

**FACTORS CONTROLLING THE
DISPERSIVITY OF SOILS AND THE ROLE
OF ZETA POTENTIAL**

A Thesis

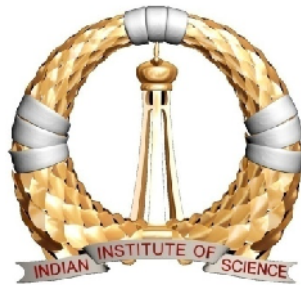
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Dedicated to
Prof N Sankar

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SYNOPSIS

Most soil particles loses cohesion and split up the soil mass into individual soil grains when they come in contact with water and get saturated. In dispersive soils the particles detach more spontaneously from each other and go into suspension even in quiet water. Thus the phenomenon of dispersion is common to most soils, the degree varying from soil to soil. Dispersive soils are abundantly found in various parts of the world such as Thailand, United States, Australia, Mexico, Brazil, South Africa and Vietnam. Several geotechnical failures such as piping due to internal erosion, erosion and gulying in relatively flat areas, collapse of sidewalls and topsoil removal have been reported worldwide due to the construction in dispersive soil. Failures as reported could be prevented if such soils are identified beforehand or if the quantification of dispersivity in the soil is done accurately.

There are several methods of measuring dispersivity in soils which include several physical tests, chemical tests and some common laboratory tests. It is reported in literature that no method could be completely relied upon to identify dispersive soils with absolute confidence. In addition, when these methods were studied in detail, several flaws surfaced needing a better estimation of dispersivity. In order to develop a new method of estimation of dispersivity, the mechanism of dispersion in soils was studied in depth, which revealed that the existing concepts regarding dispersivity are incomplete in many aspects. An exhaustive philosophy of dispersion which addresses every detail is non-existing. To solve these problems, the concept of dispersivity was investigated in detail. It was found out that the observed dispersivity is a result of repulsion in the soil overcoming the attractive force. Thus a list of factors that could possibly affect the repulsion and attraction (and hence the

dispersivity) in soils were found out. Even though literature focuses on exchangeable sodium as the principal reason for dispersivity, from fundamental theoretical considerations several other factors such as Cation exchange capacity (CEC), pH, structure of the soil, electrolyte concentration in the pore fluid, presence of organic matter, clay minerals involved in the soil and dissolved salts in the soil could possibly have an influence on dispersivity.

Several studies have reported soils of high dispersivity to possess a high pH, high CEC, high amounts of sodium. The influence of these factors on dispersivity of other soils (or generally in any soil) is not well explored. Research on understanding their mechanism of action led to the conclusion that these parameters could be generalized for any soil. Through the analysis of these parameters, it was found that the fundamental parameter governing the dispersivity of soils is the number of charges on clay particles and that the repulsion in the soils is mainly contributed by the electrostatic repulsion. The attractive force in a soil/clay mass is primarily contributed by the van der Waal's attraction and dispersion occurs when the electrostatic repulsion (resulting due to permanent and pH dependent charges) dominates over the van der Waal's attraction.

A practical estimation of charge with least effort could be possibly carried out through the measurement of zeta potential of soils. In order to verify whether the effect of all the factors is completely and sufficiently reflected in the zeta potential values, experiments were conducted on various soils. Three soils namely Suddha soil (a locally available dispersive soil), Black cotton soil and Red soil were selected for the study. These soils were chosen as the soil samples as they could display wide ranges of dispersivity values. In order to perform dispersivity tests, soil fraction finer than 75μ (75 micron meter sieve size) was fixed as the sample size as dispersivity pertaining to the finer fractions play a greater role than that of the

coarser particles. All the three soil samples were treated with sodium hydroxide and urea solutions to alter the dispersivity so that the influence of all parameters could be studied. The dispersivity of the treated and untreated soils was found out through the various conventional tests and it was found that there exists a good correlation between the dispersivity and the zeta potential of soils. It was also observed that the increase in the dispersivity is higher when treated with salts of monovalent cations. Increase in the organic content also increased zeta potential, but not as significantly.

