COMPATIBILITY OF BLENDED LITHOMARGIC CLAY AS LANDFILL LINER MATERIALS

Thesis

Submitted in partial fulfillment of the requirements for the award of the degree of

DOCTOR OF PHILOSOPHY

by

ALLAMAPRABHU S KAMATAGI



DEPARTMENT OF CIVIL ENGINEERING NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA, SURATHKAL, MANGALORE – 575 025 July, 2014

DECLARATION

by the Ph.D. Research Scholar

I hereby declare that the Research Thesis entitled "Compatibility of Blended Lithomargic Clay as Landfill Liner Materials" which is being submitted to the National Institute of Technology Karnataka, Surathkal in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy in Civil Engineering is *a bonafide report of the research work carried out by me*. The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

092014CV09F03, ALLAMAPRABHU S KAMATAGI

(Register Number, Name & Signature of the Research Scholar)

Department of Civil Engineering

Place: NITK-Surathkal Date: 05/11/2014

CERTIFICATE

This is to *certify* that the Research Thesis entitled "Compatibility of Blended Lithomargic Clay as Landfill Liner Materials" submitted by ALLAMAPRABHU S KAMATAGI (Register Number: 092014CV09F03) as the record of the research work carried out by him, is *accepted as the Research Thesis submission* in partial fulfilment of the requirements for the award of degree of Doctor of Philosophy.

Dr. Sunil.B.M Department of Civil Engineering, (Research Supervisor) Prof. Sitaram Nayak Department of Civil Engineering, (Research Supervisor)

Prof. K.N Lokesh Department of Civil Engineering Chairman – DRPC



ACKNOWLEDGEMENT

First and foremost, I express my sincere heartfelt thanks and deepest gratitude to my research supervisors **Dr. Sunil. B. M and Prof. Sitaram Nayak**, Department of Civil Engineering for their excellent guidance and kind cooperation throughout the research period, leading to successful completion of this research. Apart from the technical guidance, it was their constant affection, support and solace during the moments of despair that have been behind the successful completion of this report.

I am greatly indebted to RPAC members, Prof. Subba Rao, Department of Applied Mechanics and Hydraulics Engineering and Prof. Vijay Desai, Department of Mechanical Engineering, for their critical evaluation and very useful suggestions during the progress of the work.

I am thankful to Prof. K.N. Lokesh, Head of Civil Engineering Department and Chairman DRPC, Prof. S. Shrihari, Secretary, DRPC and Prof. A. U. Ravishankar and Prof. Katta Venkataramana, former Heads of the Department of Civil Engineering, for their continuous support, encouragement and timely help during my entire research period.

I sincerely thank Prof. Rajedra Udapa, Dr. Uday Bhat and Ms. Rashmi Department of Metallurgy Engineering, Dr. Vidya Shetty and Mrs Tritila Department of Chemical Engineering for providing me with laboratory facilities in the Department of Metallurgy and Chemical Engineering.

I gratefully acknowledge the support and all help rendered by Mr. Mohammed Zafar, Mr. Santosh Fernandes and Mr. Srinivasa (Former M.Tech students of GTE) successful completion of the experimental program. I sincerely thank the laboratory sraff Sri. Chandrashekar Karanth, Sri. Sadananda Kadri, Sri. Narayan Naik, Mr. Yathish, Sri. Manohar, Sri. Hanumanth for the help rendered during experimental stages of the work.

I also like to extend my gratitude to all the teaching faculty and supporting staff of the Civil Engineering Department, for their encouragement, help and support provided during the research work. I am very much thankful to all my friends and fellow research scholars of this institute for their continuous encouragement and suggestions during the course of my research work.

My special thanks to my friends Rachanna, Mithun, Bapugouda, Kishor, Santosh, Naveen, Poornachandra, Prasahant and Shreelaxmi for their consistent support and encouragement.

Most importantly I would like to thank my family members especially my mother, my brother Shashikant, my sisters Renuka Shivakiran and Arundhati, and sister in-law Mrs. Sujata who always supported and encouraged me in this endeavour and their support kept me going through hard times and gave me confidence, courage and inspiration.

Finally, I am grateful to everyone who have helped and encouraged me during this research work.

Allamaprabhu Kamatagi

Place: NITK Date: 05-11-2014

ABSTRACT

The present investigation is an experimental study on locally available lithomargic clay (shedi soil) and blended lithomargic clay as a suitable soil liner material for the effective containment of leachate in landfills.

The objectives of the research work were accomplished in three phases. First phase of work deals with geotechnical characterization of test soils. Hydraulic conductivity is considered as most significant factor for performance of a clay liner. Results obtained show that the hydraulic conductivity of lithomargic clay is greater than the suggested limit of $k<10^{-7}$ cm/s by various waste regulatory agencies. To reduce hydraulic conductivity of lithomargic clay, it is blended with black cotton (BC) soil and bentonite at different proportion till the required hydraulic conductivity (k <10⁻⁷ cm/s) was achieved. Lithomargic clay blended with 5% and 10% of a black cotton soil and, lithomargic clay blended with 5% and 7.5% of a bentonite satisfied the hydraulic conductivity requirement of liner material. Hence blend proportions were considered for further investigation.

The compatibility of a clay liner on interaction with contaminant depends on its capacity to retard the migration of contaminants through sorption. In the second phase studies related to adsorption characteristics of soil samples through batch tests have been carried out. The experimental results of batch adsorption tests have been analysed using three adsorption isotherms. Adsorption coefficient of study soils shows that, adsorption of potassium, lead and nickel are more on BC soil and bentonite while lithomargic clay adsorbs more chloride and chromium. As a result blending of lithomargic clay with BC soil and bentonite, the adsorption of contaminants is found to be more in the blended soils compare to parent soil. In the third phase of the research work, the effect of interaction of leachate on behaviour of lithomargic clay and blended lithomargic clay has been studied. The hydraulic conductivity has been found to decrease in both, the natural and the blended lithomargic clay due to the leachate interaction.

Blended lithomargic clays has been found to be beneficial in terms of achieving lower hydraulic conductivity, adequate strength, minimal potential to shrinkage. All these properties make blended lithomargic clay as a potential soil liner material for various geoenvironmental applications.

Keywords: Lithomargic clay, BC soil, Bentonite, Blended soil, Hydraulic conductivity, Adsorption, Leachate.

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NOMENCLATURE

Abbreviations

MSW	: Municipal Solid Waste
BC Soil	: Black Cotton Soil
BN	: Bentonite
UCS	: Unconfined Compression Strength
CEC	: Cation Exchange Capacity
XRD	: X-Ray Diffraction
SEM	: Scanning Electron Microscope
OMC	: Optimum Moisture Content
IS	: Indian Standard
BIS	: Bureau of Indian Standards

Notations

γdmax	: Maximum Dry Density
Wopt	: Optimum Moisture Content
k	: Hydraulic Conductivity
k _d	: Distribution Coefficient or Partition Coefficient
К	: Freundlich Isotherm Constant
α	: Langmuir Constant

CHAPTER 1

INTRODUCTION

1.1 GENERAL

There has been a significant increase in municipal solid waste (MSW) generation in India during the last few decades. This is mainly because of rapid population growth and economic development in the country. Due to rapid growth of urban population, as well as constraint in resources, the management of solid waste poses a difficult and complex problem for the society and its improper management gravely affects the public health and degrades environment.

Open dumping or disposal of MSW in unlined pits significantly affects the surrounding environment. Leachate from such a unlined pits has the potential to contaminate the soil and the ground water. This can in turn affect the socio- economic development of the community in the vicinity of landfills and especially in the rural regions, where people heavily depend on the ground water for drinking purpose.

Waste may consists of organic and/or inorganic constituents which may or may not be biodegradable, means the recyclable components of solid waste could be useful as a secondary resource for production processes. On the other hand, some of its toxic and harmful constituents may pose a danger if not handled properly. Source reduction, recycling and composting, waste-to-energy conversion facilities and land filling are the four basic approaches to waste management.

Even after recycle and reuse, sufficiently large quantity of waste remains, which is disposed in low-lying areas without undertaking any precautions (Bundela, 2010). This practice has led to major environmental issue, as the rainwater percolating down from the waste carries pollutants with it and joins water bodies. The contamination of water bodies decreases their dissolved oxygen level and makes the environment unsuitable for the survival of aquatic animals. Water bodies near waste dump sites are also found to be contaminated with micro-organisms which have

considerable public health implications. It has been estimated that unlined sanitary landfills in a fairly wet climate will produce leachate containing hazardous chemicals such as lead at concentrations above the drinking water standards for several thousand years. It is not surprising that the landfills constructed by the Romans about 2000 years ago are still producing leachate (Kumar and Alappat 2003).

There is an urgent need of a scientific method for disposal of waste i.e. by placing the wastes in a landfill. Engineered landfills contain the waste in such a manner that human health and the environment will not be affected (Yahia et al., 2005). Landfills usually have liner systems and other safeguards to prevent the pollution of groundwater.

1.2 ENGINEERED LANDFILLS

Worldwide the quantity of solid waste generated is increased significantly year to year. According to study (Sharholy and Ahmad 2008) India generates about 90 million tons of solid waste every year. To handle such a huge quantity of wastes, landfills are designed to dispose the generated wastes. Due to land scarcity in the urban areas, most of the landfills now find the place in the rural areas surrounding the community.

To prevent infiltration of leachate in to the surrounding ground water and then to the ground water aquifer, low permeability soils are used as bottom liners to effectively contain the leachate. Fig 1.1 shows the essential components of an engineered landfill. The basic requirements of landfill liner system, which acts as a barrier to prevent infiltration of leachate are shown in Table 1.1.

In the study region majority of the people (staying close to the landfill areas) particularly those living in rural communities, depend on ground water for drinking and agricultural purposes. Water and soil pollution by landfill leachates can seriously hamper socio-economic development. Therefore, there is a need to assess whether locally available soils proposed for liner construction are compatible with MSW landfill leachate



Fig. 1.1 Schematic of a double liner and leachate collection system for a landfill (Daniel, 1993)

Property	Limiting Value
Percentage of gravels (%)	<30
Maximum particle size (mm)	25
Percentage of fines (%)	>30
Plasticity index (%)	>10
Coefficient of hydraulic conductivity (cm/s)	<10 ⁻⁷
Unconfined Compressive Strength (kPa)	≥200

Table 1.1 Basic requirements of the liner materials (Daniel, 1993)

1.3 STUDY AREA

1.3.1 Lithomargic Clay

The lithomargic clay used in the present investigation is the name given to the locally available silty sand. The lithomargic clay (locally known as shedi soil)

constitutes an important group of residual soils existing under lateritic soils. This is a silty soil with approximately 60% of fines (silt and clay). These soils are mainly composed of hydrated alumina and kaolinite. This soil is present at a depth of 1–3 m below the lateritic soil zone throughout the Konkan belt of India (Sitaram et al. 2012). This type of soil is abundantly available in the western coastal belt of southern India, starting from to Cochin to Goa. These soils are the product of tropical or subtropical weathering. Their strength is high in dry conditions, whereas significant reduction of strength takes place when there is an increase in moisture content.

1.3.2 Vamanjoor Landfill Site

A site in Vamanjoor village where Mangalore city MSW is being dumped from few decades has been selected. Mangalore city is Headquarter of Dakshina Kannada district and is one of the fast growing cities in Karnataka state, India. The present area of the Mangalore city is about 132sq.Kms and having population of 5 lakhs approximately. The Mangalore city lies between 12°52¹ N latitude and 74°49¹ E longitude. It has an elevation of 10 to 60 meters above M.S.L. The ambient temperature ranges from 17° C to 37° C. The annual average rainfall is about 3900mm. The total quantity of MSW generated from Mangalore city has been estimated to be 300 tonne every day.

The Vamanjoor dumping yard in Mangalore city has been spreads over an area of approximately $1 \times 10^4 \text{ m}^2$. The waste dumped at this site includes domestic waste, paper, plastic, glass, cardboard, cloths, construction and demolition waste. Further waste from the fish market and non-infectious hospital waste are also being dumped. The site is a non-engineered low lying open dump yard, looks like a huge heap of waste. Waste is being dumped as per truck drivers convenience and bull dozers are used for stacking the waste to height of 3-4 mts. Bull dozers also act as compactors as they can be driven to top of the heap. No intermediate layer of soil is placed on regular basis. The dump yard receives animal carcasses, chemical, industrial and biomedical waste and being illegally dumped together, without segregation as there is no separate landfill for these wastes.

1.4 ORGANIZATION OF THE THESIS

Present work has been divided into eight chapters and compiled in this thesis for the purpose of better understanding and clarity of the proposed problem.

- Chapter 1: Introduction to various aspects of the engineered landfill and explains the necessity of the present work.
- Chapter 2: Review of available literature on the proposed work is presented in Chapter 2.
- Chapter 3: The experimental methodology adopted and the materials used for the present study are presented in Chapter 3. Basic terminology along with determination of various soil properties as per the procedure recommended by the Bureau of Indian Standards (BIS) are covered in Chapter 3.
- Chapter 4: Discussion on results of the tests carried out during the study is organized in this chapter. In order to achieve suitability of locally available soils or blended soils as landfill liner materials, geotechnical and chemical characteristics are discussed.
- Chapter 5 and 6: To examine the capacity of blended soils to adsorb various leachate constituent like sodium, chloride, potassium, chromium, lead and nickel have been presented through batch adsorption study.
- Chapter 7: This chapter provides the impact of Vamanjoor village MSW landfill leachate on hydraulic conductivity, Atterberg limits and mineralogical composition of the blended soils.
- Chapter 8: Major conclusions regarding the suitability of blended soils as a liner material for the MSW landfills have been outlined in this chapter.Recommendations for the future research have also been presented.

CHAPTER 2

REVIEW OF LITERATURE

2.1 INTRODUCTION

This literature review is to identify and summarize some of the literatures pertaining to the use of naturally available clays as an effective MSW landfill liner material. It is mandatory for a liner material to have a low hydraulic conductivity, as the key function of the liner is to reduce the flow of contaminants. Apart from low hydraulic conductivity other properties of soils (like volumetric shrinkage, unconfined compressive strength, sorption capacity etc.) play an important role in assessing the long term behaviour of the landfill liner. Different types of soil liner systems have been developed by researchers in order to deal with the local conditions. An attempt is made in this chapter to review the available literature pertaining to landfill clay liner.

2.2 APPLICATION OF CLAYEY LINERS

The earliest use of compacted clayey soils as hydraulic barriers appears to be in earthen dams for water impoundments. Since then, the specific uses of clayey liners as hydraulic barriers have grown to a wide range of applications. These applications can be found in canal linings, landfills and surface impoundments (Daniel 1993a), deposits of mine tailings, chemical liquid storage ponds, leachate storage ponds, and evaporation ponds (Daniel, 1984).

Out of the above applications, compacted clay liners (CCLs) used in sanitary landfills have received the most prominent attention in recent times resulting in a vast amount of related literature. According to Daniel (1985 and 1993a), in the United States where many of the recent developments took place, CCL were not commonly used until the early 1970s, and until about 1982 nearly all of the engineered landfills in the US were constructed of clay liners using a single layer. In 1982, the Environment Protection Authority of the US (US EPA) banned their use as sole liners for landfills and surface impoundments unless the site owner could prove they were effective. The agency apparently based its ruling largely on studies showing that clay liners failed to meet EPA's criteria of zero penetration and zero leakage of contaminants into the ground (Daniel, 1993a). It appears that this decision was largely fuelled by the earlier findings that some chemicals such as concentrated organic chemicals can affect liner clays, leading to large increases in liner hydraulic conductivity (Anderson, 1982) and the inferior performance of some liners due to poor construction practices (Daniel, 1984). However, the current US environmental legislation allows the use of clayey liners as part of a composite liner system comprising synthetic geomembranes.

2.3 DESIRABLE PROPERTIES OF COMPACTED CLAY LINER

The primary objective of a CCL is to act as an effective barrier for contaminant migration over its design lifetime. A number of researchers have examined the desirable properties of CCLs (Mitchell and Jaber, 1990; Daniel and Wu, 1993; Jessberger, 1995). The most important desirable properties can be summarised as follows:

2.3.1 Low Hydraulic Conductivity

This can be regarded as the most important requirement for CCLs. In general, the hydraulic conductivity is directly proportional to the rate of seepage flow of contaminant liquid through the liner. Hence, low hydraulic conductivity will reduce the rate of contaminant liquid release and/or release of contaminants through liquid flow from the waste containment facility and, consequently, the impact on the natural environment would be lessened. The presence of an adequate percentage of clay fractions in the soils used for CCL construction is essential to achieve a low hydraulic conductivity. This property depends on a large number of variables and may feature high variability even under strict controls.

2.3.2 Low Diffusivity

Diffusion is the other known process by which contaminants can migrate through a CCL. This is the process whereby contaminants would migrate from a

source of high concentration to points of lower concentration. In simple terms, the contaminant flux rate depends on the concentration gradient and the diffusion coefficient. Hence, as far as the liner desirable properties are concerned, low diffusivity can be achieved by maintaining a low diffusion coefficient within the liner. The diffusion of contaminants can take place without any seepage flow, meaning that achieving a low hydraulic conductivity alone may not limit the rate of contaminant release. However, the diffusion (along with dispersion) can occur simultaneously with the seepage flow.

2.3.3 High Attenuation Potential

It would be desirable if CCLs could reduce and prolong the rate of contaminant release and lessen the concentration of contaminants by chemical reaction. These processes, which are generally referred as the attenuation, include adsorption, precipitation, biological process, oxidation-reduction reactions and acid-base reactions. Analysis of all these processes can be significantly complex. Adsorption is commonly considered with diffusion where the contaminant migration is retarded by this reaction.

2.3.4 Adequate Strength and Low Compressibility

CCLs should feature adequate strength and low compressibility in order to effectively perform as barriers for contaminant release. These properties are essential to maintain the traffic ability of construction equipment during the construction phase. These are also required to maintain the integrity of the liner against the overburden stress imposed by the material above it, and to make the liner stable when employed on slopes, for example, in the side wall of a waste containment facility.

2.3.5 Long Term Stability

In waste containment facilities, CCLs are provided to limit the contaminant release into the natural environment, at least during its design lifetime. Hence, the long-term stability of a CCL is important where its desirable properties should not degrade significantly with time. Known mechanisms by which CCLs can degrade with time include creep and, more importantly, the chemical reaction with waste leachates and contaminants. Creep can lead to long term deformations, and if differential settlements were to occur, they can threaten the integrity of the liner. If the potential for chemical reaction leading to degradation of liner properties is low, it is then considered that the liner soils are "compatible" with the wastes to be contained. Hence, the tests of chemical compatibility are imperative in the liner design.

