do this, batch equilibrium testing was performed on the soils using a constant soil-water ratio and different sulfate concentrations. The procedure for the test has already been addressed in Chapter 3. Figures 5.2 and 5.3 represent the sulfate adsorption by palygorskite and blank samples at palygorskite natural pH equal 9. While Figure 5.2 indicates an adsorption of sulfate by palygorskite, Figure 5.3 compares sulfate adsorption by the same sample to a blank sample (i.e. by use of only distilled-water as a pore fluid and no soil sample). This Figure illustrates that the assumed adsorption in Figure 5.2 is less than the precision of the test. In fact, no adsorption has occurred in palygorskite at its natural pH and all the added sulfate stayed in the pore fluid of the soil. On the other hand, since sulfate is known to be among the non-potential determining ions *(Yong et al. 1992)* this, in turn, will be in agreement with the above conclusion.

Based on the above discussion, there does not seem any problem regarding the use of the modified barium chloride method to measure *CEC* of marly soils (Table 5.2). The only difficulty which remains to be discussed, is the change of the fabric of the soil due to soil washing. In fact, during the process of soil washing, the soil structure tends to be more oriented, leading to the exposure of more sites to be replaced by exchangeable cations. However, we should keep in mind that due to the pore fluid analysis of both illite and marl (as was addressed in Chapter 3) the samples show dispersive behaviour. Therefore, the role of soil washing on exposure of more surfaces to external cations will not be so significant. This can be proved by comparison of *CEC* for illite before and after sulfate removal in which we face the same range of *CEC*. As can be seen in Tables 5.1 and 5.2 for illite, while the common barium chloride method gives the *CEC* equal 40±3 *meq/100 g* of soil, the suggested modified method based on three soil washings and applying the barium chloride method ends up with *CEC* equal to 45±4. This low difference, is observed to be within the range of error existing in the *CEC* measurement *(Rhoades 1982)*.

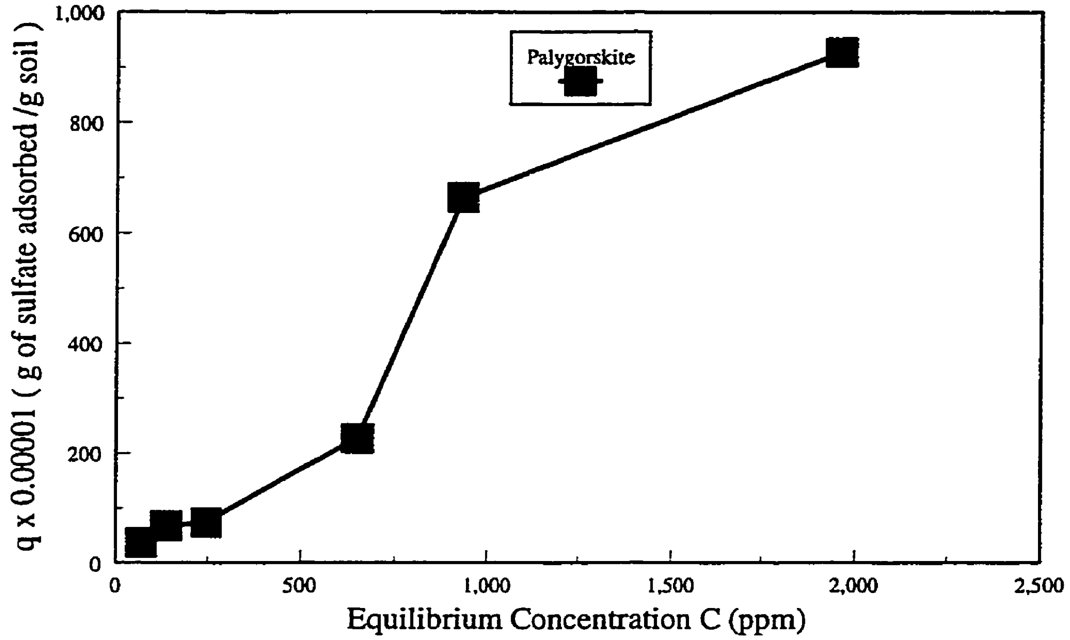


Figure 5.2: Adsorption of sulfate for a Palygorskite sample from batch equilibrium test.

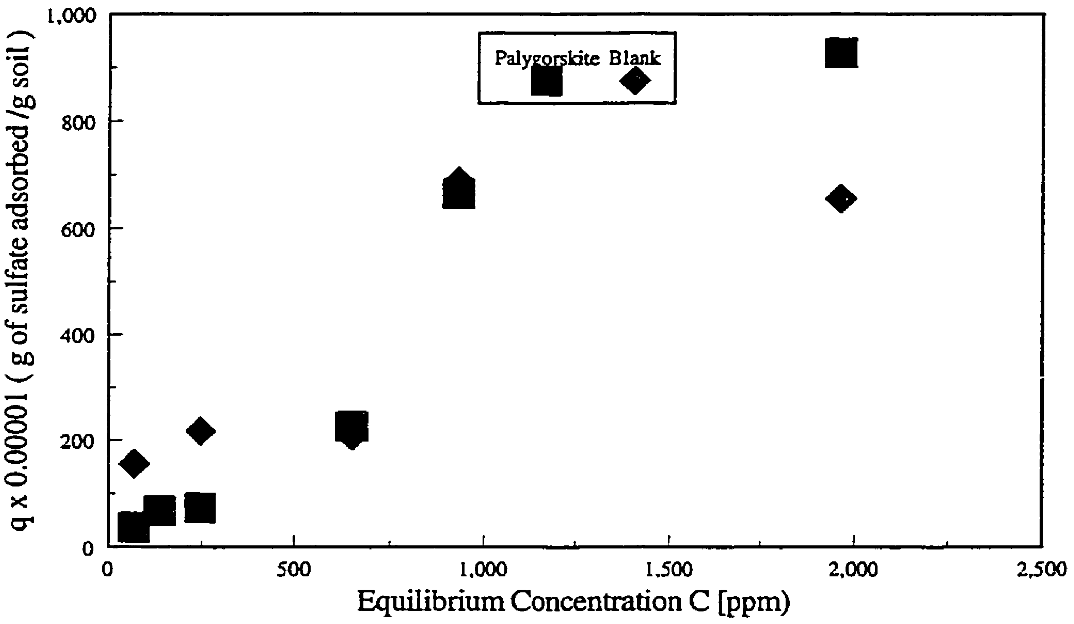


Figure 5.3: Comparison of adsorption of sulfate for Palygorskite and blank samples from batch equilibrium test.

In the ammonium acetate method (Table 5.3) even though it gives *CEC* within the range of expectable values for marly soil, its extractable parts come mostly from calcium cation, as was explained before. This happens for marly soils while for illite samples the range of released extractable calcium was within the same range as the barium chloride method giving 46 and 49 *meq/100 g* soil, respectively. It should be noted that the amount of calcite in marly soils was more than three times when compared with illite samples, as was presented in Figure 3.3. The high concentration of calcium cations in *CEC* measurement of marl with this method, could be from either exchangeable cations or dissociation of calcite, as previously addressed. Even though it was observed that, due to the trapping effect of the soil structure as was explained before, the amount of extractable sodium (the summation of soluble and exchangeable) was less than that of the soluble one! (Table 5.3). This is in good agreement with the above discussion where it was explained that this method is not useful for soil rich in calcite. The extensive dissociation of calcite, which causes a high concentration of calcium ions, has the ability to extensively depress the diffuse ion-layer of clay fraction. Following that, the development of a flocculated structure has the ability to trap some ions *(Bower 1950)*. The decrease in sodium ion concentration in the extractable stage might be due to the this trapping process caused by the high release of calcium ions in the dissociation process.

Table 5.3: The ammonium acetate method for *CEC* measurement, unit: *meq/100g* soil.

Soil Sample	**Unacceptable sodium concentration by application of ammonium acetate method**		***CEC* measurement by summation of exchangeable Na, K, Mg and Ca ions**
	Soluble Sodium	**Extractable Sodium**	***CEC***
tM2	110±10	71±6	41
mtM3	102±9	92±8	37
WM	102±9	80±7	44
Illite	1±0.1	3±0.3	54

The homoionic method *(Polemio and rhoades 1977)* was also performed on three different marl samples. Table 5.4 only indicates the amount of soluble and extractable sodium in this method. As can be seen, again surprisingly, the amount of extractable sodium is less than the measured soluble sodium. Although this method is a very time consuming method, it still does not lead to an acceptable result in marly soils (i.e. negative exchangeable sodium in Table 5.4)

Table 5.4: The homoionic method for *CEC* measurement, unit: *meq/100g* soil.

Soil Sample	**Soluble Sodium**	**Extractable Sodium**	**Exchangeable Sodium**
tM2	110±11	40±4	-70±12
mtM3	102±10	42±4	-60±11
WM	102±10	39±4	-63±11

Based upon the above discussion, and because of the various reactions obtained, it was decided that the results obtained using the modified barium chloride method were perhaps the least compromised. This provided a *CEC* measurement of about 39-42 *meq/100g* soil (Table 5.2), a value which places the marl used in the study in the high range, comparable to active chlorites. Therefore, the *CEC* for soils rich in sulfate can be achieved from the previously mentioned refinement made in the current *CEC* methods (Table 5.2). At least three soil washings will be performed upon the soil, each time measuring the rate of sulfate removal. Finally, the barium chloride method is performed, using the method previously mentioned, to measure the exchangeable cations. These suggested steps seem to be much faster than the current technique for *CEC* measurement of saline soils. Based on the results of this research, and before doing any more investigation, the maximum sulfate which can be considered to be within the safe range (in terms of not significantly affecting the *CEC* results by application of barium chloride method) seems to be 7 *meq/l*. Soils rich in potential determining ions or showing dispersive behaviour by their pore fluid analysis will be more compatible with this method since they already have an oriented structure and the final results will not be significantly affected by change in the soil fabric.

5.3 SOIL WASHING METHOD TO EXTRACT PURE PALYGORSKITE

To investigate the role of salt on marl performance, soil washing with distilled-water was used. In each step of soil washing, using plastic centrifuge tubes, pulverized marl was mixed with distilled-water in a soil water ratio of 1:5. Then the tubes were shaken on a end-to-end shaker for 24 hours. After shaking, samples were centrifuged at 60000 *RPM* for 10 minutes and then the supernatant was discarded. Following several soil washings, it was observed that the marl sample settled in a manner in which different colours of soil fraction layers were distinguishable. Continued soil washing with distilled-water removed the salt fraction. This was monitored by pore fluid analysis and is addressed in Table 5.2. Because of different soil grain sizes, the specimen settled in a manner in which the heavier fraction settled faster. After several soil washings, simple observation on the settled sample in centrifuge tube indicated that segregation of marl components happens during the soil washing process. Therefore, this process was assumed as a possible method for extraction of different marl components. Specifically, extraction of pure palygorskite which was free of calcite is of interest.

Usually, for the purpose of enhancing the gravitional force, a centrifuge is used. It has the ability to increase the rate of particle settling. In fact, the process of centrifuging, enhances the total force acting on the solid particles and finally makes the settling time shorter. By and large, concentration variation, the density of solid particles and the viscosity of fluid are known to affect the settling velocity. The role of concentration of suspended particles on the rate of settlement was evaluated by several researchers without considering the role of the soil surface charge of clay particles *(Richardson and Zaki 1954, Robinson 1961)*. However, clay particles, due to their surface charge, cause additional attraction or repulsive forces which will affect the rate of particle settlement. *Pavlik and Sansone (1973)* evaluated the role of the diffuse ion-layer of clay particles on settlement under the force of gravity. They showed that due to the distortion of the diffuse ion-layer, an electric field, opposed to the force of gravity is set up. This developed force may cause a substantial fraction of the total resistance to the movement of small particles. *Alammawi (1984)* examined, experimentally, the effect of the concentration of suspended different kaolinites on the rate of settlement with the view of finding a relationship between settlement due to the gravity and centrifugal forces. He indicated that, depending on the concentration, segregation occurs in experiments conducted under centrifugal force as a function of rotational speed. His studies also indicate the importance of the variation of concentration and centrifugal time upon the height of suspension settlement.

In the current research, to investigate the effectiveness of palygorskite extraction from marly soils over the soil washing process, *XRD* was performed on several layers of settled soil. After several soil washings, as previously described, soil fractions in the centrifuge tube were sectioned into 7 layers. To do this, based on different colours, soil samples were extracted from the tube. Then the extracted layers were air dried and pulverized for *XRD* analysis. For preparation of *XRD* slides, 0.2 grams of each sample were mixed with 10 *mL* distilled-water in a small volumetric flask, shaken for 3 minutes and placed in an ultrasound for a short period. Then, four drops of this mixture were poured on to a glass slide and analyzed with *XRD*.

For the extracted layers, Figures 5.4, and 5.5 indicate the variations of relative *XRD* peaks intensity of palygorskite, calcite and quartz. The settled soil layers in the centrifuge tubes were numbered from top to the bottom. Therefore, the upper layer in the centrifuge tube is called layer one. Layer seven is the lowest layer settled in the bottom of the centrifuge tube. As can be seen in Figure 5.4, the concentration of palygorskite is much higher in the first layer, as opposed to the other layers. At the same time, the concentrations of calcite and quartz are almost lowest in this layer. Pure palygorskite was taken from the first layer. Figure 5.4 shows that as we go along the lower layers, quartz and calcite concentrations increase. This can be attributed to the particle size effect which causes the settlement of coarser particles much faster than finer particles. In the fifth layer, we are faced with a sudden increase in palygorskite concentration. In this layer calcite and quartz concentrations tend to decrease in comparison to the fourth layer. During soil extraction from the centrifuge tube, it was visually observed that, as we go along the depth of soil deposit in the centrifuge tube, the concentration of coarser particles increases, while the concentration of clay fraction decreases. In spite of this simple observation, *XRD* analysis indicates a decrease in quartz and calcite peak intensity after the fourth layer. As previously mentioned, during sample preparation for *XRD*, a mixture of dry soil and distilled-water was kept in an ultrasonic device for a short period of time. This process will cause coarser particles to settle faster and therefore they do not appear in the soil water mixture taken for *XRD* analyses.

Therefore, we are faced with a sudden decrease in quartz and calcite peaks in the fifth layer. At the same time, due to the removal of coarser grains, the clay fraction will show an increase in concentration in this layer. On the other hand, very fine quartz and calcite, which will settle in the tube after coarser particles, seem to appear from the fourth layer as indicated from *XRD* analysis. In fact, layers four and five are the border layers for the appearance of very fine and coarse quartz and calcite. This evaluation is based on assumption that fine quartz and calcite have been taken from the volumetric flask for the *XRD* analysis, but not coarser particles. This assumption was continuously confirmed by simple observation during sample preparation. The further pattern of *XRD* analysis for calcite and quartz, which shows a lower concentration of these minerals in layers 6 and 7 when compared to layer 4 and an overall increase in concentration when compared to the whole pattern, confirms the previous discussion. By and large, in the first layer a very negligible quantity of calcite and quartz was identified (less than 1%), therefore, it seems this physical method is an appropriate way to extract pure palygorskite from marl. The *XRD* of pure palygorskite compared with a marl sample is presented in the Appendix III. As can be seen in Appendix III, all calcite, quartz and other clay minerals disappear, leading to a pure palygorskite mineral.

Particularly, this method would be very effective in separating the calcite fraction of Illitic sample (Domtar sealbond) from a pure clay mineral as is investigated in the following section.

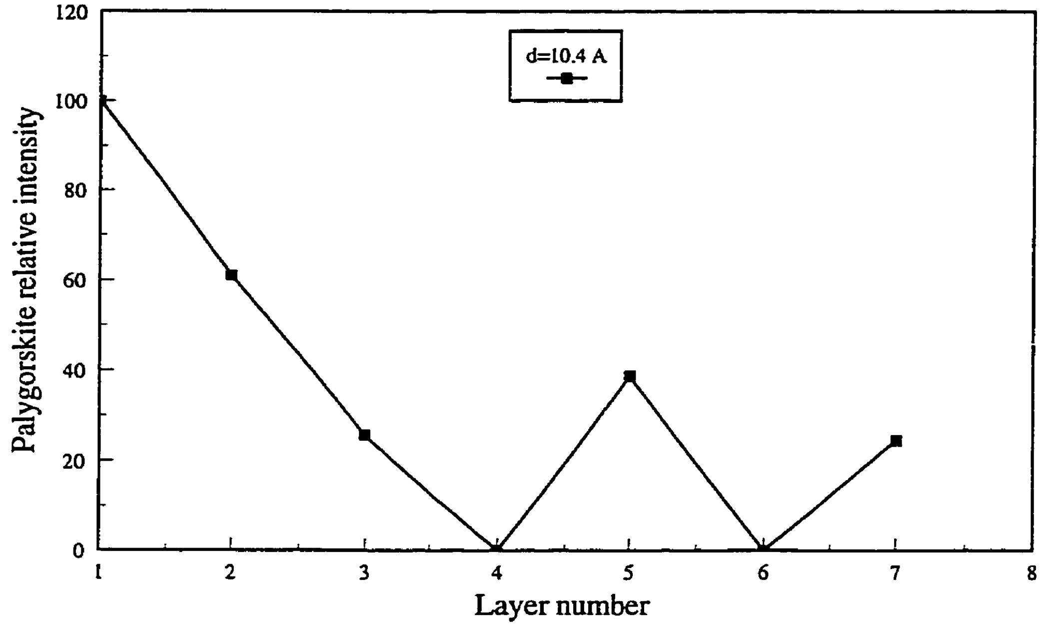


Figure 5.4: Variation of relative intensity of Palygorskite's XRD major peak from the top to the bottom of centrifuge tube for a Marl sample after several soil washings.

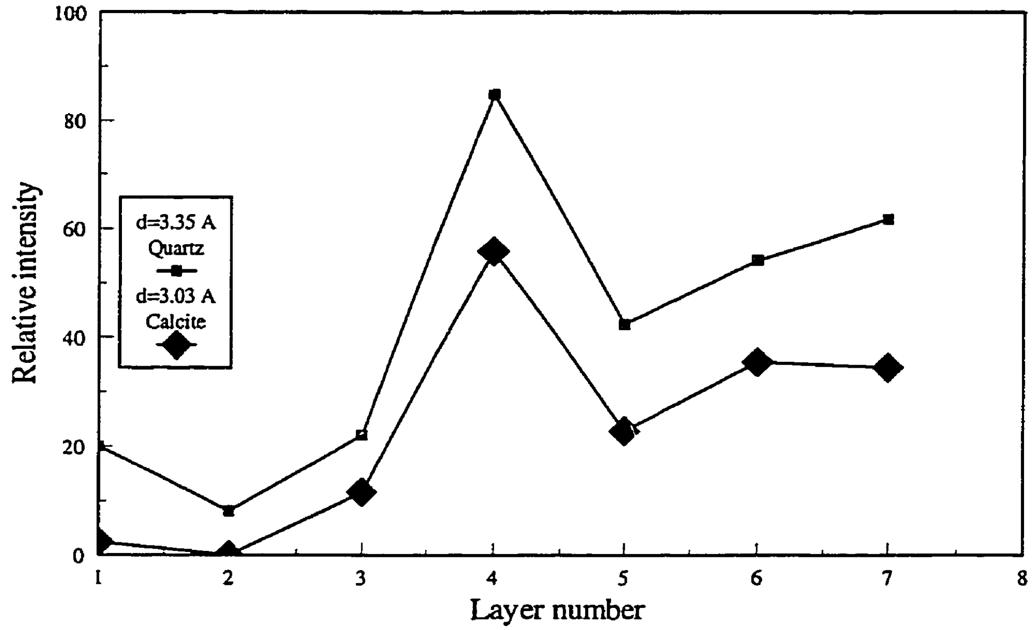


Figure 5.5: Variation of relative intensity of Calcite and Quartz's XRD major peaks from the top to the bottom of a centrifuge tube for a Marl sample after several soil washings.

5.3.1 *XRD* Evidence, Extracted Pure Illite from Domtar Sealbond

To investigate the effectiveness of the above suggested method for calcite removal, a sample of illite domtar sealbond was treated by the same process of soil washing as previously addressed in case of marl. After four soil washings, the sample was centrifuged and sectioned into the four layers. *XRD* was performed on these samples after drying and preparation as mentioned before. Figure 5.6 and 5.7 shows the variation of *XRD* peaks in these experiments. Figure 5.6 indicates the *XRD* results of illite in its basal spacing equal to 10 angstrom for those layers. Both the *XRD* peak intensity and relative peak intensity are plotted. As can be seen, after several soil washings and centrifuging, we are faced with a relatively pure illite, free of calcite in the first layer (the top layer). The relative intensity of calcite in this layer was 1.1 percentage while for the untreated sample it was 14%. In regard to the chemical analysis of the illitic sample used in this research, it was found that, based on the *XRD* results, the amount of calcite in the top layer was less than 1%. As we go to the further layers (i.e. along the bottom of the centrifuge tube), the concentration of calcite increased and illite showed a decrease in its peak intensity. The pure illite, free of calcite, found in the upper layer can be extracted easily and be used for experiments without having any chemical effect on the clay fraction of sample. Even though the lower layer samples were still a mixture of illite and calcite (Figure 5.7), achievement of pure illite, free of any calcite which was obtained in the top layer was the main aim of this step.

5.3.2 The Advantage of the Suggested Extraction Method

The advantages of the suggested extraction method, for extracting pure mineral from natural marl, are as follows:

1) This method is a physical method, therefore, the process of mineral separation does not affect the chemical properties of soil. As an example, the common method for separating calcite from soils rich in carbonate, which calls for acidification of soil, might affect the properties of clay fraction specifically when chlorite is present in the soil.

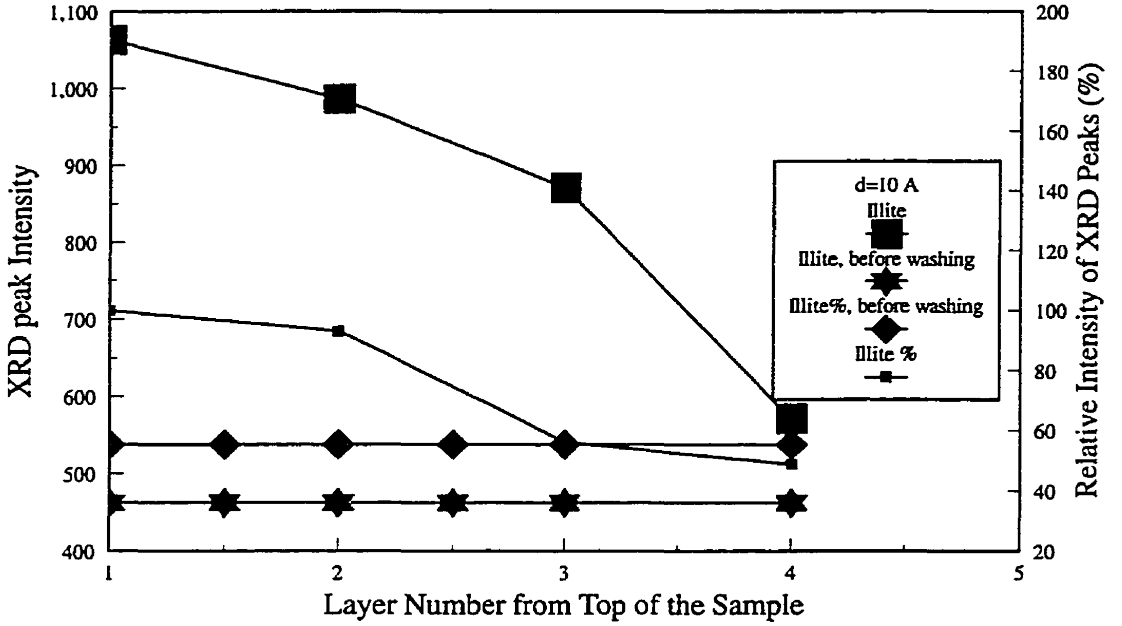


Figure 5.6: Variation of relative intensity, and intensity of Illite's XRD major peak from the top to the bottom of a centrifuge tube for an Illitic sample after several soil washings.

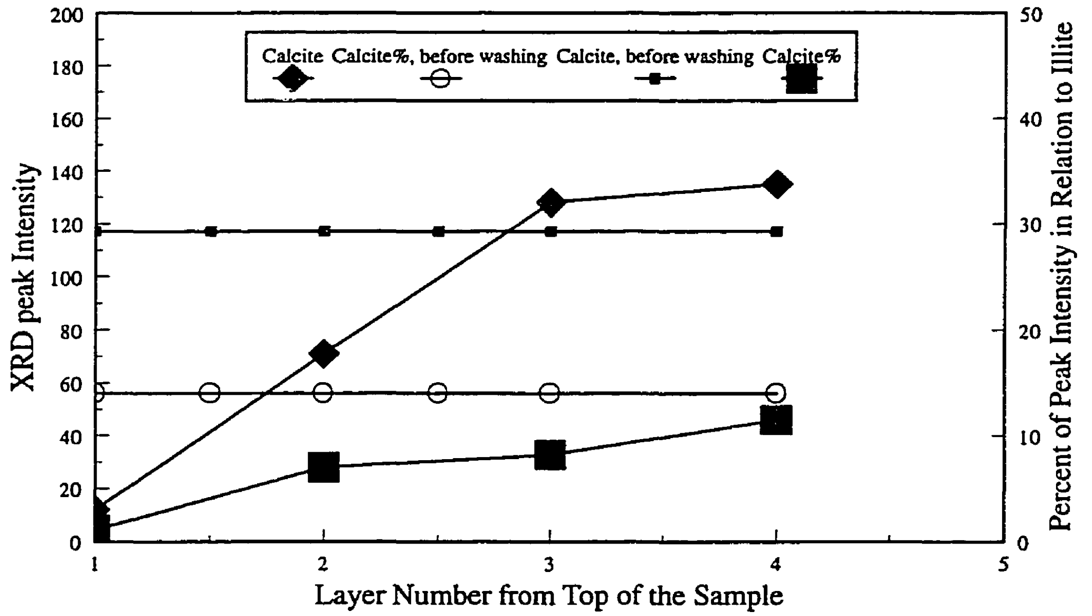


Figure 5.7: Variation of relative intensity, and intensity of Calcite's XRD major peak from the top to the bottom of a centrifuge tube for an Illitic sample after several soil washings.

2) Achieving pure palygorskite is made possible to evaluate some properties of palygorskite. This significantly helped to discover the contribution of palygorskite to marl performance, as will be addressed later in this Chapter.

5.4 THE ROLE OF MARL COMPONENTS ON ITS BEHAVIOUR

This section covers the evaluation of the role of palygorskite, sepiolite, carbonate, and salt upon marl behaviour. The wetted-state reactions of marl also will be addressed in this section. The clay fraction of marl is generally dominant in palygorskite and/or sepiolite, and it is the presence of these clay soil fractions that are the root cause of many of the problems encountered in the use of such soils as load bearing materials *(Yong and Ouhadi 1997)*. This makes it necessary to investigate the role of palygorskite and sepiolite on marly soils performance. These minerals have chain-like structures as opposed to the more classical plate-shaped type of mineral particles commonly associated with clay minerals. Furthermore, palygorskite-sepiolite are known to have the same general *XRD* and dehydration characteristics. It is therefore not uncommon to consider the performance of palygorskite as also being representative of sepiolite.

5.4.1 Diagnostic the *XRD* Properties of Palygorskite

The extent of variation in the diffraction characteristics of palygorskite is not well known *(Grim 1968)*. *XRD* tests, using different treatments as previously addressed, were performed on marl samples. The following diagnostic characteristics were observed from the palygorskite fragment of marl. *1)* In spite of the fact that palygorskite is reported to have a basal spacing of 10.40 angstrom, in all weathered states of marl samples, the presence of basal spacing of 10.07 angstrom was observed. While after several soil washings, as was addressed in section 5.3, the basal spacing of palygorskite increased to 10.40. This variation of basal spacing could be attributed to the removal of salt from the sample which caused the transformation of the soil structure to a very oriented fabric. As the number of soil washing increased the basal spacing of palygorskite got closer to 10.40. The intensity of peaks also followed the same pattern. The pure palygorskite that was finally extracted from marl after several soil washings shows the basal spacing equal to 10.40 angstrom. Therefore, in soils rich in salt, palygorskite's peaks might be mistaken for illite. *2)* Acid and heat treatment (up to 500 degrees centigrade) did not have any effect on the basal spacing of palygorskite, however, it was observed that its intensity will be affected. *3)* Glycerol treatment decreases the intensity of the basal spacing of palygorskite and magnesium-glycerol increases the relative intensity of the palygorskite's peaks. In both cases the basal spacing remained unchanged.

5.4.2 The Role of Palygorskite on Marl Behaviour

The role of palygorskite $\{(Mg, Al)_5 (Si, Al)_8 O_{20} (OH)_2 8H_2O)\}$ on soil performance has not yet been sufficiently investigated. This mineral was first found in the Urals in 1861 in the Palygorskite Range on the Popovka River and takes its name from this locality *(Ssaftchenkov 1862, Ovcharenko 1969)*. It has a fibrous texture and its cardboard or paper like appearance is due to the tangling of the fibres.

It is known as *attapulgite* in North America after it was found at Attapulgite, Georgia *(Lapparent 1935)*. *Piolite* and *lassalite* also are known to be considered as synonyms for palygorskite *(Heddle 1879, Friedel 1901, 1907)*. However, palygorskite is known as the more aluminous member *(Fersmann 1913)*. Palygorskite may be of sedimentary or hydrothermal origin. It is sometimes derived from pyroxenes and amphiboles *(Longchambon 1935)*. Some different ideal formula for palygorskite are suggested which vary depending on the amount of alumina and magnesium in its structure. It usually occurs in a mixture of carbonate deposits due to the environment in which it is formed. It is essentially white or yellowish or has a greyish yellowish, or greenish colour when wet. The main factor which distinguishes palygorskite from other clay minerals is its chain-like structure, as is presented in Figure 1.2. Water in its chain-like structure is called zeolitic water. Water is combined with cations and anions on the surface and in the zeolitic type channels of its crystals.

In the characterization part, the effect of weathering on the behaviour of marl was evaluated. To determine the amount of palygorskite in the samples and to evaluate the effect of the weathering process on the palygorskite fraction of the soil, *XRD* analysis with different treatments (acid, heat, magnesium and glycerol) were done. *X-Ray* testing results show that the clay fraction of marl is dominated by the presence of palygorskite. The consistent overlap of *XRD* peaks for three samples (each having undergone different states of weathering) indicates that all of the soil samples come from the same mineral formation (Appendix III). It should be noted, however, that the mineral concentrations vary in each sample. The *XRD* results indicate that palygorskite peaks remain present even after weathering. In fact, in all weathered states palygorskite controls the marl behaviour (Table 5.5). The amount of quartz and kaolinite with the basal spacing of about 3.35 and 7.2 angstrom, respectively, was found to be present in the following order:

$$\mathrm{WM} > \mathrm{mtM3} > \mathrm{tM2}$$

Grain size distribution analysis confirms that the amount of clay sized particles is the reverse of the above order, the results of which were confirmed by specific surface area measurement, as illustrated in Figure 3.8. The concentration of salt in the pore fluid of soil specimens is also higher in weathered samples than in unweathered soils (Figure 3.1).

Table 5.5: XRD test results for three marl samples and pure palygorskite (Data %), Different treatments including soil "as it is", acid, magnesium, and glycerol treatments have been carried out.

Sample	Quartz	Felds.	Calc.	Dolom.	Palygorskite	Chlorite	Kaolin	Illite	Montmor.,Gypsum, Arcanite,Thenardite
tM2	17	2	20	4	34	9	8	3	3
mtM3	20	2	20	3	33	7	10	3	2
WM	23	1	18	3	33	6	11	2	3

Felds.=Feldspar, Calc.=Calcite, Dolom.=Dolomite, Montmor=Montmorilonite

It seems that rain slightly washes the clay part of the soil. However, because of marl suction and capillary rise, the concentration of salt in the surface layer increases. This is quite significant, in terms of sulfate attack, in stabilized soil during the service life in any engineering construction. The regional climatic conditions appear to be responsible for increasing the kaolinite content of weathered marl. Since the organic and amorphous content of the tested marl, as indicated in Figures 3.5 and 3.6, are around 1%, it seems these parameters do not have a significant effect on the behaviour of marl. However, the presence of amorphous alumina could be responsible for the acceleration of ettringite formation in the short term.