One of the popularized theories on colloidal dispersions is the classical DLVO theory which has formulated the total interaction energy of colloidal particles by estimating the electrostatic repulsion and van der Waal's attraction energy between two particles. The total interaction energy is then expressed as the difference between them. A similar approach as taken by the DLVO is adopted in this study. The total attractive energy existing in a soil mass is mathematically derived from the expression for van der Waal's energy between two particles and the total repulsive energy from the zeta potential values. Two different approaches namely an infinitesimal particle approach and a finite particle approach is taken for finding the energy in a soil mass. In the infinitesimal particle approach, a clay particle is assumed to be infinitely small such that any soil particle of a finite radius could be conceived to be formed by a combination of infinite number of these infinitesimal particles. With this setting, the total energy in a soil mass is computed without really bothering about what exact particles constitute the mass. The increase in energy due to the increase in radius is then integrated to obtain the final expression. The dispersivity of the soil is then estimated under defined physical conditions of the soil. In the finite particle approach, each particle is considered to be of finite radius and to estimate the total energy, the total number of particle

combinations is then taken and the total energy is expressed as a sum of all the possible combinations. The dispersivity of a soil in both approaches is expressed as a release of energy when the repulsion rules over the attraction. In order to validate the derived propositions and expressions, experiments were conducted again on soils. The soils were treated with hydroxide salt of monovalent cations such as lithium, sodium and potassium. The dispersivity of the various treated and untreated soils was measured with the conventional methods and with the derived expressions of dispersivity through zeta potential. The similarity in the trend of the dispersivity values confirmed the validity of the derived expression. It was also concluded that the infinitesimal particle approach could be adopted when information about the physical properties are available and when they are not, the finite approach could be used.

An accurate determination of zeta potential is critical for representation of dispersivity with zeta potential. Thus the procedure for measurement of zeta potential was standardized. The standardization was primarily focused on establishing the ideal conditions for zeta potential measurement. The role of Brownian motion, in electrophoretic mobility measurements were studied by employing the usage of zeta deviations. Untreated, potassium hydroxide treated, sodium hydroxide treated and lithium hydroxide treated samples of Suddha soil, Black Cotton soil and Red soil (finer than 75μ) were used for the study. Zeta potential measurements on unfiltered soil water suspensions, suspensions passing 2.5μ and suspensions passing 0.45μ were conducted along with recording their zeta deviations. It was observed that soil suspensions finer than 0.45μ show acceptable values of zeta deviations and thus could be used as a standard procedure for estimating zeta potentials. It was also

concluded that the presence of Brownian motion makes the assessment of zeta potential through electrophoretic measurements easier and accurate.

In an alternate perspective it is deduced that the amount of total monovalent ion concentration in the soil (dissolved and adsorbed) could adequately serve as an ideal parameter that could be used to quantify dispersion in soils. In order to verify the speculation, the variation of repulsive pressure with monovalent cation concentration was studied for the above mentioned treated and untreated soils. Within the monovalent cations, the role of ionic size in repulsion along with physical factors was also studied with the help of Atterberg limits, compaction characteristics, and dispersivity measurements. It could be concluded that even though there are several chemical factors such as CEC, pH, electrolyte concentration, type of clay minerals, dissolved salts etc. and physical factors such as plasticity, water holding capacity, density and structure which influence dispersion in soils, these factors affect either directly forces between the particles or the surface charge of clays which again affect the forces. The two phenomena can be combined through the hydration behavior of the adsorbed cations on the clay surface in view of dispersivity. It is that force due to hydration which acts as the principal reason to separate the clay particles apart. As the radius of the inner hydration shell is higher for monovalent cations than those of higher valency ions, more force would be offered by the monovalent ions. Higher the charge and higher is the number of monovalent cations, higher will be the repulsion and thus the dispersivity. The repulsive force offered by the monovalent cations in soil was calculated through osmotic pressure differences and the dispersivity was expressed as the release of energy as earlier. In order to validate the proposal, the dispersivity of the samples as measured with the

conventional methods was compared and studied with the derived expression. The similarity in the trend of the dispersivity values confirmed the validity of the derived expressions.

Thus, it can be seen that there are primarily two different methods of quantifying dispersivity of soils. When one method estimates dispersivity by calculating the electrostatic repulsion through zeta potential, the other method gives a dispersivity value based on the repulsive pressure offered by the monovalent cations in the soil. Two methods could be regarded as two different measurements of the electrical double layer. Any method could be used based on the property that could be easily quantified.