2.3.6 Ductility

Ductility will allow the extension of a CCL without significant cracking due to tensile stresses being introduced. Cracks on the liner can act as preferential flow and contaminant release paths, and significantly compromise the effectiveness of the barrier. A CCL may be subjected to extension in situations such as at the crest of a slope or during uneven settlement. Uneven settlement is particularly important for cover liners, as the landfill can undergo substantial settlement with the degradation of wastes.

2.3.7 Low Shrink/Swell Potential

CCLs may display different levels of shrink/swell potential depending on a number of factors such as the plasticity and mineralogical properties of clay. It is desirable that this potential is low in order to minimise the probability of desiccation cracking due to moisture changes within the liner. The moisture changes can occur if liners were exposed to atmosphere during construction or to internal temperature gradients, or by evapo-transpiration in the case of cover liners.

2.3.8 Adequate Interface Strength

In waste containment systems, the stability of slopes is regarded as a major design consideration. According to slope stability theory, slopes tend to fail along the zones of lowest shear strength. It is important in the slope stability point of view that adequate interface strength is maintained between CCL and other adjacent structural components.

2.3.9 Constructability

The construction of CCLs involves the mixing of soils at moisture content generally wetter than optimum value and subsequent compaction of wet soils using heavy rollers. Hence, trafficability by various compaction equipment on wet soils is an important issue. The constructability will become a major concern if predominantly high plastic soils are used for the liner.

2.3.10 Low Freeze/Thaw Effects

In very cold climates, CCLs may undergo significant seasonal temperature changes associated with the freezing and thawing of pore liquids. This process can affect the structure of the clay liner leading to contraction cracking of the liner (Kim and Daniel, 1992). While it may be important to keep these effects to a minimum in liners constructed in very cold climates, this issue may not apply to liners constructed in countries with temperate or tropical climates (such as Australia).

2.4 PROPERTIES OF LINER CLAYS

2.4.1 General

In the previous section, an overview of the desirable properties of the clay liners for its effective performance was provided. A variety of physico-chemical properties of liner soils including clay minerals will control these properties of CCLs.

2.4.2 Clay Mineralogy

Clays are small crystalline particles of one or more members of a small group of minerals. Therefore, mineralogy is a primary factor controlling the size, shape, and physical and chemical properties of soil particles. Hence, it is not surprising that clay mineralogy plays an important role in compatibility assessment of clayey soils with various chemical liquids and leachates. Therefore, it seems important that a brief review of the desirable clay mineralogical properties is presented at this point. Clay minerals are normally formed from weathering and subsequent geological processes of parent materials such as rocks and occur in particles of small size. They are primarily hydrous silicates of aluminium, magnesium and iron, carrying a net negative charge created by either crystal structure imperfections or substitutions or from chemical reactions at the mineral surface (Goldman et al, 1990). This net negative charge plays a significant role in the physico-chemical behaviour of clays because cations in the pore water can get attracted to the surfaces of clay particles creating a diffuse double layer between the clay particles. Therefore, the attractive and the repulsive forces among the clay particles will depend on the thickness of this double layer.

On the basis of structure, clay minerals fall into a relatively small number of groups. A limited number of different minerals are found in significant abundance in the soils commonly encountered in engineering practice. In the discussion which follows, only the important clay minerals, their properties and relevance to liner clays are considered.

2.4.3 Clay Mineral Classification

Most clay minerals have a sheet-like layered crystalline structure. These sheet structures consist of two different types of basic units, namely, tetrahedral units and octahedral units. Schematic diagrams of these units along with their salient features are shown in Fig. 2.1. The silicon-oxygen unit is called a tetrahedral unit where silicon is tetrahedral coordinated with four oxygens, with the silicon atom at the centre. In octahedral sheets, aluminum or magnesium ion is octahedral coordinated with six oxygen or hydroxyl groups forming a hexagonal close packing. The oxygen atoms and hydroxyl groups lie in two parallel planes with Al or Mg atoms between these planes. As shown in Fig. 2.1, the octahedral unit is slightly bigger than the tetrahedral unit. Because of the significant similarity in crystal structure of these units, the interstratification of two or more of these unit types often leads to the formation of layered sheet which constitutes a single clay particle or mineral (Mitchell, 1976). The majority of the clay minerals can be categorised into four groups based on the height of the unit, the composition of the sheets and the kind of inter-sheet bonding (Goldman et al, 1990). These groups are kaolinite, illite, smectite, and chlorite. This grouping is particularly convenient because the members of the same group have comparable behavior. A schematic diagram of different clay mineral groups is given in Fig. 2.2.



Fig. 2.1 Basic structural units in the silicon sheet and octahedral sheet (Grim, 1959)



Fig 2.2: Schematic diagram of different clay minerals

2.4.3.1 Kaolinite mineral

The kaolinite minerals are derived from a 1:1 arrangement of silica tetrahedral sheet and an alumina octahedral sheet. The bonding between the sheets is dominated by a fairly strong hydrogen ion bond over relatively weak van der Waal forces. This strong bonding makes kaolinite minerals relatively stable or inactive against chemical attack from leachates. Furthermore, this strong bonding can also lead to relatively large particles with a small specific surface area of $15m^2/g$ and a characteristic basal spacing of 7.2Ű. A small negative charge on kaolinite particles results in a cation exchange capacity of 3-15 meq per 100 gm. Consequently, they have relatively high

hydraulic conductivity values (which are rarely less than 10^{-8} m/s) and less adsorptive capacity (Rowe et al, 1995). This leads to a fairly rapid advective transport and little retarding capacity, when hydraulic flow is considered. Therefore, these characteristics do not make it an ideal mineral for compacted clay liner construction, although it is relatively stable against many chemicals and moisture changes.

2.4.3.2 Illite mineral

This mineral is derived from stacks of 2:1 three layer units with an octahedral sheet between two silica tetrahedral sheets. These units are held together by very strong potassium (K^+) bond to form stacks of these units. Because of the potassium bonding, only a small unbalanced charge is left in the mineral surface giving a cation exchange capacity of 25 meq/100g and making it a mineral of normal activity. Rowe et al (1995) have noted that "Illite is efficiently compacted or consolidated to form clayey soils having a hydraulic conductivity of 10^{-9} to 10^{-11} m/s depending on the void ratio. Also, the CEC of 25 meq/100g is adequate to permit abundant adsorption of undesirable species such as heavy metals. Finally, there is no interlayer, c-axis (unit spacing) expansion or contraction possible, so illite is often considered to be one of the most desirable clay minerals for use in engineered clay liners for municipal solid waste". However, it should be noted that if the interlayer K^+ is leached out by acidic leachates (e.g. pH about 2 in acidic mine tailings), then the mineral structure would experience an increase in the unit spacing (i.e. swelling) and transform to a less stable vermiculite mineral (Rowe et al, 1995). The reverse is also possible where the vermiculite mineral can transform to illite by K⁺ fixation, where reduction in the unit spacing would occur with the possibility of significant cracking.

Vermiculite is a fairly common mineral with a poorly organised octahedral sheet between two silica tetrahedral sheets. Isomorphous substitution of aluminum for silicon is extensive in the tetrahedral sheet, resulting in a net negative charge on the crystal surface. The positive charge deficiency is larger than that of the layers of divalent cations and water. This larger charge deficiency results in vermiculite having the highest cation exchange capacity of all clay minerals. The primary surface area of vermiculite is 40 to 80 m/g and the secondary surface may be as high as 870 m/g.

2.4.3.3 Smectite mineral

The smectite group of clay minerals includes 2:1 three layer units comprising of an octahedral sheet in between two silica tetrahedral sheets. The bonding between the layers is provided by van der Waals forces and by cations that may be present to balance charge deficiencies in the structures. These bonds are weak and are easily separated by adsorption of water or other polar liquids. Therefore, these minerals may experience significant variations in the unit spacing (c-axis expansion and contraction), leading to swelling or cracking due to change in the moisture level, as well as when exposed to some chemicals (Goldman et al, 1990). The smectite mineral particles have a large specific surface area of up to $800m^2/g$ and have a high adsorptive capacity and can be compacted to give very low hydraulic conductivities $(10^{-11} \text{ to } 10^{-13} \text{ m/s})$. These characteristics make this mineral highly desirable for compacted clay liner constructions, but one has to be careful about the swelling and cracking they might undergo when exposed to adverse conditions.

Montmorillonite and saponites are the common minerals in this group. But the montmorillonite plays a special role in clay liner construction because this is the most common mineral in natural smectite clays, as well as the mineral used in commercially available bentonite, which is commonly used as an additive for the improvement of clays and sands. Montmorillonite comes in two types: sodium montmorillonite and calcium montmorillonite depending on the interlayer cation available. Sodium montmorillonite has the capacity to adsorb a substantial amount of interlayer water in comparison to the calcium variety. This makes Na montmorillonite significantly more reactive with the potential for a large amount of expansion or shrinkage. Because of these characteristics, sodium montmorillonite (commercially bentonite) is commonly used as an additive to improve soils and sands of low hydraulic conductivity values, in the slurry cut of walls, and as a clay mat in geosynthetic clay liners. Calcium montmorillonite is generally difficult to mix with soil, but its workability can be improved by activation with Na. With these clay minerals, the thing to watch out for is the potential of one mineral transforming to the other by ion exchange when exposed to leachate.

2.4.3.4 Chlorite mineral

Chlorite comprises a 2:1 layer (an octahedral sheet in between two silica tetrahedral sheets similar to Illite or Smectite) which is bonded to another octahedral sheet having Mg, Al or Fe in the central position. This sheet carries a net negative charge due to replacement of Mg by Al in the hydroxyl sheet Chlorite has similar engineering behaviour to illite and is considered to be effective, non-reactive barrier clay (Rowe et al, 1995). Nevertheless, chlorite minerals in clayey soils are almost always found in association with other clay minerals (Goldman et al, 1990). Chlorites are less attractive than smectite and have a cation exchange capacity of 10 to 40 meq/100g and the basal spacing is fixed at 14.2Ű.

2.5 CLAY CHEMISTRY

2.5.1 Diffuse Double Layer

Clay chemistry deals with the interactions within a clay-water-electrolyte system with mobile ions. Because the clay particle surfaces generally carry a net negative charge, the cations in the pore liquid are attracted to clay surfaces by electrostatic forces. This results in a layer of cations being held at the clay particle surface (Stern layer) and a diffuse layer of cations until the cation concentration approaches that of bulk pore liquid, giving rise to what is commonly referred to as a diffuse double layer. As shown in Fig. 2.3, the distribution of cation and anion concentrations in the diffused double layer of the bulk pore liquid are such that net negative charge at the clay surface is neutralised, and, at the other end of the layer cations and anions are balanced within the free bulk fluid. Hence, between two adjacent clay particles, the two double layers will be interacting to keep the distance between them. The most important aspect of the interaction of a clay-water-electrolyte system (e.g. Clay and leachate) is the contraction and expansion of the double layer (Rowe et al, 1995). For example, double layer contraction can cause clay particles to flocculate creating significant free void space and, therefore, leading to a substantial increase in clay hydraulic conductivity. Similarly, expansion in the double layer can cause dispersion of clay particles, thereby reducing the free void space and the hydraulic conductivity.



Fig. 2.3: Diffuse Double Layer (Das, B. M. 2006)

2.5.2 Factors Affecting Double Layer

2.5.2.1 Electrolyte concentration

The double layer thickness is inversely proportional to the square root of the electrolyte concentration. The double layer is suppressed by an increase in concentration. An increase in concentration reduces the surface potential for the condition of constant surface charge. Interparticle interactions extend to a much greater particle spacing for a low electrolyte concentration than a higher concentration. Swelling of the clay layer is related to double layer interactions and hence swelling is dependent on electrolyte concentration (Mitchell, 1976). Sitaram et al (2010) stated that a high electrolyte concentration retards full mobilization of the diffuse double layer thickness, increasing the effective void space for water which can lead to a higher hydraulic conductivity (Rao et al, 1987).

2.5.2.2 Cation valance

Thickness of the double layer will decrease with the increase of cation valance if the solutions have the same molarity and constant surface charge causing the solution to become more flocculent. Cation valance also affects surface potential of an electrolyte. The preferential adsorptions of relatively small amounts of di or trivalent cations added to clay have a significant influence on physical properties (Mitchell, 1976). If the cations are changed from monovalent to divalent or trivalent (e.g., from Na to Ca) the double layer contracts (Quigley, 1989).

2.5.2.3 Temperature

If the temperature is increased, the dielectric constant decreases and, consequentiy, there is a contraction in the double layer. This is due to the effect of temperature on the dielectric constant being more paramount than on the double layer. However, Mitchell (1976) pointed out that for water, the product ε T does not decrease markedly as the double layer, temperature is increased. Although the effect of temperature is not that significant on still the hydraulic conductivity could increase up to 6 times as the temperature is increased from 25°C to 50°C due to the changes in the viscosity and density (Airey, 1993). Therefore, it is advisable that the temperature should be maintained at a constant level during hydraulic conductivity testing.

All the above factors will cause the hydraulic conductivity to increase (sometimes dramatically) if the void ratio remains constant (ice. no overall volume change). Besides these, there are factors relating to solution properties such as pH, electrolyte type, composition and exchange phenomena as anion adsorption, selectivity of multivalent ions, and size and specific surface area of the clay particles may also affect the double layer thickness.

2.5.2.4 pH

Clay particles may have hydroxyl (OH) of the chemical structure (e.g. SiOH) exposed on their surfaces, and may have the tendency to dissociate depending on the pH of the pore fluid (Mitchell, 1976). At high pH (alkaline solutions), H can go into
the solution increasing the net negative charge on the clay surface. It can be argued that this would lead to an increase in double layer thickness, hence clay dispersion. In addition, alumina which is exposed at the edges of particles, can ionize positively when exposed to low pH (acidic) fluids. This means that the net negative charge on the clay particles will decrease (and sometimes can become even positive), and particles tend to flocculate from positively charged edges clinging to negatively charged surfaces (Mitchell, 1976). Goldman et al (1990) has pointed out that the clay minerals which derive a net negative charge mainly by chemical reactions on the surface are more likely to be affected by pH in the pore fluid. Accordingly, kaolinite, which appears to derive much of its net negative charge this way, may be more susceptible to change due to pH than other minerals.

2.5.2.5 Hydrated ion size

The thickness of the double layer depends on the hydrated ion size of cations. Therefore, from a given cation valence, the thickness of the double layer tends to increase with the increasing hydrated radii of cations (for example, hydrated radii of $Mg^{++} > Ca^{++} > Na^+ > K^+$).

2.5.2.6 Anion adsorption

Descriptions given so far assume attraction of cations to the clay particle surface. There may be situations, however, where some anions are attracted to the clay particles (e.g. edges) and thereby increase the net negative charge on the particle. This tends to increase the double layer thickness and leads to dispersion. For example, this appears to be the main mechanism by which the phosphates act as effective additives for clay dispersion or deflocculation (Mitchell, 1976).

2.5.2.7 Cation exchange capacity

The adsorbed cations around the clay particles can be exchanged by other cations in the pore fluid. The cation exchange capacity (CEC) of a soil is the sum of exchangeable cations, and is normally represented as meq/100g of soil. A high CEC generally represents high clay content and a high attenuation potential for

contaminants. Ion of one type can be replaced by another type (e.g. Ca^{++} for Na^+ or Na^+ for Ca^{++}), and the replacibility of the ions depends mainly on valence, a relative abundance of the different ion types and ion size (Mitchell, 1976). For example, monovalent ions are easily replaced by divalent ions. Common cations found in soil have the following descending order of replacing power: $Al^{+++} > Ca^{++} > Mg^{++} > K^+ > Na^+$. However, it is possible for this replacing order to be overridden if ions of lower replacing power are present in higher concentrations.

Soils with high CECs (e.g. Montmorillonite) are more prone to structural change than soils with less CECs (e.g. Kaolinite). This is because cation exchange can affect the double layer thickness and, in turn, can lead to dispersion or flocculation giving rise to changes in hydraulic conductivity of soils. Replacement of monovalent cation by a divalent cation (e.g. Na^+ by Ca^{++} or $Mg^{++)}$ can reduce the double layer thickness.

2.6 HYDRAULIC CONDUCTIVITY OF COMPACTED CLAY

Compaction is the application of mechanical energy to bring the soil into a dense and more stable condition. Soils in a dense state will have low porosity and a minimum flow path for the fluid to flow through them. Soil loses its natural fabrics and structure during the processing of soils for compaction. Compaction alters the soil fabric which, in turn, affects strongly the hydraulic conductivity of fine-grained cohesive soils. A number of factors are related to the hydraulic conductivity of compacted clays: basic physical properties, moulding moisture content and degree of saturation, method of compaction and compactive effort. These are all discussed in this sub-section.

2.6.1 Basic Physical Properties

Hydraulic conductivity is a function of the amount of clay fractions present in the liner material and it is reduced with an increase in the amount of fines. Higher liquid limit, plastic limit and surface activity are associated with soils having a greater quantity of clay particles (Mitchell, 1976). The soils containing a large quantity of highly swelling minerals generally have a high plasticity index. The liquid limit & the plastic limit reflect the consistency of the structure of cohesive soils and are a good parameter in which modification in the soil structure is detectable. All other factors being equal, more plastic clays should have lower hydraulic conductivity (Day & Daniel, 1985; Mesri & Olson, 1971). As the determination of plasticity index is quite easy and fast, it can be used for a first and qualitative evaluation of clay-permeant compatibility. Changes in the Atterberg limit due to the changes of moulding fluid were found by different investigators. Several investigators (e.g. Ridley et al, 1984; Barbour and Yang, 1993; Sitaram et al, 2010) found that plasticity of the soil is reduced due to the presence of high salt concentration in the moulding fluid. This occurred as a result of a decrease in the liquid limit and a little change in the plastic limit. Ridley et al (1984) and Sitaram Nayak et al, (2010) observed a decrease in the optimum moisture content and increases in mass density owing to the presence of high concentration of saline water as a moulding fluid.