To investigate the role of palygorskite upon marl stability, several experiments were performed on pure palygorskite extracted in the manner previously outlined. These physico-chemical tests are as follows:

Cation exchange capacity of palygorskite is known to be in the order of 9-30 *meq/100g (Van Olphen and Fripiat 1979, Mitchell 1993)*. While *Van Olphen and Fripiat (1979)* report the *SSA* of palygorskite to be 172 m^2/g when water is used as the covering material for *SSA* measurement purposes, the result of this research shows *SSA* equals 192 m^2/g where EGME is employed. In this research using barium chloride as an extractable solution, sodium was observed as the main exchangeable cation of palygorskite in which the exchangeable sodium percentage *(ESP)* was more than 50%. Soils with *ESP* greater than about 2 percent are known to be suspectable to spontaneous dispersion in water and behave as dispersive clays *(Mitchell 1993)*. For the illitic sample this ratio was measured as around 2%. Therefore, since palygorskite was known to be the major clay fraction of marl, the high dispersivity potential due to the presence of sodium ions will be one of the significant sources of marl dispersivity behaviour. This in turn will illustrate, that the dispersivity behaviour of marl is strongly governed by palygorskite performance as a major fraction of marl.

To investigate the chemical composition of palygorskite, digestion testing *(EPA 1979)* was performed. Table 5.6 represents the amount of different elements obtained after analysis of supernatant following digestion testing. The final pH of pore fluid which was used for ion concentration measurement in digestion testing, was less than 0.5.

Table 5.6: The results of digestion testing on pure palygorskite.

Description	Cations monitored in digestion experiment (*meq/100 g* soil)					
	Na	Ca	Mg	K	Si	Al
Palygorskite	80±7	9±0.8	321±21	51±5	14±1	578±54

The result of this test indicates that the amount of releasible alumina is in the order of 578 *meq/100 g* soil. This is quite significant in terms of ettringite formation, since the presence of soluble alumina is known to be one of the main elements of ettringite formation *(Mehta and Klein 1966, Yong et al. 1996)*. This will be discussed in more detail in Chapter 6. Table 5.6 (and further Table 5.7) indicate that significant quantities of magnesium and silica are associated with this type of soil, and the minerals should remain stable so long as the alkaline environment is maintained. However, should leaching of the salts in the soil occur to the extent that the alkaline environment is considerably reduced, decomposition occurs and transformed products would be likely obtained. Palygorskite was observed to be a very swelling soil. Figure 5.8 indicates the free-swelling measurement of palygorskite using oedometer testing in which after four days, 32% free swelling was observed. This might justify the swelling performance of marly soils which can be attributed to the palygorskite/sepiolite's swelling in contact with water.

5.4.3 The Performance of Pure Sepiolite

Sepiolite also might be present as a one of the main elements in marly soils *(Davis 1967)*. The investigation of the role of sepiolite on marly soils behaviour is soils behaviour is necessary to provide a comprehensive picture of the expected behaviour of marls and the role of dominant minerals of marl impacting on its instability. The role of sepiolite $\{(Mg_4\,Al_2\,Si_{10}\,O_{27}\,15H_2O)$ or $(Mg_4\,Si_6\,O_{15}\,(OH)_2\,6H_2O)\}$ on soil behaviour has not been adequately addressed in the literature. The term sepiolite which was first applied in 1847 by *Glocker*, has a Greek root meaning cuttlefish whose bone is light and porous *(Grim 1968)*. Its electron microscopy picture shows elongate lath-shaped units. In comparison to palygorskite the individual laths appear to be thicker and shorter. *Caillere et al. (1948)* reports the density of sepiolite to be 2.08.

To investigate some general behaviours of sepiolite, which are not sufficiently addressed in the literature, a series of characterization experiments were run on the sepiolite sample. The results of Atterberg limit testing including liquid limit, plastic limit, and plasticity index of sepiolite show 500, 200, and 300 respectively. The activity coefficient which is defined as the ratio of the plasticity index over the percentage of clay sizes, was calculated to be 3 for the sepiolite sample. This classifies sepiolite as a very active clay since clays having an activity coefficient more than 1.25 are known to be very active *(McCarthy 1977)*.

The compaction characteristics of sepiolite using the Harvard Miniature apparatus were measured as 0.64 Mg/m^3 and 105% for maximum dry density and optimum water content. While with application of calibration factors as presented in the Chapter 3, the maximum dry density and optimum water content will be 0.7 Mg/m^3 and 86% respectively. The *CEC* of sepiolite using the barium chloride method was measured as 10 *meq/100 g* soil. While the specific surface area with the application of the EGME method was 370 m^2/g. Very high *SSA* and low *CEC* is representative of very noticeable sepiolite and palygorskite performance in comparison to other clay minerals. The open structure of these minerals could be responsible for indicating high surface area in spite of their low *CEC*. In fact, the very high liquid limit is in good agreement with a high *SSA*, in which the open structure has a high ability to keep water. Table 5.7 indicates the results of the digestion experiment for sepiolite in which the final pH of pore fluid for ion concentration measurement was less than 0.5. As can be seen, sepiolite has a very low amount of alumina in comparison to palygorskite. In this aspect, it has a lower ability to directly affect ettringite development. This difference will be addressed in Chapter 7 where the contribution of different clay minerals for ettringite formation are addressed.

The water holding capacity of a sepiolite sample is investigated by the performance of suction testing, as presented in Figure 5.9. The result of this experiment indicates the very high water holding capacity of sepiolite in comparison to that of illitic soil. As an example, at pF 0, the water content of sepiolite shows 291% while for the illitic sample the water content at this pF indicates only 31%. This very noticeable water holding capacity of sepiolite, which is attributed to its high surface area and open structure, and availability of sulfate ions can strongly contribute to post stabilization failures, as will be addressed in Chapter 7.

Table 5.7: The results of digestion testing on pure sepiolite.

Description	**Cations monitored in digestion experiment (*meq/100 g* soil)**					
	Na	**Ca**	**Mg**	**K**	**Si**	**Al**
Sepiolite	2±0.2	1±0.1	1012±90	10±1	80±7	9±1

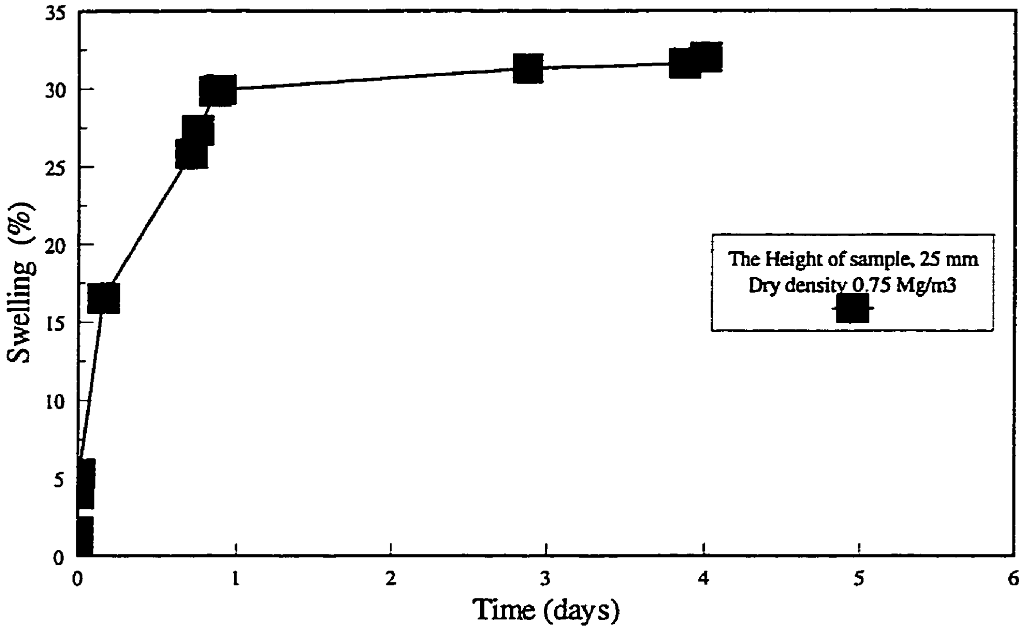


Figure 5.8: Free-swelling variation of Palygorskite using Oedometer testing.

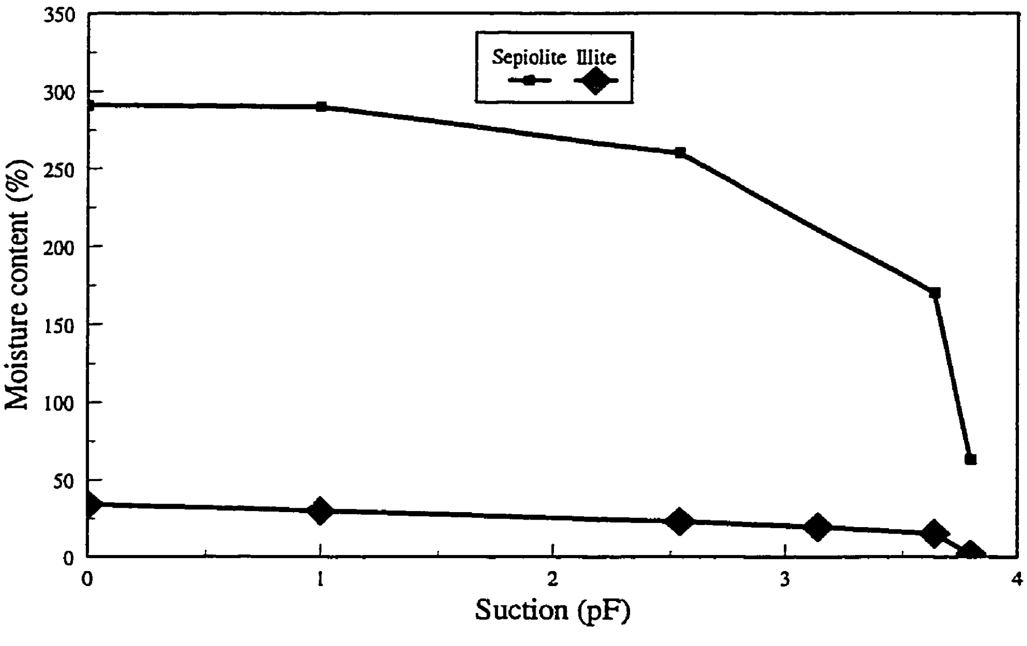


Figure 5.9: Fluid retention curves for Sepiolite and Illitic samples.

5.4.4 The Role of Carbonate on Marl Performance

The carbonate fraction of soils may form as a result of physical and chemical weathering of parent carbonate rocks including limestones, dolomites, and carbonate sandstones *(Akili 1981)*. These carbonate minerals tend to be soluble, chemically reactive, easily recrystalizable and very different in origin *(Fookes and Higginbottom 1975)*. They might behave like a cement binder in soil deposits *(Brenner et al. 1990)*. It is shown that the cementation process is directly proportional to time, temperature, and dryness *Beckwith and Hansen (1982)*. The removal of these cementing substances might cause mechanical instability of the soil mainly in a collapsed form *(Lamb 1990)*. Some typical geotechnical laboratory test results on remoulded carbonate soils are presented by *Akili(1981)*. To evaluate the role of carbonate on marl performance, the effects of adding artificial calcite to marl properties was examined. To do so, a set of mixtures of marl samples with different percentages of carbonate were prepared. Each soil sample was subjected to two sets of testing. The first set investigated the role of carbonate on the fluid retention characteristics of marl and illite and was achieved by Atterberg limit evaluation and suction measurement. The second set examined the effect of carbonate on the free-swelling performance of marl. In both cases distilled-water was used as a solution while additional carbonate was added to the marl and mixed carefully in the dry condition. As can be seen in Figure 5.10, generally by increasing the percentage of additional carbonate, both the liquid limit and the plasticity index decrease. As is shown in this Figure, adding more carbonate to marl, (up to 20 percent additional carbonate) does not significantly affect the monitored performance. It should be noted that the marl sample used in this research initially had around 25 percent carbonate. By adding more than 50 percent carbonate, the plasticity index shows significant improvement and has decreased from 24.4 to 15.4 percent. At the same time, the liquid limit decreases with the increase of percentage of calcite. The presence of carbonate in the soil fraction can affect soil behaviour in two different aspects. These aspects will be the chemical and physical influences. From the chemical point of view, carbonate might increase the calcium ion concentration in one aspect and bicarbonate concentration in another aspect, as was addressed in Chapter 2. These facts will cause conflicting performance; the tendency for depressing diffuse ion-layer on the one hand and affinity for producing a dispersive structure due to the presence of bicarbonate ions, on the other hand. As was presented in section 5.2, the results of soluble ion measurement indicate that the calcium concentration achieved from soluble measurement and extractable measurement using ammonium acetate have very noticeable differences. Since the ammonium acetate method has the ability to dissociate the calcite fraction of soil, it can be concluded that with consideration of the low concentration of calcium ion in soluble measurement, calcite does not have a significant role in terms of depressing the diffuse ion-layer. On the other hand, depending on environmental conditions, these interactions are time dependent and since these experiments were performed right after the addition of calcite, there was not enough time for development of these possible interactions. In addition, from the physical point of view, the presence of calcite replaces the clay fraction of soil. In this manner the clay fraction, with high surface area, will be replaced by carbonate leading to a lower water holding capacity and liquid limit of soil. Therefore, the simple replacement of calcite by clay fraction governs the behaviour which causes a decrease in the liquid limit and plasticity index and an overall improvement in soil performance. This is confirmed by evaluating the role of carbonate on the water holding capacity of illitic soil. Figure 5.11 indicates the effect of the addition of 30% carbonate on the suction performance of an illitic sample. As can be seen, by the addition of carbonate, the water holding capacity of soil decreases. This phenomena can be attributed to the replacement of clay fraction by carbonate which is in good agreement with the results of Atterberg limit testing. The suction performance of a marly sample is also presented in this Figure. The suction performance of the marly sample, in comparison with two others illitic soils, indicates that, not only the water holding capacity of marl is higher than an illitic soil but also the rate of removal of water by applying excess pressure is lower in the marl sample. For instance, from pF 0 to pF 3.14 (20 psi) the water content of the illitic soil decreases by

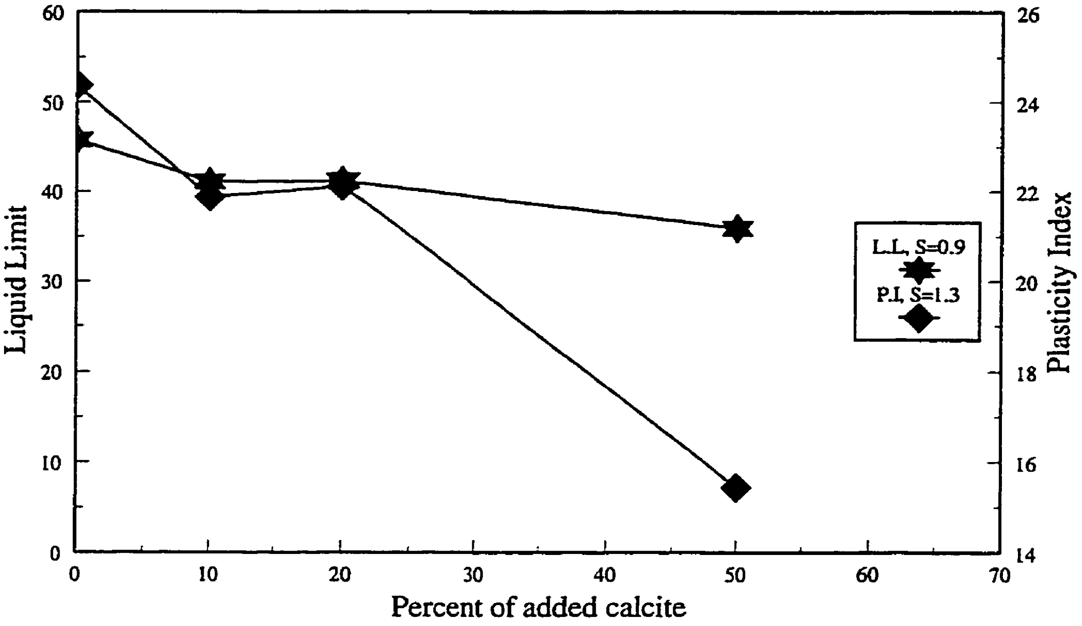


Figure 5.10: Liquid limit and plasticity index of a Marl sample mixed with different percentages of Calcite.

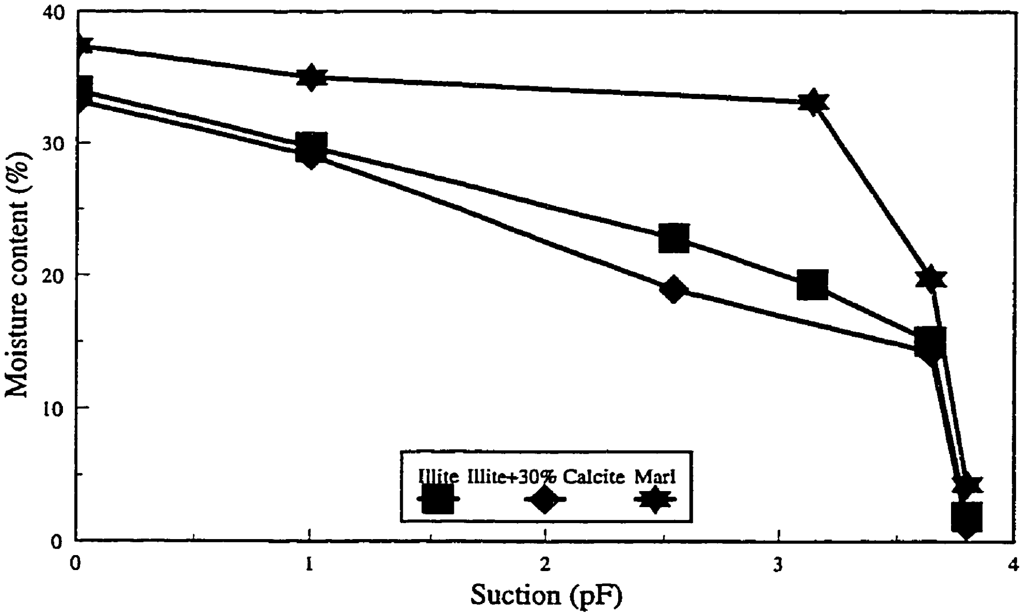


Figure 5.11: Fluid retention curves for Marl, Illitic and mixtures of Illitic/Calcite samples.

approximately 44% while in a marly sample this quantity has decreased by only 11%. This performance can be attributed to the role of the open structure of the palygorskite fraction of marl. With an increase of carbonate content one expects to diminish the water holding capacity of soil, in one aspect and, increase the rate of water removal by increasing suction in another aspect.

By and large, the increase in carbonate content of soil leads to that soil being classified as a clay with low plasticity (i.e. CL) based on the plasticity chart of unified system *(Craig 1987)*.

To have a clearer view of the carbonate effect on marl behaviour, a series of free-swelling experiments were performed. The soils used in these tests were a marl sample with 20% additional carbonate and a marl sample without any additional carbonate (i.e. marl as it is). The results of these experiments are plotted in Figure 5.12. The initial height and dry density of samples was chosen to be the same. The sample was compacted with the same range of water content and dry density, where the dry density and water content were 1.7 Mg/cm^3 and 17%, respectively. This was chosen due to the observation of small differences in the compaction characteristics of these samples achieved by the use of the Harvard Miniature apparatus. On the other hand, it was decided to compact the soil samples on the dry side of optimum water content to have the highest possible swelling *(Schroeder 1975)*. The free-swelling of samples was monitored by leaving the compacted samples to be saturated and swell under a very small surcharge, as mentioned in Chapter 3. These results indicate a decrease in free-swelling of marl with an increase in the percentage of carbonate. The relative swelling was around 6.8% in the case of 20 percent carbonate, and 9.9 percent free-swelling when no artificial carbonate was added. This can be attributed to the non-reactive performance of carbonate. In fact, the replacement of the clay fraction with an artificial carbonate tends to decrease the swelling fraction of soil, leading to a decrease in final swelling. This is in good agreement with the results presented in Figure 5.10 in which by increasing the percentage of artificial carbonate to the marl sample a decrease in Atterberg limits of samples can be observed.

A decrease in water holding capacity of a mixture of illite and carbonate in comparison to that of an illite sample as presented in Figure 5.11 supports the above discussion.

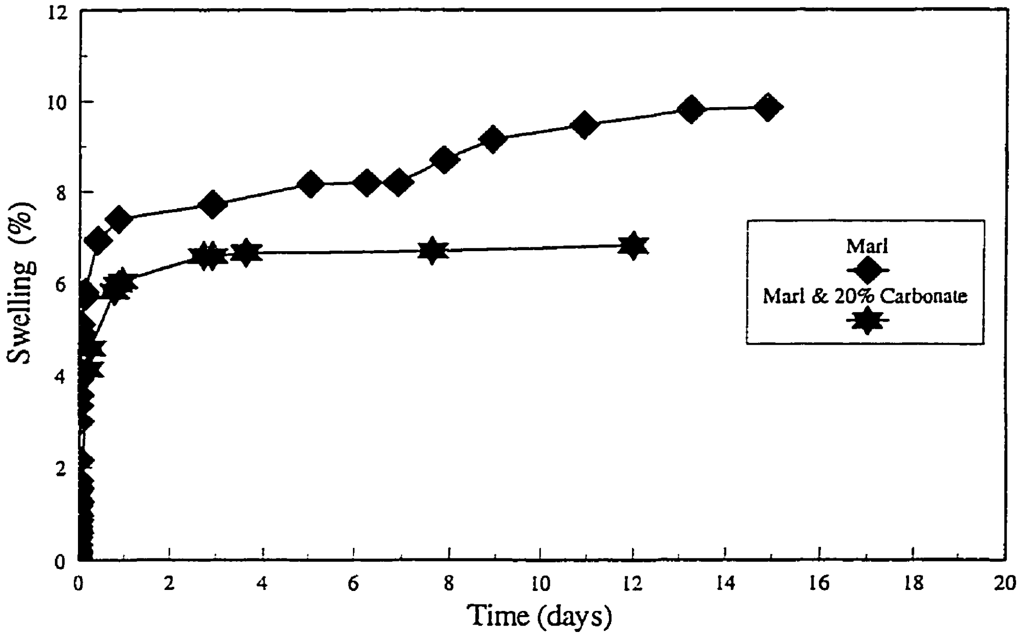


Figure 5.12: Free-swelling measurement of marl and Marl/Calcite samples using Oedoemeter testing.

5.4.5 Impact of Wetted-State Reactions

Control of marl soil performance, especially in the longterm will depend not only on the mechanical and physical interactions (normally considered important in geotechnical engineering) but also on the many physico-chemical factors. In particular, as indicated previously, the presence of swelling-type minerals (palygorskite and montmorilonite minerals) in combination with the high carbonate, sulfate (gypsum) and salt contents are all a recipe for a very interesting and challenging suite of reactions which could prove to be adverse to the longterm stability of the soil. The first indication of problems arising from physico-chemical reactions of such soils was indicated previously in the laboratory procedures required to determine the Cation Exchange Capacity (*CEC*) of marl. The combination of a high specific surface area, together with high water holding capacity, presence of carbonates, sulfates, swelling-type clay minerals, and excess salts in the pore water can only mean that careful control of water entry in the compacted or stabilized marl soil is required if degradative reactions are to be avoided.

As a simple example, Figure 5.13 shows the free swelling performance of the marl soil in the "natural" and "washed" state. The washed soil condition was obtained using the same procedure as explained in section 5.3. After several soil washings processes and discarding the supernatant, the sample was dried, ground, mixed and sieved to finer than 75 micron mesh (i.e. the same size as unwashed marl). It is immediately clear that maximum swelling for the natural sample is not significantly lesser than the "washed" sample over the longer term period. However, we note that the "washed" sample reaches the maximum swelling in at least one-fourth the time period taken by the natural sample to reach its own maximum free swell. This performance, together with the index properties shown in Table 5.8 are pieces of information which reveal the reaction effects that will contribute to strength reduction and subsequent instability for the compacted clay. The significance of the results lies in the phenomenon of leaching of the compacted soil by influent water, generally obtained as rainfall.

Whereas, one could argue that the reduction in the various salts and sulfate are considerable, and that the reductions are not reflected in comparable property changes as noted in Table 5.8, the impact of these changes need to be viewed in terms of the physico-chemical process. Before discussing the reaction consequences via mechanistic model interpretations, we can view the *XRD* peak intensity for palygorskite for the natural and washed state, as shown in Figure 5.14.

The numbers shown in Figure 5.14 adjacent to the points on the graph, are the respective "weighting factors" of the evaluated reflection lines, based on those presented by the International Centre for Diffraction Data *(ICDD, 1988)*. (In *XRD*, each mineral shows a series of peaks which are specific to each individual mineral. ASTM and ICDD classify the data for each mineral on the basis of the most intense diffraction lines which are usually called the "weighting factor"). As noted from the results shown (in the Figure), there is a significant increase in the peak intensities of the different reflection lines at the various basal spacings except at the second-last basal spacing. This could be related either to the removal of the coating effect of amorphous material around clay particles *(McKyes et al. 1974)*, or to the well oriented soil particles caused by soil washing which will cause sharper and higher intensities as can be seen in Figure 5.14. When considering the very low amount of amorphous material in marly soils (Figure 3.6), one might conclude that the salt removal and more oriented fabric are the major reasons for these differences in peak intensities. This information lends weight to the mechanistic model developed in the next subsection to describes the changes in the structure of the soil due to the wetted state reactions.

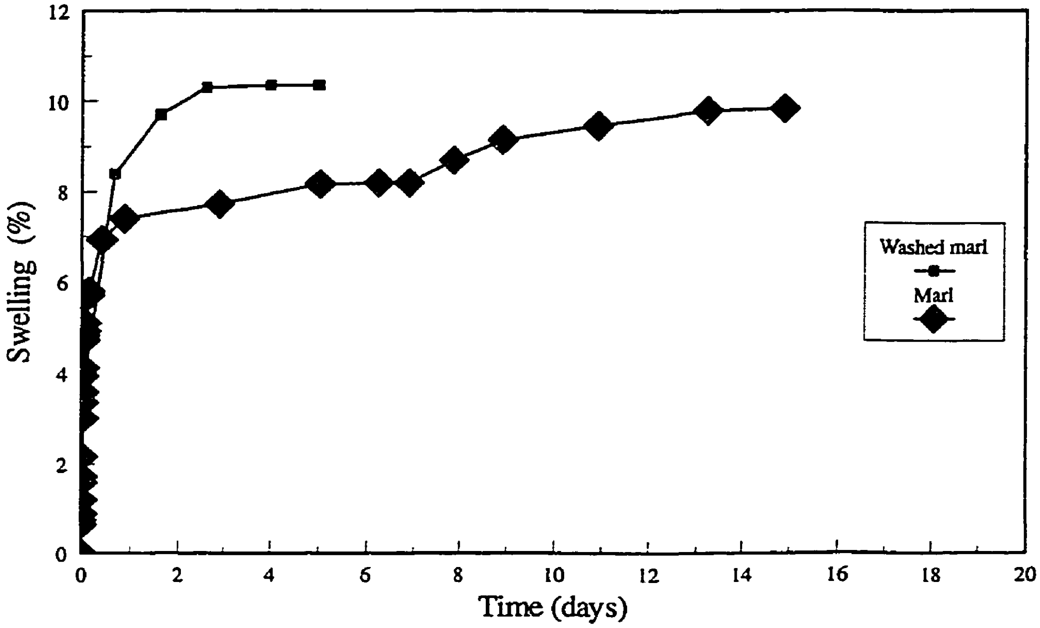


Figure 5.13: Free-swelling variation of washed and unwashed Marl samples using Oedometer testing.

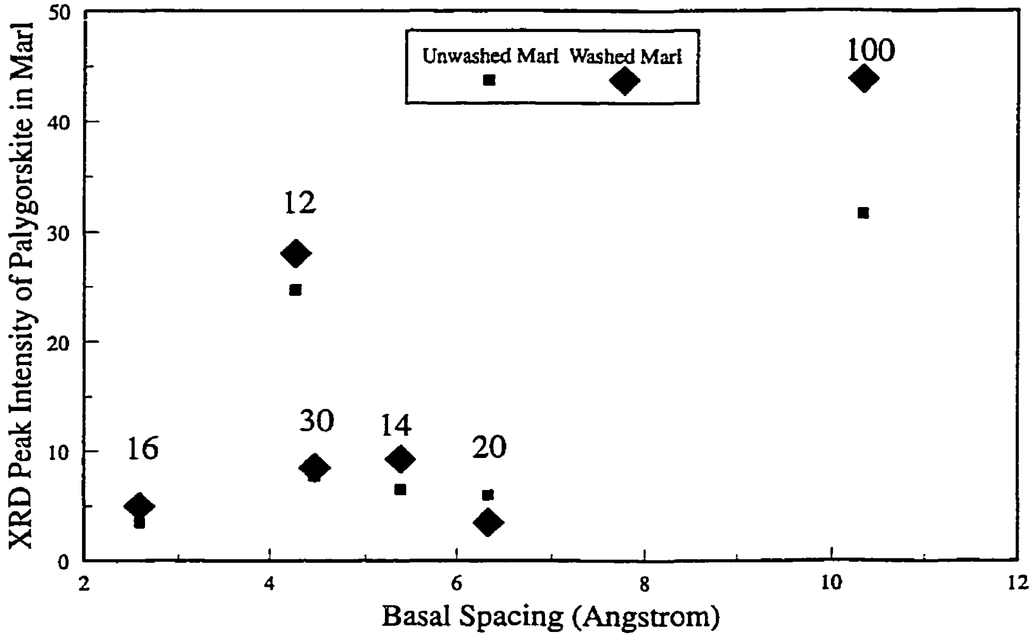


Figure 5.14: Variation of XRD peak intensity of Palygorskite in washed and unwashed Marl samples for different Palygorskite's reflection lines.

5.4.6 Wetted State Instability, Mechanistic Model

The wetted state mechanistic model, which needs to be developed to show how the changes in the integrity of the compacted natural marl soil, benefits from the collective information, presented in Table 5.8 and Figures 5.13 and 5.14. Based on these results, a mechanistic model is developed which shows that the reactions developed in the wetted state can lead to the collapse of the compacted marl, or to dispersive behaviour. The model of the natural compacted marl (not wetted) shows:

(1) precipitated carbonate and sulfate bonds forming the core of the "cementing" relationships for the flocculated structure as shown in Figure 5.15, (2) a simplistic 3-particle representation of the elements of the structural fabric, and (3) equivalent matric-osmotic pressures are developed as a result of inter-penetration of the diffuse ion-layers from adjacent particles (using the diffuse double layer model).

The "wetted-state" condition which is developed after compaction of the marl soil results in (a) weakening of the cementation effect produced by the carbonates and sulfates, and (b) significant reduction in the salt content of the soil. The destabilizing outcome of (a) and (b) occurs through the increase in the matric-osmotic pressures because of the reduction in salt concentration. This increase in matric-osmotic pressures can be predicted from diffuse double-layer theory, and should these pressures exceed the confining stress and bonding established by the "cementing bonds" swelling of the soil results, and/or self detachment of particles occurs, thereby leading to dispersive soil behaviour. Continued exposure to water in the wetted state will contribute to instability.

The free-swelling information given in Figure 5.13, together with the values noted in Table 5.8, indicate that the structural integrity established in the bonded soil has been destroyed because of wetted state reactions, as described heretofore. Confirmation of the dispersed structure is obtained by the *XRD* information shown in Figure 5.14. The sharper and higher intensities shown by the "washed" samples indicate well-oriented particle arrangements. We can therefore expect a dispersed structure for the wetted state, and a dispersive behaviour of the system. The sequence of structural change leading to instability of the unit is shown in Figure 5.16.

Table 5.8: Evaluation of the role of soil washing on the marl performance.

Test Type	Soil Sample	
	Salinity Marl	**Washed Marl**
Liquid limit (%)	45.8	49.6
Plasticity index(%)	24.4	30.3
Sulfate (ppm)	5520	290
Salt (ppm), Na	18230	230
K	310	40
Ca	670	20
Mg	410	60
Maximum dry density (Mg/m^3)[1]	1.78	1.71
Optimum water content[1] (%)	19	22.5
Maximum free-swelling (%)	9.9	10.4

[1] According to Harvard Miniature testing.