The applicability of the new approaches – calculation of monovalent cations and zeta potential- for estimating the dispersivity in soils through a complete development of philosophy of dispersion and is presented, in this thesis, in nine chapters as follows:

In **Chapter 1** the background of the study and review of literature connected with the present study is presented. The mechanism of dispersion and the geotechnical problems associated with dispersion is elaborately presented in this section. As the dispersive soils cannot be identified through conventional tests, a description about the various tests designed to identify dispersive soils is presented. Earlier works relevant to the topic and the shortcomings of those studies are discussed. Finally, the objectives of the current research along with the scope of the work are explained in the concluding part of this chapter.

Various factors that could have influence on the dispersivity of soils and their mechanism of action are presented in **Chapter 2**. The relationship of the factors with zeta potential is discussed. Theories dealing with dispersivity, conventional methods of measurement, role of geotechnical characteristics in assessing dispersivity are being presented.

Chapter 3 deals with the various materials and methods used for the study. A locally available dispersive soil called Suddha soil along with Black Cotton soil and Red soil were chosen as the soils for the study of dispersion. The basic material properties and testing programs adopted for the study are presented in this chapter. The codal procedures followed to determine the physical, chemical, index and engineering properties are described in detail.

The experimental investigations carried to bring out the role of zeta potential in dispersivity of soils are described in **Chapter 4**. Detailed analysis of the results showed estimation of zeta potential is possible and can sufficient quantify dispersivity of soils. The formulation of the equation for estimating dispersivity from zeta potential is described in **Chapter 5**. The estimation dispersivity based on attraction and repulsion energies in a soil mass is presented here. The adoption of the approach and methodologies used based on classical DLVO theory for the current work is explained in detail. The values of dispersivity obtained from the derived equation are compared with those obtained from the conventional tests. The validity of the expression is confirmed with the results of the experiments.

Chapter 6 deals with the standardization of the measurement procedure of zeta potential. Role of Brownian motion in the accurate measurement of electrophoretic mobilities are brought out here. **Chapter 7** brings out an alternate perspective of quantifying dispersivity through monovalent cations. The role of monovalent cations and the mechanism in which they contribute to the repulsive pressures (hence the dispersivity) are discussed. Experimental research design adopted has brought that the effect of monovalent and ionic size on repulsive pressures leading to dispersivity is described. The results of the experiments added with the inferences drawn are explained at the end.

The estimation of repulsive pressures for measuring dispersivity from monovalent cations is discussed in **Chapter 8**. The dispersivity of a soil mass is derived from monovalent ion concentration and experiments were carried out for verification purposes. The experimental investigation procedure adopted followed by the results are presented in this chapter. It was observed that a good co-relation exists with the dispersivity obtained from the monovalent ion concentration and that obtained from conventional methods.

Chapter 9 compares the dispersivity obtained through the various methods proposed in this thesis. The comparison is made in light of the classical electrical double layer theory. The major conclusions of the study are brought out at the end of this chapter.

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LIST OF SYMBOLS/ABBREVIATIONS

SYMBOL	DESCRIPTION
A	Hamaker constant
A_s	Specific surface area
A_v	Avogadro's number, 6.023×10^{23}
c	Equivalent concentration of monovalent cations contributing to dispersivity (cmol/kg)
C_c	Molar concentration of cations midway between the plates
C_0	Local molar concentration of the solution
d	Separation distance
D	Dispersivity
[DIVALENT]	Divalent cation concentration
e	Void ratio
E	Electric field
ϵ	Charge density per unit area
ϵ_0	Permittivity of the free space
ϵ_r	Relative permittivity of the medium
F	Dominance factor
G	Specific gravity
k	Dielectric constant
κ^{-1}	Diffused double layer thickness
[MONOVALENT]	Monovalent cation concentration

M	Mass of a soil mass
N_M	Relative number of monovalent cations that contributing to dispersion
η	Viscosity
ρ	Dry density
ρ_w	Density of water
P	Swelling pressure
Q	Total charge
r	Radius of a particle
r_h	Hydrated radius of the monovalent cation
R	Radius of the soil mass
R_g	Universal gas constant
R-A	Repulsion minus Attraction
R.E	Repulsive energy
R.F	Repulsive force
ψ_0	Surface potential
T	Temperature
TIC	Total ion concentration (cmol/kg)
U	Van der Waal's interaction energy
μ_E	Electrophoretic mobility
V_d	Equilibrium sediment volume
XRD	X-Ray Diffraction
Z.D	Zeta deviation
ζ , Z.P	Zeta potential