2.6.2. Moisture Content

Moisture content strongly influences the arrangement of clay particles under the compactive effort used. Lambe (1958) suggested that compacted clays are flocculated when compacted dry of optimum moisture content and dispersed when compacted wet of optimum moisture content. At optimum moisture content, soil can display a combination of flocculated and dispersed fabric. The differences in hydraulic conductivity between the dry side and wet side of optimum, which have the same dry density, can increase from one to three log cycles (e.g. Mitchell et al, 1965). As shown in Fig 2.4, a difference in hydraulic conductivity was found by Benson and Daniel (1990) where the tests were carried out in dry and wet side of optimum. All investigators agreed that for a good liner, water content should be on the wet side of optimum but it is uncertain how much wet of optimum it should be. The strength of compacted clay decreases with an increase in water content. Daniel & Korener (1993) suggested that the soil must not be placed at too high water content above optimum because the shear strength may become too low. This may increase the risk of desiccation cracks forming in the drying soil, and ruts may form when construction vehicles pass over the liner.

2.6.3 Compaction Effort

Soil compaction is a process in which the air and, to a lesser degree, the water void volume of a soil mass is reduced. Laboratory compaction tests are used to specify the compaction requirements for the field. Samples are compacted using a range of compaction energies and a window for moisture content and dry densities are found. The weight and type of compactor have a significant influence on hydraulic conductivity. The increasing weight of the compactor results in a greater compactive effort, more shear deformation, smaller more uniform pores and lower hydraulic conductivity. Mitchell et al. (1965) found that kneading compaction yielded hydraulic conductivity half an order of magnitude lower than static compaction at wet of optimum moisture content having the same dry unit weight. Lower hydraulic conductivity in kneading compaction attributed to larger shear stress that occurs as the foot of the kneading compactor penetrates the soil. As shown in Fig 2.5, experience from the laboratory has shown that the type of compactor can affect hydraulic conductivity. Benson et al. (1994) found that rubber tyre rollers produced hydraulic conductivity 4 times higher than sheep foot rollers. As shown in Fig 2.6, Daniel and Wu (1993) presented an acceptable zone for quality assurance on the basis of moisture content and dry density considering hydraulic conductivity, volume shrinkage and shear strength as the criteria. This could be used in the field work by plotting the curves and making sure that they fit into the acceptable zone.



Fig 2.4: Hydraulic Conductivity vs Moulding Moisture Content (Benson & Daniel, 1990).



Fig 2.5: Effect of compaction energy on hydraulic conductivity (Mitchell et al., 1965)



Fig 2.6: Acceptable Zone Based on Design Objectives for Hydraulic Conductivity, Shrinkage and Shear Strength (Daniel and Wu, 1993)

2.7 LOCALLY AVAILBLE SOILS AS LINER MATERIAL

A large number of landfills have been constructed worldwide based on the performance of the constructed facilities. Researchers have also been trying to use locally available soils as liner material in landfill. Wherever suitable low hydraulic conductivity natural clay materials are available, they provide the most economical lining material and are commonly used. Natural clays usually satisfy basic requirements of the good liner material (Osinubi and Nwaiwu 2006).

Yahia et al., (2005) studied the possibility of using crushed shales as landfill liners and reported that the crushed shales satisfy the all geotechnical properties and chemical analysis for clay liners and the compacted shales have low compressibility and no serious post construction settlement is expected for all level of compaction. <u>Taha and Kabir</u> (2005) measured certain physio-chemical properties of the granite residual soil to assess its suitability as a soil liner material. From the physio-chemical properties, it was concluded that the granite residual soil can be used as a suitable liner material for isolating waste materials in landfills and the soil satisfies all the basic requirements of a good barrier material. Though, its high plasticity (i.e 35%) proved to be an issue for workability, it exhibits small shrinkage potential upon drying. It is recommended that considerable care should be taken during the preparation of soil. Blending the soil on site with a pulverizing mixer would be helpful in reducing clod size and obtaining uniform moisture content.

Kolawole and Adrian (2005), Hydraulic conductivity tests were conducted on three samples of lateritic soil with four compactive efforts. It was concluded that to achieve a hydraulic conductivity value less than 1×10^{-7} cm/s, the lateritic soils that should be compacted to a minimum dry unit weight of 16.0kN/m³, with a minimum initial degree of saturation of 86% using a compaction energy that is at least at British Standard Light (BSL). Taha and Kabir, (2005) have suggested that the granite residual soil can be potentially utilized as compacted soil liner material. By applying Proctor compaction energy at water contents of 4.2% dry of optimum to 0.4% wet of optimum water content, it achieve the low hydraulic conductivity, adequate strength and minimal potential to shrinkage.

2.8 BLENDED SOIL AS A LINER MATERIAL

When low-permeability clay is not available locally, in-situ soils may be mixed with medium to high plasticity imported clay to achieve the required low hydraulic conductivity (Taha et al., 2005). Researchers have suggested blending of different soils to be used as a liner material (Kolawole and Adrian 2005; Kalkan 2006; Ameta and Wayal 2008; Chiu et al 1998; Sahel and Ali 2001; Moses and Afolayan 2011, Palmer et al. 2000).

Ameta and Wayal, (2008) reported that the permeability is greatly affected by adding bentonite to dune sand. Hydraulic conductivity reduced from 1×10^{-4} cm/s to 1×10^{-8} cm/s after 10% bentonite was added to the dune sand and compacted to maximum dry density at optimum moisture content. The coefficient of consolidation decreases with lower bentonite to dune sand ratios. Gueddouda et al., (2008) studied the hydraulic conductivity of dune sand with bentonite mixtures and concluded that 12% bentonite is the minimum requirement in the mix to achieve the required resistance to the percolation of water. Amedi et al. (2012) studied the acceptable hydraulic conductivity of lateritic soil blended with bentonite clay. Studies were carried out on lateritic soil treated with different percentage of 10% bentonite clay,

prepared at various compaction states (dry of optimum, optimum and wet of optimum moisture content) consider four compactive efforts (i.e., the reduced British Standard Light, British Standard Light, West African Standard and British Standard Heavy). They concluded that lateritic soil with 10% bentonite clay mixture satisfies the minimum hydraulic conductivity requirements on wet side of optimum for clay liner.

Tay et al., (2000) studied the shrinkage and desiccation cracking exhibited by bentonite-enhanced sand mixture (BES) upon air drying. Compacted bed of BES containing 10% and 20% bentonite do not exhibit desiccation cracking, if volumetric shrinkage during drying is less than about 4%. Sahel et al., (2001) has studied blending of two different kinds of locally available soils are high plastic clayey soil and medium plastic soil, which satisfies all specifications for a soil liner as shown in Fig. 2.7 and Fig. 2.8. Studies were carried by Kalkan (2006) on composite soil samples made with natural clay red mud and cement red mud. It is concluded that this composite soil can be successfully used for stabilization of clay liner.



Fig. 2.7 Compaction curves of the blended soil (Sahel et al., 2001).



Fig. 2.8 Hydraulic conductivity curves for the blended soil (Sahel et al., 2001).

Amer et al., (2006) investigated the potential use of sand-attapulgite (palygorskite) clay mixtures as a landfill liner. They analysed the results and concluded that the sand + 30% clay mixture prepared at 2% above optimum water content can be considered to satisfy the requirements for landfill liners. They also concluded that for all sand-clay mixtures improvement in shear strength was obersved.

2.9 ACCEPTABLE ZONE

After choosing a liner material the next step is to specify compaction control for the same because compaction energy and degree of saturation controls the hydraulic conductivity of the liner material.

Osinubi and Nwaiwu, (2006), Compaction proctor tests were conducted on three samples of lateritic soil with four compactive efforts. They have investigated the acceptable zones (AZ) which was constructed based on the compaction plane to meet design objectives for hydraulic conductivity, volumetric shrinkage strains, and unconfined compressive strength as shown in Fig. 2.9. The line of optimums was identified as a suitable lower boundary and zero air voids curve as the top limit for overall acceptable zones of lateritic soils. The volumetric shrinkage strain was also identified as the second most important design parameter for lateritic soils. The shapes of the acceptable zones were affected by the fines contents of the soil.



Fig. 2.9 Acceptable zones based on hydraulic conductivity (Osinubi and Nwaiwu, 2006)

2.10 ADSORPTION STUDIES

Before beginning with the literature dealing the retention of contaminants by soil liner system, it is necessary to understand the theory behind the adsorption and the means, with the help of which required parameters are determined. Adsorption of a substance involves its accumulation at the interface between two phases, such as a liquid and a solid or a gas and a solid. The molecule that accumulates, or adsorbs, at the interface is called an adsorbate, and the solid on which adsorption occurs is the adsorbent. Adsorption is important to assess the migrational characteristics of the solute in the particular soil. If the adsorption is more, the less its migration and less will be the extent of pollution. An important parameter that is used in contaminant transport analytical models, the partition coefficient (K_d), may be directly obtained from adsorption studies. Thus the attenuation characteristics (the ability to retain contaminants) of a soil for a potential liner material can be derived from the study of adsorption studies (Taha et al. 2003). Linear sorption processes govern a common approach to the simulation of transport of contaminants in porous medium (Shivakumar 2011). Many researchers conducted the sorption studies using batch

experimental test Young and Park (2011), Hai-jun et al (2008), Tanit et al., (2009), Kumar and Philip (2006), Pivato and raga (2006) Taha et al (2003).

2.10.1 Retention of Contaminants by Soil Liner System

A number of studies on hydraulic conductivity have been carried out but sorption behavior of compacted clay soils has not been carried out extensively for Indian scenario. The leachates generated may contain many toxic metal ions. Adsorption of soluble metallic species by clays, oxides and other colloidal matters appears to be an important means of controlling the trace soluble metal concentrations in the heterogeneous system. Bentonite containing good amount of clay content is considered to be an adsorbent for the removal of various heavy metal ions such as cadmium, lead, copper iron, manganese and nickel (Naik and Sivapullaiah 2012). Conventional technologies for the removal of heavy metal ions such as chemical precipitation, electrolysis, ion exchange and reverse osmosis are often neither effective nor economical. Among the physico-chemical treatment process, adsorption is highly effective, cheap and easy to adopt. Adsorption is proven to be a successful method for removal of heavy metals from landfill leachate (Tahir & Naseem, 2004).

Taha et al., (2003) studied the adsorption of phenol on granite residual soil and kaolinite and concluded that, residual soil possesses a greater adsorption capacity compared with kaolinite. A linear relationship was obtained for results involving only low concentrations. The highly non-linear relationships, which cover the whole set of data, was transformed linearly using the Linearized Freundlich and Langmuir isotherms. The linearized Langmuir plot for low concentration data may be used to estimate the maximum adsorption capacity of the soil. It is concluded that the residual soil has a great potential for use as a soil liner material. Kim (2002) conducted the laboratory batch test to determine the mechanism by which thiolane and sulfolane adsorb on soil materials. It was found that thiolane is more strongly adsorbed onto clay materials than sulfolane as K_d showed 9.1 \pm 0.41 L/kg and 1.14 \pm 0.16 L/kg, respectively.

Kim et al., (2003) has investigated the effect of the soil solids concentration in batch tests on the measured values of the partition coefficient (k_d) of organic pollutants in landfill liner material. It was suggested that the soil solids concentration is less than a certain value (e.g. 100g/l), the measured partition coefficients will not properly simulate the field situation and retardation factors of landfill liner systems will be overestimated. Hai-jun et al., (2009) studied the effect of soil-solids concentration and temperature in batch tests on the adsorption of Cr(VI) onto landfill liner materials, and concluded that the values of isotherm parameters measured using batch tests under low soil-solids concentrations will not properly simulate the field situation, and retardation factors of clay landfill liners systems will be overestimated. Therefore, a sufficiently high soil-solids concentration should be conducted in batch tests in order to obtain isotherm parameters close to the results from the field situation.

Tanit et al., (2009) studied the potential use of lateritic and marine clay soil as landfill liners to retain heavy metals. It was reported that the marine clay soil had better adsorption capacity than that of the lateritic soil and its hydraulic conductivity was lower. In addition, the hydraulic conductivities of both soils when permeated with low concentration of heavy metal (Cr, Pb, Cd, Zn and Ni) solutions were below 1×10^{-7} cm/s and when permeated with heavy metal solutions, the retardation factors of the lateritic soil and the marine clay soil ranged from 10 to 98 and 37 to 165 respectively. For lateritic soil and the marine clay soil, Cr and Pb were retained relatively well, while Cd, Zn and Ni were more mobile. The marine clay soil had higher retardation factors and its hydraulic conductivity was more compatible with Chromium solution, than that of the lateritic soil. In general, the properties of the marine clay soil indicate that it has significant advantages over the lateritic soil as landfill liner material.

Sezer et al., (2003) studied the mineralogical and sorption characteristics of Ankara clay. The effect of clay mineral types and their concentrations are clearly reflected in the cation exchange capacity values of mineral barriers. The presence of oxides in its composition enhances the retention of heavy metal ions. It was concluded that the Ankara clay can be effectively utilized as a component of barrier design in sanitary landfill because of its suitable chemical and mineralogical characteristics.

2.10.2 Sorption Isotherms

Sorption refers to contaminants attached to mineral grains and organic matter in the soil. The relationship between contaminants absorbed and present in pore water is expressed graphically by using isotherms. There are different kinds of isotherms but in this study we have mainly three isotherms that are

- i. The linear isotherm
- ii. The Freundlich isotherm
- iii. The Langmuir isotherm

2.11 EFFECT OF LEACHATE ON GEOTECHNICAL PROPERTIES OF CLAY LINER

Clay liners are now commonly used to limit or eliminate the movement of leachate and landfill gases from the landfill site. The liners are exposed there to various chemical, biological and physical events, and they are affected by the resulting leachate. To assess the durability of the liner material, it is important to study the chemical compatibility of the liner material with different pore fluids, or the leachate that the liner may be subject to (Mitchell and Jaber, 1990; Olson and Daniel, 1981; Mitchell and Madsen, 1987; Sivapullaiah and Lakshmikantha, 2004). In this sense, when attempting to define the geotechnical characteristics of clay liners, the use of distilled water or tap water is far from being representative of the in-situ conditions. For this reason, to properly use the compacted clays as impermeable liners, more theoretical and experimental study is needed to investigate the variation of engineering properties with chemicals.

2.11.1 Landfills Leachate

In most countries, sanitary landfills are nowadays the most common way to eliminate Municipal Solid Wastes (MSW). In spite of many advantages, generation of heavily polluted leachate, presenting significant variations in both volumetric flow and chemical composition, constitutes a major drawback (Renou et al., 2008). Leachate may be defined as liquid that has percolated through solid waste and has extracted, dissolved or suspended materials. In most landfills leachate is composed of the liquid that has entered the landfill from external sources, such as surface drainage, rainfall, groundwater, and water from underground springs and the liquid produced from the decomposition of the wastes, if any. When water percolates through solid wastes that are undergoing decomposition, both biological materials and chemical constituents are leached into solution. The chemical composition of the leachate will vary greatly depending on the age of the landfill and the events before the time of sampling. A large body of work on the chemical composition of landfill leachate can be found in Manimekalai and Vijayalakshmi (2012), Ehrig (1988), Tchobanoglous et al. (1993), Renou et al. (2008). The characteristics of the MSW leachate (as shown in Table 2.1) at a dump yard (this yard is being operated for 15 years) were reported by Ravishankar et al. (2004).

2.11.2 Effect of Leachate on Consistency Limits of Soil

It should be pointed out that there has not been a general consensus regarding the effect of chemicals on the consistency limits of clays. Arasan and Yetimoglu (2008), based on their experimental study on a CL clay, pointed out that both the liquid limit and the plastic limit somewhat increased when the concentration of salt solutions was increased. Sivapullaiah and Manju (2005) investigated the same geotechnical properties of a low plasticity soil (w_L = 38%) using NaOH solution. They reported that the liquid limit of the test soil was increased with increasing NaOH concentration due to forming of new swelling compounds. Sitaram et al. (2010) studied that liquid limit and plasticity index of the soils tested decrease as a result of interaction with sodium chloride solution. Rao and Mathew (1995) based on their experimental study with marine clay, indicated that the clay particles were dispersed when the clay interacted with chemicals. Due to dispersion and deflocculation of clay, the geotechnical properties (especially, hydraulic conductivity) of clay were significantly changed. Hence, the increase in consistency limits could be attributed to dispersion of the clay particles when CL clay was permeated with salt solutions. Additionally, salt solutions might cause to form new swelling compounds and these new compounds might have increased the liquid limit of CL clay as indicated in Sivapullaiah and Manju (2005).

Some researchers have indicated that the liquid limit decreased with increasing salt concentration for CH clays (Sridharan et al., 1986; Bowders and Daniel, 1987; Daniel et al., 1988; Edil et al., 1991; Gleason et al., 1997; Lin and Benson, 2000; Sridharan and Prakash, 2000; Schmitz et al., 2004).

Substances extracted	Maximum concentration in mg/L
Total solids	10,300 to 14,530
Total dissolved solids	6700 to 10,530
BOD	200 to 1200
COD	22,125
Ammonia-N	900
Sodium (Na)	1000
Potassium (K)	1000
Iron content	50
pH	8.1

Table 2.1 Typical leachate composition (Ravishankar et al. 2004)

2.11.3 Effect of Leachate on Hydraulic Conductivity of Soil

It is well known that the hydraulic conductivity of clays can be strongly affected by the clay-fluid system interaction (Mitchell, 1993). A great number of experimental studies dealing with the effects of chemicals on hydraulic conductivity of compacted clays are available in the literature. Sitaram et al. (2010) reported that, hydraulic conductivity and void ratio increases with the increase in the sodium chloride concentration for laterite and shedi soil. Suppression of diffuse double layer is responsible for the steep increase in hydraulic conductivity of the soil. Most of the researchers pointed out that the hydraulic conductivity increased when the concentration of chemical solutions was increased for high plasticity clays. In some cases, interactions between the permeating liquid and the clay can result in significant increases in the hydraulic conductivity of the clay relative to that based on water (Mitchell and Madsen, 1987, Sitaram et al, 2007). This increase in hydraulic conductivity of the soil is attributed to chemical reaction between the leachate and the clay minerals. It is reported in literature that strongly acidic and strongly basic liquids can dissolve clay minerals (Uppot and Stephenson, 1989). Flocculated and dispersed structures have different hydraulic conductivities. The thickness of the diffused double layer can influence the soil structure, resulting in permeability changes. The thickness of this diffused double layer can be affected by parameters such as the dielectric constant of the medium, cation valence, electrolyte concentration, and so on. When fluids containing various chemicals or leachate permeate underlying clay liners, they may change various factors that can influence the thickness of the diffused double layer and hence the permeability of the permeated clays (Sharma and Levis, 1994). Yilmaz et al. (2008) studied the effect of inorganic salt solutions (NaCl, NH₄Cl, KCl, CaCl₂ and FeCl₃) on the hydraulic conductivity of CL and CH class clays. It was indicated that the hydraulic conductivity decreased when the concentration of the salt solution was increased for CL clays. Similarly, some experimental tests on kaolinite clay showed that hydraulic conductivity decreased when clay samples were permeated with chemical solutions such as acetone, benzene, diethylene glycol, nitrobenzene, phenol (Dragun, 1988). Rao and Mathew (1995), based on their experimental study with marine clay, indicated that the reduction in hydraulic conductivity was related to the dispersion and deflocculation of clay. Also, Park et al. (2006), after conducting an experimental study on low plasticity kaolinite clay, reported that the hydraulic conductivity was not significantly affected, but slightly decreased due to pore clogging and the high viscosity of the solutions. Hence, the decrease in hydraulic conductivity could be attributed to dispersion of the clay particles when CL clay was permeated with inorganic salts. It could be also said that the decrease in hydraulic conductivity is due to formation of new swelling type of compounds as well (Sivapullaiah and Manju, 2005).