In any particular case, standard deviation is as addressed in Chapters 3 and 6.

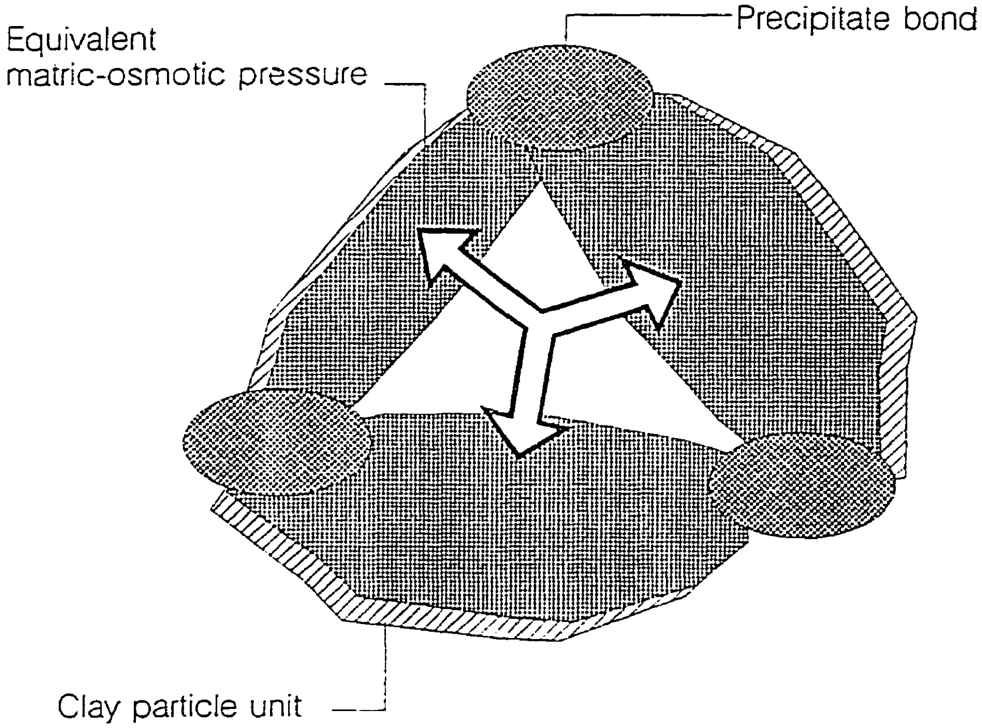
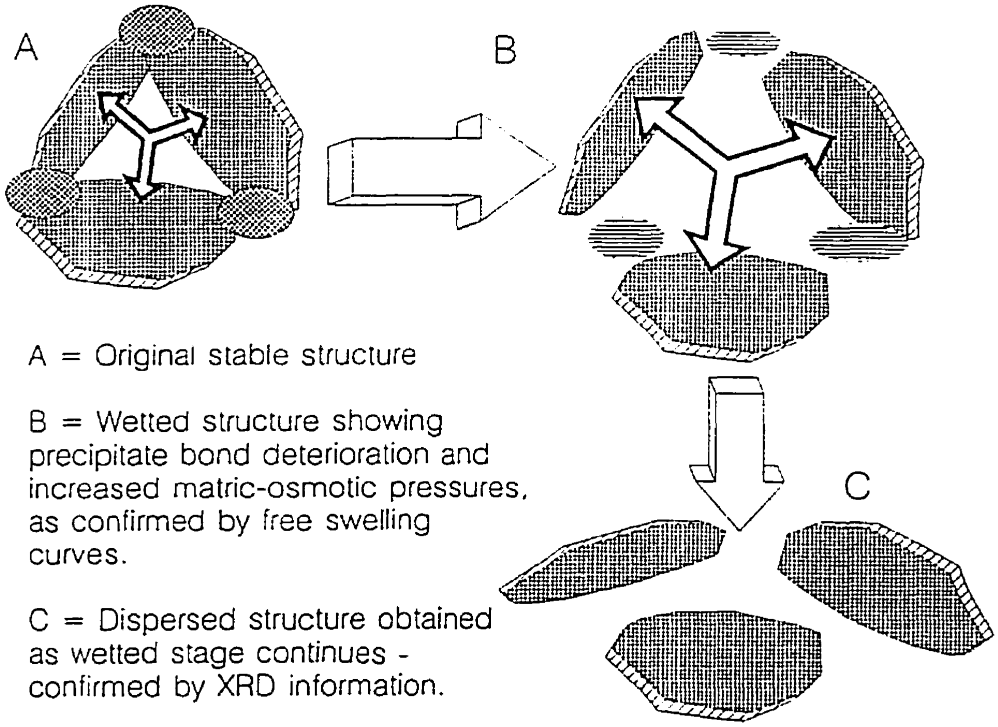


Figure 5.15: Schematic of 3-particle unit showing precipitate bonds and matric-osmotic pressures affecting stability of unit *(Yong and Ouhadi 1997A)*.



A = Original stable structure

B = Wetted structure showing precipitate bond deterioration and increased matric-osmotic pressures, as confirmed by free swelling curves.

C = Dispersed structure obtained as wetted stage continues - confirmed by XRD information.

Figure 5.16: Soil structural changes due to wetted state reactions, leading to instability.

5.5 NEW DEFINITION AND CLASSIFICATION OF MARLY SOILS

As discussed, marly soils are defined as a soil or rock with 35-65% carbonate and a complementary content of clay *(Barth et al. 1939, Pettijohn 1975)*. However, this definition cannot be universally applied to many of the rocks in Britain, the Persian Gulf area, U.S or other countries which are often referred to as marls. As examples, most of the marls of the Keuper series contain less than 20% carbonate material *(Bells 1978)*, while Ontario and Quebec marl is reported to have more than 70% calcite *(Guillet 1969)*. Such soils, according to the classification of clay-lime carbonate mixtures, are marly clays *(Barth et al. 1939)*. Furthermore, this definition does not consider the type of clay fraction in marls. The literature review indicates that usually the clay fraction of marl is dominated by the presence of palygorskite or sepiolite which governs marl behaviour. Persian Gulf marl is dominated by the presence of palygorskite *(Kassler 1973, Yong et al. 1993, Ouhadi et al. 1996)*. In the reported post-stabilization failure in the United States, where lime was used as the agent, sepiolite was the most abundant, while montmorilonite and kaolinite were also present. Calcite, gypsum, thenardite and arcanite were also identified *(Hunter 1988)*. U.S. marl in the Virginia region is dominated by the presence of palygorskite. Palygorskite is the dominant clay fraction of Russian marl deposits *(Ovcharenko 1969)*. The clay mineralogy of Keuper marl also includes sepiolite *(Keeling 1956)*. Palygorskite and sepiolite have a chain-like structure (Figure 1.2). The zeolitic water of palygorskite and sepiolite, which is the water in channels located within their structure, can accommodate different ions giving rise to a high degree of selectivity in the ion adsorption process. This produces the so-called molecular sieve structure.

By and large, based on above explanations and the results of this Chapter, it can be concluded that palygorskite and sepiolite significantly control marl behaviour. Therefore, their presence in combination with carbonate makes the clay-carbonate mixture more distinguishable from any other clay-carbonate mixture. Therefore, it seems that the current definition of marl, which considers any combination of clay and carbonate *(Barth et al. 1939)*, must be improved. This improvement should take into account the type of clay fraction of marl. In this view point, not all combinations of clay-carbonate will be considered a marly soil, but the presence of palygorskite or sepiolite will be a necessary condition, as the governing clay fraction, for this categorization. This can be done with a modification to the definition suggested by *Barth (1939)* (Figure 5.17). As such, a new definition based on the suggested classification by previous researchers, and the results of this study, is necessary. This is illustrated by means of the triangular diagram in Figure 5.18. This suggested classification has the following advantages:

a) It considers the presence of palygorskite or sepiolite a necessary condition for marly soils. This is in order to take into account the significant and noticeable role of these two minerals on marl behaviour before and after stabilization, as was explained in this Chapter and will be further investigated in the Chapter 6.

b) The suggested classification can be applied to all marly soils classified by *Barth et al. (1939), Fookes and Higginbottom (1975), and Pettijohn (1975).*

c) By including the percentage of silt or sand in the classification, the expected behaviour of marl in terms of swelling, dispersivity or collapsible performance can be obtained. All seven possible combinations of marly soils suggested by *Fookes and Higginbottom 1975* are plotted on the same triangular graph in Figure 5.18. These seven regions are called pure clay or mudstone, clay, clayey marl, marl, limey marl, marly limestone and pure limestone, respectively. The base of the triangle includes the suggested classification by *Barth* in which the percentage of silt or sand will be zero. By considering all combinations of soil fractions including clay, carbonate and silt/sand, all the above different marly soils can be considered in the areas numbered 1 to 7 in Figure 5.18, respectively. Some of the available information in the literature, including the results of the research conducted by *Davis 1967, Hunter 1989, Ismael 1993, Yong et. al 1993, Ouhadi et. al 1993, Mohammed 1995,* and *Yong et. al 1996* which include more than 30 samples, lie in the regions 4 and 9. In all these cases, silt and sand are present.

While in only three cases, the coarse fraction of soil is dominated by the presence of sand, in the rest of the cases the coarse fraction is mainly silt. It was observed that in these available case studies, 30 samples lie within region 4 and 9, while only 3 samples, in which the coarse fraction is dominated by sand, lie in region 11. As was explained in this Chapter, marly soils are known to show a possible collapsible, dispersive and swelling behaviour. According to an extensive study conducted by *Rollins et al. (1994)* regions 8 and 11 (marly silt or marly sand) have a high possibility of collapsible behaviour. By increasing the percentage of clay fraction to more than 20 percent, silt content <50% and carbonate content >50%, the collapsible potential decreases. Region No. 10 (silty marl or sandy marl) which has mainly more than 30 percent clay, 20 to 50% silt and carbonate content <20%, is principally governed by swelling performance *(Rollins et al. 1994)*. Region No. 9 and 4 behave as transition zones between collapsible and swelling soils. On the other hand, with regard to pore fluid properties of soil, a highest potential for dispersive behaviour can be obtained while the potential for collapsible or swelling behaviour exists. The latter behaviour increases when soil composition lies in regions 8 and 10. The samples studied in this research correspond to region 9. Regions 9 and 4 are compatible with the general collapsible, dispersive and swelling behaviour of marly soils. Other regions can be suspected of having different behaviours.

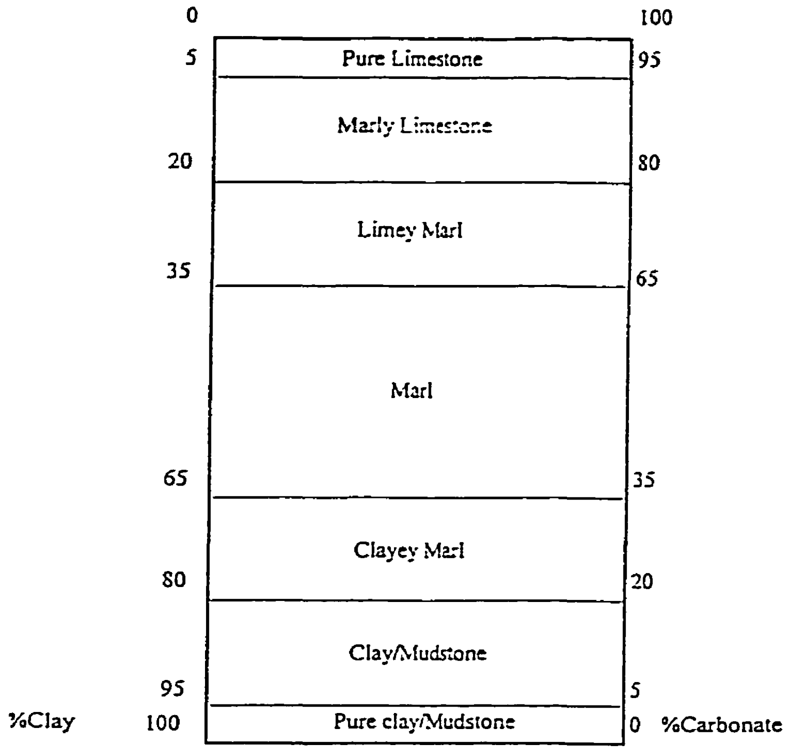


Figure 5.17: Classification of Marly soils suggested by *Barth et al. 1939.*

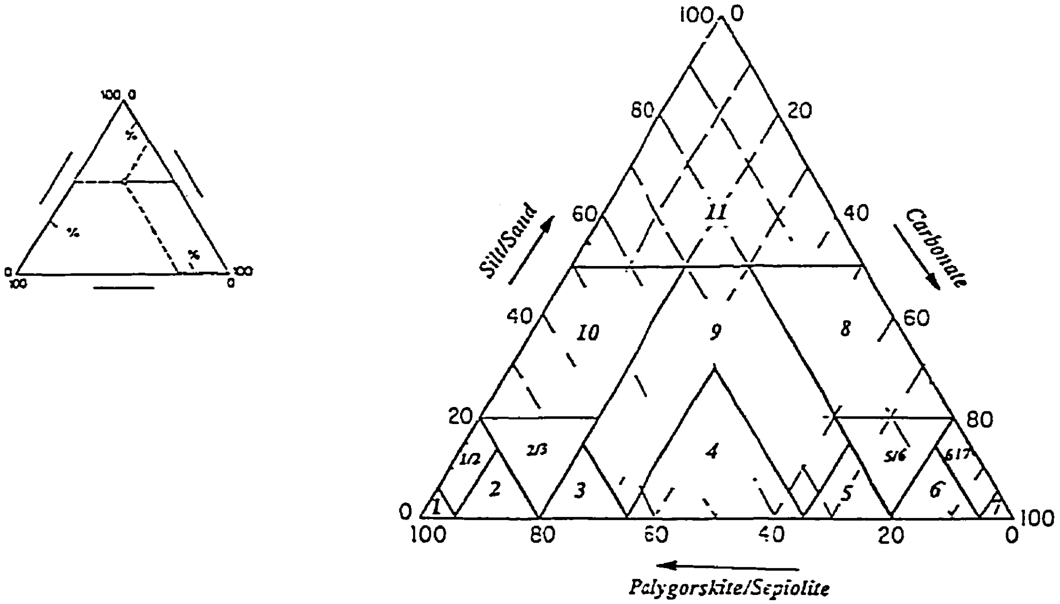


Figure 5.18: Proposed classification for Marly soil.

5.6 SUMMARY

The significant role of palygorskite and sepiolite on marl behaviour and the wetted-state reaction of marly soils were addressed in this Chapter. A modification of *CEC* measurement of soils rich on sulfate and having relatively dispersive structures due to their pore fluid characteristics, is suggested. By the application of the suggested method, based on several soil washings and by *XRD* analysis, the separation of different components of marly soils and illitic soil (domtar sealbond) are evaluated. By use of *XRD* analysis, it is shown that, this technique has the ability to extract pure palygorskite and illite from marly and illitic samples respectively, which are free of calcite. Based on the literature review conducted and the results of this research (showing very distinguishable performance and behaviour of palygorskite and sepiolite) a new classification for marly soils is presented in this Chapter. This classification focuses attention on the presence of palygorskite or sepiolite as the major fraction of marl which governs its behaviour.

CHAPTER 6

MINERAL TRANSFORMATION OF PALYGORSKITE, AND ETTRINGITE DEVELOPMENT IN STABILIZED SOIL

6.1 INTRODUCTION

This Chapter focuses attention on mineral transformation and ettringite $\{Ca_6Al_2(SO_4)_3(OH)_{12},26H_2O\}$ development in marl stabilization and their impact upon some geotechnical responses. Soil stabilization from both the mechanical and chemical points of view is evaluated. The deficiencies of geotechnical evaluation of marl stabilization are addressed. In the chemical and mineralogical aspects of soil stabilization, the mineral transformation is monitored using an evaluation of pore fluid chemistry and by conducting *XRD*, at different time intervals under different curing conditions. Mineral transformation is achieved by monitoring the change in palygorskite's *XRD* peak intensities and its transformation to ettringite. Performing *XRD* tests at different time intervals and under different conditions allowed the monitoring of the variation of these peaks and the formation of new peaks.

6.2 STABILIZATION FROM MECHANICAL ASPECTS

Usually traditional soil stabilization evaluates soil performance, mainly from a mechanical point of view. This includes focusing attention on stabilization to assess how the stabilizer agents affect the mechanical properties of soil. The common geotechnical criteria emphasize Atterberg limits evaluation, *CBR* or unconfined strength measurements, and pH variation *(ASTM 1990, 1992)*. The strong tendency to use mechanical consideration of soil stabilization has created much previous research where, even the evaluation of chemical stabilizer agents mainly focuses on mechanical responses of soils *(Michaels and Tausch 1960, Moh et al. 1962, Kezdi 1979, Rao et al. 1993, Amoudi 1994A)*. However, in this research main attention was given to the physico-chemical aspects of soil stabilization. While the current geotechnical evaluation criteria for soil stabilization are carried out on stabilized samples, the deficiency of these criteria are addressed. To evaluate the role of additives on stabilized marl performance from the geotechnical point of view, Atterberg limits, *CBR* and pH tests are carried out as follows:

6.2.1 Geotechnical Criteria of Marl Stabilization

Figures 6.1 and 6.2 indicate the variations in liquid limit and plasticity index for a single marl sample stabilized with varying degrees of lime, cured at 20 degrees centigrade and saturated humidity for different time intervals. Since, in the curing period, samples were kept in the humid condition, they were initially wet before performing of the Atterberg limits experiments. In each step following the curing period, a certain amount of distilled-water was added to the samples and Atterberg limits were measured. In soil stabilization using lime, changes in Atterberg limits show a disordered trend with the addition of lime to marl. Atterberg limits, after one day curing, indicate the effect of ion exchange on soil performance caused by the addition of lime. This will produce a flocculated structure due mainly to the replacement of sodium ions by calcium ions. The significant role of soil pore fluid on the distribution features of the electric potential and the counter-ion charge is expressed by the double layer theory *(Gouy 1910, Chapman 1913)* as presented in Chapter 2. Initially, in a soil sample before the addition of additives the interaction between interpenetrating diffuse ion layers from adjacent particles, from adsorbed water layers, and from interaction between like charges will cause the development of repulsion forces in clays *(Yong and Warkentin 1975)*. This repulsion force will cause the particles to become separated and will produce a dispersive structure. According to the double layer theory the diffuse ion-layer thickness is governed

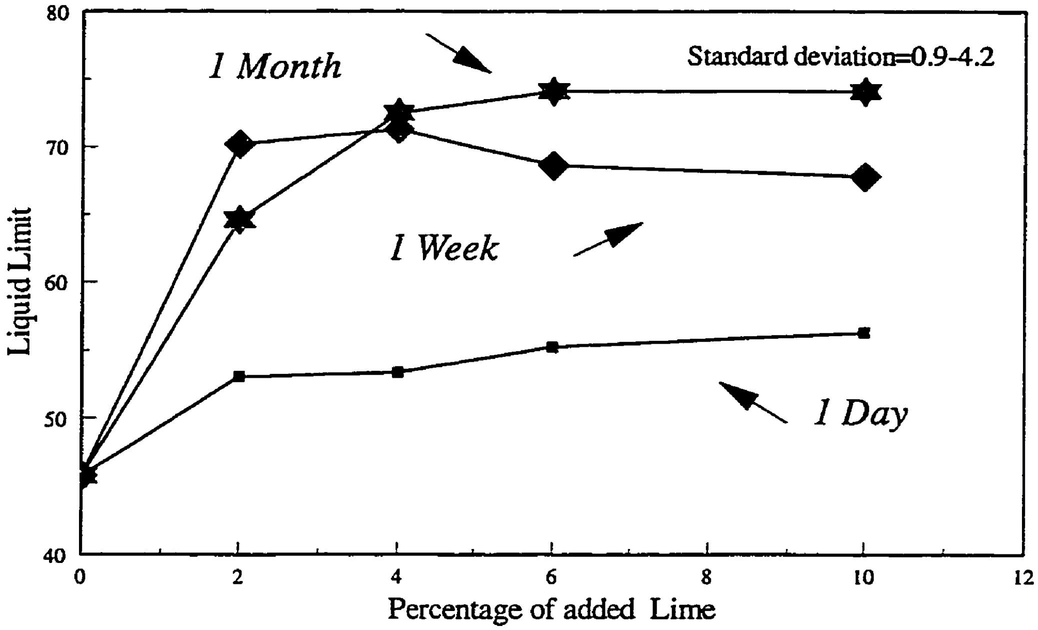


Figure 6.1: Liquid limit measurement for stabilized Marl samples at different curing intervals.

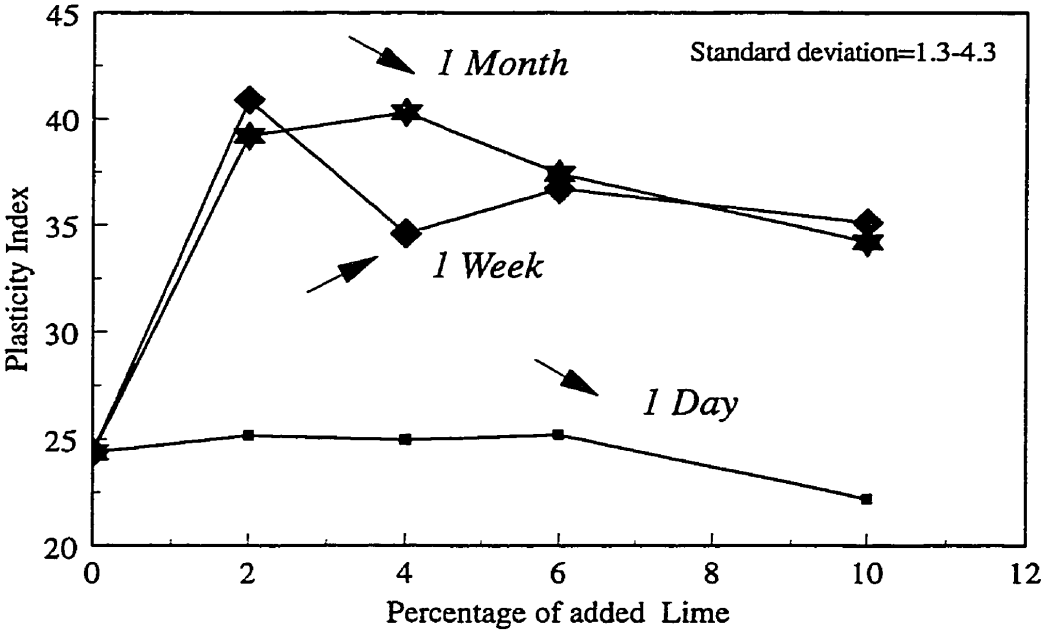


Figure 6.2: Plasticity index measurement for stabilized Marl samples at different curing intervals.

by factors including concentration and valence of the ions. Usually the higher the electrolyte concentration and the higher the valence of the cations, the more the diffuse ion-layer thickness will be reduced. Over the stabilization period, the addition of lime will cause an increase in calcium ion concentration. Therefore, since Ca^{2+} has a higher valence and lower hydrated radius than Na^+, the replacement of Na^+ by Ca^{2+} will cause a decrease in the diffuse ion-layer thickness and this in turn will produce a flocculated structure *(Quric and Schofield 1955)*. In fact, sodium clays are likely to display a higher degree of dispersion. Therefore, the major source of repulsion forces decreases. Once this process occurs the forces of repulsion are decreased, and the forces of interparticle attraction will act. This will cause the clay particles to get closer and finally the clay flocculates. This process will finally cause an improvement in soil performance from the mechanical point of view.

On the other hand, the chemical aspects of soil stabilization will cause further improvement in soil behaviour as follows. The solubility of silica and alumina versus variation of pH is presented in Figure 6.3 *(Keller 1964)*. As pH increases, the solubility of both the silica and alumina fraction of clays increase. Therefore, as time goes on, the high pH environment, induced by addition of lime, will solubilize the alumina and silica of the clay fraction. The interaction of alumina and silica with calcium ions will produce two cementing agents called *CAH* (calcium alumina hydrate $\{3CaO.Al_2O_3.Ca(OH)_2).12H_2O\}$) and *CSH* (calcium silica hydrate $\{3CaO.2SiO_2.3H_2O\}$), respectively *(Thompson 1966, 1968)*. These cementing agents are responsible for the improved soil behaviour after stabilization. This improvement is caused by enhancing and cementing the flocculated fabric, and consequently decreasing the exposed surface area to the water.

The potential of soils to keep water is a function of two factors: (1) the extent of exposed surface of soils where, if increased, the ability of soil to keep water will increase, and (2) the extent and size of soil pores. These in turn will affect the liquid limit of soils. The addition of lime in one aspect decreases the exposed surface area of soil, due to the formation of a flocculated structure, and this in turn tends to decrease the liquid limit. On the other hand, because of the carbonate-type bonding for the flocculated structure (section 2.8.1) the amount of trapped water within the soil structure will increase leading to a further increase in liquid limit. This will be further addressed through the evaluation of the water holding capacities of soils, in Chapter 7. Therefore, while for soils with a very high liquid limit it can be expected that there will be a noticeable decrease in liquid limit upon addition of lime, for soils with moderate to low liquid limit, the addition of lime not only will not decrease the liquid limit, but also, as is presented in Figure 6.1, the liquid limit increases. This increase could be even more than the initial amount, resulting from the significant role of developed pores to keep water. This is in good agreement with the conclusion made by *Kezdi (1979)* in which the decrease or increase in the liquid limit of a stabilized sample is related to the magnitude of the initial liquid limit of soil (i.e. to the magnitude of the liquid limit of soil before stabilization). Still a soil sample keeps its trend with an overall decrease in plasticity index by the further addition of lime in both the short-term and long-term evaluation which is representative of an overall improvement of soil performance. With approximately 4 to 5 percent of lime added, the plasticity index starts to decrease and no noticeable further increase in liquid limit is observed (Figure 6.2). These results are confirmed by the increase of *CBR* resistance of the stabilized soil where different percentages of lime were added (Figures 6.4 and 6.5). Figure 6.4 presents the variation of *CBR* resistance of a stabilized marl sample versus the addition of lime in dry, wet, and curing conditions. The dry condition indicates the performance of a test following compaction of samples according to their optimum water content and maximum dry density. Performing *CBR* in wet conditions applies to conducting experiments in which, compacted samples have already been kept for 96 hours in distilled-water. These experiments were performed on two series of samples in which no curing and seven days curing was used. Figure 6.5 represents the *CBR* resistance of marly soil where the samples are stabilized with 4% lime and tested after different curing time intervals in the wet condition. The major conclusions which can be made from these experiments can be summarized as follows:

a) As the percentage of added lime increases, the *CBR* resistance of stabilized marl increases. This is valid for both wet and dry samples.

b) As Figure 6.4 and 6.5 indicate, the curing condition causes a noticeable increase in resistance of stabilized soil. As an example, for a sample stabilized with 4% lime, the *CBR* of soil increases more than 300% after 30 days curing. However, the major increase in resistance is achieved after 30 days. Following the first 30 days the soil strength increases at a very slow rate where the difference between the *CBR* after 75 and 30 days shows only 4% increase.

c) Performing the experiments on dry samples gives a higher resistance than in wet samples, keeping other conditions similar. However, as curing conditions are applied on samples, wet *CBR* shows even higher resistance than on an uncured dry sample. This might commonly be attributed to the speeding up of the cementing process caused by soil stabilization.

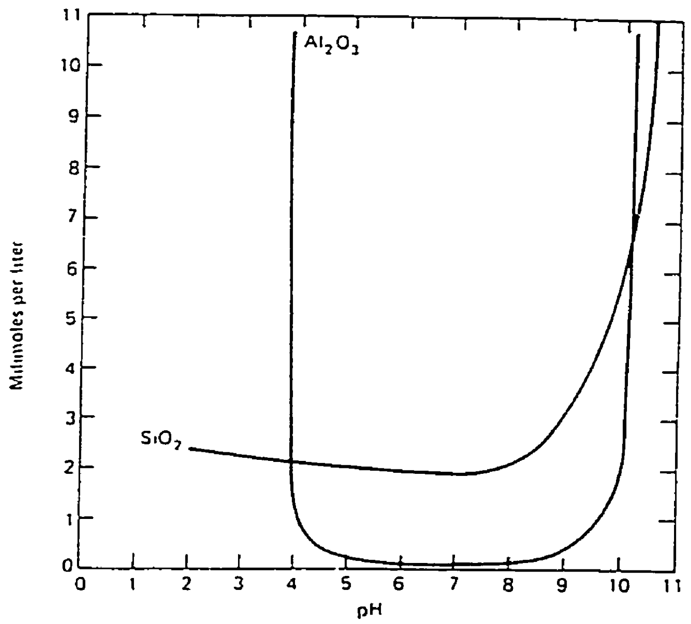


Figure 6.3: Solubility of silica and alumina versus variation of pH (Keller, 1964).

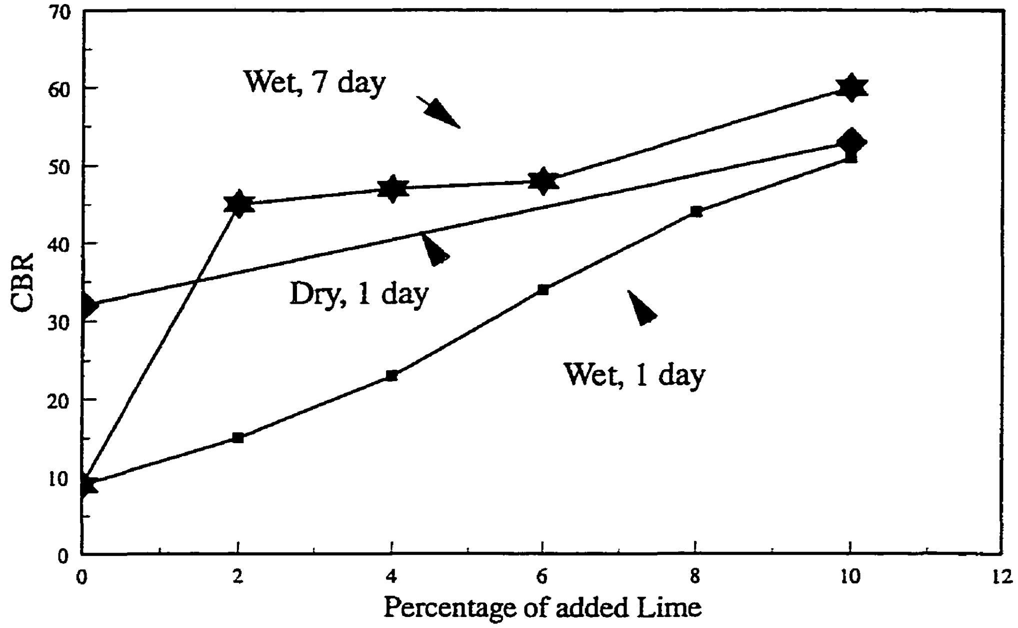


Figure 6.4: Dry and wet *CBR* of stabilized Marl samples at different curing intervals.

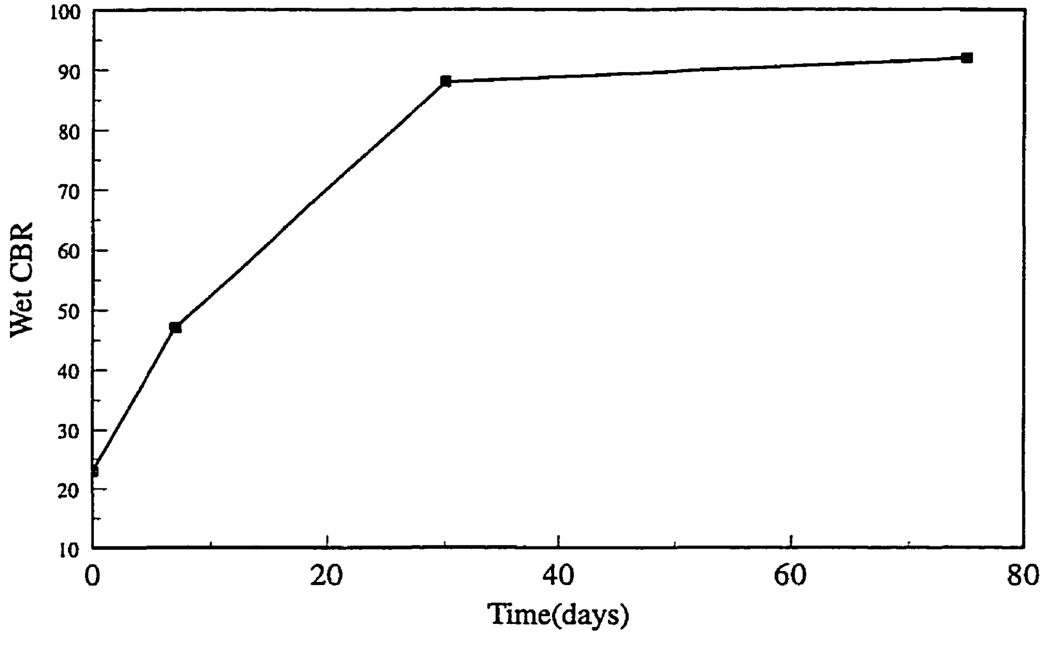


Figure 6.5: Wet CBR of a Marl sample stabilized by 4% Lime, after different curing intervals.