CHAPTER 1

INTRODUCTION

1.1 GENERAL BACKGROUND

A thorough knowledge about the nature and behavior of soil is very important especially in areas where the soil interacts with large volumes of water such as embankments, irrigation canals, earth filled dams, and channels. As soils and their horizons differ from one another, different soil groups have different characteristics which are related to their engineering properties. Wide variation is seen in the behavior of soils because of the complexities involved during their geological formation. Civil engineers planning to build structures have to understand the characteristics of different soils that they need to deal with.

The dispersion characteristics of soils play a major role in the geotechnical application especially where erosion is prominent. Earlier, it was considered that clays were non-erosive by nature and is resistant to erosion. However, it was found that highly erosive soils such as dispersive clays are abundant in various parts of Thailand, United States, Australia, Mexico, Brazil, South Africa and Vietnam (Decker 1977). Soils possessing high amounts of dispersivity are generally unstable where the amount of water content interacting with, is high. Dispersive soils when used for construction in hydraulic structures such as roadway embankments, dams, canals or other structures can create severe problems if they are not well identified (Rengasamy et al. 1984). Various threats occurred to such structures due to the usage of dispersive soils have been reported worldwide.

Numerous investigations on dispersive soils and their properties have been carried out and reported in literature. Dispersion in clays was first reported by agronomists over 100

years ago and their fundamental behavior was moderately understood by soil scientists and agricultural engineers nearly 50 years ago (Volk 1937; Richards 1954). However, until the early 1960's the relevance of the topic in the perspective of civil engineering was recognized not well enough. Various researches have been performed to improvise the procedures for identifying dispersive soils. Results show that there can be great variations possible regarding the erodibility of the material having similar texture and index properties even if the samples are taken from neighboring locations.

1.1.1 Existence of dispersive soils

Dispersive clays are commonly encountered in alluvial clays in the form of slope wash, lake bed deposits, loess deposits, and flood plain deposits; no specific geological origin been claimed for such soils (Jansen 2012). In some areas, marine deposits formed of claystone and shales have similar dissolved salts as dispersive clay, and their residual soils are dispersive. Dispersive clays have even been associated with granites and sandstones in countries such as Zimbabwe as well (Clarke 1986). There are easily identifiable surface erosion of rugged undulating corrugations and rapidly developing deep channels and tunnels in areas where dispersive soils are present (Jansen 2012). Even then, the absence of such surface erosion patterns, the characteristic quintessentially attributed to dispersive clays does not necessarily prove that dispersive clays are not present. Though normally, dispersive soils are associated with red, brown, gray or yellow complexions, they are found as a resultant of various combinations of these colours also (Rengasamy and Olsson 1993). In the past, dispersion was identified in soils formed in arid or semiarid climates and in areas of high alkalinity. Recently problems associated with dispersion have been found in humid climates in various geographic locations such as Australia, Tasmania, Mexico, Trinidad, Vietnam, South Africa,

Thailand, Israel, Ghana, Brazil, Venezuela, and many parts of the Southern United States. As per Elges (1985), dispersive soils are found in

- (i) Low lying areas where in the seepage water has high SAR (Sodium adsorption ratio)
- (ii) Areas where in the original sediments contain high illitic or other 2:1 minerals with high ESP (Exchangeable sodium percentage values)
- (iii) Areas where there is high leaching so as to remove the excess salts present in soils with high SAR.

Usually, 2:1 clay minerals mainly montmorillonite is the principal element in dispersive clays (Bell and Maud 1994). Recent studies have shown that some illites are also highly dispersive (Bell and Walker 2000).