2.11.4 Shear Strength

The shear strength of the landfill is one of the important parameter. The liner material should be strong enough to sustain the static load exerted by the overlying body of waste (Kenney et al., 1992). Limited information is currently available on the shear strength of clay liners interacted with chemicals. However, some of the researchers were focused on the investigation of the shear strength of lower activity clays such as kaolinite, sub soil or red earth. Ayininuola et al. (2009) investigated the shear strength of subsoil saturated with $CaSO_4$ at different concentrations. The laboratory results of this study showed that there were initial increase in soil angle of friction and cohesion due to presence of CaSO₄ salt. Similarly, Sivapullaiah and Lakshmikantha (2005) investigated on the utilization of Indian red earth (kaolinitic soil) as a liner material with bentonite and lime addition. It was found that the peak stress of the liner in NaOH and water are higher than those of HCl and NaCl. They indicated that the lower strength of the soil with NaCl solutions was due to reduction in soil cohesion by reduced water adsorption capacity consequent on reduced thickness of the diffused double layer. Park et al. (2006) also indicated the addition of the electrolyte solutions caused an increase in electrolyte concentration, which decreased the double layer thickness. The large increase in interparticle attraction made possible by the reduction of the diffuse double layer was responsible for the flocculation of the clay mixture on mechanical remolding. This effect resulted in increased strength of kaolinite mixtures.

2.12 LITERATURE SUMMARY

From the literature review it was found that the studies carried out on soil as a liner material by various researchers are site specific. Each problem is unique by itself and the behaviour of the soil depends on many factors (eg: leachate constituent etc.)

After the review of available literature, it is found that the selected compaction method should be the one which has no adverse effects on the physical properties of the soil layer and the initial compaction water content and the compactive energy have a significant role in imparting a particular structure to the compacted soil. Several studies have been conducted to minimize the hydraulic conductivity. To achieve this, soils should be compacted on the wet side of optimum moisture content. Clod size in soil should be minimized to the extent possible to prevent preferential flow pathways for leachate. Soils must be protected against desiccation both prior to and after compaction.

Natural clays usually satisfy the specification for liner material; however, highly plastic clays that desiccate are not preferred because the desiccation cracks can lead to the leakage of leachate. The hydraulic conductivity of clays containing less reactive clay minerals such as kaolinite and illite were found to be unaffected by chemical solutions. The effect of clay mineral types and their concentrations are clearly reflected in the cation exchange capacity values of mineral barriers.

2.13 RESEARCH OBJECTIVES

The concept of engineered landfill is being promoted in India and setting up of landfills is usually contemplated outside the urban localities. In rural areas majority of the population depend on ground water. Hence to prevent contamination of soil and water it is therefore landfill with bottom liner necessary to design a proper disposal system for the generated wastes applicable to the local climatic conditions. Liner acts as a barrier to prevent or minimize the migration of pollutants into the environment from the landfill. Liners are usually constructed using naturally clayey soils or composite materials (geosynthetics and natural soils).

The following objectives are proposed for the current research investigation:

- 1. Suitability of locally available soils or blended soils as landfill liner material.
- 2. To specify compaction control for the blended soil.
- 3. To examine the capacity of soil to adsorb various leachate constituent through batch adsorption tests
- 4. To study the impact of municipal solid waste (MSW) landfill leachate on hydraulic conductivity of the blended soils.
- 5. Evaluation of potential effectiveness of blended soil as landfill liner material based on the laboratory test results.

CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 GENERAL

The methodology adopted for soil characterization wherein, all the tests pertaining to physical, chemical, and geotechnical properties of soil are explained. All the tests are performed as per procedure recommended by the Bureau of Indian Standards. Also the procedure adopted to determine the adsorption characteristics of test soils and leachate characterization are the other highlights of this chapter.

3.2 SOIL SAMPLING AND TESTING

In the present study lithomargic clay (locally called shedi soil) has been procured from Haleangadi, approximately 6 kilometres away from National Institute of Technology (NITK), Surathkal, India and black cotton (BC) soil from Hebsur village, 20 km from Hubli city, Karanataka state, India. Commercially available bentonite (BN) was also used for the study. The index and engineering properties of test soils are determined as per relevant Indian Standards.

The soils were transferred to separate plastic containers with proper nomenclature on the containers. The procured soil samples from the site were air dried in shade and stored in plastic bags to avoid contamination. Index properties of the soil were determined by selecting a representative soil sample. Soil samples were prepared as per IS 2720 (Part 1)-1983.

Commercially available bentonite was used for the study. Sodium bentonites have been used more extensively than calcium bentonite because of its superior swelling capacity, higher cation exchange capacity and its very low hydraulic conductivity to water.

3.3 METHODS FOR GEOTEHNICAL CHARACTERIZATION OF SOILS

The index and engineering properties of test soils are determined as per relevant Indian Standards. A brief overview of the methodology adopted for soil testing is presented in the following sections.

3.3.1 Index Properties

The natural moisture content and in situ field density of soil were determined as per IS 2720 (Part 2)-1973 (reaffirmed 1997) and IS 2720 (Part 29)-1975 (reaffirmed 1995) respectively. The specific gravity of soil solids were determined as per IS 2720 (Part 3/ section 1)-1980 (reaffirmed 1997). The grain size analysis of test soils were done as per IS 2720 (Part 4)-1985 (reaffirmed 1995). The liquid limit of the test soils using standard liquid limit apparatus was determined as per IS 2720 (Part 5)-1985 (reaffirmed 1995). The plastic limit was determined as per IS 2720 (Part 5)-1985(reaffirmed 1995). The shrinkage limit of the test soils was determined as per IS 2720 (Part 6)-1972(reaffirmed 1995).

3.3.2 Determination of Compaction Characteristics of Test Soils.

The compaction characteristics of lithomargic clay, BC soil and bentonite were studied in the laboratory using standard proctor test (light compaction test) as per IS 2720 (Part-7)-1980 (reaffirmed 1987). The equipment used in the test consists of cylindrical mould (with detachable base plate) having an internal diameter of 100 mm and 127.5 mm effective height, whose internal volume is 1000 ml. The rammer used has a mass of 2.6 kg with a drop of 310 mm. The number of blows required to achieve Proctor energy per layer is 25 (total in three layers). After compaction of third layer the collar was removed and the soil was trimmed level with the top of the mould. Weight of the sample in the mould was then found out. Water content of the representative sample was found out. The compaction was repeated and the results of compaction test were then plotted as dry density against water content to obtain compaction curve. From the plot, maximum dry density (γ_{dmax}) and optimum moisture content (w_{opt}) were read corresponding to the peak of the compaction curve.

3.3.3 Hydraulic Conductivity

Falling head permeability tests were carried out on saturated soil sample to study the hydraulic conductivity of test soils (shedi soil, BC soil and bentonite) as per IS 2720 (Part 17)-1986 (reaffirmed 1997). To stimulate the field condition, all the permeability test were conducted on samples remoulded to standard Proctor maximum dry density and optimum moisture content. Fig. 3.1 shows the apparatus and schematic diagram of varying head permeability.



Fig.3.1 Apparatus and schematic diagram of varying head permeameter

3.3.4 Unconfined Compression Strength (UCS)

In this study, unconfined compression strength (UCS) test on study soils were carried out on soil samples having a diameter and length of 38mm and 76mm, respectively. This test was carried out on soil samples by moulding the soil at different initial water content, to assess the change of compressive strength with change in water content. Unconfined compression test was conducted as per IS: 2720

(part 10)-1991 (reaffirmed 1995). Fig. 3.2 shows the instruments used for the unconfined compressive strength.



Fig. 3.2 Unconfined compression testing machine

3.4 CHEMICAL CHARACTERISTICS OF STUDY SOIL

Chemical parameters of soil that are essential for adsorption studies were determined. These are pH, cation exchange capacity, organic matter, conductivity, sulphate, silica content, iron oxide content, aluminium oxide content, calcium and magnesium oxides in soil and the methods and instruments used for the test are tabulated in Table 3.1. All the tests pertaining to chemical characteristics were carried out on soil passing through 425 micron IS sieve.

Parameters used	Methods	Instruments used	References
рН	Electrometric method (Standard method)	Electrometric method (Standard method) pH meter	
Conductivity (mS/cm)	Potentiometric method	Conductivity meter	IS 2720 part 26-1987, pp 239-241
Organic matter	Modified Walkley & Black method	-	IS 2720 part 22-1972, pp 260-261
Cation Exchange Capacity (meq/100g)	Rapid Method	-	IS 2720 part 24-1976, pp 244-245
Silica (SiO ₂)	Gravimetric method	-	IS 2720 part 25-1982, pp 256-257
Iron Oxide (Fe ₂ O ₃)	Gravimetric / Colorimetric method	Spectrometer	IS 2720 part 24-1976, pp 256-257
Aluminium Oxide (Al ₂ O ₃)	Gravimetric method	-	IS 2720 part 24-1976, pp 256-257
Sulphates (SO ₄)	Turbidimetric method	Spectrometer	IS 2720 part 27-1977, pp 254-255
Magnesium Oxide (MgO)	E.D.T.A Titrimetric method	-	Standard Methods pp. 3–83 (As explained in Appendix I)

Table 3.1 Methodology and instruments used in determining chemical characteristics of soil.

3.5 ADSORPTION STUDIES

Adsorption is a phenomenon in which a solute attaches itself to the surface of a solid material. The compatibility of a clay liner on interaction with contaminant depends on two factors, i) the ability of the clay liner to resist any increase in hydraulic conductivity due to the contaminant interaction and ii) its capacity to retard the migration of contaminants through sorption. Adsorption is proven to be a successful method for removal of heavy metals from landfill leachate (Julita et al. 2005). Adsorption is important to assess the migration characteristics of the solute. If the solute is adsorbed more, the less would be its migration and hence lower the extent of pollution (Taha et al. 2003). Thus the attenuation characteristics (the ability to retain contaminants) of a soil for a potential liner material can be derived from the study of adsorption tests. Adsorption characteristics of soil samples were studied through batch tests. After the test, adsorption isotherms were plotted. The parameters initial concentration (C_0) and final/equilibrium concentration (C_e) of solute were used to plot the linear and nonlinear isotherms.

The tests were carried out by first measuring the initial concentration of standard solution (C_i) and later measuring the final concentration of the contaminant (C_e) in the solution after equilibrium time of about 2 weeks as shown in Fig. 3.3.



Fig. 3.3 Test soil samples for adsorption studies.

After determining the initial and final concentration of contaminant (i.e. C_i and C_e), the mass of contaminant adsorbed on soil surface is calculated using Eqn. 3.1.

$$S = \frac{(C_i - C_e) \times V_f}{M_s}$$
 3.1

Where, S – Mass of contaminant sorbed per unit dry mass of soil (mg/kg)

 C_i – Initial concentration of contaminant in solution (mg/L)

C_e – Concentration of contaminant in solution at equilibrium (mg/L)

M_s– Mass of soil (g)

 V_f -volume of solute (ml)

Detailed procedure is given in Appendix II

3.6 LEACHATE STUDIES

The extent of the effect of solid waste leachate on soil properties is mainly depends on the quality and quantity of the leachate generated from solid waste, which in turn depends on the decomposable matter in the solid waste, age of landfill, quantity of rain fall, runoff characteristics, etc,. For present study, Mangalore city MSW dumping area has been selected (Fig. 3.4). The Mangalore city MSW is being dumped at Vamanjoor village from past three decades. The characterization of Mangalore city MSW has been done and the methodology followed is mentioned in this section.



Fig 3.4 Leachate collection at municipal solid waste dumping yard

3.6.1 Leachate Sampling and Testing

Leachate samples were collected randomly from three different locations at the base of the dumping yard and were mixed prior to its analysis. The samples were immediately stored in refrigerator with proper nomenclature on the containers. The analysis was started without delay in laboratory based on the priority to analyze parameters. Various physico-chemical parameters of the leachate samples studied and its methods/instruments used are shown in Table 3.2.

Parameters used	Methods	Instruments used	References
рН	Electrometric method (Standard method)	Digital pH meter Systronic make, Model- 335	Standard Methods 4–85
Electrical conductivity in milli siemens	Potentiometric method	Conductivity meter Systronic make, Model- 307	Standard Methods 2–44
Total dissolved solids (TDS) in mg/L	Conductimetric method	Conductivity meter Systronic make, Model- 307	Standard Methods 2–56
Total hardness expressed in terms of CaCO ₃ in mg/L	Titrimetry method	-	Standard Methods 2–37
Calcium (Ca) in mg/L	Titrimetry method	-	Standard Methods 3–64
Chemical oxygen demand (COD) in mg/L	Closed reflux titrimetry method	Lovibond Model- ET125	Standard Methods 5–15
Bio chemical oxygen demand (BOD) in mg/L	Polarographic DO Probe method	DO meter, WTW make Model-OXI96	Standard Methods 5–3
Ammonium nitrogen (NH ₄) in mg/L	Nesslers method	Spectrometer Lovibond make, Model- PC Spectro	Standard Methods 356
Sodium (Na) in mg/L	Flame Photometric Method	Flame photometry Systronic make, Model-128	Standard Methods 3-98
Potasium (K) in mg/L	Flame Photometric Method	Flame photometry Systronic make, Model- 128	Standard Methods 3-87
Chloride (Cl) in mg/L	Argentometric method	-	Standard Methods 4-67
Zinc (Zn) in mg/L			
Chromium (Cr) in mg/L	Atomic absorption	AAS-Tifac make	Standard Methods
Lead (Pb) in mg/L	ead (Pb) in mg/L spectrometer		3-17
Copper (Cu) in mg/L	method		

Table 3.2 Leachate parameters and methods/instruments used for its determination

3.7 X- RAY DIFFRACTION (XRD) ANALYSIS

The X-ray diffraction (XRD) analysis was conducted to determine mineral content of the soil. The analysis was carried out using a diffractometer. To identify mineral types, quantitative assessment was made by comparing the diffraction pattern of each sample with the standard patterns. The X-ray diffraction (XRD) is a versatile,

non-destructive technique that reveals information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD is the direct and analytical method for determining the presence and absolute amounts of mineral species in a sample. Based on the principle of X-ray diffraction, A wealth of structure, physical and chemical information about the mineral investigated can be obtained. X-ray, which are electromagnetic radiations, are produced when high speed electrons collide with metal target. Whenever a wave motion is of the same magnitude of the repeat distance between scattering centres, the diffraction occurs. Hence the crystalline substance can diffract x-rays.

The powder diffraction can yield a great deal of structure information's about the material under investigation. Basically this method involves the diffraction of monochromatic x-rays by a powder specimen. The diffraction pattern of an unknown substance can be obtained in two ways, namely, continuous scan process. From the analyses, a curve of intensity vs 2θ of range of interest is plotted. The identification of the unknown begins with recording of the diffraction pattern.

Today about 50,000 inorganic and 25,000 organic single component, crystalline phases, and diffraction patterns have been collected and stored on magnetic or optical media as standards. The main use of the powder diffraction is to identify the components in a sample by a search/match procedure. Furthermore, the areas under peak are related to the amount of each phase present in the sample. In the powder or polycrystalline diffraction it is important to have a sample with a smooth plane surface. If possible, we normally grind the sample down to particles of about 0.002mm to 0.005mm cross section. The ideal sample is homogeneous and the crystallites are randomly distributed. The sample is pressed into a sample holder so that we have a smooth flat surface.

XRD study was under taken on the basic soil (lithomargic clay) and blended soil (before and after leachate interaction). This study was undertaken to know the formation of new minerals after leachate interaction. The analysis was carried out on Diffractometer- JEOL- Model DX-GE-2P. the diffraction was varied from 5° to 90° at scanning speed of 4°/min and operated at 30kV.

The International Centre Diffraction Data (ICDD), formerly known as (JCPDS) Joint Committee on Powder Diffraction Standards, is the organization that from diffraction equipment manufacturers or from ICDD direct. Currently the database is supplied either on magnetic or optical media. Two database versions are available: the PDF I and the PDF II. The database format consists of a set number and sequence number starts from 1 every year. The yearly releases of the database are available in September of each year. For the analysis 1994 JCPDS- International Centre Diffraction Data was used.

3.8 SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

Scanning electron microscope study was undertaken to study the microfabric component of the soil structure before and after the leachate interaction. Scanning electron microscope (SEM) operates under high vacuum and has an electron gun as a source of electrons. It has two or more condenser lenses. To evaluate the influence of fabric on the behaviour of soil, SEM analysis was carried out on the before and the after leachate interaction shedi and blended soil samples. The analysis was carried out on the JEOL scanning electron microscope [Model JSM – 6380LA (Fig 3.5)], which provide fabric appraisal. Each sample is held in an aluminium sample holder and sputter - coated with a fine gold film. The sputter coater is designed primarily for sputtering conducting gold layers on to sample to prevent charging effects in the scanning electron microscope.

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of material making up the sample. In most applications, data are collected over a sleeted area of the surface of the sample, and a two-dimensional image is generated that displays spatial variations in these properties. Areas ranging from 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 500X to approximately 10,000X, spatial resolution of 50 to 100nm).



Fig. 3.5 Analytical scanning electron microscope

The SEM has a large depth of field which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution which means that closely spaced feathers can be examined at a high magnification. Preparation of the sample is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in the research areas today.

CHAPTER 4

GEOTECHNICAL CHARACTERIZATION OF TEST SOILS

4.1 GENERAL

In the present work, locally available natural soil (i.e. lithomargic clay), black cotton soil and commercial available bentonite and its blends were studied to assess the compatibility as landfill liner. The natural soil samples were obtained from Dakshina Kannada district and Dharward district of Karnataka state. After sampling, the soil samples were transported to the laboratory and air dried in shade. The tests were carried out as per the procedure recommended by the Bureau of Indian Standards (BIS).