6.2.2 Marl Stabilization Considering pH Criteria

Monitoring the pH is one of the common criteria for evaluating the performance of lime and cement as a stabilizer agents. For instance, according to ASTM C977 in soil stabilization using lime, if the pH readings are 12.40 or higher, the lowest percentage that gives a pH of 12.40 is the amount of lime required to stabilize the soil. The idea is to achieve a pH in which the cementitious caused by chemical interaction between additives and soil starts.

To examine this criteria, the pH variation of a single marl sample stabilized with different percentages of additives is illustrated in Figure 6.6. This Figure compares the variation of pH where lime and cement are used as stabilizer agents. As can be seen in this Figure for all cases soil stabilized with lime shows a higher pH than a sample stabilized by cement. However, the difference is not significant and in all cases the difference is less than 6%. On the other hand, while the initial pH of soil was 8.7, even the addition of 2 percent of lime increases the pH to as high as 12.80. By increasing the percentage of additives from 2% to 10%, the pH increases only less than 4%. While, with the addition of 10 percent lime, the pH was 13.30. The use of more than 10% additive for soil stabilization is considered to be uneconomical. With application of the pH criteria, even 2% cement or lime seems to be able to overcome marl associated problems.

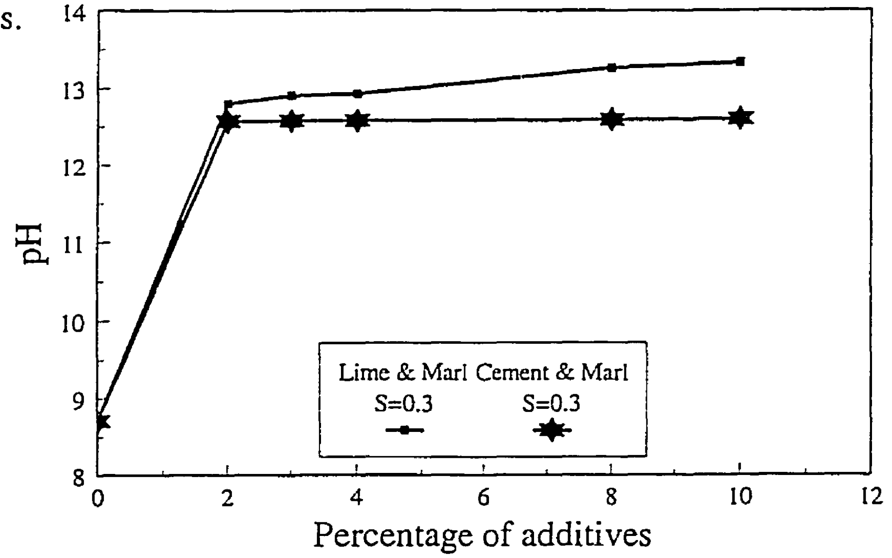


Figure 6.6: pH variation of stabilized Marl with different percentages of Lime and Cement.

6.2.3 Deficiency of Geotechnical and pH Criteria for Soil Stabilization

Based on the discussion in sections 6.2.1 and 6.2.2, the required geotechnical conditions might be achieved by application of only 2% additives. For instance, this amount of stabilizer agent causes a flocculated fabric, as can be seen in the results of the Atterberg tests in Figures 6.1 and 6.2, causing a higher liquid limit after curing. Furthermore, as Figure 6.4 indicates the addition of 2% lime increases the *CBR* up to 500% more than the initial wet *CBR* of marl. This is just the measured resistance in the wet condition and after 7 days curing. In addition, stabilization with 2% cement or lime, raises the pH as much as 12.8 and 12.6, respectively. Different common geotechnical criteria indicate that 2% additive can overcome marl problems. To further evaluate these criteria a series of slaking experiments was performed on stabilized marl. The procedure was as follows. Samples were mixed with different percentages of additives and after keeping for equilibrium they were compacted according to their maximum dry density and optimum water content. Then they were cured for 30 days using the previously mentioned curing conditions. After preparation of samples and following the curing period, samples were kept in water for 24 hours to evaluate their slaking behaviour. The results of these experiments for samples stabilized by cement and lime are presented in Tables 6.1 and 6.2, respectively. The percentage of slaking used in these Tables is defined as the ratio of the dry weight of sample after keeping in water for 24 hours over its initial dry weight. This, in fact, is representative of the weight loss of samples measured after being kept in water for 24 hours. The curing period of 30 days was chosen to provide sufficient time to ensure the achievement of chemical interaction between soil and additives. As the Tables indicate, in spite of current geotechnical criteria previously addressed, the application of 2% additive will not be reliable, in which 100% percentage of slaking in water will happen. While the behaviour is relatively uniform for cement stabilization (with the addition of cement the rate of slaking decreases), this pattern does not seem to be uniform in terms of lime stabilization. Even though the required pH for pozzolanic reaction is achieved, sufficient *CBR* resistance is reached, and obtaining flocculated fabric is displayed by Atterberg limits evaluation, slaking performance after 30 days curing indicates unsatisfactory behaviour. The higher slaking of a sample stabilized by 8 or 10% lime in comparison to that of a sample stabilized by 4 or 6% lime (Table 6.1) can be attributed to the presence of the excess quantity of lime which does not interact with soil fraction or may be attributed to the variation of ettringite formation in the stabilized marl as a function of available calcium ions as will be discussed later in this Chapter and in Chapter 7. By and large, it seems that the geotechnical criteria are not capable of evaluating the required percentage of additives in marl stabilization. It should be noted that based on the results of Tables 6.1 and 6.2, cement has a better response than lime when used as a stabilizer agent. This will be addressed in Chapter 7 where the soil water potential of stabilized marl is discussed.

Table 6.1: Slaking behaviour of stabilized marl with lime, after 30 days curing.

% of Lime	**Curing (Days)**	**Slaking after keeping samples in water for 24 hrs.**				
		%0	**%25**	**%50**	**%75**	**%100**
0	30					*
2	30					*
4	30			*		
6	30			*		
8	30				*	
10	30				*	

Table 6.2: Slaking behaviour of stabilized marl with cement, after 30 days curing.

% of Cement	Curing (Days)	Slaking after keeping samples in water for 24 hrs.				
		%0	%25	%50	%75	%100
0	30					*
2	30					*
4	30			*		
6	30			*		
8	30		*			
10	30	*				
15	30	*				

6.3 CHEMICAL AND MINERALOGICAL ASPECTS OF STABILIZATION

Specific surface area (*SSA*) measurement is used as an another tool for soil stabilization performance in the current research. For the same samples under the same curing condition, the variation of *SSA* and percentage of added lime were evaluated. Samples were mixed with additives and distilled-water. After any specific curing condition, the samples were dried and processed for *SSA* measurement. Figure 6.7 represents the variation of specific surface area for samples stabilized with different percentages of lime under the same curing condition. This series of experiments was performed after different time intervals. Figure 6.7 shows that with an increase in the percentage of added lime in marl stabilization, there is an increase in the surface area after one hour of curing. This can be attributed to the dispersive structure resulting from high pH right after the addition of additives. In fact, while a low pH promotes a positive edge to negative surface interaction which creates a flocculation structure, dispersion of clay particles often happens with high pH conditions. In other words, increasing the pH will make the surface charge density more negative since the surface concentration of OH^- will be increased. The relatively significant quantity of kaolinite, as a pH dependent fraction of marl, will contribute to this process. In fact, since the edge of the kaolinite is known to possess a pH dependent charge, as a result of high pH, the edges will be negatively charged contributing to a more dispersive structure. It should be emphasized that at the same time an ion exchange effect will occur. This phenomenon, due to the addition of lime, is not as quick as increasing the pH, since it is usually fulfilled after 7 days curing *(Kezdi 1979)*. Therefore, while increasing pH governs the short term behaviour of marl stabilization in terms of variation of *SSA*, ion exchange controls the mid-term performance in terms of decreasing the surface area due to increasing the percentage of added lime, causing an improvement in the mechanical response of the soil being stabilized. That is why, as is shown in Figure 6.7, the behaviour is followed by a decrease in the surface area after one week of curing of stabilized samples. In view of the promotion of cementing resistance in the soil stabilization process, we would commonly expect a further decrease in the soil surface area. This decrease in surface area can be related to the progress of cementious effects of additives. The cementatious process, in fact, reduces the amount of the exposed surface of the soil. Furthermore, in long-term behaviour of soil-additive interaction, prior research indicates a significant decrease in specific surface area which is attributed to the formation of a crystalline structure of calcium silica hydrate *(Kondo et al. 1967)*. However, as is illustrated in Figure 6.7, surprisingly we are faced with an increase in the surface area after one month of curing. A similar behaviour is observed when sea-water is used instead of fresh-water (Figure 6.8). While these achievements are in conflict with the geotechnical results, they indicate an agreement with the slaking performance response of tested samples.

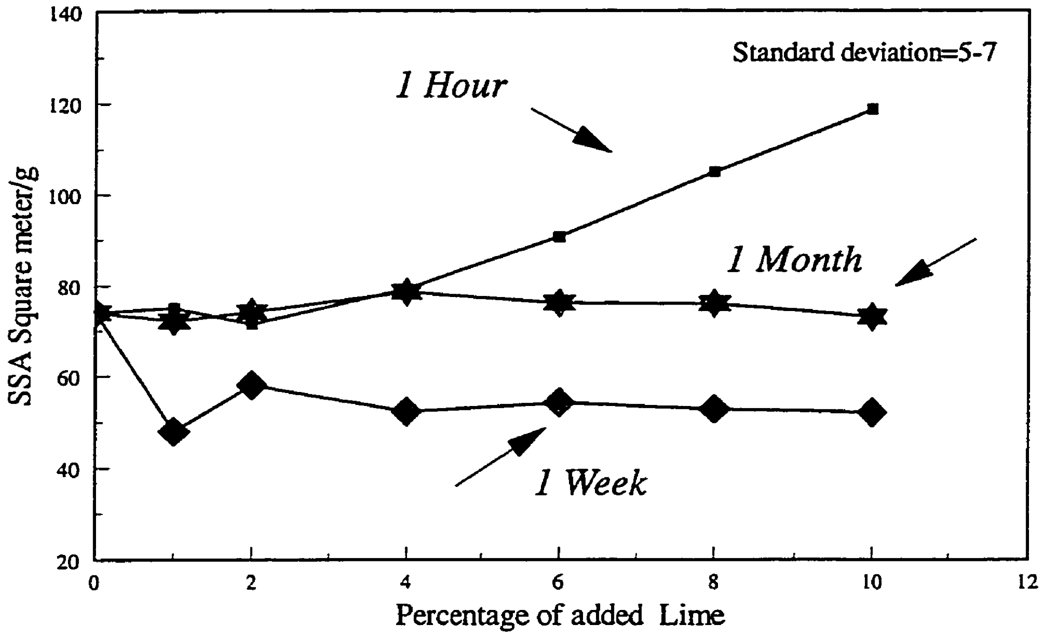


Figure 6.7: Specific surface area (SSA) of stabilized Marl samples with different percentages of Lime, measured at different curing times.

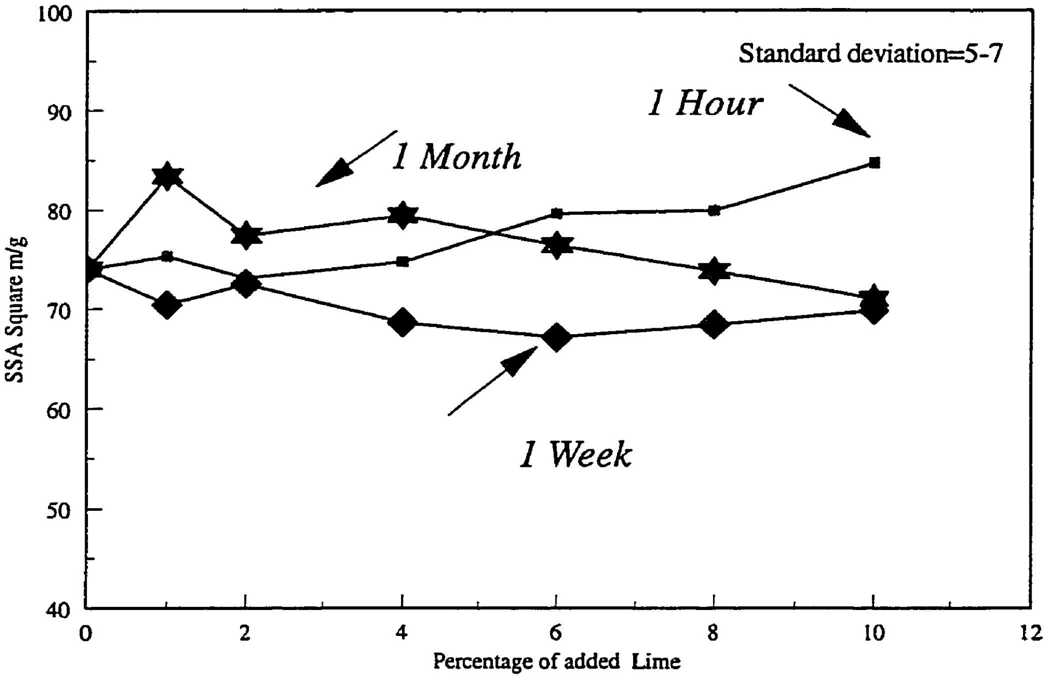


Figure 6.8: Specific surface area of stabilized Marl samples with different percentages of Lime, mixed with sea-water and measured at different curing times.

6.4 ETTRINGITE FORMATION INDICATED BY *XRD* ANALYSIS

To interpret these conflicting results, *XRD* tests were performed on the cured samples, under the previously indicated conditions. The *XRD* spectra were obtained by scanning in the 2θ range of 5 to 70 degrees. At the end of the required moist-curing periods, the samples were taken from the humid-room for immediate processing. In this series of experiments the reflection lines of palygorskite, *CSH*, *CAH* and ettringite are monitored and will be explained in the following.

6.4.1 Palygorskite's Peak Intensity Variation Over Stabilization Period

Figure 6.9 indicates the variation of palygorskite's peak intensity for its five reflection lines, under different curing time intervals. These reflection lines are 10.4, 6.33, 5.38, 4.46, and 3.17 angstrom, as were previously addressed in Chapter 2. The variation of the reflection lines of palygorskite are monitored after 1, 7, and 30 days curing following marl stabilization with 10% lime, and are compared with the initial values for palygorskite (Figure 6.9) corresponding to zero days of curing. After different curing time intervals, a portion of sample was taken and analyzed by *XRD*. As can be seen in Figure 6.9, over the curing period, palygorskite's peak intensity starts to diminish with the addition of lime. Only the variation of peak intensity for the reflection line equal to 3.17 does not follow the other patterns and will be explained in the next section (6.4.2). This reflection line is the same for palygorskite and *CSH*. The overall pattern of decreasing palygorskite peak intensity can be attributed to the solubility of the silica and alumina fraction of palygorskite at high pH reaction. In fact, as was presented in Figure 6.3, the solubility of clay minerals increases as the pH of pore fluid goes to around 12. This released alumina and silica will be available for further chemical reaction. The second reason which contributes to the mid and long term decreasing of palygorskite peak intensity will result from ion exchange interaction causing a flocculated structure. It was already explained (Figure 5.14) that for a single sample having different degrees of orientation, the well oriented structure indicates a relatively higher peak intensity than that of a less oriented structure. Therefore, the phenomenon of ion exchange can contribute to the diminishing of palygorskite peak intensity as the curing period progresses.

6.4.2 *CSH* and *CAH* Formation Over Stabilization Period

As was previously addressed, two cementing agents are known to form in the stabilization process and are responsible for the improvement of soil behaviour. In this process, the released alumina and silica of clay fraction are responsible for the development of cementious agents called *CSH* and *CAH* through their interaction with lime.

The formation and growth of *CSH* can be found by observing the increase in the peak intensity of its major basal spacing (d=4.15 angstrom) over different time intervals as displayed in Figure 6.10. The variation of the second basal spacing of *CSH* (d=2.67 angstrom) confirms the progress in *CSH* formation. Another reflection line of *CSH* which is in the same order of magnitude of that of the palygorskite reflection lines, was also monitored. This reflection line, which is 3.17 angstrom, is presented in Figure 6.9. Following the prior explanation of palygorskite and *CSH* peak intensity over the stabilization period, the disordered pattern of this reflection line can be speculated on and can be explained as follows. Due to the solubility of palygorskite in all curing conditions, this mutual peak indicates a decrease in intensity after one and seven days curing. In a one month cured sample, the apparent intensity from *CSH* formation, as was confirmed with its others reflection lines, overcomes the decreased palygorskite peak intensity of this mutual reflection line. This will cause a noticeable increase of intensity at 3.17 angstrom spacing after one month period.

The formation and growth of *CAH* is evaluated by monitoring its major reflection line at 7.6 angstrom *(Rao et al. 1993)*. As is presented in Figure 6.10, the formation of calcium aluminate hydrate *(CAH)* was observed after seven days curing by achieving

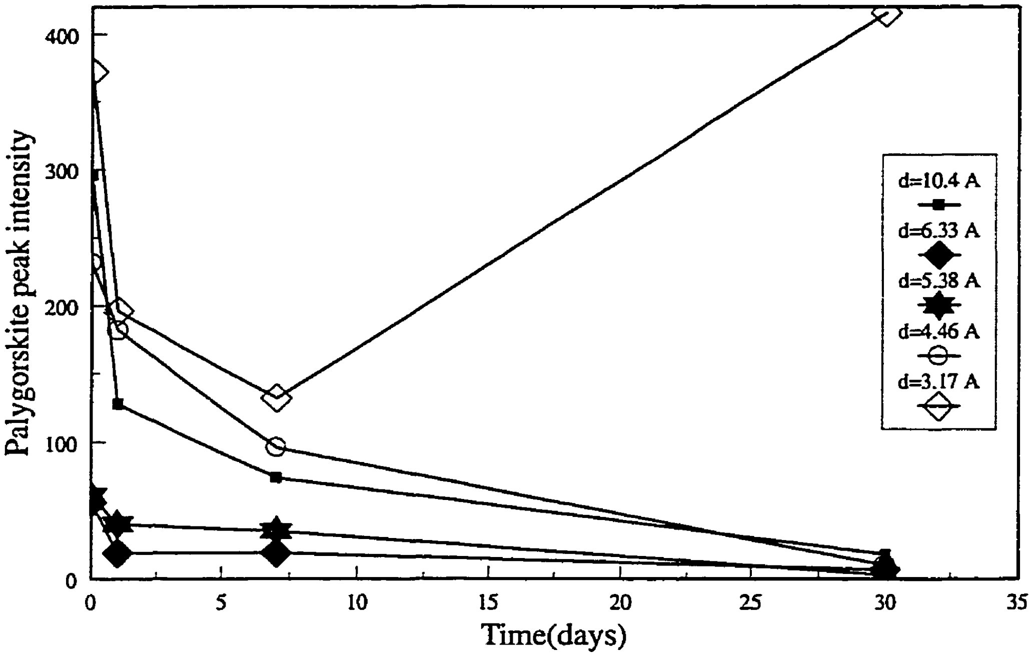


Figure 6.9: Variation of Palygorskite's peak intensity for its five reflection lines, in stabilized Marl with 10% Lime, after different curing intervals.

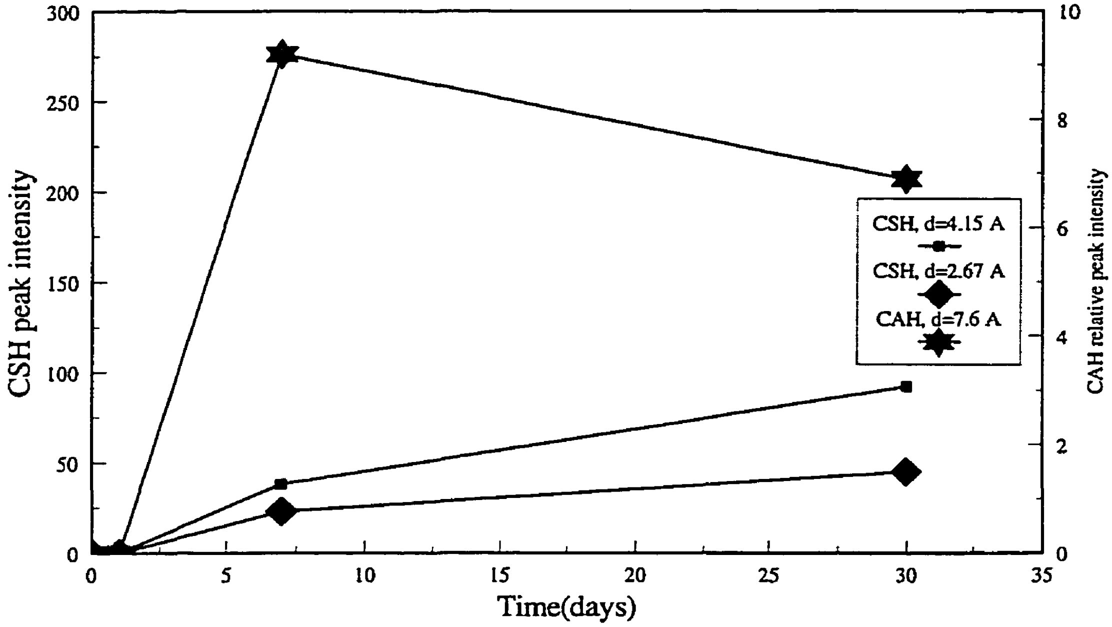


Figure 6.10: Variation of *CSH* and *CAH*'s peak intensity for their three reflection lines, in stabilized Marl with 10% Lime, after different curing intervals.

9.2% relative peak intensity. Surprisingly, in spite of expectation of an increase in its intensity, the one month cured sample revealed a decrease in the relative peak intensity of the *CAH* major reflection line. The one month cured sample shows a relative peak intensity equal to 6.9% for this reflection line. More explanation of this performance will be addressed in the following.

6.4.3 Ettringite's Peak Intensity Variation Over Stabilization Period

As was explained before, the availability of dissolved alumina in the presence of sulfate and calcium might provide a favourable condition for ettringite formation. As presented in Figure 6.11, with increasing time, ettringite mineral forms in marl stabilization. The ettringite is formed due to the provision of dissolved alumina from palygorskite fraction of marl, calcium ion from added lime, and the sulfate present in the pore fluid of marl. As was previously addressed, the high pH environment caused by the addition of lime is necessary for this reaction. On formation of ettringite the rate of ettringite growth increases leading to an increase in surface area resulting from the high surface area of the ettringite. Ettringite, with a basal spacing of 9.72 angstrom, appears after seven days of curing. The variation of reflection lines of 5.61 and 2.77 angstrom also are shown in this Figure. It would seem that while ettringite, with its high swelling characteristics, produces failure in a stabilized soil, its needle-like structure in some manner contributes to the geotechnical response of the soil behaviour. The formation and growth of *CSH* (Figure 6.10) also helps to achieve a high strength in common geotechnical testing. On the other hand, the variation of the *CAH* reflection line and its decrease in intensity which coincides with the increase in ettringite intensity, strengthen the possibility of the contribution of *CAH* to ettringite formation as time goes on. This contribution happens through the provision of alumina for ettringite formation.

The *XRD* analysis indicated no other byproduct formation, which may typically include monosulfate or thaumasite. This factor was evaluated by performing *XRD* tests on both wet and dry samples. Monosulfate peaks in *XRD* analysis, disappear upon drying of sample, while ettringite peaks are stable in both wet and dry circumstances. The results of the solubility of the alumina fraction of marl, which are measured at different soil washing with acid and base, are presented in Figure 6.12. The procedure of tests has already been addressed in Chapter 3. After each process of soil washing the amount of soluble alumina and silica were measured. As can be seen, the release of soluble alumina is very time dependent. The results of this experiment also show a good agreement with the time dependency of ettringite growth in soil stabilization. In fact, as time goes on more alumina will be available which will contribute to the continuous ettringite formation. These alumina are usually responsible for the formation of *CAH* as a cementing agent in soil additives interactions.

6.4.4 Necessary Conditions for Ettringite Formation and Its Stability

Ettringite mineral is repeatedly reported to be stable above pH of 10.5 *(Gabrisova et al. 1991, Havlica et al. 1991)*. To ensure the occurrence of the required condition for ettringite stability, the pH of two samples stabilized by 4 percent lime and 10 percent cement are compared in Figure 6.13. As can be seen, with increasing duration, the pH decreases showing how the hydration process contributes to the stabilization process. It is quite significant that even after one month the pH is still greater than 10.5, which is the minimum pH required for ettringite formation.

Some of the appropriate conditions for ettringite formation, in cement hydration, were previously investigated *(Mehta and Klein 1966)*. This research indicates that in the system having the required elements for ettringite development, achieving a molar ratio of Al_2O_3/SO_4 less than 1.0 is a favoured condition for ettringite formation. Based on the alumina solubility pattern of soil, as was presented in Figure 6.12, the release of soluble alumina does not have an instantaneous pattern. In fact, depending on the environmental conditions, in terms of pH and availability of moving water, the amount of released alumina can vary. In other words, the above mentioned ratio might be continuously changed over the leaching process. This fact can justify the different concentrations of ettringite being formed at different places, having similar initial conditions located in the single case study. In the road failure reported in U.S. due to the ettringite formation *(Hunter 1988)*, at different places, having similar initial conditions but different availability of water, different concentration of developed ettringite was observed.

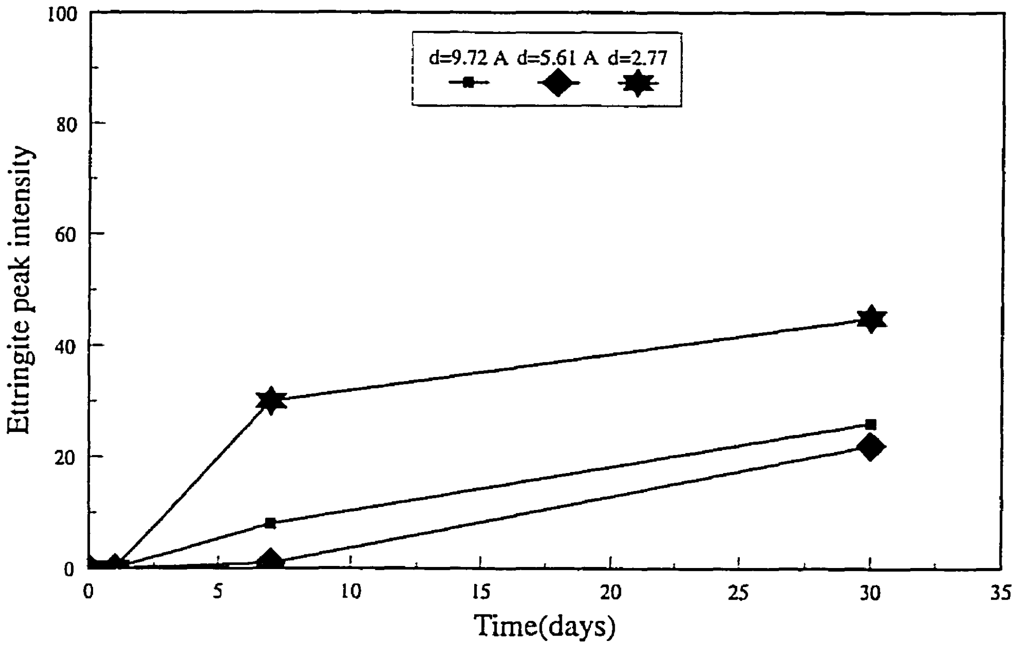


Figure 6.11: Variation of Ettringite's peak intensity for its three reflection lines, in stabilized Marl with 10% Lime, after different curing intervals.

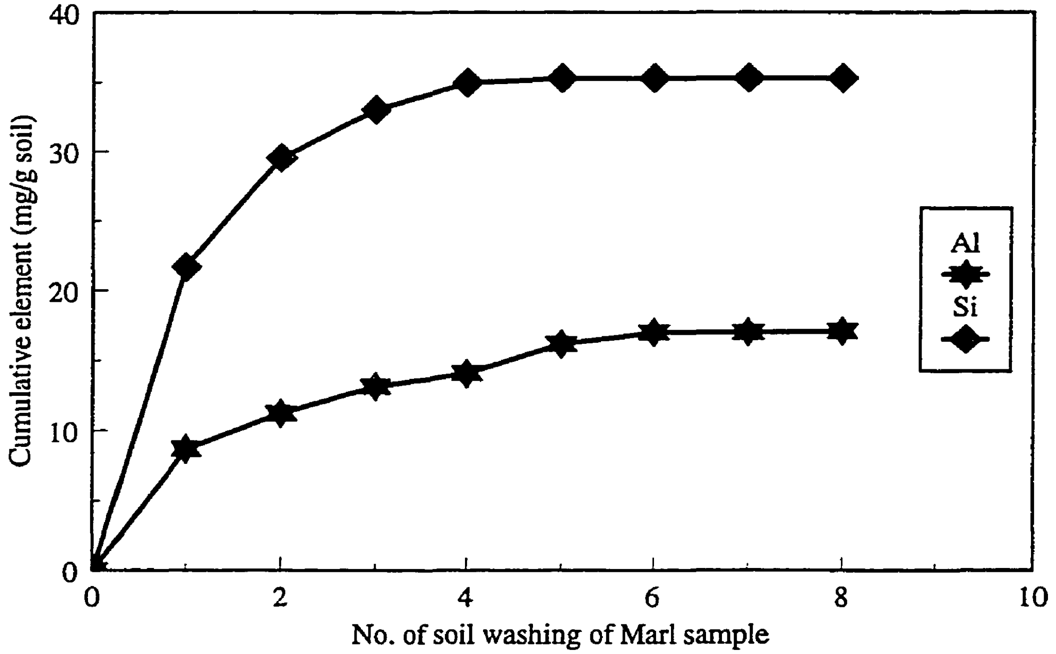


Figure 6.12: Variation of released alumina and silica from a Marl sample at different soil washing steps, using acid and base.

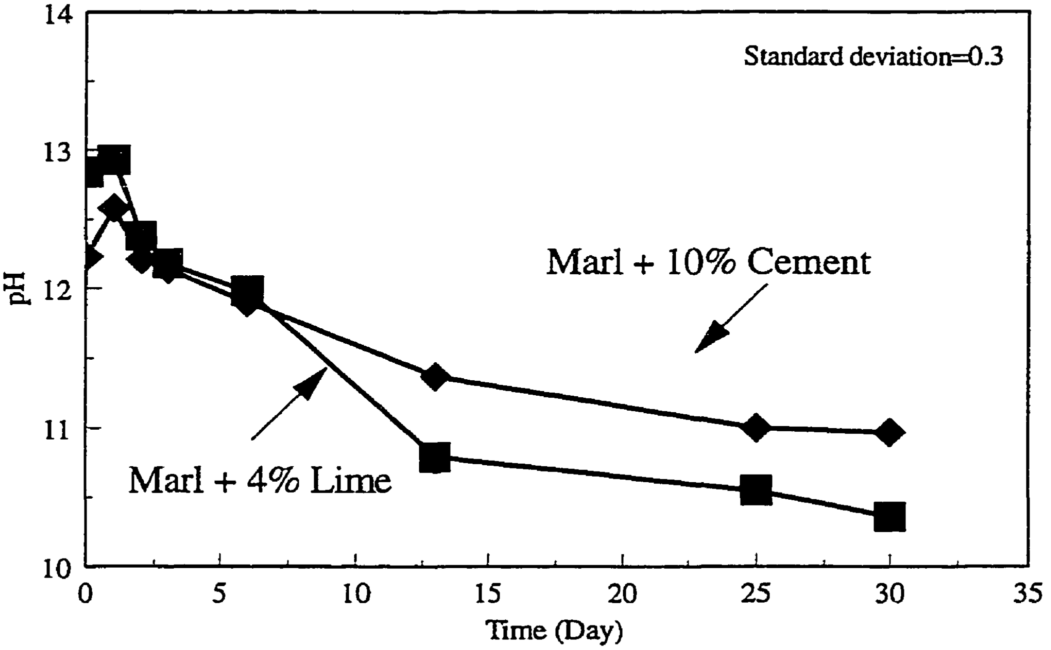


Figure 6.13: pH variation of stabilized Marl with 4% Lime and 10% Cement at different time intervals.