4.2 CHARACTERIZATION OF TEST SOILS

4.2.1 Index Properties of Test Soils

The index properties of the test soils are presented in Table 4.1

Grain Size Analysis

Wet sieve analysis was conducted on the test soils and its blends. Table 4.1 gives the grain size distribution of lithomargic clay, black cotton soil and bentonite analysed in the laboratory. Lithomargic clay contains mainly 59.5% of fines passing through 75microns and 40.5% retained on the 75 microns sieve. Black cotton soil contains 99.5% of fines passing thorough 75micron and only 0.5% is retained on 75microns sieve. Bentonite contains 80% of clay and the remaining 20% is silt content. Fig 4.1 shows grain size distribution curve of test soils. Based on the test results the lithomargic clay is classified as MI i.e. inorganic silts of intermediate plasticity and black cotton soils and bentonite are classified as inorganic clay of high plasticity (CH).

Parameters	Lithomargic clay	Black cotton soil	Bentonite
Insitu field density, $\gamma \text{ kN/m}^3$	16	15.85	-
Natural moisture content (%)	15.7	31	-
Field dry density, $\gamma_{dfield} kN/m^3$	13.83	12.1	-
Specific gravity	2.58	2.61	2.36
Atterberg's limits (%)			
Liquid limit (w _L)	45	109	297
Plastic limit (w _P)	32	42	45
Shrinkage limit (w _S)	27	2.5	10.5
Plasticity index (I _p)	13	67	252
Particle size distribution (%)			
Gravel size	2.5	0.0	-
Sand size	38.0	0.5	-
Silt size	44.5	70.5	20
Clay size	15.0	29.0	80
Soil classification	MI	СН	СН
Max dry density, γ_{dmax} (kN/m ³)	16.5	13	13.1
Optimum moisture content (OMC) %	19.5	36	33

Table 4.1 Index properties of the test soils

Specific Gravity

The specific gravity of test soils was determined and the results are provided in Table 4.1. As shown in Table 4.1 the test soils have a specific gravity values ranging between 2.36 to 2.61.

Atterberg Limits:

Plasticity characteristics of soils are very useful in classification of soils. During this research work, Atterberg limits were determined as per the procedure recommended by BIS. The results are presented in Table 4.1.



Fig. 4.1 Particle size distribution curve of lithomargic clay, BC soil and bentonite clay

4.2.2 Compaction Characteristics of Test Soils

Clay liner is one of the important components of the engineered landfill. During the construction stage of landfills, the usual procedure is to compact the bottom liner to obtain maximum density and reduced permeability.

The compaction characteristics of test soils were studied in the laboratory using light compaction test [IS: 2720 (Part-7)-1980 reaffirmed 1997]. The results of maximum dry density (γ_{dmax}) and optimum moisture content (OMC) are presented in Table 4.1. Also, the compaction characteristics of test soils plotted as dry density versus OMC are shown in Fig 4.2. From the Fig. 4.2, it is observed that maximum dry density and OMC for lithomargic clay is 16.5 kN/m³ and 19.5%, for black cotton soil is 13 kN/m³ and 36% and for bentonite is 13.1 kN/m³ and 33%.



Fig 4.2 Compaction characteristics of test soils

4.2.3 Hydraulic Conductivity of Test Soils

Landfill liner materials are usually chosen based on the hydraulic conductivity of soils. Low hydraulic conductivity soils are usually preferred.

Permeability test were carried out to study the hydraulic conductivity of lithomargic clay, BC soil and bentonite. To simulate the field conditions the soils were remoulded to standard proctor maximum dry density i.e. γ_{dmax} and OMC. The apparatus used for the permeability tests is shown in Fig. 4.3. Table 4.2 shows the hydraulic conductivity of test soils.

Table 4.2 Hydraulic conductivity of lithomargic clay, black cotton soil and bentonite

Sl	Compaction		Hydraulic conductivity (cm/s)			
no	Type of soil	test	(w _{opt} -4) %	(w _{opt}) %	(w _{opt} +2) %	(w _{opt} +4)%
1	Lithomargic clay	Standard Proctor	7.2×10 ⁻⁶	2.4×10 ⁻⁶	9.2×10 ⁻⁷	4.8×10 ⁻⁶
2	Black cotton soil	Standard Proctor	-	Impermeable	-	-
3	Bentonite	Standard Proctor	-	Impermeable	-	-



Fig 4.3 Apparatus used for the permeability tests

The criterion for choosing clay as liners and cover materials is primarily based on the hydraulic conductivity achievable under field conditions. Clayey soil that can be compacted to obtain a low hydraulic conductivity (1x10-7cm/s or less), when compacted to 90-95% of the maximum Proctor's dry density on wet of optimum moisture content is chosen for a land fill liner construction. Table 4.2 shows that the hydraulic conductivity of lithomargic clay is greater than that of the requirement for liner material (k $< 1 \times 10^{-7}$ cm/s Daniel, 1993 and Rowe et al. 1995). For this reason, the locally available lithomargic clay is blended with suitable soil (BC soil and bentonite) in order to achieve a lower hydraulic conductivity ($\leq 1 \times 10^{-7}$ cm/s), which is a basic requirement for a liner material. The blend proportion of the BC soil and bentonite soil with base soil are shown in Table 4.3. Lithomargic clay mixed with black cotton soil and bentonite at different proportions satisfied criteria as a liner material. Black cotton soil and bentonite very much satisfies the requirement of permeability but its use is restricted because of presence of active clay minerals. They have the tendency to expand and shrink with changes in moisture may lead to significant volume changes and dessication cracks.

Mix ID	Lithomargic clay (Shedi soil) (%)	Black cotton soil (%)	Bentonite (%)
Shedi soil + 5% BC	95	5	-
Shedi soil + 10% BC	90	10	-
Shedi soil + 5% BN	95	-	5
Shedi soil + 7.5% BN	92.5	-	7.5

 Table 4.3 Mix proportion of blended soil

4.3 CHEMICAL CHARACTERISTICS OF TEST SOILS

From Table 4.4, pH value of the soil shows that the lithomargic clay is acidic, black cotton soil and bentonite is slightly basic. As soil acidity increases (pH value decreases), more H⁺ ions are attached to the colloids and push other cations from the colloids into the soil solution thereby decreasing cation exchange capacity (CEC).When soils become more basic (pH increases), the available cations in solution decreases because there are lesser H⁺ ions to push cations into the soil solution from the colloids thereby increasing the CEC. Cation exchange capacity of Lithomargic clay is 3.7 meq/100g, which does not satisfy the requirement (i. e. 10 meq/100g of soil) recommended by various researchers (Rowe et. al., 1995) for the liner material.

4.4 COMPACTION BEHAVIOUR OF BLENDED SOILS

The compaction characteristics of blended lithomargic clay mixed with 5% and 10% BC soil and 5% and 7.5% bentonite were studied using standard proctor compaction test. Fig. 4.4 shows the compaction behaviour of blended test soils. The results of compaction test with varying percentage of black cotton soil and bentonite added to lithomargic clay are shown in Table 4.5. From Table 4.5, it is observed that when 95% of lithomargic clay is mixed with 5% BC soil, γ_{dmax} is 16.45kN/m³ and OMC is 20.5%. 90% of lithomargic clay mixed with 10% BC soil yielded γ_{dmax} of 16.40kN/m³ and OMC of 21%. When 95% of lithomargic clay mixed with 5% bentonite, γ_{dmax} is 16.43kN/m³ and OMC is 20.33%, where as 92.5% of lithomargic clay mixed with 7.5% bentonite, resulted γ_{dmax} of 16.40kN/m³ and OMC of 20.5%.
Parameters	Lithomargic clay	Black cotton soil	Bentonite
рН	5.40	7.9	8.40
Cation Exchange Capacity (meq/100g)	3.70	41.5	91.00
Organic content (%)	0.14	1.02	1.39
Conductivity (milli siemens)	0.09	0.78	1.52
Sulphate (%)	0.009	0.015	0.236
Silica (%)	73.20	53.10	37.80
Iron oxide (%)	0.48	8.50	10.83
Aluminium oxide (%)	0.52	6.70	1.37
Calcium oxide (%)	0.01	1.46	0.17
Magnesium oxide (%)	0.02	0.3	0.24

Table 4.4 Chemical properties of study soils



Fig 4.4 Compaction behaviour of blended test soils

Blended proportion of BC soil and bentonite (%)	Dry unit weight (kN/m ³)	Optimum Moisture Content (%)	Permeability in (cm/s)
100% Lithomargic clay	16.50	19.5	2.40×10^{-6}
95% Lithomargic clay + 5% BC soil	16.45	20.5	1.4 × 10 ⁻⁷
90% Lithomargic clay + 10% BC soil	16.40	21.0	8.1×10^{-8}
97.5% Lithomargic clay + 2.5% bentonite	16.45	20.0	3.51×10 ⁻⁷
95% Lithomargic clay + 5% bentonite	16.43	20.3	8.51× 10 ⁻⁸
92.5% Lithomargic clay + 7.5% bentonite	16.40	20.5	5.83× 10 ⁻⁸

Table 4.5 Compaction characteristics and variation of hydraulic conductivity of lithomargic clay blended with black cotton soil and bentonite

4.5 HYDRAULIC CONDUCTIVITY OF BLENDED SOILS

When lithomargic clay alone did not satisfy the hydraulic conductivity requirement, it is blended with black cotton soil and commercial available bentonite. Table 4.5 shows the compaction characteristics and hydraulic conductivity with respect to addition of black cotton soil and bentonite. From Table 4.5, it is evident that lithomargic clay mixed with 10% BC soil and lithomargic clay blended with 5% and 7.5% of bentonite satisfies the hydraulic conductivity required for soil liner. In field lowest hydraulic conductivity of clayey soil is achieved when the soil is compacted at water content which is slightly higher than the optimum moisture content (Mitchell et al. 1965, USEPA 1989, Daniel and Benson1990). This is due to the development of a large water film around the particles, which causes swelling of the clay, exert pressure lightly against the surrounding particles, consequently the effective pore size reduces resulting in an apparent low hydraulic conductivity. Hence, it is decided to study the lithomargic clay mixed with black cotton soil and bentonite at wet side of the optimum.



Fig. 4.5 Variation of hydraulic conductivity of blended soils with moulding water content

The relationship between hydraulic conductivity and corresponding moulding water content for lithomargic clay blended with 5% and 10% black cotton soil and also lithomargic clay blended with 5% and 7.5% bentonite is presented in Fig. 4.5. Moulding water content taken in the study are $(w_{opt}-4)$ %, $(w_{opt}-2)$ %, $(W_{opt})\%$, $(w_{opt}+2)$ % and $(w_{opt}+4)$ % for the corresponding soil combination. From Fig. 4.5 it is found that the lithomargic clay blended with 10% black cotton soil and lithomargic clay blended with 5% and 7.5% bentonite satisfies the criteria for hydraulic conductivity (k < 1×10^{-7} cm/s) at optimum moisture content and 2% wet side of optimum moisture content, whereas lithomargic clay blended with 5% black cotton soil satisfies the criteria for hydraulic conductivity at 2% wet side of optimum moisture content. The hydraulic conductivity changes with the change of moulding water content. Soils compacted at dry of optimum water content tend to have relatively high hydraulic conductivity whereas soils compacted at wet of optimum water content tend to have lower hydraulic conductivity, Benson and Daniel (1990) describes that increasing water content generally results in an increased ability to breakdown clay aggregate and to eliminate inter aggregate pores. Moreover,

increasing water content results in reorientation of clay particles and reduction in the size of inter particle pores (Lambe 1954).

4.6 UNCONFINED COMPRESSIVE STRENGTH (UCS) OF BLENDED SOILS

The variation of unconfined compression strength with moulding water content is shown in Fig. 4.6. Compacted soils used for waste containment liners must have adequate strength for stability and also resist compressive stress exerted by the waste material on the liner system. The compressive stress acting on the liner system depends on the height of the landfill and the unit weight of waste. Hence to support the maximum compressive stress in a landfill, Daniel and Wu (1993) reported that soil used for soil liners should have minimum unconfined compression strength of 200 kPa. From Fig 4.6 it is observed that the UC strength of compacted soil decreases with the increase of moulding water content. Similar observation were reported by Daniel and Wu (1993); Taha and Kabir (2005). In the present study, it is found that (Fig. 4.6) blended soil possesses higher strength (> 200kPa) than the recommended minimum strength, at optimum moisture content and 2% wet side of optimum moisture content.



Fig. 4.6 Variation UCS with moulding water content

4.7 ACCEPTABLE WATER CONTENT

An important step in design of compacted clay liners is to determine the range of acceptable water content for field compaction of the soil. If the soil is too dry during compaction, desired hydraulic conductivity would not be obtained and in case of soil being too wet, it will cause difficulty in compaction as well as may lead to desiccation cracks due to volumetric shrinkage. Thus, it is very important to specify the acceptable range of water contents within which the compacted soil will exhibit hydraulic conductivity $\leq 1 \times 10^{-7}$ cm/s, volumetric shrinkage $\leq 4\%$ and unconfined compressive strength ≥ 200 kPa.

Here γ_{dmax} indicates the maximum dry density that can be achieved with standard compaction and γ_{dmin} indicates the minimum dry density at which soil mixture has an unconfined compressive strength of 200 kPa. The specified range is the range of moulding water content corresponding to the dry density at which hydraulic conductivity was found to be less than 1×10^{-7} cm/s. Therefore the area covered between these limits is the acceptable zone as shown in Fig.4.7 and Fig 4.8. The acceptable zone is a range of paired dry unit weight and moisture content values that will result in low values of hydraulic conductivity when effective and proper compaction is achieved.

4.8 INDEX PROPERTIES OF BLENDED SOILS

Many researchers have proposed the desirable index properties for a liner material based on the experience and performance study of the landfill liner materials. In this study, an effort was made to bring out the index properties of blended liner material to assess its behaviour. Table 4.6 lists the index properties of lithomargic clay blended with black cotton soil and bentonite.



Fig 4.7 Acceptable zone based on hydraulic conductivity, standard compaction and unconfined compressive strength for shedi blended with 10% black cotton soil.



Fig. 4.8 Acceptable zone based on hydraulic conductivity, standard compaction and unconfined compressive strength for lithomargic clay blended with 7.5% bentonite.

Parameters	Lithomargic clay	95% Lithomargic clay + 5% black cotton soil	90% Lithomargic clay + 10% black cotton soil	95% Lithomargic clay + 5% bentonite	92.5 Lithomargic clay + 7.5% bentonite
Specific gravity	2.58	2.57	2.57	2.56	2.53
<u>Grain size</u> analysis					
Gravel (%)	2.5	2.5	2.0	1.5	2.0
Sand (%)	38.0	34.0	33.0	38.0	37.0
Silt (%)	44.5	47.5	46.0	42.0	40.0
Clay size (%)	15	16.0	19.0	18.5	21.0
Atterberg's limits (%)					
Liquid limit (w _L)	45	47	49	48	51
Plastic limit (w _P)	32	29	27	27	27
Shrinkage limit (w _s)	27	24.5	24	21	20
Plasticity index (%)	13	18	22	21	24
IS classification	MI	MI	CI	CI	СН
Activity	0.86	1.12	1.16	1.13	1.14

Table 4.6 Basic physical properties of blended test soils

A marginal increase in plasticity index and percent fines was observed in blended soil compared to that of natural lithomargic clay as shown in Table 4.6. The plasticity index increased by 38.5% and 69.2% for lithomargic clays blended with 5% and 10% of black cotton soil and percentage of fines increased by 6.7% and 26.05% respectively. The plasticity index increased by 61.5% and 84.6% for lithomargic clays blended with 5% and 7.5% bentonite and percentage of fines increased by 1.7% and 2.5% respectively. The plasticity index and the percentage fines are the most important criteria for selection of soil for liner system construction. They are the key property in achieving low hydraulic conductivity. Literature suggests that plasticity index greater than 10% have been used successfully to construct soil liners with extremely low in-situ hydraulic conductivity and, Daniel (1993) states that if the plasticity index is less than 35, low shrinkage can be expected. Soils with inadequate fines typically have too little silt and clay sized particles to produce high hydraulic conductivity. Hence a minimum of 50% fines is usually recommended for achieving low hydraulic conductivity.

In addition, shrinkage potential of a soil is directly related to its shrinkage limit. The shrinkage limit of the lithomargic clay blended with 5% and 10% of black cotton soil are 24.5% and 24% respectively, where as lithomargic clay mixed with 5% and 7.5% of bentonite obtained from laboratory tests are 21% and 20% respectively. Soils with high shrinkage limit will show little volume change potential. Shrinkage limit obtained from blended soil sample is close to the range of water content required to achieve the hydraulic conductivity of 1×10^{-7} cm/s, which signifies that the blended soil sample is less susceptible to volume change. The plasticity index of the blended soils is greater than 15% which indicates that the soil is workable. Thus the blended soil would be preferable as the liner material.

The Activity of blended soils is listed in Table 4.6. According to Skempton's classification it is classified as normal clay. Activity is an index of the surface activity of the clay fraction. Soils with higher activity are likely to consist of smaller particles having larger specific surface area and thicker electrical double layer. Therefore hydraulic conductivity generally decreases with increasing activity. However soils with high activity are more readily affected by pollutant if they are used in containment structures hence less active clayey soils are preferred for landfill liners (Rowe et al. 1995).

Compacted soil liners are subjected to frequent desiccation due to loss of water by evaporation. Desiccation leads to development of shrinkage cracks. Cracks provide pathways for moisture migration into the landfill cell, which increases the generation of waste leachate, and ultimately increases the potential for soil and ground water contamination, thus, the soil liner significantly losses its effectiveness as an impermeable barrier. Literature suggests that a soil liner does not exhibit desiccation cracking if the volume change upon drying of the compacted soil used as the liner is less than 4% (Daniel et al. 1990 and Wu et al. 1993). Test results indicate that the optimum moisture content is less than the shrinkage limit hence volumetric shrinkage does not play any role in deciding the acceptable zone.

4.9 CHEMICAL PROPERTIES OF BLENDED SOILS

Based on the chemical characteristics of the soil, its behaviour as a landfill liner material can be predicted; hence it is important to evaluate the chemical characteristics of the soil to be used as a landfill liner material. Table 4.7 lists the chemical properties of lithomargic clay blended with black cotton soil and bentonite.