6.5 SUMMARY

The mineral transformation of a palygorskite fraction of marl over the soil stabilization process was addressed in this Chapter. The results of this Chapter indicate the significant deficiency involved in the current common geotechnical criteria for soil stabilization evaluation.

From current mechanical evaluation of soil stabilization, three criteria are usually used to evaluate the soil stabilization process. These include, pH evaluation, Atterberg limit variation, unconfined compressive strength, and/or *CBR* testing. That is why common soil stabilization evaluation criteria emphasize achieving a high pH (more than 12.80), improving Atterberg limits, and increasing *CBR* or unconfined strength. The results of the current study indicate that the very common method of soil stabilization, which focuses attention on mechanical aspects of soil performance, is not capable of evaluating the failures and instability of stabilized marl due to the ettringite formation. Specific surface area measurements, in conjunction with *XRD*, are two valuable means to evaluate marl stabilization from the physico-chemical point of view. Ettringite formation, whose presence appears in *XRD* could explain the conflicting results between the mechanical and physico-chemical evaluations of marl stabilization. It would seem that while ettringite, with its high swelling characteristics, produces failure in a stabilized soil, its needle-like structure in some manner contributes positively to the geotechnical response of the soil behaviour. Any other source of sulfate may also augment the possibility of ettringite formation. The necessary conditions to provide for ettringite formation and its stability were also examined in this Chapter. The very time dependent pattern of releasable alumina and silica fraction of clay soils were examined. In which this pattern can provide a very flexible and variable molar ratio of Al_2O_3/SO_4 over the stabilization process, which might directly affect the possibility and rate of ettringite formation.

CHAPTER 7

KINETICS OF ETTRINGITE AND FLUID RETENTION OF STABILIZED MARL

7.1 INTRODUCTION

Equations for the rate of ettringite formation have been derived by many investigators. There exists few experimental studies for validation of these derivations. Furthermore, comparing the pattern of the kinetics of ettringite, formed from different possible sources, specifically in stabilized soil, will help to obtain not only a clear picture of the kinetics of ettringite from the different sources, but also to have a clear expectation of ettringite formation and growth in soil stabilization. This will be another aspect of the physico-chemical evaluation of soil stabilization. *XRD* analysis can be used to monitor the process of formation and growth of ettringite minerals. In such an evaluation, the establishment of the contribution of different clay minerals to ettringite formation will provide a general expectation of the possibility of soil instability when the clay mineral of soil fraction is known.

Among several factors involved, soil fluid retention plays an essential role in the process of ettringite formation as it can provide permanent access to the environment's sulfate source. In terms of environmental conditions, pore fluid of marl is usually accomplished by the presence of chloride ions. As previously discussed in Chapter 2 (section 2.8.3), the availability of chloride ions during the leaching process may affect the extent of ettringite formation. In this Chapter, by the use of a series of physico-chemical tests the above addressed key points are investigated.

7.2 KINETICS OF ETTRINGITE FORMATION

Several investigators have tried to derive and establish equations for the rate of ettringite formation. The equation suggested by *Jander (1927)* is the most frequently used. This equation is as follows:

$$[1-(1-\alpha)^{1/3}]^N=Pt \tag{7.1}$$

where α is the reaction ratio, t is time and P is a rate constant. This equation is based on the assumption that ettringite forms when substance A reacts with substance B to form product AB. While *Jander* reported that the N value was equal to 2, *Mori & Minegishi (1968)* observed that kinetics of ettringite formation, and consequently the value of N, are dependent on the variation of temperature. *Ginstling & Brounshtein (1950)* defined a more precise derivation. Their equation is as follows:

$$1-2/3\alpha-(1-\alpha)^{2/3}=Pt \tag{7.2}$$

where α, t and P are the same as in the *Jander* expression. This equation has the ability to consider the size of particles which participate in the interaction process. *Plowman & Cabrera (1984)* investigated the kinetics of ettringite formation using tri-calcium aluminate which was extracted from cement. In this instance the rate of ettringite formation, presumably at room temperature, followed the following form:

$$[1-(1-\alpha)^{1/3}]=(Pt-c)^{1/2} \tag{7.3}$$

In a recent study by *Brown & LaCroix (1989)*, the kinetics of ettringite formation were evaluated by the use of tri-calcium aluminate as a source of ettringite formation. They used a rearranged form of the equation suggested by *Jander (1927) and Mori & Minegishi (1968)* as follows:

$$[1-(1-\alpha)^{1/3}]=Pt^{N} \tag{7.4}$$

in which N=0.5 implies diffusion control, while N=1 implies surface area control. Among the above suggested equations, the latter seems to be more practical because it takes into consideration both the diffusion and the surface area of the chemicals involved in the interaction. In other words, from the beginning, Equations 7.1 and 7.3 assume that the process of interaction is governed by the diffusion role of the elements present in the chemical interaction.

In the current research, by application of *XRD* analysis, the kinetics of ettringite formation is monitored in two different cases. First, the rate of artificial ettringite formation is evaluated using alumina sulfate and lime at the different time intervals. Second, the kinetics of ettringite formation on stabilized soil are evaluated.

7.2.1 Kinetics of Artificial Ettringite

The theoretical basis of kinetics of artificial ettringite has previously been addressed by several researchers, as was pointed out in the section 7.2. Most of the pervious experimental studies were performed by application of tri-calcium aluminate*(Mehta 1976, Plowman & Cabrera 1984, Older & Maula 1984, Grusczscinski et. al 1993)*. However, the two major sources of artificial ettringite formation are known to be by use of tri-calcium aluminate and alumina sulfate.

By and large, few experimental studies exist on the evaluation of the kinetics of ettringite formation. For instance, there is a need to evaluate the kinetics of ettringite formation by the use of alumina sulfate and lime, in which calcium ions are produced from the same source as those in the soil stabilization condition. Furthermore, such an evaluation will help to extend the established criteria for favoured conditions of ettringite formation. For this purpose the kinetics of ettringite formation is experimentally evaluated in this section by the use of alumina sulfate and lime. To investigate the kinetics of artificial ettringite formation when alumina sulfate and lime are used as the source of mineral formation, a series of *XRD* tests were performed on mixtures of these two elements and distilled-water at different time intervals. Artificial ettringite was prepared using the method suggested by *Older and Maula (1984)*. For complete mineral formation, 48 hours of agitation of prepared mixtures was performed. To monitor and establish the rate of ettringite formation, at different time periods, a sample was taken from the prepared mixture, dried and analyzed by *XRD*. For these experiments, Figure 7.1 indicates the variation of reaction ratio of ettringite formation versus time. The reaction ratio is calculated based on the peak intensity of the major reflection line of ettringite at each period, divided by its final achieved peak intensity after equilibrium of chemical reactions. Ettringite formation was monitored at the time intervals of 1 min., 5 min., 15 min., 45 min., 24 and 48 hours. Analyses of the relation between reaction ratio versus time are performed by application of non-linear least square regression applied by *TableCurve Software (Jandel Scientific TableCurve, Version 3.01, 1991)*. The four different equations suggested by *Jander (1927)*, *Ginstling & Brounshtein (1950)*, *Plowman & Cabera (1984)*, and *Brown & LaCroix (1989)*, as was addressed in previous section, are applied on the achieved data. The coefficients introduced in equations, 7.1, 7.2, 7.3, and 7.4 are presented in Table 7.1.

The results of *XRD* analysis indicate that ettringite forms after 1 min. of mixing. *Brown & LaCroix (1989)* in the study of the kinetics of ettringite formation using tricalcium aluminate report the appearance of ettringite peaks after 10 minutes. The value of N obtained in the current research (Table 7.1) is consistent with the value obtained by *Plowman & Cabera (1984)* and *Brown & LaCroix (1989)*. However, the values of P indicated in Table 7.1 are much smaller than values reported by the above mentioned authors. A comparison of the results, indicated in Table 7.1 and previous works, shows that as the time required for ettringite formation increases the value of P decreases. It should be noted that by rearrangement of Equation 7.4 to the form of Equation 7.1 the coefficient of N will be 1/0.63 or 1.59 and coefficient of P will be 0.00033, which are in the same order of magnitude as those of the other equation coefficients presented in

Table 7.1. The values of *N*, obtained in this study, lie within the range predicting the rate of ettringite growth to be diffusionally controlled. While in previous research, tri-calcium aluminate, was used as a source for production of ettringite, the general mechanism of mineral transformation is in accord when alumina-sulfate and lime are used as the sources of ettringite formation. The faster formation of ettringite in the current research may be attributed to the faster availability of alumina and sulfate ions (when alumina-sulfate is used as a source of ettringite formation) and is due to the higher solubility of alumina sulfate in comparison with that of tri-calcium aluminate. Gypsum was found to form mainly at relatively higher concentrations than ettringite in the very earlier stages. However, its concentration rapidly decreased after 48 hours when equilibrium was achieved. The final concentration of gypsum was estimated to be less than 10%. The pH of prepared ettringite in a 1:10 solution was 12.3.

Table 7.1: Application of experimental results on the theoretical equations for kinetics of ettringite.

Coefficients	**Applied Equations for Kinetics of Ettringite Formation**			
	Equation (7.1)	**Equation (7.2)**	**Equation (7.3)**	**Equation (7.4)**
P	0.00033	0.00012	0.00034	0.0065
N	2	-	-	0.63
c	-	-	0.02	-
r[1]	0.92	0.94	0.92	0.93

[1] r=Coefficient of correlation

7.2.2 Kinetics of Ettringite on the Stabilized Soil

As was discussed in Chapter 6, in marl stabilization, ettringite may form after 7 days of curing. Its formation was monitored up to 30 days in the current research (Figure

6.11). *Mitchell and Dermatas (1992)* report the continuation of ettringite formation for more than 20 months. In the failure reported in the lime-treated subbase of roadways in the U.S., damage due to the ettringite formation visually started within six months following construction and severely increased by the end of two years *(Hunter 1988, Mitchell 1986)*. As the results of the current research and previous works indicate, the rate of ettringite formation in stabilized soil is much slower than that of artificial ettringite. Data presented by *Mitchell and Dermatas (1992)* were used for a quantitative comparison of the kinetics of ettringite formation in soil stabilization with the data presented in section 7.2.1. It was previously pointed out that the coefficients of the Equations 7.1 through 7.4 express the features of kinetics of ettringite. Table 7.2 represents these coefficients for previously addressed Equations regarding kinetics of ettringite in soil stabilization. For calculation of the coefficients presented in Table 7.2, the data plotted in Figure 7.2 are used. In this evaluation, reaction ratios are calculated with the assumption that ettringite formed after 20 months curing, is the equilibrium condition in terms of the maximum quantity of ettringite which may form under these specific conditions. These data were used because of the longer period of monitoring of ettringite mineral in soil stabilization.

It should be noted that by rearrangement of Equation 7.4 to the form of Equation 7.1 the coefficient of N will be 1/0.904 or 1.1 and coefficient of P will be 1.2×10^{-6}. As mentioned in section 7.2, Equation 7.4 has the advantage that it takes into consideration, both the surface area and diffusion roles in the ettringite formation process. The range of values of N obtained by application of Equation 7.4 indicates that in spite of artificial ettringite, the ettringite formation in soil stabilization is accomplished with surface area control.

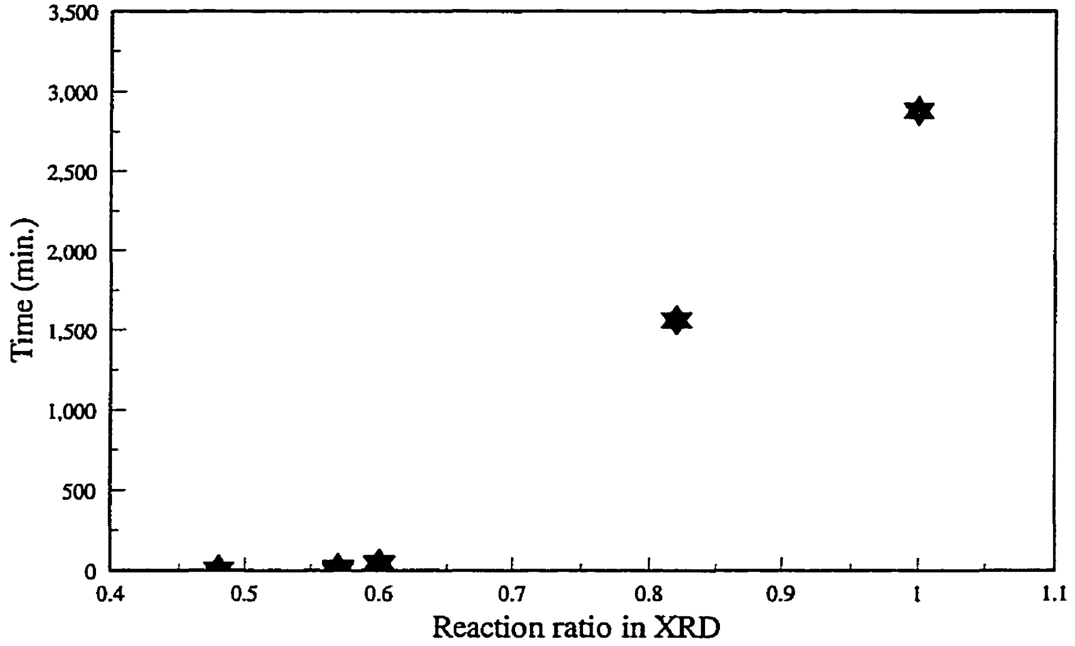


Figure 7.1: The variation of reaction ratio and time to establish the kinetics of artificial Ettringite.

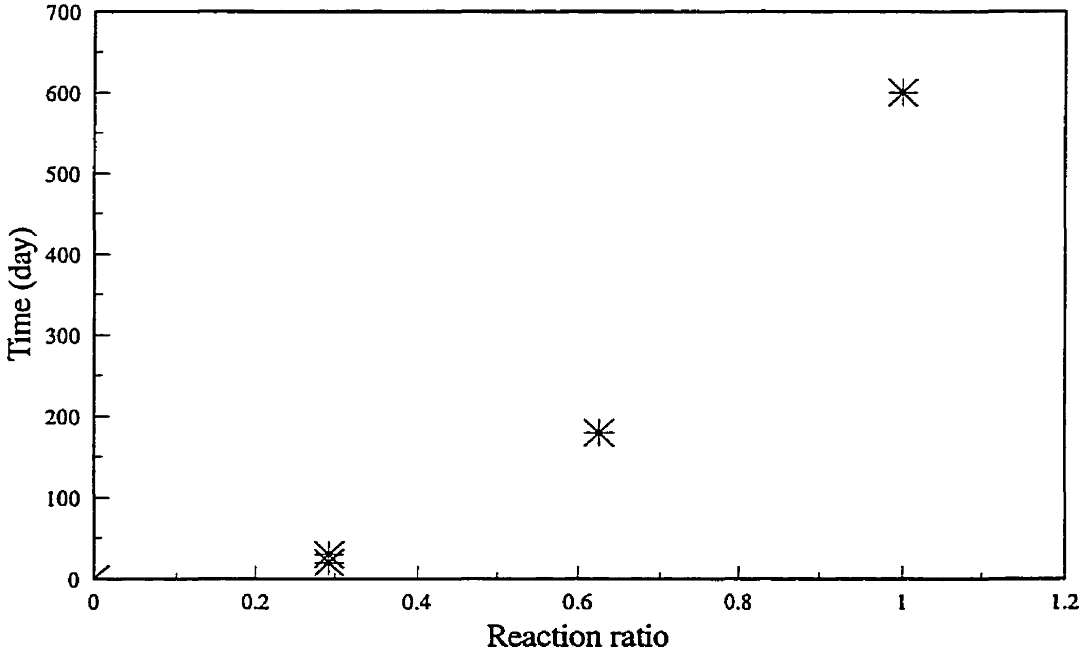


Figure 7.2: The variation of reaction ratio and time calculated based on experimental data of *Mitchell and Dermatas (1992).*

Table 7.2: Application of experimental results on the theoretical equations for kinetics of Ettringite in soil stabilization.

Coefficients	**Applied Equations for Kinetics of Ettringite Formation in Stabilized Soil**			
	Equation (7.1)	**Equation (7.2)**	**Equation (7.3)**	**Equation (7.4)**
P	1.13	3.78	1.26	$4.3\text{x}10^{-6}$
N	2	-	-	0.904
c	-	-	0.1	-
r[1]	0.97	0.99	0.98	0.99

[1] r=Coefficient of correlation

7.3 THE ROLE OF DIFFERENT IONS ON ETTRINGITE FORMATION

To investigate the role of different ions including, alumina, sulfate and calcium on ettringite formation, and to evaluate the extent of ettringite formation in the system of alumina-sulfate/lime/distilled-water, tests were carried out on samples by varying the following constituents: alumina sulfate, slaked lime, and distilled-water. The variation of these elements takes into account the role of change on the main elements present in the ettringite structure. For this purposes, eight different mixtures of alumina-sulfate, hydrated lime and distilled-water were prepared, kept to equilibrate and monitored for the quantity of ettringite minerals by application of *XRD* analysis. The process of sample preparation followed the method suggested by *Older and Maula (1984)*. In addition to ettringite, monosulfate may also form in the presence of alumina sulfate, and calcium ions *(Mehta and Klein 1966)*. While *Lea (1970)* reports that the peaks, verifying the presence of monosulfate hydrate, occurs at 8.92 and 4.46 angstrom, *Berman and Newman (1963)* found *XRD* lines at 9.5-10, 5.7, and 4.7 to 4.9 angstrom for wet monosulfate hydrate which was confirmed by *Mitchell and Dermatas (1992)*. To take into consideration these reported findings, and to avoid any mistakes (in terms of similar basal spacing of monosulfate and ettringite) *XRD* was performed on wet samples after preparation of samples and following equilibrium. This was done to monitor the possibility of monosulfate formation which is reported to have a similar major basal spacing as ettringite and is stable only in wet condition. No noticeable quantity of monosulfate formation was observed in these experiments. Later, samples were air dried and processed for *XRD* in the dry condition (the details of preparation were addressed in Chapter 3). In dry samples, the reflection lines of ettringite were monitored. Figure 7.3 indicates the variation of *XRD* intensity of ettringite peak versus variation of concentration of sulfate for a series of samples having 0.12 *mol* calcium in the mixtures. The first three major reflection lines of ettringite are plotted in this Figure. As can be seen, by increasing the sulfate concentration, the intensity of ettringite peak increases up to 0.06 *mol* of added sulfate where a maximum peak intensity is achieved. Following this point, by increasing the sulfate concentration, the intensity of ettringite peaks decreases. The same pattern was observed when the role of alumina concentration on the quantity of ettringite formation was evaluated for a series of mixtures having 0.12 *mol* calcium in the mixture (Figure 7.4). Furthermore, when the concentration of alumina and sulfate were fixed at 0.04 and 0.06 *mol*, respectively, varying the concentration of calcium follows the above described pattern for ettringite peak intensity. It was noted that in all these points, where the maximum quantity of ettringite's *XRD* peak is achieved, the concentration of different elements including, sulfate, alumina and calcium lies exactly in accordance with the *"stoichiometric"* relations of these elements required for ettringite formation. Moreover, in this series of experiments the formation of ettringite seems to be more sensitive to the variation of available sulfate and alumina ions rather than that of calcium concentrations. This can be concluded by comparing the slope of the graphs and the variation range of horizontal axis's values in Figures 7.3, 7.4, and 7.5.

Based on above discussion, one may come to the conclusion that when the formation of ettringite is possible, due to the sulfate concentration in pore fluid of soil, small variations of calcium concentration, in which in soil stabilization may happen, do not play a noticeable role in preventing ettringite development. In other words, it seems that in soil stabilization, when sulfate is present in the pore fluid of soil, application of lime may lie in the range of high risk for ettringite formation even if mechanical/physical experiments indicate the achievement of better properties. This conclusion is in good agreement with the results of an investigation presented by *Mehta & Klein (1966)* in which they found only in the case of very high ratios of calcium ion, formation of ettringite may not be stable. However, even though the previous studies *(Mehta and Klein 1966)* reported that ettringite formation is favoured when the molar ratio of Al_2O_3/SO_4 does not exceed 1, the results of the current research presented in Figures 7.3 through 7.5 indicate that ettringite formation may lie in the critical range even if the above ratio is 1.33. The use of various sources for ettringite formation can be responsible for these differences. It should be noted that the important effect of solubility of major elements of ettringite mineral, which directly affect the rate and extent of ettringite formation, can be another reason for these differences. This fact has been addressed in Chapter 6.

The final conclusion (achieved from Figures 7.3 to 7.5) is achievement of a higher intensity of the first basal spacing of ettringite (i.e. d=0.973 *nm*), in comparison with other basal spacings presented in these graphs. The major basal spacing of minerals show the highest possible intensity and this is a characteristic of well crystallized minerals *(Cullity 1967)*. The general achieved pattern in which basal spacing of d=0.973 *nm* has the highest intensity, can be an indicator of the assessment of relatively complete crystal formation of an ettringite mineral. Therefore, the *XRD* diffraction follows the general pattern of completely formed ettringite crystal.

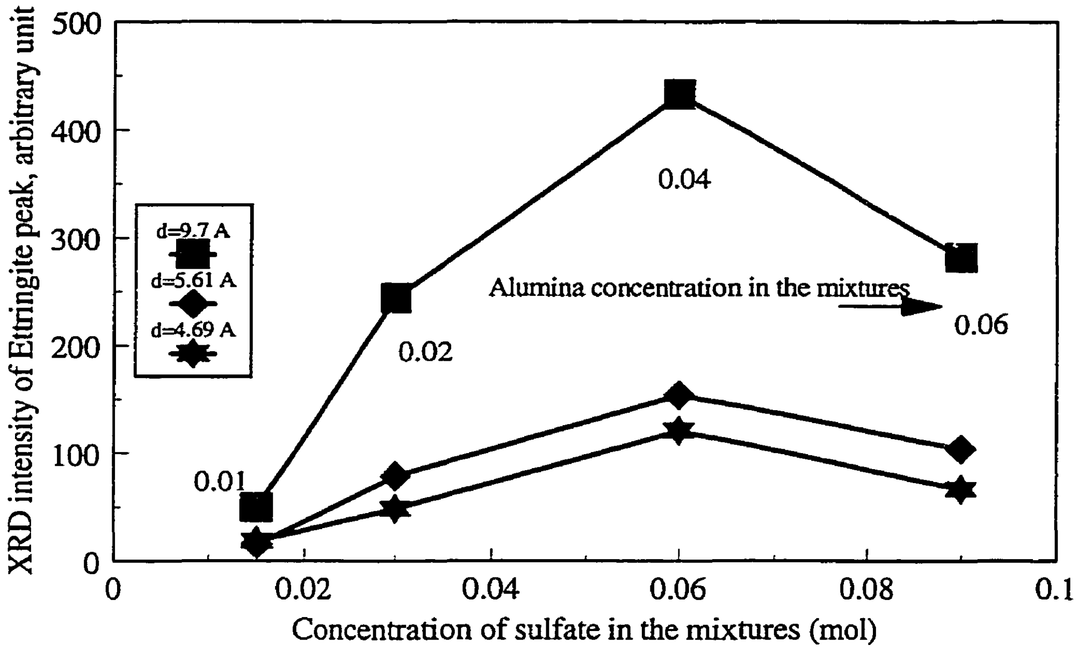


Figure 7.3: The role of sulfate concentration on the quantity of Ettringite formation, having 0.12 mol calcium in the mixtures.

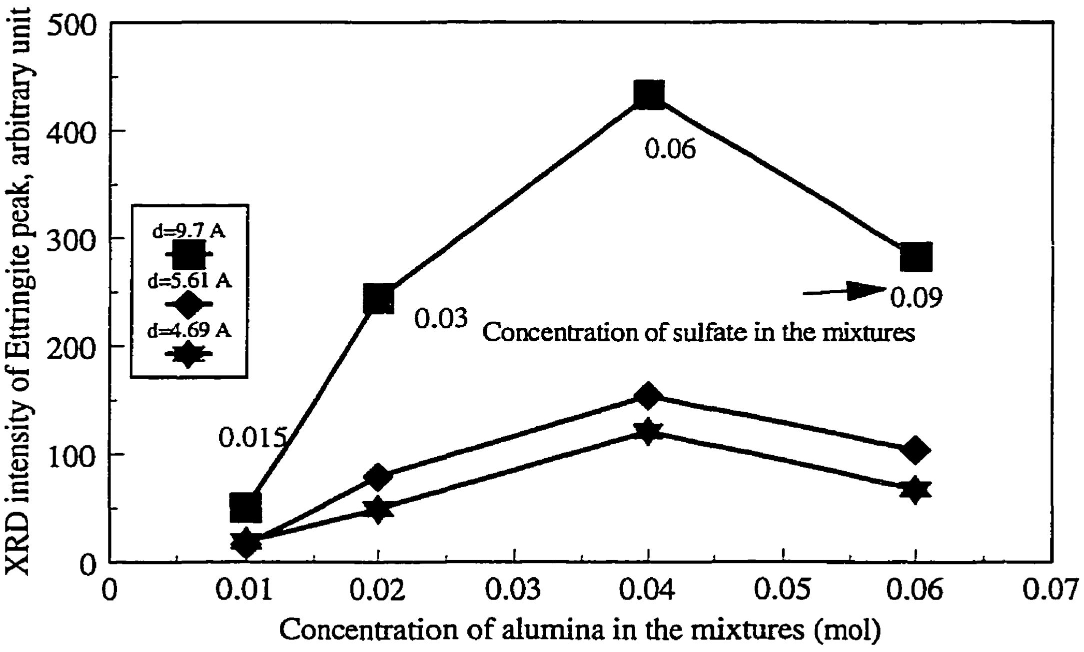


Figure 7.4: The role of alumina concentration on the quantity of Ettringite formation, having 0.12 mol calcium in the mixture.

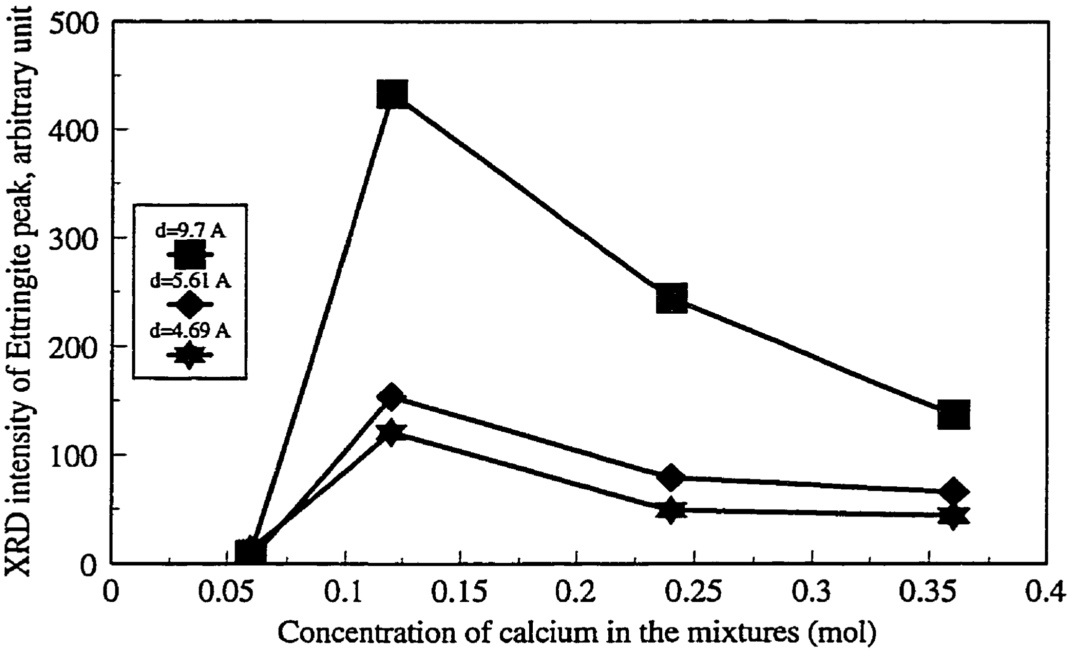


Figure 7.5: The role of lime concentration on the quantity of Ettringite formation, having 0.04 mol alumina and 0.06 mol sulfate in the mixtures.

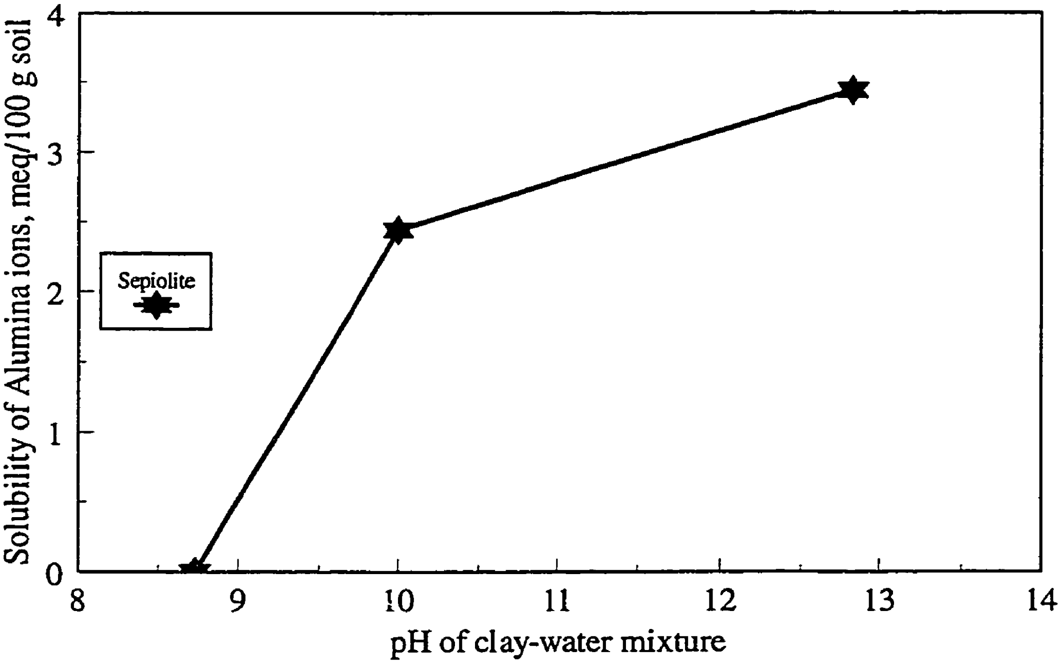


Figure 7.6: Solubility of Sepiolite at different pH.

7.4 CLAY MINERALS CONTRIBUTION TO ETTRINGITE FORMATION

As shown in Chapters 1 and 6, released alumina ions in the clay fraction constitute the main elements for ettringite formation. To investigate the possible contribution of different clay minerals on ettringite formation, two series of experiments were performed, as follows:

1) The maximum amount of releasable alumina of different clay minerals was measured through a series of digestion tests *(EPA 1979)*. Achieving pH less than 0.5 in this experiment made it possible to dissolve all releasible alumina from the clay fraction.

2) Since the quantity and the rate of releasible alumina of clay minerals is a function of pH *(Keller 1964)*, a set of experiments was conducted to investigate the amount of releasible alumina of clay minerals by variation of pH. In this series of tests, by application of *1 N NaOH* and *1 N HCl*, the different clay-water mixtures were adjusted to different pH levels. Following equilibrium, the solubility of alumina ions was measured by the use of *AAS*. The results of these experiments are explained in sections 7.4.1 and 7.4.2.

7.4.1 Total Releasible Alumina of Clay Minerals

Table 7.3 compares the results of digestion tests in terms of the measurement of total released alumina of different clay minerals. The results of these experiments indicate that palygorskite has the highest ability to release alumina ions in comparison with the different clay minerals studied in the current research. This confirms that the extent of ettringite formation might be highest when palygorskite is present in the clay fraction of soil, assuming all necessary conditions for ettringite formation are met. Even though sepiolite has a very low quantity of releasible alumina, its very noticeable water holding capacity can strongly contribute to the post-stabilization failure, as was addressed in Chapter 5. This would occur by provision of sulfate ions for chemical interaction due to the high water holding capacity of soil (Figure 5.9). The very noticeable water holding capacity of sepiolite, which is attributed to its open structure, can provide availability of sulfate ions as a necessary element for ettringite formation. The expected effects caused by the presence of other ions in the structure of palygorskite, sepiolite, and marl on soil behaviour, were previously addressed in Chapter 5.

Table 7.3: The results of digestion testing on different clay minerals.

Clay minerals	**Cations monitored in digestion experiment (meq/100 g soil)**					
	Na	**K**	**Mg**	**Ca**	**Si**	**Al**
Palygorskite	80±7	51±5	321±21	9±0.8	14±1	578±54
Sepiolite	2±0.2	10±1	1012±90	1±0.1	80±7	9±1
Marl	305±20	12±1	260±20	370±25	23±2	270±20
Illite	8±0.8	16±1	139±10	62±6	18±1	288±20
Kaolinite	5±0.8	0	0.3±0.1	0	16±1	88±7

7.4.2 Releasible Alumina of Clay Minerals at Different pH

Figure 7.6 indicates the variation of soluble alumina in sepiolite versus different pH of soil-water mixtures. As can be seen, the amount of soluble alumina of sepiolite, at the initial pH of soil, is almost zero. By adding *1N NaOH* to the soil-water mixture, the quantity of this soluble alumina increases as pH rises. In the range of pH studied, around 20% of total alumina in sepiolite is released. This may contribute to the early formation of ettringite minerals, assuming all necessary conditions are met. However, according to the results of Chapter 6 and the long-term performance of stabilized soil, most parts of the clay fraction will be solubilized. Therefore, the total quantity of alumina ions in clays, as was described in Chapter 6, seems to govern the extent of ettringite formation.

On the other hand, a possible difference exists in the quantity and rate of releasible alumina in clays (Table 7.3), which may cause a different rate of ettringite formation. Therefore different coefficients of kinetics may be expected once ettringite forms with an alumina source of different clay minerals.

7.5 FLUID RETENTION DURING ETTRINGITE FORMATION

In this section, the fluid retention potential of different soil samples will be evaluated. In addition, the effect of clay loss on the retention potential of marly soil and sepiolite will be studied. Precise evaluation of the long-term behaviour of stabilized soil with regard to ettringite formation will be accomplished by evaluating the soil fluid retention, and by assessing the minerals' transformation effects on this retention potential. In fact, these properties of soil can provide access to the sulfate and water from the environment to extend mineral transformation.

As was discussed before, the growth of ettringite, as a new mineral which forms after soil stabilization, occurs slowly. Therefore, the effect of mineral transformation on the retention potential of soil also is of interest. To investigate the role of ettringite formation on soil solute retention, artificial ettringite was formed, and its formation was confirmed by *XRD*. It was then compacted in a suction mold for measurement of fluid retention potential. To provide similar initial conditions to other suction experiments, the compaction characteristics of ettringite were measured, using a Harvard Miniature apparatus. These compaction characteristics were used to compact ettringite in a suction mold. Performing compaction testing by use of Harvard Miniature apparatus revealed the optimum water content of ettringite equals 78% and its maximum dry density equals 0.83 Mg/m^3. Therefore by application of the calibration coefficient presented in section 3.5.2, (to achieve the corresponding optimum water content and maximum dry density if the standard test is done) one will get an optimum water content of 58% and a maximum dry density of 0.89 Mg/m^3. Samples were compacted on the wet side of the compaction curve, as was shown in Chapter 3. For these experiments, Figure 7.7 compares the fluid retention characteristics of pure artificial ettringite with that of a marly sample. The standard deviation of these measurements is established based on the coefficient of variation calculated by measurement of the retention potential of 11 illitic samples at pF=0. The mean value of these measurements was 36.7, standard deviation was calculated to be 1.3, and coefficient of variation (*COV*) was calculated as 0.04. This coefficient of variation can be used to calculate the standard deviation of the fluid retention potential in suction measurement testing. It is interesting to note that this *COV* is equal to the upper limit of *COV* for compaction testing as is presented in Appendix *I*.

As Figure 7.7 shows, the fluid retention potential of ettringite is noticeably high. For instance, as can be seen in Figure 7.7, in all different pressures applied on samples, the fluid retention of ettringite is significantly higher (as much as 400%) than that of the marl sample. In other words, as ettringite grows in stabilized soil, its presence may enhance the water retention of soil, providing more sulfate for further interaction with the clay fraction of soil. This in turn strengthens the conclusion previously derived with regard to the existence of a difference between the pattern of kinetics of ettringite formation. In fact, in the post-stabilization process, one may expect to have continuous fluctuation of the molar ratio of sulfate, alumina and calcium. This will happen not only due to the variation of concentration of alumina ions over the post-stabilization period (as was addressed in Chapter 6) but also due to the variation of sulfate concentration due to the increase in fluid retention of soil as ettringite grows in stabilized soil. The process of ettringite formation and its contribution to providing more sulfate for soil additive interaction may be another justification for the pattern of the kinetics of ettringite formation in stabilized soil.

This conclusion is in good agreement with the field observation reported by *Hunter (1988)* in which in a single site in the U.S. where post-stabilization was observed, the variable degrees of mineral transformation to ettringite and thaumasite occurred at different cross sections of the site.

7.5.1 Free-Swelling Measurement of Ettringite

For further investigation of the role of ettringite on the stability of soils, the free-swelling measurements of artificial ettringite were evaluated. For this purposes, ettringite was formed and its purity was confirmed by *XRD* analysis (Appendix *III*). Following grinding of the dried ettringite, it was compacted to its maximum dry density and optimum water content in an Oedometer testing apparatus. Figure 7.8 shows the free-swelling measurement of pure ettringite in comparison with that of a palygorskite sample. By and large, there exists two major schools of thought regarding the expansion associated with ettringite formation. These are the crystal growth theory and the swelling theory *(Cohen 1983)*. While the first theory relates the expansion caused by ettringite to its crystallization pressure, the second impression attributes the expansion to the water-adsorption and swelling characteristics of ettringite *(Mehta 1973)*. The very high swelling of ettringite, which is in the order of 50%, strengthens the latter school of thought that expansion produced by ettringite formation is mainly due to its swelling or water-adsorption characteristics. Zeta potential evaluation showed that the artificial ettringite holds a negative charge. This mechanism is associated with the water holding capacity of ettringite, as was shown in Figure 7.7. Where, following ettringite formation, the fluid retention of soil increases leading to more water in soil structure. Consequently, due to the high swelling characteristics of ettringite and its high water adsorption, it swells leading to the stabilized soil failure.

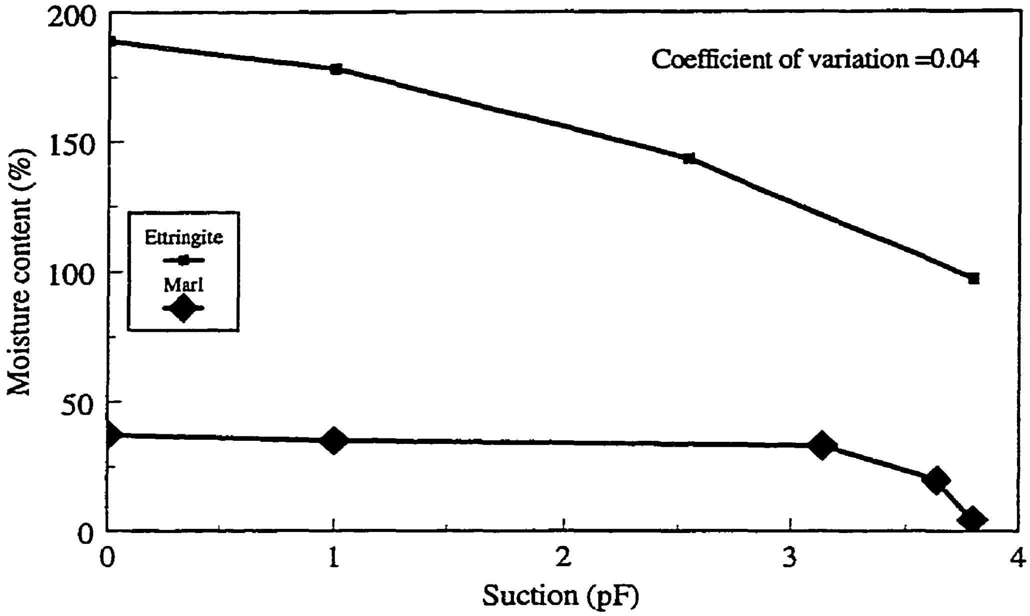


Figure 7.7: Fluid retention curve for artificial pure Ettringite in comparison to that of Marl sample.

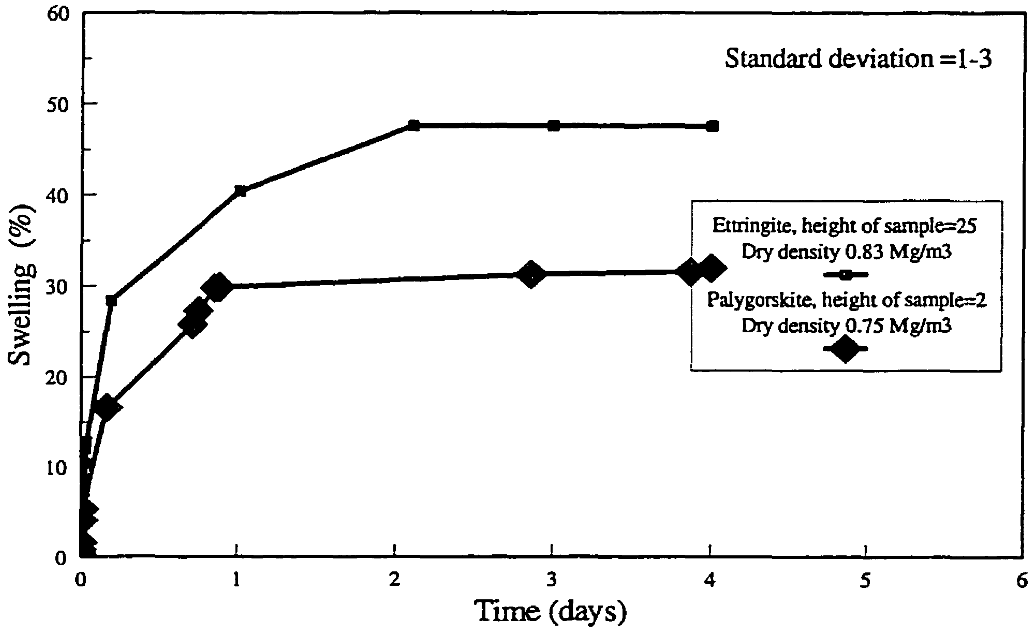


Figure 7.8: Free-swelling variation of pure Ettringite using Oedometer testing.

7.5.2 Differentiation of the Performance of Cement and Lime

The achievement of conditions necessary for ettringite formation is associated with provision of sufficient water in the stabilized soil. The fluid retention of soil can play an essential role in this matter. It can also help with the availability of sulfate ions for soil additive interactions. Therefore, even though one may achieve an improvement in geotechnical responses of soil without considering the extent of fluid retention of soil, the extent of water capacity may play a critical role in the long-term performance of a stabilized soil.

Figure 7.9 compares the fluid retention potential of stabilized marl, when two series of stabilized marl samples are compared with an un-stabilized marl sample. In this series of experiments two set of marl samples were stabilized by 4% cement and 4% lime, respectively. No curing condition was applied to the samples. After dry mixing of soil and additives, distilled-water was added to the soil samples. Following a further mixing period, the samples were compacted in suction molds and fluid retention was monitored at different suction potentials. To increase the accuracy of the results, each soil-additive mixture was prepared separately for each individual mold. As can be seen in Figure 7.9, the stabilized marl with 4% lime indicates a higher water retention than that of stabilized marl with 4% cement. It is quite significant that the sample stabilized with 4% lime shows an even relatively higher fluid retention than that of the unstabilized marl. In some steps of the experiments, the fluid retention of a sample stabilized with 4% lime, goes up to around 20% more than that of stabilized marl with 4% cement. *XRD* performed on these samples indicated no ettringite formation. This can be related to either the non-existence of a curing condition, as explained in Chapter 6, or the absence of sufficient water due to the application of external air pressure for removal of water as part of the test procedure. Both factors may prevent or delay the extent and rate of ettringite formation.

Based on above explanation, the higher fluid retention of stabilized marl with lime in comparison with that of a sample stabilized with cement, can be related to the soil structure after lime treatment in which the cementation action provides "carbonate-type" bonding for flocculated and agglomerated soil particles. To confirm this conclusion, the Atterberg limits of these samples were measured. In spite of the test procedure employed in Chapter 6, in which Atterberg limits were performed directly following the curing period, in this part, after the application of additives and a waiting period, samples were dried and sieved. Then, the Atterberg limit tests were performed on these samples. Since each suction measurement takes around one month, a one week waiting period was employed for performance of Atterberg limit testing following the preparation of samples. During this time interval, no curing was performed on samples. Table 7.4 shows the results of these experiments. A comparison between data presented in Table 7.4 and Figures 6.1 and 6.2 where curing was applied to samples, indicates that a curing condition plays an essential role on the results of Atterberg limits testing. Achieving a high liquid limit upon stabilization in soils with moderate liquid limit, as was explained in Chapter 6, is influenced by curing conditions. For instance, the application of 10% additives in uncured samples, will not reach the same range of liquid limit as a sample stabilized with 2% lime and cured one week (Table 7.4 and Figure 6.1). As Figure 6.1 indicates, the liquid limit for a sample stabilized with 2% lime and cured one week is 70.2, which is higher than all data achieved in the results shown in Table 7.4 for uncured samples. These differences may be attributed to more progress of chemical interaction of soil-additives in cured samples which provides "carbonate-type" bonding (section 2.8.1) for the flocculated structure. In other words, due to the ion exchange effects in the longterm performance of soil-additive interactions which are governed by the dissociation of the $Ca(OH)_2$ into Ca^{2+} and OH^- ions, the electrical surface forces of the clay minerals are being modified. This creates the occurrence of the flocculated structure. Afterwards, the "carbonate-type" bonding for the flocculated structure forms, where it provides the ability for the new structure of soil to retain more water. Two other points should be kept in mind. First, the possible role of ettringite minerals on the results indicated in Figures 6.1 and 6.2, and secondly, the difference between the procedure of these two series of experiments, in which a part of the cementation between particles is broken, upon drying, grinding and sieving of stabilized samples evaluated in Table 7.4.

Another difference between the role of cement and lime in marl stabilization is the achievement of a higher liquid limit and plasticity index for samples stabilized with lime in comparison with those stabilized with cement. One may conclude that achieving higher pH in lime stabilization in comparison to that of cement stabilization, when similar percent of additives is used (Figure 6.6), provides more calcium ions to modify the electrical surface forces of the clay minerals. Furthermore the extent of the previously mentioned carbonate-type bonding for flocculated particles increases leading to more water being trapped in the soil structure of lime treated soils. This finding is in good agreement with the results of fluid retention (Figure 7.9) in which samples stabilized with lime, show higher fluid retention than samples stabilized with cement.

In addition to the above discussion, the results and explanation pointed out in section 6.2.3 confirm that cement has a better influence on stabilized marl performance. This may be attributed to the high strength achieved from hydration products of soil-cement interaction as explained in the Section 2.8.2. On the other hand, the higher fluid retention of marl stabilized with lime, may provide a larger quantity of water and sulfate to chemically react with the soil and stabilizer agents. This will enhance the possibility and extent of ettringite formation for a sample stabilized with lime in comparison with that stabilized with cement.

Table 7.4: Atterberg limits of stabilized marl with cement and lime.

Soil Sample	**Atterberg Limits**	
	Liquid Limit	**Plasticity index**
Marl	45.8	24.4
Marl & 2% Lime	58.3	30
Marl & 10% Lime	62	32.6
Marl & 2% Cement	47	21
Marl & 10% Cement	39.7	12.7

7.5.3 The Role of a Stabilizer upon Zeolitic Water

To investigate the role of a stabilizer on the zeolitic water performance, a series of fluid retention measurements were performed on a sample stabilized with sepiolite. To take, as much as possible, into account only the role of the stabilizer on the zeolitic water behaviour, it was decided to prevent ettringite or thaumasite formation during the test period. For this purpose, no curing condition was applied to samples. Performing *XRD* on samples following fluid retention measurement indicated the achievement of this decision. Figure 7.10 represents the results of this series of experiments when pure sepiolite samples are stabilized by 4% lime and 4% cement, respectively. Comparing the fluid retention behaviour of sepiolite stabilized by cement and lime, indicates relatively higher fluid retention of samples containing lime in comparison with those of samples containing cement. This performance, which is similar to the pattern shown in Figure 7.9, strengthens the conclusion made in section 7.5.2. Furthermore, comparing the fluid retention potential of sepiolite and mixtures of sepiolite/additives indicates a decrease of around only 60% in water content, following the application of stabilizer agents. In other words, stabilizer agents have not completely controlled the zeolitic water influences of sepiolite over the stabilization process. This in turn makes questionable the use of cement and lime as additives for controlling zeolitic water performance of sepiolite and presumably palygorskite. The same pattern of high fluid retention of stabilized marly soil by cement and lime (Figure 7.9) in which the water capacity of soil is not well controlled by the application of additives supports this conclusion.

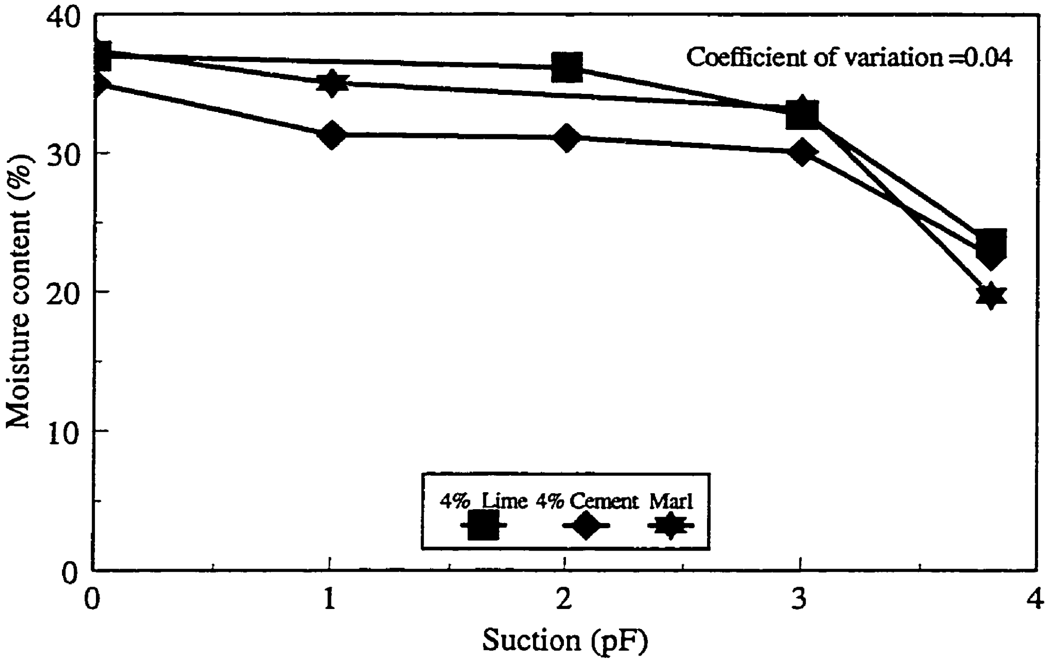


Figure 7.9: Fluid retention curves for Marl samples stabilized by 4% Lime and 4% Cement, respectively.

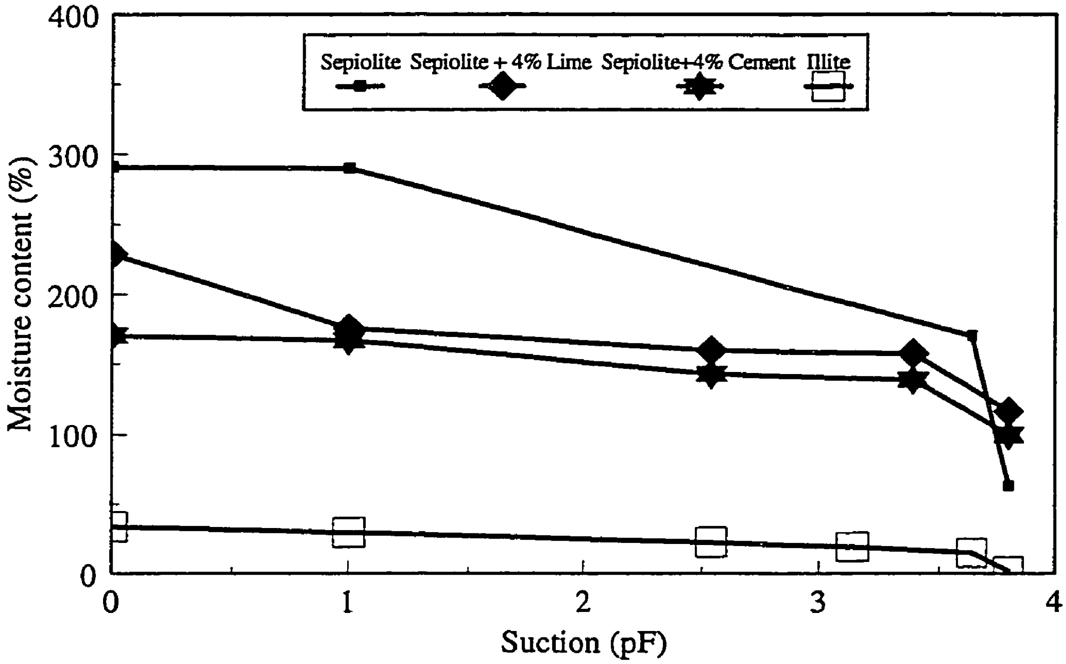


Figure 7.10: Fluid retention curves for Sepiolite and stabilized Sepiolite by 4% Cement and 4% Lime, respectively.

7.6 LEACHING BEHAVIOUR OF MARLY SOIL

The leaching behaviour of unstabilized and stabilized marl are examined to study the possible interaction of chloride ions, clay fraction, and lime. For this purpose, a series of mixtures of marl and silica sand were prepared. Silica-sand passing sieve No. 16 was chosen to decrease the time required for passing several pore volumes of distilled-water during the leaching process. A mixture of 40% marl and 60% sand was used as a blank sample. Two more samples were studied which were mixed with 4% lime and 2% artificial ettringite, respectively. The passing of each pore volume took several weeks. Figure 7.11 indicates the relative chloride concentration in the effluent collected during the leaching process in relation to the cumulative pore volume. On the vertical axis, C/C_o represents the ratio of the effluent chloride concentration C to the initial concentration of the soil C_o. The cumulative pore volume indicates the cumulative volume of water which passes through the sample during the leaching process.

7.6.1 Leachability of Chloride Ions in Stabilized Soil

The chloride concentrations in the collected effluent are seen to increase slowly in unstabilized marl. On the other hand, in the two samples mixed with lime and ettringite, respectively, the chloride concentration in the collected effluent is observed to increase sharply in the early pore volumes. For instance, in the blank sample (soil sample without any additive) all chloride is discharged after passage of 15 pore volumes. However, in the two other mixtures of marl and additives after passage of one pore volume all chloride ions are discharged. Furthermore, it was observed that the time required for passage of one pore volume in unstabilized marl (few weeks) was much smaller than that in marl and additive mixtures (few months). The slow movement of chloride ions in the marl sample can be attributed to the zeolitic water effect of palygorskite. A previous study by *Warith (1987)* showed that all chloride ions passed through the illitic and kaolinite samples after around three pore volumes. By adding additive to the marl sample as was explained in section 7.5.2 and 7.5.3, a part of the zeolitic water role of accumulating different ions and water, is overcome. In this case the behaviour of soil in the leaching process got close to the soil containing plate-shaped type of mineral particles (i.e. illite and kaolinite). In addition, a high pH reaction will solubilize a part of palygorskite fraction of soil (as it was discussed in Chapter 6), and in this manner part of the zeolitic water effects of palygorskite will be eliminated. Even though the possibility for formation of trichloride-alumina-hydrate was addressed in Chapter 2, the very quick discharge of chloride ions indicates that there did not exist a noticeable interaction for its possible formation.

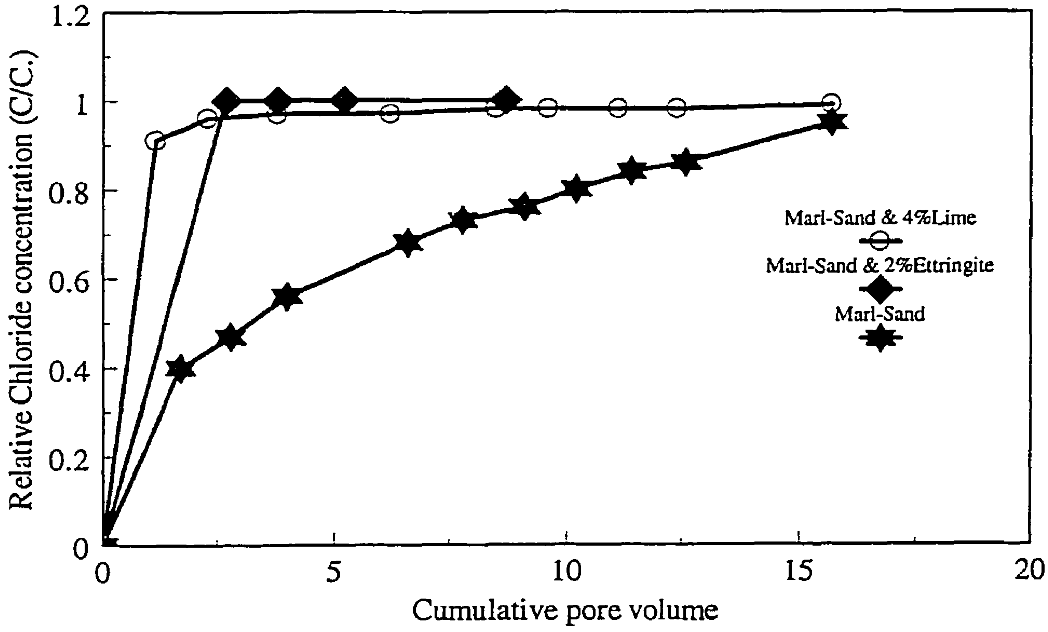


Figure 7.11: Relative Chloride concentration in effluents collected during leaching in distilled-water, Marl as it is, Marl & 2% Ettringite, Marl & 4% Lime.

7.7 SUMMARY

A set of *XRD* tests were performed to investigate the kinetics of ettringite formation when different sources of material are used to supply the major elements of ettringite. The kinetics of ettringite formation were compared in three different cases. It is shown that while the values of equation coefficients representing kinetics of artificial ettringite lie within the range predicting the rate of artificial ettringite growth to be diffusionally controlled. In soil stabilization, the rate of ettringite formation is much slower than that of artificial ettringite. In addition, in soil stabilization the rate of ettringite formation is governed by the role of surface area over its process of formation. In this Chapter, the role of concentration variation of ettringite's major elements on its formation, is investigated. The results indicated that the formation of ettringite seems to be more sensitive to the variation of available sulfate and alumina ions rather than calcium concentration. This conclusion once again, as indicated in Chapter 6, confirms that choosing the appropriate percentage of additives for soil stabilization when the formation of ettringite is in doubt, should be made by use of a physico-chemical evaluation rather than simply by mechanical assessment.

The extent and importance of the contribution of different clay minerals to ettringite formation was investigated through a series of digestion and fluid retention tests. Among several clay minerals studied in this research, it is shown that palygorskite has the highest ability to contribute to the ettringite formation. Fluid retention studies by the use of suction experiments revealed the different roles of cement and lime on the zeolitic water performance. Furthermore, in terms of the fluid retention potential of soil, it was observed that the application of cement and lime did not completely control the role of zeolitic water. In addition, in this Chapter some geo-environment characteristics of artificial pure ettringite were addressed. Finally, the leaching performance of stabilized marly soil in regards to leachability of chloride ions was investigated.

CHAPTER 8
SUMMARY AND CONCLUDING REMARKS

8.1 SUMMARY

This thesis investigated the role of marl components and ettringite mineral on the stability of marly soils. The use of lime and/or cement in the stabilization of marl can often lead to adverse results in the post-stabilization periods. The presence of palygorskite or sepiolite in marl, contributes significantly to its unique behaviour, and also to the problems which arise in the post stabilization stage. Whereas the presence of salts and sulfates in marl soil is important in the establishment or development of stability, these can contribute to the extent of mineral transformations after stabilizing the soil.

This study has focused on the development of ettringite, an expansive mineral, which forms from the transformation of the palygorskite clay fraction in the marl soil as a result of post stabilization circumstances in the presence of lime and cement as stabilization agents. Ettringite produces high swelling, which can be in the order of up to 30 centimetres in roads constructed from stabilized marl. Reactions between lime, alumina (released from the clay fraction of soil) and sulfates present in the soil pore fluid can cause the formation of ettringite. These reactions have been responsible for the failure of several soil stabilization projects.

In this study, the roles of palygorskite, sepiolite, and pore fluid chemistry on marly soils behaviour have been evaluated in relation to the development of stability or instability (failure) of the stabilized marl.

A literature review was conducted in this research and a summary of that was addressed in ***Chapter 2*** and revealed a strong need for conducting physico-chemical research regarding evaluation of these kinds of post-stabilization failures. ***Chapter 3 addressed*** the materials and experimental methods used in this study. Chapters 4, 5, 6, and 7 include the results and discussions of this investigation. In the following, a summary of the investigation presented in Chapters 4 through 7 are pointed out.

Chapter 4 covered the necessary criteria for quantitative *XRD* analysis of marly soils and ettringite. This Chapter included two major parts.

1) In the first part of Chapter 4, through the experimental studies, current *XRD* techniques for quantitative mineral analysis are evaluated. The accuracy of these methods are investigated by the preparation of a series of artificial soil mixtures. By performing *XRD* analysis on these artificial samples, the deficiencies involved in the quantitative analysis using areas under peaks are explained. Analyses based on identical mass adsorption are investigated and it is shown that this method is not capable of quantitatively analysing artificial mixtures having sepiolite and palygorskite. The problems involved in the use of only major reflected lines in the quantitative mineral evaluation is addressed. Then mineral diagnosis using the internal and external standard methods are investigated. It was shown that by application of the external standard method, and aim of only the major reflection line, palygorskite shows a lower peak intensity in its major basal spacing when compared to sepiolite, leading to underestimation of its presence in the mineral quantification when this method is used. Through the calculation of the coefficient of correlation, the poor accuracy of these methods in the evaluation of an artificial multi-phase system of marly soils is addressed.

2) Finally in Chapter 4, a quantitative *XRD* method for marly soils and ettringite is proposed. The theoretical basis of the proposed quantitative *XRD* analysis is based on the relationship established between the intensity and the absorption coefficient of the soil sample as suggested by *Klug and Alexander (1954)* and *Brindley (1961)*. By introducing a coefficient defined as the "average weighted intensity" and by use of the reflection lines with an intensity weighting factor of equal or more than 30, the above mentioned

theoretical basis is developed. By performance of *XRD* on a series of artificial marly samples having ettringite, a series of practical graphs for *XRD* mineral quantification of marly soils and ettringite is presented. Validation of these established graphs for *XRD* quantification were investigated by the use of 6 artificial mixtures of palygorskite, sepiolite, calcite, kaolinite and ettringite. The coefficient of correlation found between predicted and quantity of minerals present in the mixtures was 90%.