Parameters	Lithomargic clay	95% Lithomargic clay + 5% BC soil	90% Lithomargic clay + 10% BC soil	95% Lithomargic clay + 5% Bentonite	92.5% Lithomargic clay + 7.5% Bentonite
рН	5.40	6.5	6.7	5.65	5.69
Cation Exchange Capacity (meq/100g)	3.70	9.56	10.8	24.16	24.80
Organic content (%)	0.14	0.17	0.24	0.33	0.36
Conductivity (milli siemens)	0.09	0.38	0.45	0.44	0.57
Sulphate, (SO ₄) %	0.01	0.016	0.025	0.019	0.026
Silica (SiO ₂) %	73.20	70.3	68.8	66.90	61.70
Iron oxide (Fe ₂ O ₃) %	0.48	1.76	2.72	1.87	2.00
Aluminium oxide (Al ₂ O ₃) %	0.52	0.83	1.08	0.53	0.80
Calcium oxide (Cao) %	0.01	0.20	0.37	0.03	0.04
Magnesium oxide (Mgo) (%)	0.02	0.03	0.04	0.03	0.04

Table 4.7 Chemical properties of the blended soil

Soils used in landfill liner systems should have adequate contaminant attenuation capacity. The attenuation of organic contaminants through a compacted soil liner is a function of cation exchange capacity (CEC) of the liner material. Higher CEC of a liner material will result in a greater amount of inorganic contaminants being removed from the leachate (Kayabali 1997). Hence some researchers (Rowe 1995 and Kayabali 1997) have recommended that the soil liner material should atleast have a CEC of 10 meq/100g.

Table 4.7 shows cation exchange capacity of the lithomargic clay blended with black cotton soil and bentonite. Cation exchange capacity of the lithomargic clay blended with 5% black cotton soil is 9.56 meq/100 g, which is very close to the minimum requirement. CEC of the lithomargic clay blended with 10 % black cotton soil and bentonite was greater than the 10 meq/100g which indicates that the blended soil possess a good contaminant attenuation property. Thus from the CEC or contaminant adsorption point of view, the blended soils are more suitable for liner material.

4.10 SUMMARY

Lithomargic clay satisfies the basic properties for clay liners except the hydraulic conductivity parameter, which is considered to be the most important property of liner material. Hence the lithomargic clay was blended with black cotton soil and bentonite, which are rich in clay, to achieve hydraulic conductivity lower than 1×10^{-7} cm/sec.

Black cotton soil and bentonite very much satisfy the requirement of permeability ($k < 1x10^{-7}$ cm/sec) but it can not be used because of the fact that it may lead to significant volume changes, dessication cracks etc.

The lithomargic clay was blended with different proportion of black cotton soil and bentonite and a suitable mix was found at which the desired permeability was achieved. It was found that blending of 5%, 10% black cotton soil and 5%, 7.5% bentonite to lithomargic clay satisfied the requirement of a good barrier.

CHAPTER 5

ADSORPTION STUDIES ON LITHOMARGIC CLAY BLENDED WITH BLACK COTTON SOIL

5.1 GENERAL

In geoenvironmental engineering adsorption is important to assess the migration characteristics of the solute in the particular soil. More the contaminant it adsorbs on the soil particle, the less is its migration and less extensive will be the extent of pollution. Conventional clay liners are designed with the focus on minimizing permeation of leachate through the liner. Thus the ability of soil to retain the contaminants is established through adsorption studies. The differences in the adsorption characteristics of naturally available soils are because of their different origins and chemical compositions. In connection with any possible applications, knowledge of the behavior of blended soils as landfill liner material is required and hence the present investigation. Hence adsorption tests were conducted on lithomargic clay, black cotton soil and lithomargic clay blended with 5% and 10% black cotton soil to study the attenuation characteristic of the soils to be proposed as a liner material.

In this study, adsorption of sodium (Na), potassium (K), lead (Pb), nickel (Ni), chloride (Cl) and chromium [Cr (VI)] on the blended test soils were studied using batch adsorption tests.

5.2 ADSORPTION ISOTHERMS

The experimental results of batch adsorption tests are analysed using three adsorption isotherms (i.e linear, Freundlich and Langmuir adsorption isotherms). The parameter used to plot the adsorption isotherms are the amount of contaminant sorbed, S, and the equilibrium concentration, C_e . When the relationship between S and C_e can be approximated by a straight line a linear adsorption isotherm is established. Mathematically, linear adsorption isotherm is expressed as

$$\mathbf{S} = \mathbf{k}_{\mathrm{d}} \mathbf{C}_{\mathrm{e}} \tag{5.1}$$

where,

S is the mass of contaminant sorbed per unit dry mass of solid (mg/kg).

 C_e is the concentration of contaminant in the solution at equilibrium (mg/L)

k_d is the known as distribution coefficient or partition coefficient.

Nonlinear adsorption, which are used to fit experimental data from the adsorption test are grouped as Freundlich adsorption isotherm and Langmuir adsorption isotherms. Mathematically Freundlich adsorption isotherms is expressed as

$$S = KC_e^{\frac{1}{n}}$$
(5.2)

where *K* is Freundlich isotherm constant (mg/g) which indicate the extent of adsorption and n is adsorption intensity or empirical constant. Usually values of n<1 refers to unfavorable sorption and n > 1 indicates a favorable sorption.

K and n are evaluated by plotting linearized form of Eqn 5.2, i.e.

. .

$$Log S = Log K + 1/n Log C_e$$
(5.3)

Langmuir Adsorption Isotherm mathematically expressed as

$$S = \frac{\alpha \beta C_e}{1 + \alpha C_e} \tag{5.4}$$

This nonlinear adsorption isotherm has been developed based on the concept of finite number of adsorption sites on a solid surface. According to Langmuir sorption occurs till all sorption sites are filled. In the above Eqn 5.4

 α = adsorption constant/ Langmuir constant related to the binding energy (L/kg) β = maximum amount of solute that can be adsorbed by the soil (mg/kg)

To get the Langmuir adsorption parameters (i.e. $\alpha \& \beta$) a plot of $C_e / S Vs$ C_e is used.

The results of batch adsorption tests using sodium (Na), potassium (K), lead (Pb), nickel (Ni), chloride (Cl) and chromium [Cr (VI)] are shown in Tables 5.1 to 5.6. The results shown in Tables 5.1 to 5.6 were obtained by conducting batch adsorption tests on individual soil samples. The amount of adsorbate

adsorbed by the soil particles was calculated using Eqn 3.1. The initial pH values and final pH values of the solution used is also shown in the Tables 5.1 to 5.6.

The linear adsorption isotherms sodium, potassium, lead, nickel, chloride and chromium on lithomargic clay interaction is shown in Fig 5.1. The coefficient of distribution (k_d) values (along with R^2 value) for the interaction of varies contaminants on the lithomargic clay are shown in Table 5.7. For example the corresponding values for the interaction of sodium on the lithomargic clay is about 0.43 (R^2 =0.98). Except for lead and chromium, the interaction of other cations/anions on the lithomargic clay is less than 1. This indicates that the lithomargic clay has greater affinity to lead and chromium.

Similarly, the interaction of various contaminants on the black cotton soil and lithomargic clay blended with 5% and 10% BC soil are shown in Table 5.7. It is observed again from the k_d values that the BC soil has a greater affinity for contaminants when compared with the k_d values lithomargic clay. This may be attributed to the presence of higher clay size fraction percentage fines in BC soil. Also the blended lithomargic clay shows a greater affinity to adsorb contaminants when compared with the control test soil. The results are shown in Table 5.7.

Freundlich adsorption isotherm for the test soils are shown in Figs. 5.2(a) - 5.2(f). The linearized data shown in Tables 5.1 to 5.6 are also used to plot the Freundlich isotherm.

The Freundlich adsorption parameters (i.e K and n) for lithomargic clay, BC soil and blended lithomargic clay are shown in the Table 5.7. Further, from Table 5.7 it is observed that constant K is significantly higher for the BC soil when compared to the lithomargic clay or blended lithomargic clay. Thus it indicates that the BC soil has greater affinity for contaminants (in this case Na, K, Pb and Ni). This may be attributed to greater clay size fraction in BC soil (see Fig 4.1). Usually n > 1 indicates a favourable sorption (Mohan and Karthikeyan 1997). Thus from Table 5.7, it is observed that n values is always greater than 1 which indicates a good sorption on the soil particles.

Langmuir adsorption isotherm is a non-linear isotherm based on the concept that a solid surface has a definite number of adsorption sites. When all the adsorption sites are fill no adsorption can occur.

The linearized Langmuir adsorption isotherm for test soils are shown in Figs 5.3(a) – 5.3(f). The corresponding values of parameters α and β along with R² values are shown in Table 5.7.

Overestimation of adsorption data is observed for test soils (Table 5.7) when compared with linear and Freundlich adsorption isotherm. Overall, it is found that the adsorption of contaminants is greater in case of BC soil. Hence BC soil is blended with lithomargic clay. The adsorption test results of blended soils also shown in the Table 5.7.

The permeability of blended lithomargic clay is 8.1X10⁻⁸cm/s. Based on the permeability, UCC strength and adsorption test results, it may be concluded that the blended lithomargic clay has greater potential as a soil liner material for the construction of engineered landfills.

5.3 SUMMARY

The adsorption of landfill constitutes like sodium, potassium, lead, nickel, chloride and chromium on the test soils are studied. The adsorption isotherms (linear, Freundlich and Langmuir) parameters indicate that adsorption capacity of cations on blended soils increases as the percentage of BC soil increases. Adsorption of anions is more in the lithomargic clay. Hence as the blending percentage of BC soil increases the adsorption capacity of anions on lithomargic clay decreases.

Sodiu concentr	um ration	Lithomarg	gic clay	Black cot	ton soil	on soil 95% Lithomargic clay + 5% BC soil		90% Lith clay + 10%	omargic 6 BC soil
`Initial conc, C _i (mg/L)	Initial pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH
30	7.1	23	6.4	2.9	8.1	22.0	7.4	21.0	7.8
40	7.1	32	6.1	5.1	8.1	30.7	7.6	29.3	7.7
50	7.0	41	5.6	7.0	8.1	39.3	7.4	37.6	7.9
60	7.0	50	5.7	9.5	8.1	48.0	7.4	46	7.8
80	7.0	68	5.8	14	8.1	65.3	7.3	62.6	7.8
100	6.9	86	5.6	19	8.0	82.7	7.4	79.3	7.9
200	6.9	175	5.4	55	8.0	169	7.2	163	7.8
300	6.9	265	5.3	105	7.9	257	7.2	249	7.7
400	7.1	355	5.3	170	7.6	346	7.0	336.5	7.9
600	7.1	538	5.0	280	7.2	525	7.0	512	7.8
800	6.9	723	4.9	421	7.8	708	7.0	693	7.7
1000	6.9	908	5.0	550	7.8	890	6.9	872.2	7.8
1200	7.0	1096	4.8	680	7.8	1075	7.0	1054.4	7.8
1400	6.7	1285	5.8	820	7.7	1262	7.0	1239	7.7
1500	6.6	1380	4.8	940	7.7	1358.	6.9	1330.0	7.8

Table 5.1 Adsorption test results for sodium – soil interaction

Potassii concentra	um ation	Lithomarg	ic clay	Black cotto	on soil 95% Lithon clay + 5% B		margic BC soil	90% Lithomargi clay + 10% BC soil	
Initial conc, C _i (mg/L)	Initial pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH
30	7.1	16.0	6.1	1.7	7.9	15.3	6.8	14.5	7.1
40	7.1	22.5	5.3	2.4	8.0	21.5	6.9	20.5	7.0
50	7.0	29.0	5.2	3.4	8.2	27.7	6.5	26.4	8.1
60	7.0	36.0	5.2	4.4	8.1	34.4	6.8	32.8	7.2
80	7.0	50.0	5.1	6.4	8.1	47.8	6.7	45.6	7.2
100	6.9	65.0	5.1	8.5	8.1	62.2	6.7	59.4	7.1
200	6.9	149.5	4.8	17.8	8.1	143.0	6.7	136.0	7.1
300	6.9	237.5	4.7	32.0	8.1	227.0	6.4	217.0	7.0
400	7.1	327.0	4.7	51.0	8.1	313.0	6.8	299.0	7.0
600	7.1	510.0	4.6	95.0	8.0	489.3	6.4	469.0	6.9
800	6.9	689.0	4.6	156.0	8.1	662.0	6.6	636.0	6.9
1000	6.9	870.0	4.5	206.0	8.1	837.0	6.6	804.0	6.8
1200	7.0	1050.0	4.5	270.0	8.2	1011.0	6.6	972.0	6.9
1400	6.7	1230.0	4.4	330.0	8.1	1185.0	6.6	1140.0	6.8
1500	6.6	1320.0	4.3	360.0	8.1	1272.0	6.6	1224.0	6.9

Table 5.2 Adsorption test results for potassium – soil interaction

Lead	l	Lithomarg	gic clay	Black cotte	on soil	95% Litho clay + 5%	95% Lithomargic clay + 5% BC soil		margic % BC
Initial conc, C _i (mg/L)	Initial pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH
0.2	7.2	0.12	6.1	0.037	6.6	0.117	6.1	0.113	6.1
0.4	7.1	0.24	5.9	0.075	6.2	0.236	5.9	0.227	5.9
0.6	7.1	0.37	5.8	0.113	6.5	0.355	5.8	0.343	5.8
0.8	7.0	0.49	5.7	0.152	6.4	0.476	5.7	0.459	5.7
1	6.8	0.62	5.5	0.191	6.8	0.600	5.5	0.578	5.5
2	6.7	1.25	5.9	0.384	6.9	1.207	5.9	1.163	5.9
4	6.6	2.53	5.6	0.770	7.0	2.437	5.6	2.350	5.6
6	6.1	3.82	4.8	1.162	5.8	3.684	4.8	3.552	4.8
8	6.4	5.14	4.4	1.556	6.8	4.956	4.4	4.777	4.4
10	6.1	6.46	6.2	1.953	7.5	6.234	6.2	6.008	6.2
20	6.5	13.15	5.8	3.926	7.1	12.685	5.8	12.224	7.0
40	6.4	26.50	5.6	7.904	7.3	25.574	6.6	24.644	6.8
60	6.1	40.23	5.1	12.004	6.8	38.821	6.3	37.409	6.4
80	5.8	54.38	4.5	16.259	6.6	52.472	6.1	50.566	6.4
100	5.7	68.78	4.4	20.622	6.5	66.367	5.9	63.960	6.1

Table 5.3 Adsorption test results for lead – soil interaction

Nick	cel	Lithomargi	c clay	Black cotton soil		95% Litho clay + 5%	omargic BC soil	90% Lithomargic clay + 10% BC soil	
Initial conc, C _i (mg/L)	Initial pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH
2	4.1	1.005	5.5	0.020	8.5	0.956	7.6	0.906	7.7
4	3.9	2.154	5.4	0.045	8.6	2.049	7.4	1.943	7.5
6	3.2	3.453	5.4	0.069	8.7	3.284	7.5	3.115	7.4
8	3.0	4.989	5.1	0.095	8.7	4.744	7.5	4.500	7.3
10	2.9	6.842	5.0	0.121	8.4	6.506	7.4	6.170	7.3
20	2.6	16.010	4.7	0.246	8.5	15.222	7.4	14.434	7.0
40	2.6	35.155	4.2	0.554	8.5	33.425	7.2	31.695	6.8
60	2.5	54.023	3.5	0.860	8.2	51.365	6.8	48.707	6.8
80	2.4	73.145	3.4	1.222	7.8	69.549	6.7	65.953	6.5
100	2.4	92.267	3.1	1.600	7.9	87.734	6.5	83.200	6.3

Table 5.4 Adsorption test results for nickel – soil interaction

Chloride con	centration	Lithomarg	gic clay	Black cott	Black cotton soil95% Lithomargic clay + 5% BC soil		margic BC soil	90% Lithomargic clay + 10% BC soil	
Initial conc, C _i (mg/L)	Initial pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH
46	6.8	39.0	6.1	40.5	7.4	40.0	6.8	40.5	6.9
61	7.2	52.4	6.0	53	7.4	52.5	6.9	53.5	6.9
76	7.0	66.0	6.0	68	7.4	67.9	6.7	67.9	6.8
92	7.2	80.2	5.9	82.4	7.4	82.3	6.7	82.2	6.8
122	7.2	107.0	5.9	110	7.4	109.0	6.7	109.7	6.8
152	6.8	135.0	5.9	140	7.4	138.0	6.7	137.7	7.0
310	7.4	280.0	5.9	290	7.3	290.0	6.7	284.1	6.8
465	6.8	425.0	5.8	445	7.3	440.0	6.7	435.0	6.8
620	7.3	570.0	5.8	580	7.3	570.0	6.6	567.0	6.8
930	7.4	860.0	5.8	885	7.3	870.0	6.7	871.0	6.8
1250	7.2	1160.0	5.7	1185	7.2	1160.0	6.7	1165.0	6.8
1550	7.5	1442.0	5.7	1476	7.3	1445.0	6.7	1450.0	6.8
1850	7.4	1722.0	5.7	1767	7.3	1730.0	6.6	1734.0	6.8
2150	7.4	2005.0	5.7	2100	7.3	2065.0	6.5	2065.0	6.8
2300	6.7	2145.0	5.7	2240	7.2	2210.0	6.7	2205.0	6.8

Table 5.5 Adsorption test results for chloride – soil interaction

Chromium conc	entration	Lithomargic	c clay	Black cotto	ack cotton soil 95% Lithomargic clay + 5% BC soil		90% Lithomargic clay + 10% BC soil		
Initial conc, C _i (mg/L)	Initial pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH
0.1	7.8	0.01	5.4	0.0	7.9	0.04	6.5	0.05	6.7
0.2	7.8	0.02	5.2	0.1	8.0	0.09	6.7	0.11	6.7
0.4	7.8	0.06	5.0	0.3	8.2	0.20	6.7	0.22	6.8
0.6	7.8	0.10	5.0	0.4	8.1	0.32	6.7	0.35	6.5
0.8	7.8	0.15	4.9	0.6	8.1	0.44	6.6	0.48	6.8
1	7.8	0.24	5.4	0.8	8.1	0.57	6.8	0.62	6.9
2	7.8	0.7	5.0	1.8	8.1	1.17	6.6	1.26	6.7
4	7.8	1.82	5.0	3.9	8.1	2.4	6.7	2.6	6.6
6	7.7	3.07	5.0	6.0	8.1	3.7	6.8	3.95	6.7
8	7.7	4.2	4.9	8.0	8.0	5.1	6.6	5.4	6.7
10	7.6	5.5	5.1	10.0	8.1	6.6	6.7	6.9	6.8
20	7.4	13.2	5.0	20.0	8.1	14.3	6.7	14.5	6.9
30	7.1	21	4.7	30.0	8.2	22.4	6.8	22.5	6.7
40	7.0	29	4.7	40.0	8.1	30.5	6.8	30.5	6.8
50	6.8	37.5	4.6	50.0	8.1	38.5	6.8	39	6.8