Chapter 5 comprised four major aspects of marly soils behaviour before stabilization, as follows:

1) In the first part of Chapter 5, several *CEC* measurement methods were used on marl samples. By the use of illitic soil as a control sample, it was observed that these common methods lead to incorrect results in the *CEC* measurement of marly soil. This is attributed to the zeolitic water performance of palygorskite and the presence of sulfate in pore fluid of marl. A refinement in the barium-chloride method for *CEC* measurement of this type of soil, specifically when potential determining ions presents in soil pore fluid, is suggested.

2) In the second section of Chapter 5, the results of *X-ray* tests indicate that the clay fraction of marl is dominated by the presence of palygorskite. By application of the proposed method based on several soil washing processes, pure palygorskite clay mineral was extracted from marly soil where its purity was confirmed by *XRD* analysis. This helped to investigate the role of pure palygorskite on the marl performance. The general applicability of the suggested method for separating different fractions of soil was confirmed by separating pure illite from illitic soil which is rich in calcite and other clay minerals.

3) In the third part of Chapter 5, the role of marl components on its behaviour is evaluated. By conducting a set of physico-chemical tests, the fundamental performance of sepiolite and palygorskite as distinguished clay minerals was investigated. In other clay minerals there is a relation between soil cation exchange capacity (*CEC*), specific surface area (*SSA*), and water sorption capacity. For instance, as the *CEC* and *SSA* increase, the

water sorption capacity of soil increases. However, sepiolite and palygorskite in spite of their low *CEC*, show high surface area and fluid retention in comparison with the fluid retention of other clay minerals which is attributed to the zeolitic water performance. Following application of modified barium-chloride method, as an extractable solution, sodium was observed as the main exchangeable cation of palygorskite in which the exchangeable sodium percentage (*ESP*) was more than 50%. This suggests that even before stabilization, palygorskite may be one of the significant sources of marl dispersivity performance.

4) Finally in Chapter 5, based on performing a literature review and the experimental results of this research, which indicate the noticeable performance of palygorskite and sepiolite, a new classification for marly soils is presented. This classification focuses attention on the presence of palygorskite or sepiolite as the major fractions of marl which control marl behaviour. It is speculated that the very noticeable fluid retention of palygorskite and sepiolite, chemistry of pore fluid and presence of *PDI* in conjunction with high swelling performance of these minerals, contribute to the instability of marl before stabilization. In addition after stabilization, the very noticeable pore fluid holding capacity of marl which can accommodate sulfate in the zeolitic water of palygorskite/sepiolite and the high alumina content of palygorskite, can strongly contribute to the post stabilization failure of marl by formation of ettringite mineral.

Chapter 6 discussed the mineral transformation of palygorskite, and ettringite development in stabilized marl. This Chapter covers soil stabilization evaluation from the mechanical, chemical, and mineralogical aspects. Three criteria have been used to evaluate the stability of the stabilized marl soil. These include, pH evaluation, Atterberg limit variation, unconfined compressive strength, and/or *CBR* testing. The results of this Chapter indicate that the general geotechnical mechanical/physical criteria used to evaluate stabilized soil performance may not be reliable for the evaluation of stabilized marl because of the possible formation of ettringite and its resultant behaviour. A set of physico-chemical studies which include specific surface area measurements (*SSA*), and *x-ray* diffraction (*XRD*) are needed for a more complete and realistic evaluation of the long-term stability of stabilized marl. Finally the necessary conditions for ettringite formation and its stability are investigated.

Chapter 7 included the evaluation of kinetics of ettringite and fluid retention of stabilized marl and ettringite. This Chapter consists of four major parts.

1) In the first part of Chapter 7, the major differences of kinetics of ettringite when artificially formed are compared with that of stabilized soil. It is shown that when the kinetics of artificial ettringite formed from different sources is diffusionally controlled, in soil stabilization the rate of its formation and growth is governed by surface area. Then the role of sulfate, alumina, and calcium on the ettringite formation was investigated. It was observed that in all different mixtures of samples producing artificial ettringite, the maximum value of ettringite's *XRD* peak was achieved when the concentration of elements lies in accordance with the stoichiometric concentration of these elements. Moreover, in this series of experiments the formation of ettringite was found to be more sensitive to the variation of available alumina and sulfate ions rather than calcium concentration.

2) In the second part of Chapter 7, the contribution of different clay minerals on ettringite formation is investigated. This was performed by evaluation of the total releasible alumina of clay minerals and releasible alumina of clays at different pH. Among the clay minerals studied, palygorskite was found to be richest in alumina, providing the highest source of alumina for ettringite formation.

3) In the third part of Chapter 7, the noticeable fluid retention and swelling of ettringite is addressed. In terms of fluid retention, the performance of stabilized soil by cement and lime is compared and the role of stabilizer agents upon zeolitic water are investigated.

4) Finally in the last part of Chapter 7, the leaching behaviour of marly soils with a significant attention to the availability of chloride ions over the leaching period was investigated. That was done by analysing the concentration of chloride in effluent, after

passing of different pore volumes of solution through the soil leaching column. This element usually exists in a marl environment and is known to affect the extent of ettringite formation.

8.2 CONCLUDING REMARKS

The main concluding remarks which were derived from this research can be summarized as follows:

1. Soil washing technique has the ability to separate different fraction of soils. Specifically the separation of pure clay fraction from calcite was achieved and confirmed by *XRD*.

2. The role of soil fabric has to be considered in the clay identification by *XRD*. For instance, in marly soil it was observed that the role of salt on soil fabric will not only affect the magnitude of the reflection lines of the palygorskite, it also alters the intensity of mineral's peaks. In such a case, soil washing will provide a more oriented soil structure which has the highest possibility for achieving theoretic reflection lines. The use of parallel physico-chemical experiments jointly with *XRD* in clay identification, will help to decrease the possibility of identifying minerals by mistake. As an example, the basal spacing of palygorskite in salty marl was observed to be 10.07 angstrom (around that of illite) which increased to 10.4 after several soil washing. The latter basal spacing corresponds to the theoretical value for palygorskite.

3. In clay mineral identification by *XRD*, the use of parallel experiments, including soil characteristic evaluation, are strongly suggested. This will help to avoid common mistakes in soil mineral identification which occur due to the similarity of reflection lines of minerals. As an example, for a soil sample from which during the treatment process the amorphous and organic materials are removed, and known to be rich in illite and quartz (very common in soils in eastern Canada), the very low surface area or *CEC*, will

confirm that soil is mainly rich in quartz rather than illite. Even though in such a case the first major reflection line of quartz might be mistaken for illite's reflection line. It is noticeable that in some illitic soils, the major reflection line is known to be around 3.35 angstrom instead of 10 angstrom. Specific surface area measurement, *CEC* evaluation, Atterberg limit testing and soil classification can strongly help to avoid these significant sources of error.

4. Among the clay minerals studied in this research, it was observed that palygorskite has the highest ability to release alumina ions in a high pH environment. Even though sepiolite has a very low quantity of releasable alumina, as one of the major elements for ettringite formation, the high water holding capacity of sepiolite, providing sulfate ions for chemical interaction, contributes to the post-stabilization failure caused by ettringite formation. This noticeable water holding capacity is attributed to the open structure of these minerals.

5. The very common method of soil stabilization, which focuses attention on the mechanical aspects of soil performance, is not capable of evaluating the failures and instability of stabilized marl due to ettringite formation.

6. Ettringite formation, whose presence appears in *XRD*, could explain the conflicting results between mechanical and physico-chemical evaluation of soil stabilization. Furthermore, the observation of high swelling of pure ettringite which was measured in the order of 50%, strengthens this school of thought that expansion produced by formation and presence of ettringite is mainly due to the swelling and water-adsorption characteristics of ettringite.

7. Palygorskite and sepiolite minerals significantly control marl behaviour. Therefore, their presence in combination with carbonate makes the clay-carbonate more distinguishable than any other clay-carbonate mixtures. From this view point, no combination of clay-carbonate will be considered as marly soil, but the presence of palygorskite or sepiolite would be necessary to expect the common instability of marly soils. In this relation, the proposed mechanistic model is able to explain the changes in

the integrity of the compacted natural marly soils caused by their wetted-state (i.e. the simultaneous collapsible, dispersive, and swelling behaviour of marly soils in their compacted natural state following wetting).

8. For quantitative clay mineral identification by *XRD*, the use of all major reflection lines of minerals having a weighting factor equal to or more than 30, provides good agreement between the computed and the real quantity of each mineral present in the artificial marly soil and ettringite samples.

9. The kinetics of artificial ettringite formation using alumina sulfate follows the pattern of its formation when tri-calcium aluminate is used as a source of ettringite formation. Even though in the former case ettringite forms faster, in both cases the rate of ettringite growth is diffusionally controlled. In soil stabilization it was observed that the rate of ettringite formation is controlled by the surface area in chemical interaction.

10. The formation of ettringite was found to be more sensitive to the variation of available sulfate and alumina ions rather than the calcium concentration. This is particularly significant in terms of the importance of the physico-chemical evaluation of soil stabilization rather than the mechanical/physical assessment when sulfate is present in the pore fluid of soil.

11. In terms of controlling fluid retention of soil and the role of *PDI*s, cement shows a better influence on stabilized marl performance in comparison to lime. Stabilized marl by lime has a higher fluid retention than that of cement. The slaking behaviour follows the same pattern.

12. Over the post-stabilization period, the very time dependent pattern of releasable alumina and silica fraction of clay soils provides a very flexible and variable molar ratio of major elements required for ettringite formation. This may directly affect the extent and rate of ettringite formation in soil stabilization. In such a case, the common established molar ratio for ettringite formation, in cement hydration, is not applicable in soil stabilization evaluation.

8.3 STATEMENT OF ORIGINALITY

The major contributions and originality derived from this research are as follows:

1. Prior classifications of marly soil were developed and a new classification for marly soils is presented.
2. The impact of structural changes of stabilized marl on its performance are assessed. In this matter, some basic aspects and physico-chemical characterization of palygorskite, sepiolite and ettringite are quantitatively presented. The possible contribution of palygorskite and sepiolite to the post-stabilization failure due to ettringite formation was investigated.
3. An experimental *XRD* analysis method was developed for marly soils and ettringite. A series of practical graphs for quantification of mineral transformation in marly soils and ettringite formation are suggested.
4. A soil washing method to extract pure palygorskite or clay fraction from the soil mixture was developed and validated by *XRD* analysis.
5. The deficiency of the current mechanical-geotechnical evaluation method of soil stabilization are experimentally indicated. It was shown that physico-chemical investigation including *XRD* analysis is the best and mandatory tool for evaluating stabilized soil performance when lime or cement are used as a stabilizer agents and sulfate is present in the pore fluid of soil or soil environment.

8.4 SUGGESTIONS FOR FURTHER STUDIES

By and large, the study of the formation and role of ettringite on the stability of soils has received little attention within international soil literature. In other words, still many aspects remain to be investigated. Further research can be performed on the following issues:

1. The role of amorphous materials on the early formation of ettringite can be studied by preparation of artificial samples and use of *XRD*. In Chapter 6, some major key points have already being addressed.
2. Sepiolite due to its high quantity of silica may be critical due to the formation of thaumasite $\{Ca_6[Si(OH)_6]_2.(CO_3)_2.(SO_4)_2.24H_2O\}$ following soil stabilization. The extent and rate of thaumasite formation and its contribution to the deterioration of stabilized soil has not been investigated yet.
3. Quantitatively investigating the role of chloride ions on the magnitude and kinetics of ettringite formation can be another issue for future studies.

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Appendix I

ERROR ANALYSIS

I.1 INTRODUCTION

This section includes a brief application of the formulation used for error analysis in the evaluation of experimental results of this research. Most of this Appendix is cited from two references by *Ang & Tang (1975)* and *Harr (1977)*.

I.2 THE NORMAL DISTRIBUTION

The best-known and most widely used probability distribution is the normal distribution. The normal distribution has a probability density function given by :

$$f_x(x)=\frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right]\quad -\infty<x<\infty \tag{I.1}$$

where μ and σ are the parameters of the distribution of the variate, which are also the mean and standard deviation, respectively. A normal distribution with parameters $\mu=0$ and $\sigma=1.0$ is known as the standard normal distribution

I.2.1 Mean or Expected Value, Variance and Standard Deviation

The mean or expected value is the weighted average of the different values of the random variable which may be associated with different probabilities or probability densities. Therefore, if X is a random variable with a probability mass function (PMF) $p_x(x_i)$, its "weighted" average value, denoted as E(X), is:

$$E(X)=\sum_{all\,x_i} x_i p_x(x_i) \tag{I.2}$$

Similarly, for a continuous random variable X with a probability density function $f_x(x)$, the mean value is as follows:

$$E(X)=\int_{-\infty}^{\infty} x f_x(x)dx \tag{I.3}$$

The next most important quantity of a random variable is its measure of dispersion or variability. That is, the quantity which gives a measure of how closely the values of the variate are clustered (or conversely, how widely they are spread) around the central value. The variance which is a measure of such a dispersion is calculated as follows:

$$Var(X)=\sum_{all\,x_i} (x_i-\mu_x)^2 p_x(x_i) \tag{I.4}$$

in which μ_x=E(X). In other words, it is simply the weighted average of squared deviations. If X continues with probability density function of $f_x(x)$, the variance is as follows:

$$Var(X)=E[(x-\mu_x)^2]=\int_{-\infty}^{\infty}(x-\mu_x)^2 f_x(x)dx \tag{I.5}$$

Dimensionally, a more convenient measure of dispersion is the square root of the variance, or the standard deviation σ which is as follows:

$$\sigma_x=\sqrt{Var(X)} \tag{I.6}$$

Since, solely on the basis of the variance or standard deviation, it is hard to say whether the dispersion is large or small, the measure of dispersion relative to the central value is more useful. In other words, whether the dispersion is large or small is meaningful only relative to the central value. For this reason, the coefficient of variation (COV), is defined as follows:

$$COV=\frac{\sigma_x}{\mu_x} \tag{I.7}$$

This is often a preferred and convenient non-dimensional measure of dispersion or variability.

The other parameter used in the evaluation of experimental results is the correlation factor which is defined as follows:

$$r=\frac{SS_{xy}}{\sqrt{SS_x SS_y}} \tag{I.8}$$

in which SS_x and SS_y are variances calculated similar to Equation I.4, and SS_{xy} is the co-variance of the data which can be calculated as follows:

$$SS_{xy}=\frac{\sum_{i=1}^{n}(x_i-\underline{x})(y_i-\underline{y})}{N} \tag{I.9}$$

I.2.2 Mean and Variance of a Linear Function

Assuming the linear function as $Y=aX+b$, where a and b are constants. Then according to Equation I.3, the mean value of Y is the mathematical expectation of $aX+b$, or

$$E(Y)=E(aX+b)=\int_{-\infty}^{\infty}(aX+b)f_x(x)dx=a\int_{-\infty}^{\infty}xf_x(x)dx+b\int_{-\infty}^{\infty}f_x(x)dx=aE(X)+b \tag{I.10}$$

whereas the variance of Y according to the Equation I.5 is as follows:

$$Var(Y)=E[(Y-\mu_y)^2]=E[(aX+b-a\mu_x-b)^2]=a^2\int_{-\infty}^{\infty}(x-\mu_x)^2 f_x(x)dx=a^2Var(X) \tag{I.11}$$

Furthermore, if $Y=a_1X_1 \pm a_2X_2$, where a_1 and a_2 are constants, then similar to the above derivation, one will get:

$$E(Y)=a_1E(X_1)\pm a_2E(X_2) \tag{I.12}$$

That is, the expected value of a sum is the sum of the expected values. The corresponding variance is:

$$Var(Y)=a_1^2Var(X_1)+a_2^2Var(X_2)\pm 2a_1a_2Cov(X_1,X_2) \tag{I.13}$$

If X_1 and X_2 are statistically independent, $Cov(X_1,X_2)=0$ and the latter Equation reduces to:

$$Var(Y)=a_1^2(X_1)+a_2^2Var(X_2) \tag{I.14}$$

I.2.3 Mean and Variance of a General Function

For a general function of a random variable X, in which $Y=g(X)$, according to Equation I.3 and I.5, the mean and variance would be:

$$E(Y)=\int_{-\infty}^{\infty}g(x)f_x(x)dx \tag{I.15}$$

and

$$Var(Y)=\int_{-\infty}^{\infty}[g(x)-E(Y)]^2f_x(x)dx \tag{I.16}$$

To obtain the mean and variance of the function Y with the above relations, information on $f_x(x)$ is needed. In many applications, however, the density function $f_x(x)$ may not be known, information may be limited to the mean and variance of the original variate X. Furthermore, even when $f_x(x)$ is known, the integration indicated above may be difficult to perform. For these reasons, the approximate mean and variance of the function Y would be particularly useful and may be obtained as follows. If one expands g(X) in a Taylor series about the mean value μ_x, one will follow:

$$Y=g(\mu_x)+(X-\mu_x)\frac{dg}{dX}+\frac{1}{2}(X-\mu_x)^2\frac{d^2g}{dX^2}+\dots \tag{I.17}$$

where the derivatives are evaluated at μ_x.

If the series is truncated at the linear terms, one obtains the first-order approximate mean and variance of Y as follows:

$$E(Y)\approx g(\mu_x) \tag{I.18}$$

and according to the Equation I.11, and having g(μ_x) and μ_x as a constant, one will get:

$$Var(Y)\approx Var(X-\mu_x)(\frac{dg}{dX})^2\approx Var(X)(\frac{dg}{dX})^2 \tag{I.19}$$

In the general case, if Y is a function of several random variables, that is

$$Y=g(X_1,X_2,\dots,X_n) \tag{I.20}$$

similar to the previous derivation one can get the mean and variance of Y as follows:

$$E(Y)\approx g(\mu_{X1},\mu_{X2},\dots,\mu_{X3}) \tag{I.21}$$

which says that the mean of the function is equal (approximately) to the function of the means; and

$$Var(Y)\approx\sum_{i=1}^{n}(\frac{\partial g}{\partial X_i})^2 Var(X_i) \tag{I.22}$$

assuming the variables are independent and consequently the covariances are zero.

The coefficient of variation (COV=$\sigma/\underline{x}$) that is likely to occur in the results of certain common tests, is shown in Table I.1 (*Stamatopoulos 1985*). These coefficients of variation may be used to calculate the quantity of σ for the above formulation.

Table I.1: Typical values of the coefficient of variation *V* for Laboratory results.

Property	**Range of V**
Natural water content	0.15-0.63
Liquid limit	0.12-0.40
Modulus of compressibility	0.18-0.65
Coefficient of consolidation	0.56-1.01
Unconfined compressive strength	0.41-1.00
Unconsolidated undrained triaxial compressive strength	0.22-0.51
Percentage fines (fraction passing sieve no 200)	0.12-0.87
Organic content	0.76-0.93
Maximum dry density from compaction test	0.02-0.04
Specific gravity of solids	0.01-0.02

I.3 CONFIDENCE LIMITS

From the study of sample statistics, μ ($\mu=\Sigma X_i/N$) and σ ($\sigma^2=\Sigma(X_i-\mu)^2/N$) are representative of the best estimates of the population parameters. In which N is the sample size. However, the sample parameters will not exactly be equal to those of the population. An interval estimate, which provides a measure of the possibility that a parameter lies within a certain interval of values, is called confidence limits. On the other hand, this leads to the definition of confidence levels (i.e. 90% confidence which is used in this research). Confidence level is the measure of the reliability of the confidence interval which includes the population parameter under study (i.e. interval between lower confidence level, L, and upper confidence level U). Therefore, the confidence level, q, that a parameter p will be included in the interval L to U is as follows:

$$P[L \le p \le U] = 1 - \alpha = q \tag{I.23}$$

The choice of the value of q is a matter of the risk that one is willing to take in accepting an erroneous value of a parameter. The value of α is the probability that the interval L to U will not include the parameter.

I.3.1 Confidence Intervals for μ (σ Known)

When sampling from a normal population with unknown mean, μ, and known variance σ^2, one obtains the expected value of the sample, $\underline{X}$, which has a standard deviation of σ/N. Hence the variable,

$$Z = \frac{X - \mu}{\sigma/\sqrt{N}} \tag{I.24}$$

has a standardized normal distribution, and

$$P[-Z_{\alpha/2} \le Z \le +Z_{\alpha/2}] = 1 - \alpha = q \tag{I.25}$$

where $-Z_{\alpha/2}$ and $+Z_{\alpha/2}$ are tails representing the areas under the standardized normal curve. For instance, by assuming a confidence level of q=0.90%, and using Equation I.23 in which, $1-\alpha=0.90$, one will get $\alpha=0.1$. Then by use of Table I.2, the area up to point Z will be $0.5-\alpha/2=0.5-0.1/2=0.45$. Finally by finding the quantity of area equals 0.45 and by use of Table I.2, one can read the quantity of $Z_{\alpha/2}$ to be equal to 1.64.

By combination of the Equations I.24 and I.25, one can come up with the following Equation:

$$P[(X - Z_{\alpha/2}\sigma/\sqrt{N}) < \mu < (X + Z_{\alpha/2}\sigma/\sqrt{N})] = 1 - \alpha = q \tag{I.26}$$

Equation (I.26) is valid for any sample size given that σ is known, and the parent population is normal.

I.3.2 Confidence Intervals for μ (σ Unknown)

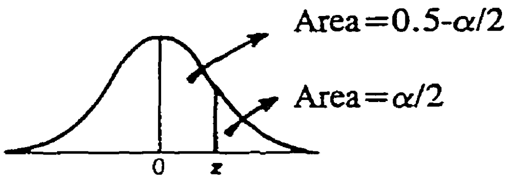
When sampling from a normal distribution with unknown variance, it can be shown that the random variable $(\underline{X}-\mu)/(s/\sqrt{N})$, where s=standard deviation of the sample, has a *t*-distribution (Student's *t*-distribution, Table I.3). N-1 which appears in the calculation of *s* is called the degrees of freedom. The *t*-distribution resembles the normal distribution, being symmetrical and bell-shaped, but is lower in the centre and higher at the extremes (at the left and right hand of two sides of the distribution curve). When $N \geq 30$, the *t*-distribution and the normal distribution are almost identical.

Accordingly, using the *t*-distribution, Equation (I.26) becomes:

$$P[(X-t_{\alpha/2}s/\sqrt{N})<\mu<(X+t_{\alpha/2}s/\sqrt{N})]=1-\alpha=q \tag{I.27}$$

In this research, the quantity of standard deviation is either determined based on data presented in the Table I.1 and the calculated mean of experiments, or is computed directly by calculation of the standard deviation of sampling. In some cases, such as fluid retention measurement and *XRD*, several experiments were performed on control samples to establish the coefficient of variation for these experiments. Later on, these established coefficients of variation are used to calculate the standard deviation of certain cases.

Table I.2: Areas under the Standard Normal Curve from 0 to z.

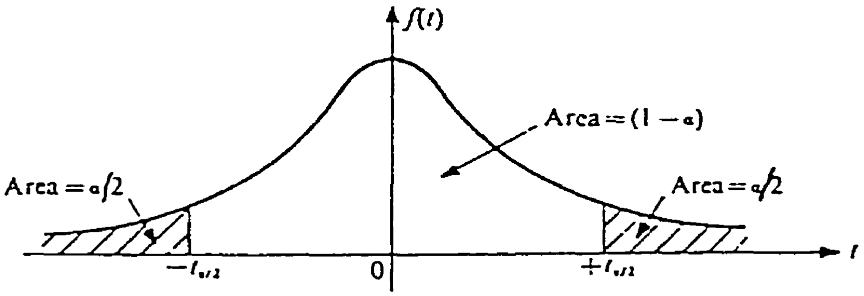


Confidence level (1-α)	$Z_{\alpha/2}$
90	1.64
95	1.96
95.45	2.00
98	2.33
99	2.58
99.5	2.81
99.73	3.00
99.9	3.29
99.99	3.89
99.994	4.00

z	.00	.01	.02	.03	.04	.05	.06	.07	.08	.09
0.0	.0000	.0040	.0080	.0120	.0160	.0199	.0239	.0279	.0319	.0359
0.1	.0398	.0438	.0478	.0517	.0557	.0596	.0636	.0675	.0714	.0753
0.2	.0793	.0832	.0871	.0910	.0948	.0987	.1026	.1064	.1103	.1141
0.3	.1179	.1217	.1255	.1293	.1331	.1368	.1406	.1443	.1480	.1517
0.4	.1554	.1591	.1628	.1664	.1700	.1736	.1772	.1808	.1844	.1879
0.5	.1915	.1950	.1985	.2019	.2054	.2088	.2123	.2157	.2190	.2224
0.6	.2257	.2291	.2324	.2357	.2389	.2422	.2454	.2486	.2517	.2549
0.7	.2580	.2611	.2642	.2673	.2704	.2734	.2764	.2794	.2823	.2852
0.8	.2881	.2910	.2939	.2967	.2995	.3023	.3051	.3078	.3106	.3133
0.9	.3159	.3186	.3212	.3238	.3264	.3289	.3315	.3340	.3365	.3389
1.0	.3413	.3438	.3461	.3485	.3508	.3531	.3554	.3577	.3599	.3621
1.1	.3643	.3665	.3686	.3708	.3729	.3749	.3770	.3790	.3810	.3830
1.2	.3849	.3869	.3888	.3907	.3925	.3944	.3962	.3980	.3997	.4015
1.3	.4032	.4049	.4066	.4082	.4099	.4115	.4131	.4147	.4162	.4177
1.4	.4192	.4207	.4222	.4236	.4251	.4265	.4279	.4292	.4306	.4319
1.5	.4332	.4345	.4357	.4370	.4382	.4394	.4406	.4418	.4429	.4441
1.6	.4452	.4463	.4474	.4484	.4495	.4505	.4515	.4525	.4535	.4545
1.7	.4554	.4564	.4573	.4582	.4591	.4599	.4608	.4616	.4625	.4633
1.8	.4641	.4649	.4656	.4664	.4671	.4678	.4686	.4693	.4699	.4706
1.9	.4713	.4719	.4726	.4732	.4738	.4744	.4750	.4756	.4761	.4767
2.0	.4772	.4778	.4783	.4788	.4793	.4798	.4803	.4808	.4812	.4817
2.1	.4821	.4826	.4830	.4834	.4838	.4842	.4846	.4850	.4854	.4857
2.2	.4861	.4864	.4868	.4871	.4875	.4878	.4881	.4884	.4887	.4890
2.3	.4893	.4896	.4898	.4901	.4904	.4906	.4909	.4911	.4913	.4916
2.4	.4918	.4920	.4922	.4925	.4927	.4929	.4931	.4932	.4934	.4936
2.5	.4938	.4940	.4941	.4943	.4945	.4946	.4948	.4949	.4951	.4952
2.6	.4953	.4955	.4956	.4957	.4959	.4960	.4961	.4962	.4963	.4964
2.7	.4965	.4966	.4967	.4968	.4969	.4970	.4971	.4972	.4973	.4974
2.8	.4974	.4975	.4976	.4977	.4977	.4978	.4979	.4979	.4980	.4981
2.9	.4981	.4982	.4982	.4983	.4984	.4984	.4985	.4985	.4986	.4986
3.0	.4987	.4987	.4987	.4988	.4988	.4989	.4989	.4989	.4990	.4990

Table I.3: Confidence coefficients, t distribution.

Degrees of freedom	Confidence level $(1-\alpha)$ for two-tailed distributions, %				
	90	95	98	99	99.9
	$\alpha/2$: 0.05	0.025	0.01	0.005	0.0005 (α for one-tailed distributions)
1	6.314	12.706	31.821	63.657	636.619
2	2.920	4.303	6.965	9.925	31.598
3	2.353	3.182	4.541	5.841	12.941
4	2.132	2.776	3.747	4.604	8.610
5	2.015	2.571	3.365	4.032	6.859
6	1.943	2.447	3.143	3.707	5.959
7	1.895	2.365	2.998	3.499	5.405
8	1.860	2.306	2.896	3.355	5.041
9	1.833	2.262	2.821	3.250	4.781
10	1.812	2.228	2.764	3.169	4.587
11	1.796	2.201	2.718	3.106	4.437
12	1.782	2.179	2.681	3.055	4.318
13	1.771	2.160	2.650	3.012	4.221
14	1.761	2.145	2.624	2.977	4.140
15	1.753	2.131	2.602	2.947	4.073
16	1.746	2.120	2.583	2.921	4.015
17	1.740	2.110	2.567	2.898	3.965
18	1.734	2.101	2.552	2.878	3.922
19	1.729	2.093	2.539	2.861	3.883
20	1.725	2.086	2.528	2.845	3.850
21	1.721	2.080	2.518	2.831	3.819
22	1.717	2.074	2.508	2.819	3.792
23	1.714	2.069	2.500	2.807	3.767
24	1.711	2.064	2.492	2.797	3.745
25	1.708	2.060	2.485	2.787	3.725
26	1.706	2.056	2.479	2.779	3.707
27	1.703	2.052	2.473	2.771	3.690
28	1.701	2.048	2.467	2.763	3.674
29	1.699	2.045	2.462	2.756	3.659
30	1.697	2.042	2.457	2.750	3.646
40	1.684	2.021	2.423	2.704	3.551
60	1.671	2.000	2.390	2.660	3.460
120	1.658	1.980	2.358	2.617	3.373
∞	1.645	1.960	2.326	2.576	3.291



Appendix II
DETAILED DESCRIPTION OF SOME OF THE EXPERIMENTS

II.1 SPECIFIC SURFACE AREA MEASUREMENT

The surface area of soil samples was determined using ethylene glycol mono-ethyl ether *(EGME)* following the procedure described by *Eltantawy and Arnold (1973)*, and *Carter et al. (1986)*. This method is based upon the assumption that the *EGME* forms a mono-molecular layer on the soil particles. It is known that the amount of *EGME* required to cover 1 m^2 of the soil particle surface is 2.86×10^{-4} g EGME per m^2 of the surface *(Carter et al. 1986)*. Therefore the surface area of the soils could be determined by monitoring the variation of weight of the sample before and after the addition of *EGME*. Before the addition of *EGME*, one gram of soil was completely dried. This was ensured by drying the sample to constant weight in an evacuated desiccator over phosphorus pentoxide (P_2O_5). Periodic measurement confirmed that constant weight was obtained. Then *EGME* was added to soil and the same process was followed while desiccator was evacuated over $CaCl_2$. Each time evacuation was performed for 45 minutes, then the sample was reweigh at successively longer intervals until a constant weight was reached. Finally, by having the amount of *EGME* required to cover 1 m^2 of the soil particles' surface, and the amount of *EGME* used to cover the soil sample's surface in this test, the specific surface area of soil can be calculated.

II.2 DETERMINATION OF AMORPHOUS MATERIAL

The main issue in determination of amorphous material is whether or not an extraction of amorphous material from a representative soil sample would attack the crystalline fraction of soil. *Segalen (1968)* suggested a method based upon a different soil washing process with acid and base. This technique is based on the fact that the amorphous portion, due to its high surface area, is rapidly dissolved while during this process, crystalline material fraction dissolved by almost a steady dissolution rate and the dissolution happens after amorphous removal. *Yong and Wang (1990)* based on the experimental results of natural-artificial sediments, and by the addition of known amounts of synthesized amorphous material, indicated that the *Segalen* method is quite acceptable.

The sample of 1 *gr* oven-dried soil was mixed and shaken with 30 *mL* of 8 *N* HCl solution for 30 minutes. This provided low pH is appropriate for dissolving the alumina and iron. Then the sample was mixed with distilled water, shaken and centrifuged to remove and discard the excess HCl. This was proceeded by adding 0.5 *N* NaOH, and keeping the sample in a hot water bath for 5 minutes to accelerate dissolution of silica and alumina. The whole procedure of alternate washing of acid and base was repeated eight times on the same soil sample. The amorphous material content can be calculated based on the non-linear fraction of dissolution curve as is presented in Figure 6.12. Getting to the linear fraction of the dissolution curve is a sign of amorphous material removal and the indicator of the steady state dissolution of the pure crystalline minerals. Finally the amount of different fraction of amorphous material was colorimetrically measured.

II.3 ORGANIC CONTENT EVALUATION

Organic content measurement was performed using the hydrogen peroxide (H_2O_2) oxidation technique. This method requires treatment of soil with H_2O_2 and reporting the weight loss of the sample which will be due to the organic removal. To do so, an oven-dried soil sample, was placed in a beaker and a small quantity of hydrogen peroxide was added. To accelerate organic removal, the beaker was warmed on a hot plate and the sample left to react overnight. This process was performed periodically, until no more reaction was observed. Finally the sample was washed with distilled water and centrifuged to remove the excess hydrogen peroxide. The settling sample was oven-dried and the difference in weight was reported as an organic content and calculated in terms of ratio to the initial dry weight of the soil. This process was used to remove the organic content of soil sample before performing *XRD* analysis.

Another method carried out to measure the organic content of soil, was based on the addition of potassium dichromate to the sample. Potassium dichromate ($K_2Cr_2O_7$) is a strong oxidation material which removes the organic matter. Titration technique was carried out to measure the required amount of potassium dichromate to eliminate organic matter of a certain amount of dry soil sample. This method is suggested for organic measurement of soils containing low quantity of organic

II.4 SOIL CARBONATE CONTENT MEASUREMENT

Several methods are presented for carbonate measurement of soils *(Hesse 1979, Quigley et al. 1982)*. The *XRD* analysis and rapid titration method *(Hesse 1979)* were used to measure the carbonate content of soil samples. This method is based on titration of a sample with *1 M* hydrochloric acid and sodium hydroxide solution, respectively. This method is reported to be suitable for the routine analysis of a large number of samples where an accuracy of about 1 % is sufficient.

Appendix III

XRD PATTERNS OF SOIL SAMPLES AND ETTRINGITE

III.1 INTRODUCTION

This Appendix includes some of the *XRD* patterns of soil samples and ettringite which were performed in the current research. Due to the numerous *XRD* analyses conducted in this study, only a part of them are presented in this section. These are shown in the following pages.

Table III.1: Mineral Identification, Marl sample.

hkl	Observed *d* Spacing	Identification
-	14-14.4	Chlorite, Montmorilonite
-110	10-10.4	Palygorskite
-	7.1	Chlorite, Kaolinite
-	6.33	Palygorskite, Feldspars
-	5-5.38	Palygorskite, Illite
-	4.46-4.92	Chlorite, Kaolinite, Montmorilonite, Palygorskite
-	4.27	Quartz, Gypsum
-	4.03-4.3	Feldspars, Palygorskite
012	3.85	Calcite
	3.56-3.88	Feldspars
-	3.34-3.35	Quartz, Illite
-	3.20	Palygorskite, Feldspars
-	3.04	Calcite, Palygorskite
013	2.9	Arcanite
-	2.87	Arcanite, Gypsum, Dolomite
341	2.58	Palygorskite
-	2.49-2.53	Palygorskite, Arcanite
-	2.28	Quartz, Kaolinite, Chlorite, Montmorilonite
200	2.13	Quartz
-	2.09-2.19	Calcite, Dolomite
116	1.87	Calcite
-	1.82	Quartz, Dolomite
122	1.60	Calcite
211	1.54	Quartz
203	1.37	Quartz

Table III.2: Mineral Identification, Extracted Pure Palygorskite.

hkl	**Observed *d* Spacing**	**Identification**
-110	10.4	Palygorskite
200	6.33	"
130	5.38	"
040	4.46	"
-221	3.65	"
-231	3.35	"
-311	3.22	"
-151	2.88	"
341	2.59	"
440	2.54	"

Table III.3: Mineral Identification, Sepiolite Sample.

hkl	**Observed *d* Spacing**	**Identification**
110	12.1	Sepiolite
130	7.47	Sepiolite
040	6.73	Sepiolite
150	5.01	Sepiolite
060	4.5	Sepiolite
131	4.31	Sepiolite
260	3.75	Sepiolite
080	3.37	Sepiolite
331	3.2	Sepiolite

Table III.4: Mineral Identification, soil washing method, layer 1 (Chapter 5).

hkl	**Observed *d* Spacing**	**Identification**
-110	10.4	Palygorskite
200	6.33	"
130	5.38	"
040	4.46	"
-221	3.65	"
-231	3.35	"
-311	3.22	"
400	3.17	"
-151	2.88	"

Table III.5: Mineral Identification, soil washing method, layers 5 & 7 (Chapter 5).

hkl	**Observed *d* Spacing**	**Identification**
-110	10.4	Palygorskite
-	7.1	Chlorite, Kaolinite
200	6.33	Palygorskite
130	5.38	Palygorskite
-	4.5-4.9	Chlorite, Kaolinite
100	4.26	Quartz
-	4.03-4.3	Feldspars, Palygorskite
012	3.85	Calcite
-	3.56-3.88	Feldspars
101	3.34	Quartz
-	3.24	Feldspars, Palygorskite
104	3.03	Calcite

Figure III.1: *XRD* peaks for the three samples of Marl, different stages of weathering.

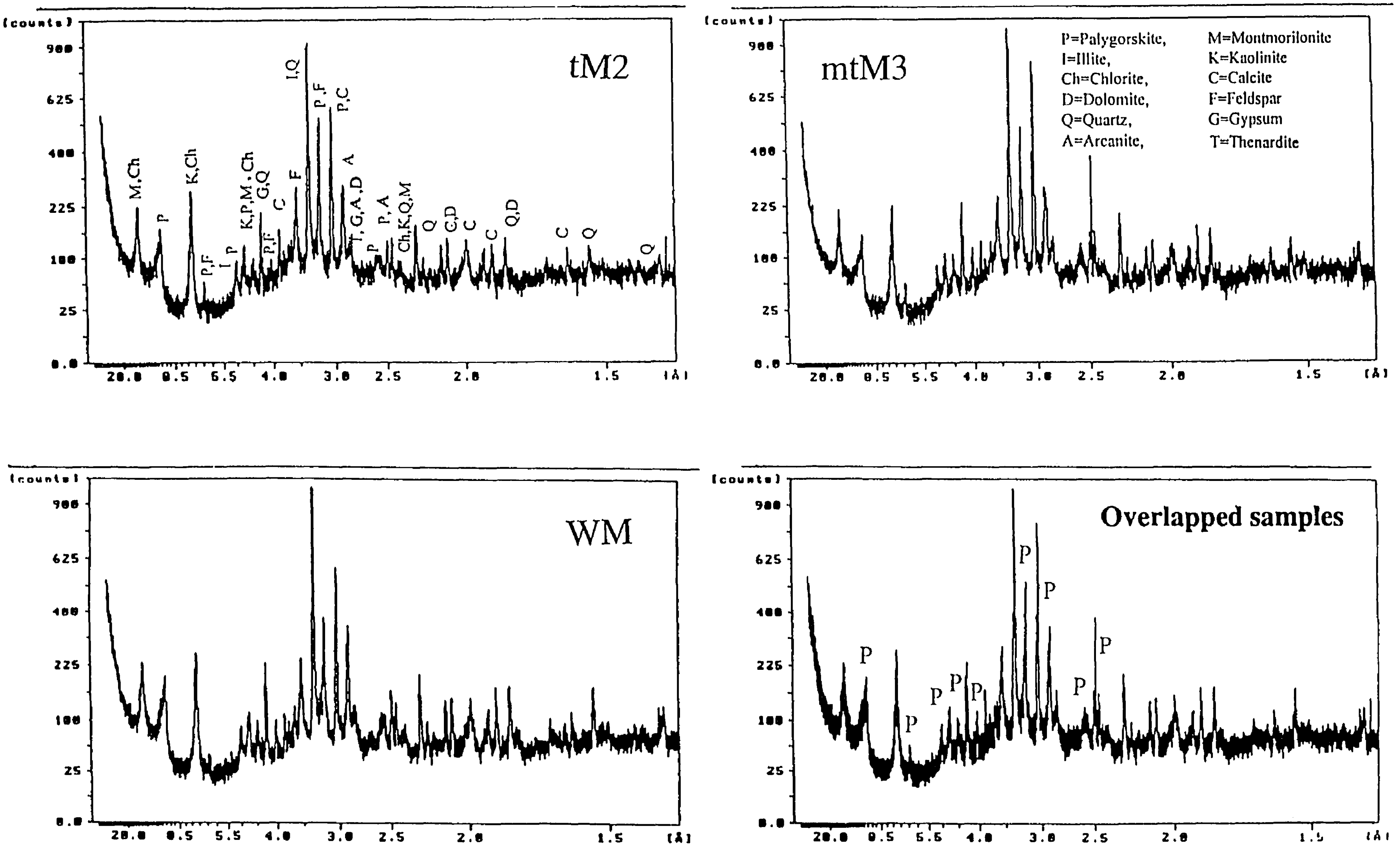


Figure III.2: *XRD* diffractogram, extracted Palygorskite sample.

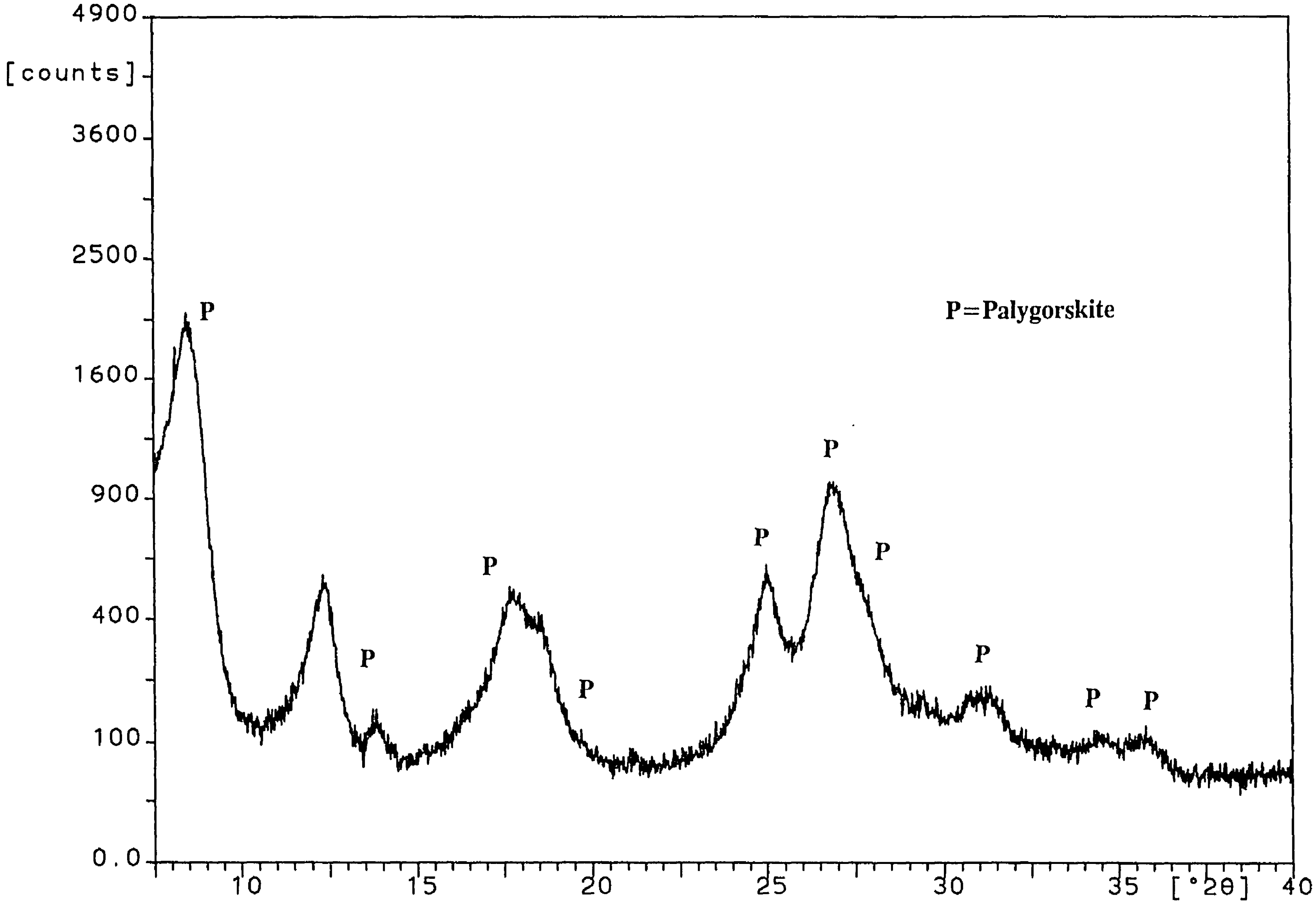


Figure III.3: *XRD* diffractogram, Sepiolite sample.

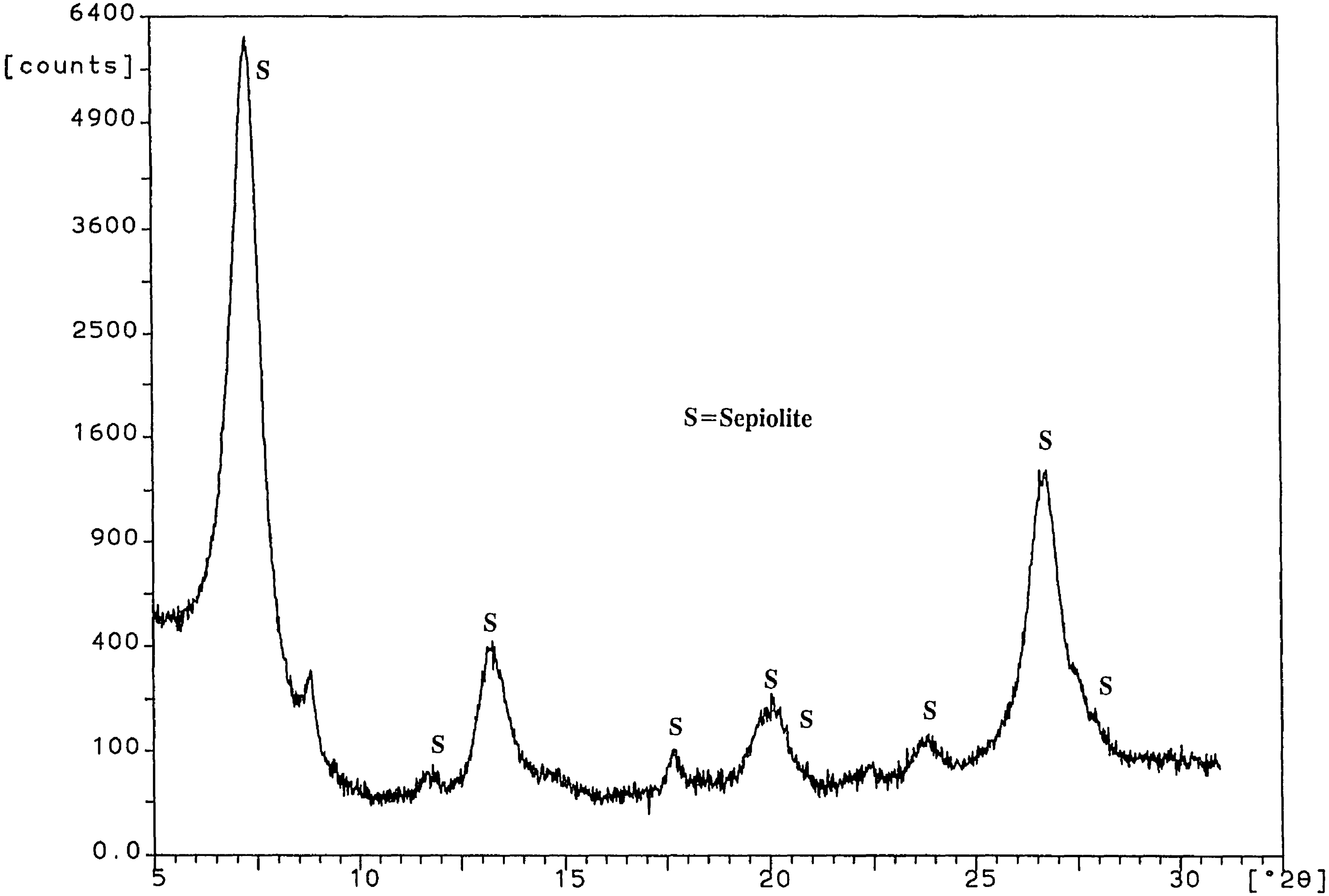


Figure III.4: *XRD* diffractogram, Ettringite sample.

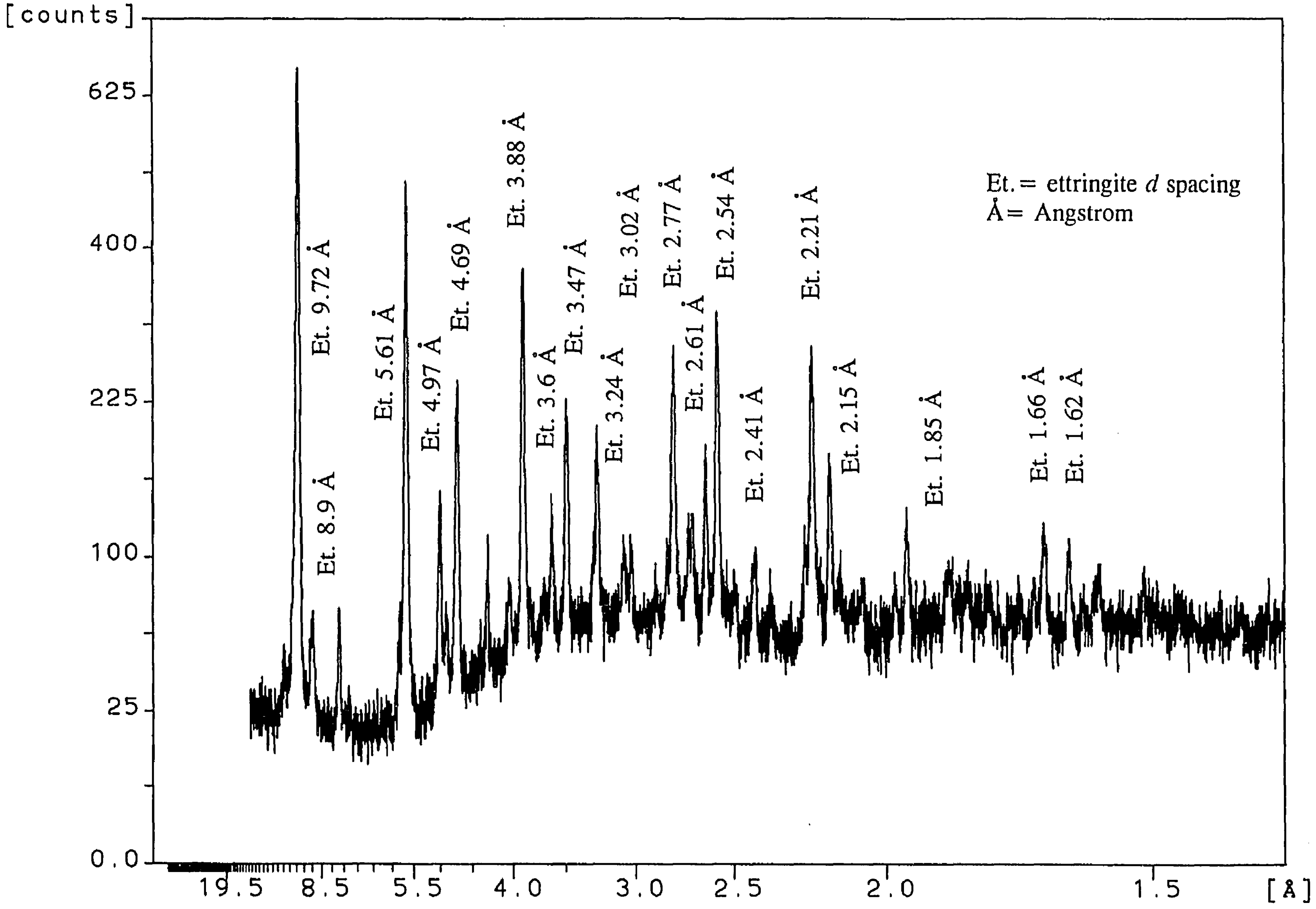
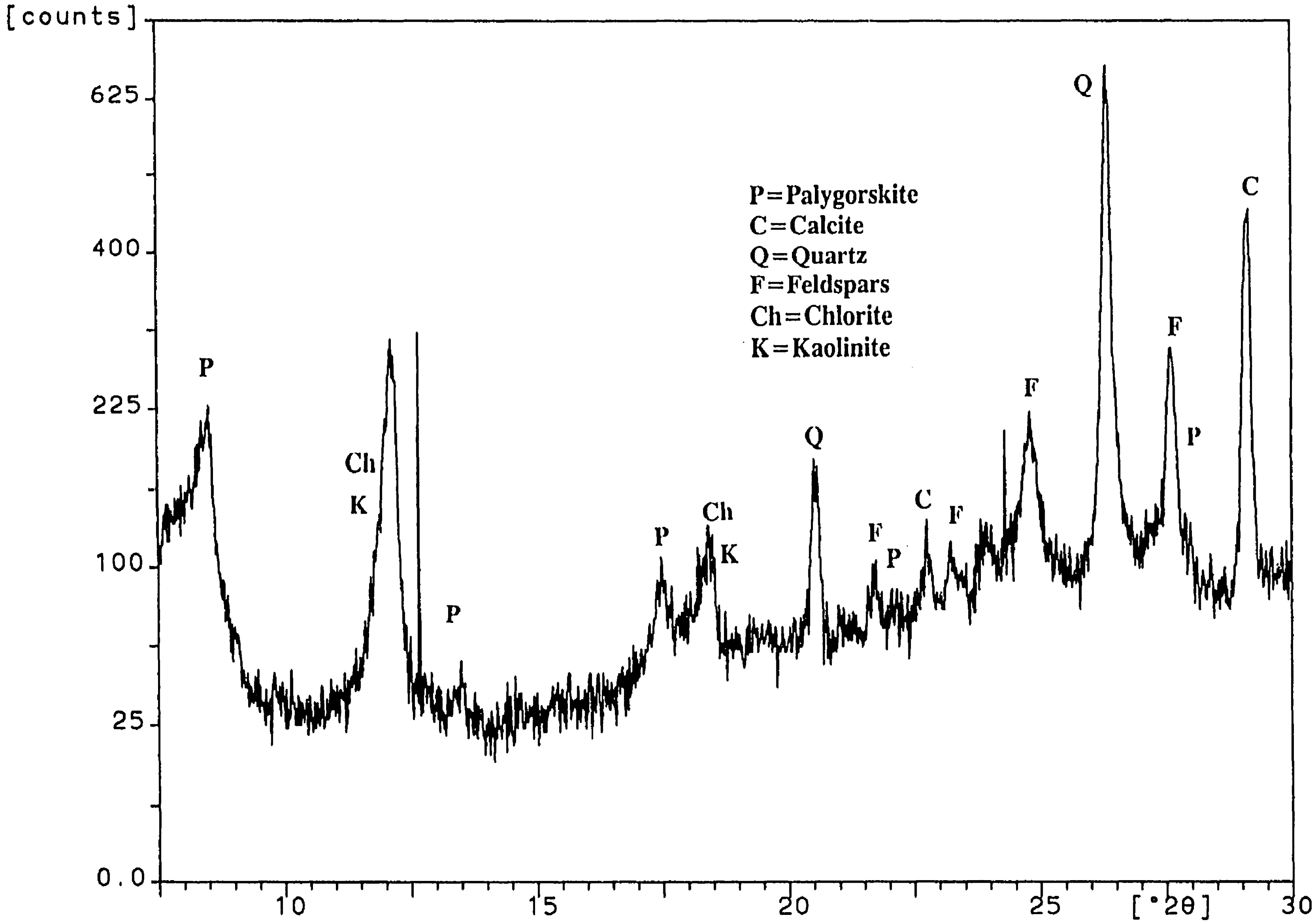


Figure III.5: *XRD* diffractogram, soil washing method, layer 5 (section 5.3).



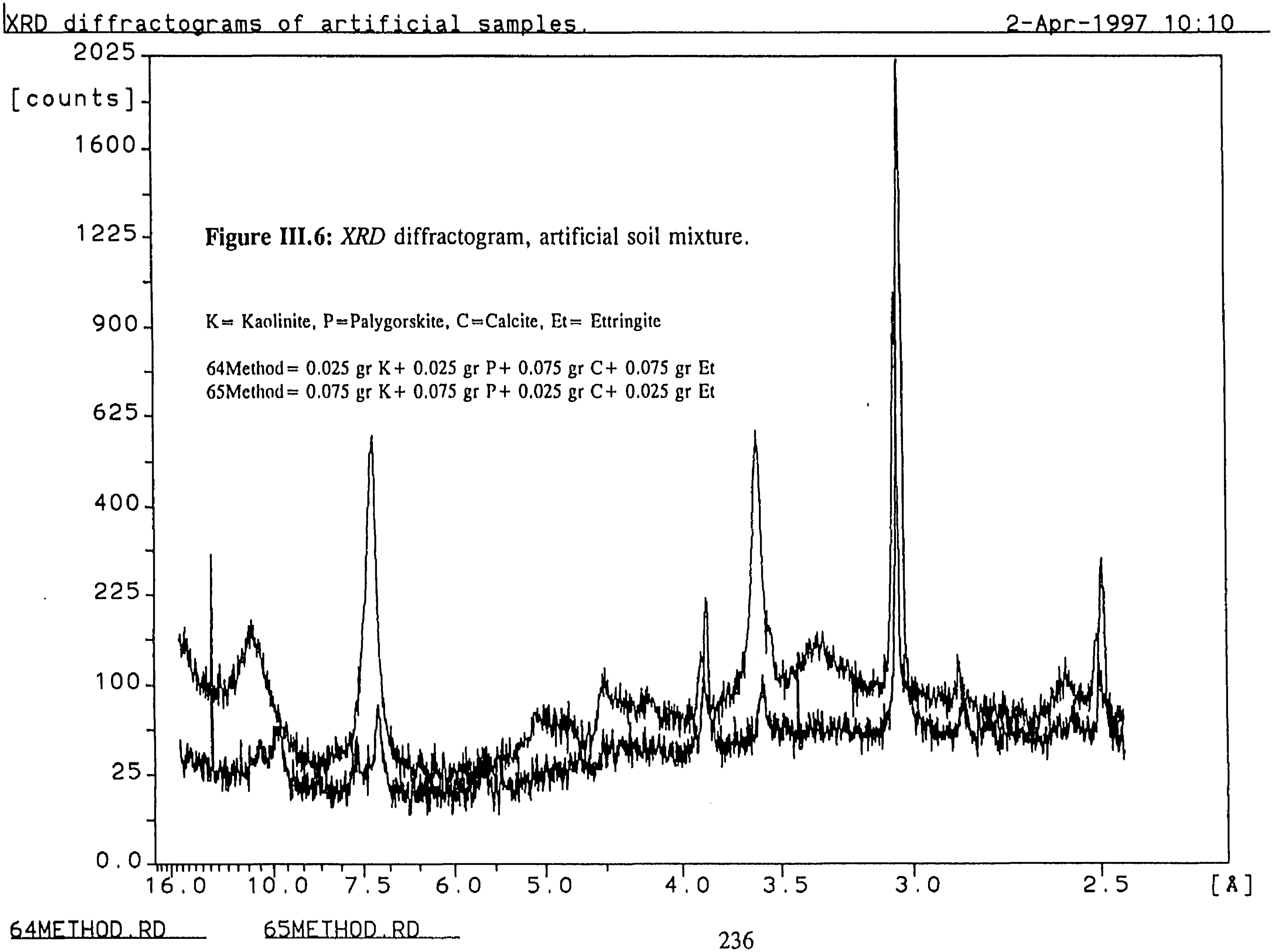
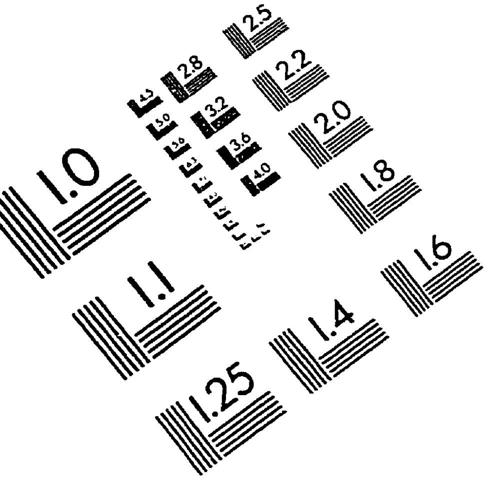


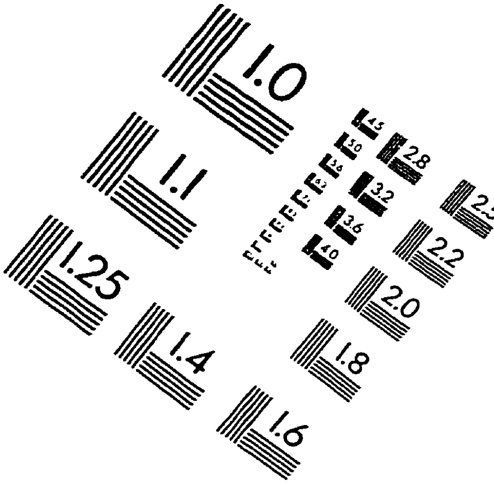
Figure III.6: *XRD* diffractogram, artificial soil mixture.

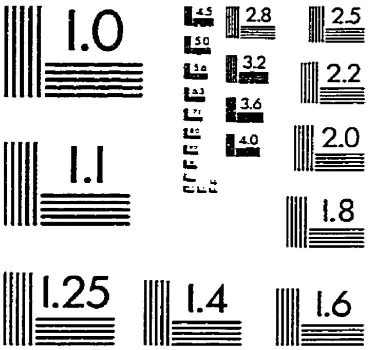
K= Kaolinite, P=Palygorskite, C=Calcite, Et= Ettringite

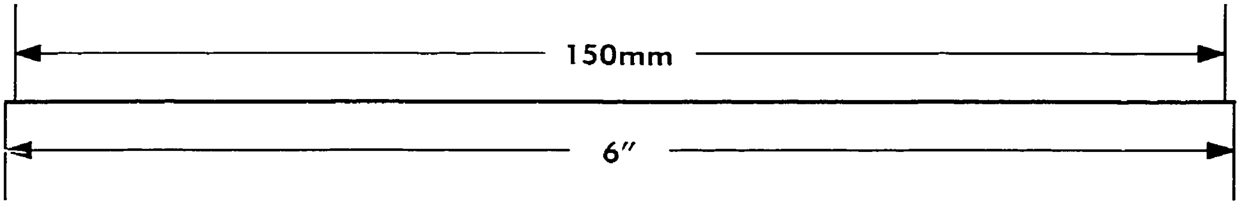
64Method= 0.025 gr K+ 0.025 gr P+ 0.075 gr C+ 0.075 gr Et
65Method= 0.075 gr K+ 0.075 gr P+ 0.025 gr C+ 0.025 gr Et

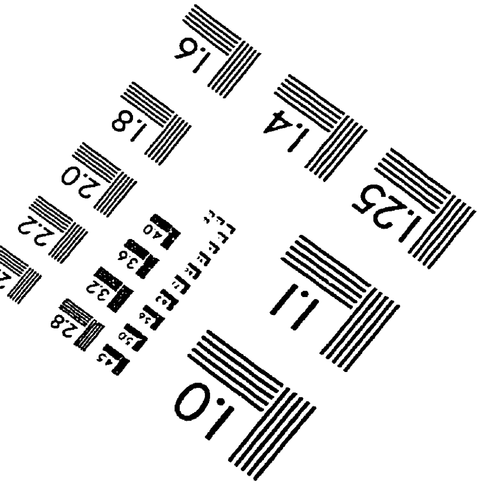
IMAGE EVALUATION
TEST TARGET (QA-3)

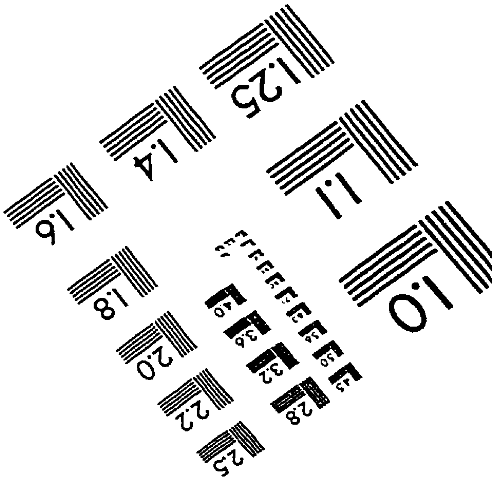












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