Table 5.6 Adsorption test results for chromium – soil interaction

Tupo of soil	Contomi	Line Isothe	ar erm	Freundli	ch isot	herm	Langmuir Isotherm			
Type of son	nants	K _d (L/kg)	R^2	K (mg/kg)	n	R^2	α (L/kg)	β (mg/kg)	\mathbf{R}^2	
	Sodium	0.43	0.98	2.97	1.43	0.99	98x10 ⁻⁶	1000	0.89	
	Potassium	0.61	0.98	16.4	1.82	0.99	2.7×10^{-3}	1000	0.90	
100% Lithomorgia	Lead	2.32	0.99	3.00	1.06	0.99	0.005	555.55	0.86	
clay	Nickel	0.32	0.92	6.68	2.56	0.95	0.093	39.53	0.97	
	Chloride	0.35	0.99	3.27	1.30	0.97	55x10 ⁻⁶	1250	0.97	
	Chromium	1.69	0.95	8.1	1.75	0.99	17×10^{-3}	64.1	0.91	
	Sodium	3.21	0.97	76.54	1.85	0.99	5.7×10^{-3}	3333.3	0.93	
	Potassium	15.46	0.97	106.3	1.45	0.99	5.8×10^{-3}	10000	0.94	
100% BC	Lead	19.45	0.99	20.7	1.02	0.99	0.004	5000	0.84	
soil	Nickel	309.4	0.99	332.3	1.11	0.99	0.304	1428.5	0.91	
	Chloride	0.22	0.99	2.04	1.54	0.99	93x10 ⁻⁶	714	0.92	
	Chromium									
	Sodium	0.52	0.99	3.69	1.37	0.99	1.1×10^{-3}	1111.1	0.91	
050/	Potassium	0.82	0.99	14.78	1.69	0.99	2.8×10^{-3}	1428.5	0.89	
95% Lithomargic	Lead	2.58	0.99	3.28	1.05	0.99	0.005	666.67	0.85	
clay + 5%	Nickel	0.59	0.97	6.70	2.04	0.98	0.057	65.36	0.93	
DC SOII	Chloride	0.31	0.99	2.40	1.37	0.99	63x10 ⁻⁶	1111.1	0.88	
	Chromium	1.49	0.98	3.58	1.28	0.99	54×10^{-3}	76.33	0.90	
	Sodium	0.62	0.99	4.43	1.37	0.99	1.2×10^{-3}	1250	0.92	
000/	Potassium	1.05	0.99	15.25	1.61	0.99	2.9×10^{-3}	1666.6	0.88	
Lithomargic	Lead	2.86	0.99	3.58	1.05	0.99	0.005	714.28	0.85	
clay + 10%	Nickel	0.90	0.98	6.785	1.78	0.98	0.043	94.34	0.90	
DU	Chloride	0.30	0.99	2.27	1.34	0.99	65×10^{-6}	1111.1	0.92	
	Chromium	1.46	0.98	3.00	1.22	0.99	39×10^{-3}	84.75	0.89	

Table 5.7 Adsorption coefficient of lithomargic clay and blended lithomargic clay



Fig 5.1 (a) Linear adsorption isotherm for sodium - soil interaction



Fig 5.1 (b) Linear adsorption isotherm for potassium – soil interaction



Fig 5.1 (c) Linear adsorption isotherm for lead – soil interaction



Fig 5.1 (d) Linear adsorption isotherm for nickel - soil interaction



Fig 5.1 (e) Linear adsorption isotherm for chloride- soil interaction



Fig 5.1 (f) Linear adsorption isotherm for chromium – soil interaction



Fig 5.2 (a) Freundlich adsorption isotherm for sodium – soil interaction



Fig 5.2 (b) Freundlich adsorption isotherm for potassium – soil interaction



Fig 5.2 (c) Freundlich adsorption isotherm for lead- soil interaction



Fig 5.2 (d) Freundlich adsorption isotherm for nickel - soil interaction



Fig 5.2 (e) Freundlich adsorption isotherm for chloride- soil interaction



Fig 5.2 (f) Freundlich adsorption isotherm for chromium – soil interaction



Fig 5.3 (a) Langmuir adsorption isotherm for sodium - soil interaction



Fig 5.3 (b) Langmuir adsorption isotherm for potassium- soil interaction



Fig 5.3 (c) Langmuir adsorption isotherm for lead- soil interaction



Fig 5.3 (d) Langmuir adsorption isotherm for nickel- soil interaction



Fig 5.3 (e) Langmuir adsorption isotherm for chloride- soil interaction



Fig 5.3 (f) Langmuir adsorption isotherm for chromium- soil interaction

CHAPTER 6

ADSORPTION STUDIES ON LITHOMARGIC CLAY BLENDED WITH BENTONITE

6.1 BENTONITE

Bentonite is a natural clay mineral and is found in many places of the world. Bentonite clays have certain desirable material properties such as swelling ability and high sorption capacity. These properties depend on the mineralogy and geochemistry of the material. There are various potential commercial bentonite products available in the markets but they are not necessary similar in respect to mineralogy and chemical composition. The differences between the mineralogy and geochemistry of different bentonites are usually due to differences in the geological history of the source occurrences. Bentonites are usually formed by alteration of volcanic ash or tuff, mainly rhyolitic or dacitic, either in situ or transported and redeposited. Characteristic for bentonites is that they are mainly composed of smectites, a group of expandable clay minerals with a wide range of chemical compositions. The desired material properties of bentonites, like swelling ability, plasticity, cation exchange capacity etc are dependent on the amount of smectite minerals in the bulk material, smectite species and on the exchangeable cations in the interlayer position. The basic structure is composed of two tetrahedrally coordinated sheets of silicon ions surrounding by a sandwiched octahedrally coordinated sheet of aluminum ions. The isomorphs substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay. Compared with other clay types, it has excellent sorption properties and possesses sorption sites available within its interlayer space as well as on the outer edges.

6.2 ADSORPTION STUDY

From chapter 4, it is concluded that the lithomargic clay blended with 5% and 7.5% bentonite satisfies the basic requirements (hydraulic conductivity $\leq 1 \times 10^{-7}$ cm/s) for a liner material. Adsorption plays a major role in assessing the migration

characteristics of the solute in the soil liner system. Higher the adsorption, lower will be the migration and pollution due to contamination. Hence in this study, adsorption of potassium (K), lead (Pb), nickel (Ni) and chromium (Cr (VI)) on the blended test soils were studied using batch adsorption tests.

The results of batch adsorption tests using sodium (Na), potassium (K), lead (Pb), nickel (Ni), chloride (Cl) and chromium [Cr (VI)] are shown in Tables 6.1 to 6.4. The results shown in Tables 6.1 to 6.4 were obtained by conducting batch adsorption tests on individual soil samples. The amount of adsorbate adsorbed by the soil particles was calculated using Eqn 3.1. The initial pH values and final pH values of the solution used is also shown in the above tables. The experimental results of batch adsorption tests are analyses using three adsorption isotherms (i.e linear, Freundlich and Langmuir adsorption isotherms). These isotherms are discussed in the chapter 5. Equations 5.1 to 5.5 were used to plot the adsorption isotherm.

The linear adsorption isotherms potassium, lead, nickel and chromium on lithomargic clay interaction are shown in Fig 6.1. The coefficient of distribution (k_d) values (along with R^2 value) for the interaction of varies contaminants on the lithomargic clay are presented in Table 6.5. For example k_d value for the interaction of sodium on the lithomargic clay is about 0.61 (R^2 =0.98). Except for lead and chromium, the interaction of other cations/anions on the lithomargic clay is less than 1. This indicates that the lithomargic clay has greater affinity to lead and chromium.

Similarly, the interaction of various contaminants on the bentonite and lithomargic clay blended with 5% and 7.5% BN soil are shown in Table 6.5. It is observed again from the k_d values that the bentonite has a greater affinity for contaminants when compared with the k_d values of lithomargic clay. This may be attributed to the presence of higher clay size fraction percentage fines in bentonite. Also, the blended lithomargic clay shows a greater affinity to adsorb contaminants when compared with the control test soil. The results are shown in Table 6.5.

Freundlich adsorption isotherm for the test soils are shown in Figs. 6.2(a) to 6.2(d). The linearized data shown in Table 6.1 to 6.4 are also used to plot the Freundlich isotherm.

The Freundlich adsorption parameters (i.e K and n) for lithomargic clay, bentonite and blended lithomargic clay are shown in the Table 6.5. Further, from

Table 6.5, it is observed that constant K is significantly higher for the bentonite when compared to the lithomargic clay or blended lithomargic clay. Thus it indicates that the bentonite has greater affinity for contaminants (are K, Pb and Ni). This may be attributed to greater clay size fraction in bentonite (Fig 4.1). Usually n > 1 indicates a favourable sorption (Mohan and Karthikeyan 1997). Thus from Table 6.5, it is observed that n values is always greater than 1 which indicates a good sorption on the soil particles.

Langmuir adsorption isotherm is a non linear isotherm based on the concept that a solid surface has a definite number of adsorption sites. When all the adsorption sites are fill no adsorption can occur.

The linearized Langmuir adsorption isotherms for test soils are shown in Figs 6.3(a) to 6.3(d). The corresponding values of parameters α and β along with R² values are shown in Table 6.5.

Overestimation of adsorption data is observed for test soils (Table 6.5) when compared with linear and Freundlich adsorption isotherm. Overall, it is shown that the adsorption of contaminants is greater in case of bentonite. Hence bentonite is blended with lithomargic clay. The adsorption test results of blended soils also shown in the Table 6.5.

Also, the permeability of blended lithomargic clay is 5.83×10^{-8} cm/s. Based on the permeability, UCC strength and adsorption test results it may be concluded that the blended lithomargic clay has greater potential as a soil liner material for the construction of engineered landfills.

6.3 SUMMARY

Studies are carried out adsorption of potassium, lead, nickel and chromium on the test soils are studied. The adsorption isotherms (linear, Freundlich and Langmuir) parameters indicate that as the percentage of bentonite increases adsorption capacity of potassium, lead and nickel on blended soils increases. Lithomargic clay showed more adsorption of chromium. As the blending percentage of bentonite increases the adsorption capacity of chromium on lithomargic clay decreases.

Potassi concentra	um ation	Lithomarg	gic clay	Benton	ite	95% Lithomargic clay + 5% BN soil		92.5% Lithomargic clay + 7.5% BN soil	
Initial conc, C _i (mg/L)	Initial pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH
30	7.1	16	6.1	4.2	7.9	5.3	6.8	4.5	7.1
40	7.1	22.5	5.3	5.7	8.0	7.3	6.9	6.2	7.0
50	7.0	29	5.2	7.3	8.2	9.4	6.5	8.0	8.1
60	7.0	36	5.2	9.0	8.1	11.8	6.8	9.8	7.2
80	7.0	50	5.1	15	8.1	17.2	6.7	13.5	7.2
100	6.9	65	5.1	25	8.1	25.5	6.7	18.0	7.1
200	6.9	150	4.8	70	8.1	87	6.7	67.5	7.1
300	6.9	237.5	4.7	137	8.1	171	6.4	137.5	7.0
400	7.1	327	4.7	217	8.1	254.5	6.8	217.5	7.0
600	7.1	510	4.6	380	8.0	440	6.4	390	6.9
800	6.9	689	4.6	540	8.1	620	6.6	566	6.9
1000	6.9	870	4.5	700	8.1	796	6.6	740	6.8
1200	7.0	1050	4.5	860	8.2	980	6.6	910	6.9
1400	6.7	1230	4.4	1010	8.1	1156	6.6	1090	6.8
1500	6.6	1320	4.3	1080	8.1	1240	6.6	1180	6.9

Table 6.1 Adsorption test results for potassium – soil interaction

Lead		Lithomargic clay		Bentonite		95% Lithomargic clay + 5% BN soil		92.5% Lithomargic clay + 7.5% BN soil	
Initial conc, C _i (mg/L)	Initial pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH
0.2	7.2	0.12	6.1	0.072	7.5	0.119	6.1	0.114	6.1
0.4	7.1	0.24	5.9	0.145	7.6	0.239	5.9	0.229	5.9
0.6	7.1	0.37	5.8	0.219	6.8	0.361	5.8	0.346	5.8
0.8	7.0	0.49	5.7	0.293	7.0	0.483	5.7	0.463	5.7
1	6.8	0.62	5.5	0.370	6.9	0.608	5.5	0.584	5.5
2	6.7	1.25	5.9	0.744	7.4	1.225	5.9	1.175	5.9
4	6.6	2.53	5.6	1.490	6.8	2.473	5.6	2.373	5.6
6	6.1	3.82	4.8	2.247	8.0	3.739	4.8	3.587	4.8
8	6.4	5.14	4.4	3.012	6.3	5.029	4.4	4.825	4.4
10	6.1	6.46	5.2	3.815	6.7	6.327	5.2	6.070	4.2
20	6.3	13.15	4.7	7.685	6.7	12.873	4.9	12.352	4.7
40	6.1	26.50	4.1	15.705	6.5	25.964	4.7	24.909	4.6
60	5.9	40.23	4.0	23.857	6.3	39.413	4.5	37.811	4.4
80	6.0	54.38	4.2	32.104	6.7	53.264	4.4	51.102	4.5
100	5.7	68.78	4.5	40.621	6.0	67.367	4.1	64.632	4.2

Table 6.2 Adsorption test results for lead – soil interaction

Nickel		Lithomargic clay		Bentonite		95% Lithomargic clay + 5% BN soil		92.5% Lithomargic clay + 7.5% BN soil	
Initial conc, C _i (mg/L)	Initial pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C_e (mg/L)	Final pH
2	4.1	1.005	5.5	0.068	5.5	0.958	5.5	0.935	5.5
4	3.9	2.154	5.4	0.161	5.4	2.054	5.4	2.005	5.4
6	3.2	3.453	5.4	0.255	5.4	3.293	5.4	3.213	5.4
8	3.0	4.989	5.1	0.400	5.1	4.760	5.1	4.645	5.1
10	2.9	6.842	5.0	0.607	5.0	6.530	5.0	6.374	5.0
20	2.6	16.010	4.7	1.339	4.7	15.276	4.7	14.910	4.7
40	2.6	35.155	4.2	3.438	4.2	33.569	4.2	32.776	4.2
60	2.5	54.023	3.5	6.231	3.5	51.633	3.5	50.439	3.5
80	2.4	73.145	3.4	10.206	3.4	69.998	3.4	68.425	3.4
100	2.4	92.267	3.1	15.567	3.1	88.432	3.1	86.515	3.1

Table 6.3 Adsorption test results for nickel – soil interaction
Chromium concentration		Lithomargic clay		Benton	iite	95% Lithon + 5% B	nargic clay N soil	92.5% Lithomargic clay + 7.5% BN soil	
Initial conc, C _i (mg/L)	Initial pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH	Final conc, C _e (mg/L)	Final pH
0.1	7.8	0.01	6.5	0.1	8.8	0.1	6.0	0.1	6.8
0.2	7.8	0.02	6.4	0.2	8.9	0.1	6.0	0.1	6.9
0.4	7.8	0.06	6.1	0.4	8.9	0.2	6.2	0.3	6.6
0.6	7.8	0.11	6.3	0.6	8.7	0.4	6.0	0.4	6.4
0.8	7.8	0.15	6.3	0.7	9.0	0.5	6.0	0.6	6.3
1	7.8	0.24	6.3	0.9	8.8	0.6	6.2	0.8	6.7
2	7.8	0.7	6.2	1.9	8.8	1.4	6.6	1.5	6.6
4	7.8	1.8	6.2	4.3	8.9	2.8	6.1	3.1	6.6
6	7.7	3.1	6.2	6.3	9.0	4.4	6.6	4.7	6.6
8	7.7	4.2	6.1	8.4	9.0	6.0	6.5	6.2	6.4
10	7.6	5.5	6.0	11.2	8.9	7.7	6.9	7.8	6.4
20	7.4	13.2	5.7	22.1	8.9	16.0	6.2	16.5	6.0
30	7.1	21	5.6	33.5	8.8	25.0	6.2	25.5	6.8
40	7.0	29	5.5	44.0	8.6	34.2	6.1	35.0	6.3
50	6.8	37.5	5.3	54.5	8.3	43.5	6.0	44.5	6.4

Table 6.4 Adsorption test results for chromium – soil interaction

Turne of soil	Contoninonto	Linear Isotherm		Freundlich isotherm			Langmuir Isotherm		
Type of som	Contaminants	K _d (L/kg)	R^2	K (mg/kg)	n	R^2	α (L/kg)	β (mg/kg)	\mathbf{R}^2
	Potassium	0.61	0.98	16.4	1.82	0.99	2.7×10^{-3}	1000	0.90
100%	Lead	2.32	0.99	3.00	1.06	0.99	50x10 ⁻³	555.55	0.86
Lithomargic	Nickel	0.32	0.92	6.60	2.56	0.95	93x10 ⁻³	39.53	0.97
clay	Chromium	1.69	0.95	8.1	1.75	0.99	17x10 ⁻³	64.1	0.91
	Potassium	13.32	0.96	679	2.22	0.99	$7x10^{-3}$	16666.7	0.93
100%	Lead	7.38	0.99	8.36	1.03	0.99	40×10^{-3}	2000	0.88
Bentonite	Nickel	27.8	0.95	70.21	1.43	0.99	180x10 ⁻³	555.56	0.96
	Chromium								
05%	Potassium	0.84	0.90	89.58	2.70	0.97	9.7×10^{-3}	1250	0.97
Lithomargic	Lead	2.47	0.99	3.16	1.05	0.99	05×10^{-3}	625	0.86
clay + 5% Bentonite	Nickel	0.55	0.97	6.65	2.13	0.98	60x10 ⁻³	61.73	0.94
	Chromium	1.49	0.98	2.40	1.35	0.99	69x10 ⁻³	41	0.95
92.5% Lithomargic clay + 7.5% Bentonite	Potassium	1.16	0.89	95.94	2.45	0.97	10×10^{-3}	1666.6	0.97
	Lead	2.78	0.99	3.5	1.05	0.99	05×10^{-3}	714.3	0.85
	Nickel	0.67	0.98	6.72	1.96	0.98	53x10 ⁻³	73.53	0.93
	Chromium	1.46	0.98	1.70	1.25	0.99	48×10^{-3}	39.84	0.96

Table 6.5 Adsorption coefficient of lithomargic clay and blended lithomargic clay



Fig 6.1 (a) Linear adsorption isotherm for potassium - soil interaction



Fig 6.1 (b) Linear adsorption isotherm for lead- soil interaction



Fig 6.1 (c) Linear adsorption isotherm for nickel - soil interaction



Fig 6.1 (d) Linear adsorption isotherm for chromium – soil interaction



Fig 6.2 (a) Freundlich adsorption isotherm for potassium - soil interaction



Fig 6.2 (b) Freundlich adsorption isotherm for lead – soil interaction



Fig 6.2 (c) Freundlich adsorption isotherm for nickel - soil interaction



Fig 6.2 (d) Freundlich adsorption isotherm for chromium - soil interaction



Fig 6.3 (a) Langmuir adsorption isotherm for potassium- soil interaction



Fig 6.3 (b) Langmuir adsorption isotherm for lead- soil interaction



Fig 6.3 (c) Langmuir adsorption isotherm for nickel- soil interaction



Fig 6.3 (d) Langmuir adsorption isotherm for chromium- soil interaction

CHAPTER 7

EFFECT OF LEACHATE ON TEST SOILS

7.1 GENERAL

Leachate is waste emanating from landfills. When water water percolates/infiltrates through solid waste, it dissolves various components from the solid waste. The hazardous nature or toxicity of the leachate is attributed to various complex biochemical reactions within a landfill. Some of the health effects of the landfill leachate are shown in Table 7.1. When leachate comes in contact with soil or ground water it has the potential to contaminate the soil and ground water systems. Researchers conclude (Sivapullaiah and Savitha 1997 Sitaram et al. 2007, Sitaram et al. 2010) that when leachate comes in contact with soil it also has some effect on hydraulic conductivity and other properties of the soil. Hence it becomes important to study the hydraulic characteristics of soil liner permeated with leachate. In other words, the compatibility of liner system with leachate has to be assess prior to its use as a liner material in the landfills. Hence it is proposed to study the compatibility of lithomargic clay and its blends, permeated with leachate.

Contaminant Potential	Health effects from exposure above the MCL
Arsenic	Skin damage; circulatory system problems; increased
Barium	Risk of cancer
Fluoride	Bone disease (fluorosis).
Mercury	Kidney damage
Nitrate	Methemoglobinemia (blue-baby syndrome).

Table 7.1 Health effects of landfill leachate (EPA, 2003)

* Maximum Contaminant Level (MCL)

7.2 LEACHATE COLLECTION AND ITS ANALYSIS

In the present work it is proposed to study the effect of leachate collected from the existing landfill. Accordingly, leachate was sampled from the drains of a existing municipal solid waste situated at Vamanjoor village near Mangalore (12°52¹ N latitude and 74°49¹ E longitude). This particular landfill is in operation from past three decades. Solid waste is collected all the locations in and around Mangalore city and is disposed at Vamanjoor dumping area (dumping yard). Samples of leachate were collected at three different locations at base of dumping yard. About 50 litres of natural leachate was collected and stored in the plastic container. The samples were transported to the environmental engineering laboratory and stored in deep freezer for further analysis. Certain chemical parameters like pH, electrical conductivity, bio chemical oxygen demand were determined in the laboratory immediately after sampling. The detailed chemical analysis and methods adopted to determine each parameter is shown in the Table 7.2. It is observed from Table 7.2 that the leachate consists of various organic and inorganic chemicals. The pH value is 7.9.

7.3 EFFECT OF LEACHATE ON LIQUID LIMIT, PERMEABILITY AND UCS OF LITHOMARGIC CLAY AND BLENDED LITHOMARGIC CLAY.

The effect of soil-leachate interaction on hydraulic conductivity and geotechnical properties of liner material was evaluated by allowing the compacted lithomargic clay with black cotton soil and bentonite mixtures to interact with leachate for a period of one month. After soil mixtures interact with leachate for a sufficient time, change of hydraulic conductivity was evaluated in the laboratory using falling head permeability test. Table 7.3 shows the geotechnical properties of test soils permeated with leachate.

7.3.1 Effect of Leachate on Liquid Limit

The effect of leachate interaction on the liquid limit of the parent soil and blended soils are shown in Table 7.3. It is observed that the liquid limits of blended soils increases after interaction with leachate. This can be explained in terms of the inter particle forces that play a prominent role in determining the liquid limit. Sharma and Lewis (1994) reported that the net electrical forces between clay mineral layers were affected by the concentration and valence of cations. In the case of lithomargic clay, because of its low cation exchange capacity, the effects due to changes in diffuse double layer are negligible. However, the increase in liquid limit (w_L) of the lithomargic clay are mainly due to increase in clay content of the lithomargic clay.

7.3.2 Effect of Leachate on Hydraulic Conductivity (k)

The effect of soil-leachate interaction on hydraulic conductivity of liner material was evaluated permeating lithomargic clay and blended lithomargic clay with leachate for a period of one month. After soil mixture interact with leachate for a sufficient time, change of hydraulic conductivity was evaluated in the laboratory. The effect of soil-leachate interaction on hydraulic conductivity is the major factor which determines the satisfactory performance of a landfill liner. The variation of hydraulic conductivity of compacted soil mixtures after contact with leachate is showed in Table 7.3. It can be seen that hydraulic conductivity of original parent soil (lithomargic clay) has decreased from 2.4×10^{-6} to 1.1×10^{-6} cm/s after the interaction with the leachate. However, with the increase of black cotton soil and bentonite percentage, the hydraulic conductivity has been significantly decreased. This reduction of hydraulic conductivity after contact with the leachate is mainly associated with the clogging of soil particle tops due to precipitation of the suspended particles existing in the leachate and formation of a less permeable thin layer at the top. It can be noted that these interactions with soil were found in the upper position of specimen for a thickness lower than 1 mm (observed at the end of the test after the disassembling of permeameter and shown in Fig. 7.1). This result is in agreement with Stern and Shackelford (1998) and Broderick and Daniel (1990) who suggested that the hydraulic conductivity of clay soils containing less reactive clay minerals such as kaolinite, and attapulgite (palygorskite) was unaffected by chemical solutions. Also, the effect of ions interaction on the hydraulic conductivity might be less significant for compacted clay (Hyang-Sig 2009).



Fig 7.1 Formation of precipitates from pollutants in the soil due to leachate flow

7.3.3 Effect of Leachate on UCS

The soil used for liner system should have minimum unconfined compressive strength of 200 kPa. From Table 7.3 it is observed that, after leachate interaction all the blended soils possess higher strength unconfined compressive strength (i.e.> 200kPa) than the recommended minimum strength, at OMC and OMC +2% water content. The decrease in the UCS is mainly due to the reduction in the thickness of diffused double layer.

7.4 MINERALOGICAL STUDIES OF TEST SOILS USING X- RAY DIFFRACTOMETER (XRD)

The mineralogical comparisons of the lithomargic clay and blended lithomargic clay permeated with landfill leachate have been studied using X- ray diffractometer (XRD) and Scanning Electron Microscope (SEM). The XRD method is the most widely used technique for identification of clay/non clay minerals.

7.4.1 XRD Analysis of Parent Soil and Blended Soils

The XRD results indicate that the main mineralogical compositions of test samples are kaolinite and montmorillonite. The scans of the clay are more or less similar (Fig. 7.2).

7.4.2 XRD Analysis of Landfill Leachate Interacted Soil

The X- Ray diffraction method is the most widely used technique for identification and detection of the clay and non-clay minerals which are present in the soil. All clay minerals have essentially the same general scheme of structure and their diffraction patterns are similar. But the most characteristic differences are provided by their d-value. The X- ray diffractometer used in the present study is type JEOL-Model DX-GE-2P. In this method, the material is exposed to a filtered X- ray beam. The X- ray passes into the material and causes the electrons in the atoms of the minerals to vibrate and reflect the beam through the successive planes. The method involves increasing of incidence angle and monitoring the intensity of the diffracted X- radiation until a maximum value of the diffracted intensity is achieved. Qualitative study by using XRD is carried out to investigate the reaction products of the contaminated soil during the interaction process. The leachate contaminated soil sample after 30 days of contact period have been used in this investigation.



Fig 7.2 (a) X-ray diffraction pattern of lithomargic clay before and after leachate interaction



Fig 7.2 (b) X-ray diffraction pattern of lithomargic clay blended with 5% BC soil before and after leachate interaction



Fig 7.2 (c) X-ray diffraction pattern of lithomargic clay blended with 10% BC soil before and after leachate interaction



Fig 7.2 (d) X-ray diffraction pattern of lithomargic clay blended with 5% bentonite before and after leachate interaction



Fig 7.2 (e) X-ray diffraction pattern of lithomargic clay blended with 7.5% bentonite before and after leachate interaction

The X-ray diffraction pattern of uncontaminated and contaminated soils shows the same counts at same 2θ degree angle indicating there is no significant influence of landfill leachate with parent soil and blended lithomargic clay.

7.5 IMAGE ANALYSIS USING SCANNING ELECTRON MICROSCOPE

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high – energy beam of electron in a faster scan pattern. The electrons interact with the atoms that make up the sample producing the signals that contain information about the sample's surface topography and composition.

A morphological study was conducted on test soil samples. The analyses were carried out on the contaminated and uncontaminated soil samples. Scanning electron microscope, which provided fabric appraisal and gave an elemental description using EDS.









(b)







Fig 7.3 (a) SEM micrographs of lithomargic clay

(b) SEM micrographs of lithomargic clay blended with 5% and 10% BC soil(c) SEM micrographs of lithomargic clay blended with 5% and 7.5% bentonite

Figs. 7.3 (a-c) below show SEM micrographs of a group of natural soil specimens. Some of these SEM micrographs clearly show the interaction between the silt/clay size particles. The micrographs in Figs. 7.3 (a-c) also show that the individual soil particles oriented at random and smaller particles are seen adhering to the surfaces of the larger particles.

During this study, photomicrographs of test soils were taken before and after contamination with leachate [Figs. 7.3 (a-c) and Figs. 7.3(d-f)]. It is observed from Figs. 7.3(d-f) that the structure of the leachate contaminated soil samples appeared to be dispersed in SEM analysis. The dispersed structure decreases the effective pore space and thus decreases the k.



(d)





(e)



(f)

Fig 7.3 (d) SEM micrographs of lithomargic clay

(e) SEM micrographs of lithomargic clay blended with 5% and 10% BC soil

110 pm

(f) SEM micrographs of lithomargic clay blended with 5% and 7.5% bentonite

Table 7.2 Physico-chemical parameters of leachate sample results.

Sl.no	Parameters	Results
1	pH value	7.90
2	Electrical conductivity in milli siemens	1.81
3	Total dissolved solids (TDS) in mg/L	1120
4	Ammonium nitrogen (NH ₄) in mg/L	633
5	Total hardness expressed in terms of CaCO ₃ in mg/L	4650
6	Calcium (Ca) in mg/L	214
7	Chemical oxygen demand (COD) in mg/L	9625
8	Bio chemical oxygen demand (BOD) in mg/L	1200
9	Sulphate (SO ₄) in mg/L	33
10	Sodium (Na) in mg/L	2030
11	Potasium (K) in mg/L	2213
12	Chloride (Cl) in mg/L	3333
13	Zinc (Zn) in mg/L	0.51
14	Chromium (Cr) in mg/L	0.20
15	Lead (Pb) in mg/L	0.77
16	Cadmium (Cd) in mg/L	0.01
17	Copper (Cu) in mg/L	0.26

Type of soil	Geotechnical properties	Liquid	Plasticity	Clay %	Permeabili	ty (cm/sec)	UCC (kPa)		
	Leachate Interaction	limit %	index %		(w _{opt})%	(w _{opt} +2)%	(w _{opt}) %	(w _{opt} +2) %	(w _{opt} +4) %
100% Lithomargic clay	Before Leachate Interaction	45	13	15	2.4x10 ⁻⁶	9.2×10 ⁻⁷	353	257	171
	After Leachate Interaction	47	15	16	1.1×10 ⁻⁶	8.0×10 ⁻⁷	338	240	150
95% Lithomargic clay + 5% BC soil	Before Leachate Interaction	47	18	16	1.4×10^{-7}	8.5×10^{-8}	325	252	168
	After Leachate Interaction	48	21	17	1.2×10 ⁻⁷	5.1×10^{-8}	308	225	156
90% Lithomargic clay + 10% BC soil	Before Leachate Interaction	49	22	19	7.9×10^{-8}	2.3×10^{-8}	330	251	165
	After Leachate Interaction	50	22	20	3.8×10^{-8}	9.3×10 ⁻⁹	280	210	147

Table 7.3 Properties of lithomargic clay and blended lithomargic clay before and after permeation with leachate

Type of soil	Geotechnica 1 properties	Liquid limit %	Plasticity index %	Clay %	Permeabilit	ty (cm/sec)	UCC (kPa)		
	Leachate Interaction				(w _{opt})%	(w _{opt} +2)%	(w _{opt}) %	(w _{opt} +2) %	(w _{opt} +4) %
95% Lithomargic clay + 5% Bentonite	Before Leachate Interaction	47	20	18	8.51×10 ⁻⁸	5.18×10 ⁻⁸	332	244	160
	After Leachate Interaction	49	17	20	6.6×10 ⁻⁸	3.2×10 ⁻⁸	313	219	142
92.5% Lithomargic clay + 7.5% Bentonite	Before Leachate Interaction	51	24	21	5.83×10 ⁻⁸	4.94×10 ⁻⁸	302	207	133
	After Leachate Interaction	58	26	23	3.2×10 ⁻⁸	2.3×10 ⁻⁸	275	201	111

Table 7.3 (Cntd.)

CHAPTER 8

SUMMARY AND CONCLUSIONS

In this work, an attempt has been made to study the suitability of locally available lithomargic clay (local name shedi soil) as liner material for the construction of landfills.

During initial characterization of test soil, it was found that shedi soil satisfies the basic requirements for construction of clay liner except the hydraulic conductivity (k). In the construction of clay liners, hydraulic conductivity of soil(s) is considered to be the most important property because of the permeation or leachate migration. Regulatory limits specify that the minimum hydraulic conductivity of soil liner should be less than 10^{-7} cm/s and hence soils having $k>1x10^{-7}$ cm/s are not considered to be suitable for the construction of bottom soil liner in landfills. Because of the above mentioned reason, it was decided to blend shedi soil with other types of soils namely, the black cotton soil and bentonite. Black cotton soil is again locally available and bentonite used in this study is commercially available. It was found from laboratory tests that both BC soil and bentonite satisfy the regulatory limit of permeability (i.e. $k < 1 \times 10^{-7}$ cm/sec). Therefore, the shedi soil was blended with BC soil and bentonite soil to obtain the desired permeability. It was established from laboratory studies that the addition of 5%, 10% black cotton soil and 5%, 7.5% bentonite satisfied the regulatory limit required for the construction of soil liner in landfills. Further, batch adsorption tests were conducted to determine the adsorption characteristics of the test soils and blended soils. Analyses were made using three adsorption isotherms, linear, Freundlich and Langmuir. Finally, compatibility of natural lithomargic clay and blended lithomargic is studied through leachate permeation tests using real landfill leachate. It is worth noting that BC soil and bentonite very much satisfy the requirement of hydraulic conductivity (i.e. $k < 1 \times 10^{-7}$ cm/sec) but their use as a sole soil liner is not justified because of the fact that BC soil and bentonite are both susceptible to significant volume change behaviour and lead to desiccation cracks due change in moisture content.

Based on the study results following important conclusions are made:

- 1. The permeability of lithomargic clay blended with 10% black cotton soil and 5%, 7.5% bentonite satisfied the criteria for hydraulic conductivity (i.e. $k < 1x10^{-7}$ cm/sec) when the blend was subjected to maximum dry density by standard compaction at optimum moisture content and wet side of optimum (i.e. at w_{opt} and w_{opt} + 2%).
- 2. To obtain hydraulic conductivity less than 1×10^{-7} cm/s, the lithomargic clay blended with 5% BC soil shall be compacted to a dry density on the wet side of optimum i.e. $(w_{opt} + 2\%)$.
- Through this study, it is concluded that the blended soils compacted to maximum dry density by standard compaction at optimum moisture content and wet side of optimum (i.e. at w_{opt} and w_{opt} + 2%) exhibited UCC more than 200kPa and also exhibited minimal shrinkage.
- 4. Low hydraulic conductivity, adequate strength, minimal potential to shrinkage make blended shedi soil a potential soil liner material for various geoenvironmental applications
- 5. Freundlich's constants (K and n) for adsorption of contaminants indicate that the lithomargic clay blended with black cotton soil and lithomargic clay blended bentonite shows the favourable sorption (n<1). Freundlich's constant K for lithomargic clay, BC soil, bentonite and blended soils shows that the adsorption contaminants increases with increase in the blending percentage of black cotton soil and bentonite.
- 6. From the adsorption isotherms, it concluded that adsorption of potassium, lead and nickel are more on the BC soil and bentonite while lithomargic clay adsorb more chloride and chromium. As a result blending of lithomargic clay with BC soil and bentonite, the adsorption of contaminants will be more in the blended soils.
- 7. When natural lithomargic clay is permeated with leachate, it is observed that liquid limit increases from 45% to 47% and plasticity index increases from

13% to 15% respectively. This increase is due to increase in clay content of the lithomargic clay.

- 8. Hydraulic conductivity of leachate permeated test soils (natural and blended lithomargic clay) decreases from 2.4×10^{-6} to 2.3×10^{-8} cm/sec after interaction with landfill leachate. This decrease in hydraulic conductivity of test soils is attributed to the clogging of soil particle tops due to precipitation of the suspended particles existing in the leachate and form a less permeable thin layer at the top.
- After leachate interaction, the UCC strength of all blended lithomargic clay possess higher UCC strength (> 200kPa) than the recommended minimum strength, at OMC and OMC +2% water content.

SCOPE FOR FUTURE WORK

Scopes for future work are listed below:

- 1. To study the impact of alternate wetting and drying on long term durability of blended lithomargic clay liner.
- 2. To study the usage potential of locally available soils or blended soils for the construction of landfill cap.
- 3. To examine the factors affecting the performance of cap systems, with emphases on improving their durability.

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