1.1.2 Behavior of dispersive soils

Dispersive soils are those soils in which the clay particles detach spontaneously from each other and go into suspension even in quiet water (Mitchell 1976). In earlier days, clays were considered to be resistant to erosion but now, studies have proven that erosive clayey soils do exist. The tendency of clays to deflocculate depends on the type of clay and soil chemistry (Decker 1977). The rate of erosion in such clays by slow-moving water is much higher even when compared to cohesionless fine sands and silts. When such soils come in contact with water, the clay fractions behave almost like single-grained particles; that is, the clay particles have a minimum electrochemical attraction and fail to closely adhere to other soil particles (Sanaz and Masoud 2014). Water molecules are drawn in-between the clay platelets which forces the clay particles apart. The binding force is overcome making the clay to swell to such an extent that individual clay platelets are separated from the aggregate (Hardie 2009) as attractive forces become lesser than the repulsive forces in saturated

condition. Thus, the individual clay platelets are split off and get carried away when the dispersive clay soil erodes in the presence of flowing water. The critical mechanism of a failure consists of developing a tension crack as the open channel of water flows, and then the gradual scouring of soil particles within the mass (Ismail and Mukri 2008). Erosion in the field may start in a drying crack, settlement crack, hydraulic fracture crack, or other channels possessing high permeability.

Thus it is quite clear from the discussion that dispersive soils are not of rare occurrence and is not limited to remote areas or the damages arising from dispersion secluded from common geotechnical problems. The mechanism of dispersion, geotechnical challenges faced, quantification or measurement of dispersivity added with their drawbacks are discussed in the subsequent sections.

1.2 THE MECHANISM OF DISPERSION

Understanding the mechanism of dispersion in soils is essential to overcome the problems with dispersive soils. Hence many studies are directed to understand mechanism of dispersivity of soils world over. Dispersive soil mass splits up into individual soil grains and go into suspension even in quiet water. They are dislodged easily and rapidly in flowing waters of low salt concentration and hence it is necessary to identify them and to quantify the amount of dispersion occurring beforehand so that the devastation caused can be regulated or avoided.

There are basically two types of soils which are prone to dispersion viz., silty soils and clayey soils. In silty soils as the cohesion is less, shearing stress induced by a fluid flow is higher than resistance offered by the submerged weight of the sediment (Umesh et al. 2011) thus making the soil dispersive. Water when comes in contact with the soil enters into

the pores and exerts pressure on the soil grains. As there is minimal cohesive force between the soil particles in silty soils the pressure exerted by the water molecules easily dominates over the attractive force ultimately leading to dispersion. Loss of cohesion upon saturation is identified as the principal reason for dispersivity in silty soils.

On the hand the reason for dispersivity in clays is mainly attributed to the presence of exchangeable sodium in the soil (Bell and Maud 1994; Bell and Walker 2000; Bhuvaneshwari et al. 2007; Umesha et al. 2009). When soils with high sodium content or high exchangeable sodium percentage come in contact with water, the clay fractions work as individual clay platelets; that is, the attraction between the clay particles is reduced to a minimum thus failing to closely bond with the other soil particles. When a sodic soil interacts with water of low salt concentration, water molecules are drawn in between the clay platelets which causes the clay to swell to such an extent that the individual particles gets separated from the aggregate. Water molecules enter in-between the clay platelets which causes these ions to hydrate which forces the clay particles to move away from each other (Figure 1.1).

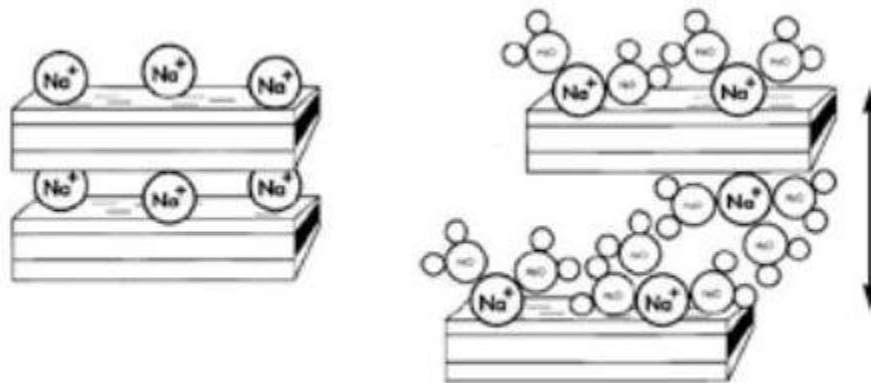


Figure 1.1 Behavior of sodic soils in water. (Hardie 2009)

The attractive force is reduced to a minimum making the clay to swell to such an extent that individual clay platelets are separated from the aggregate (Hardie 2009).

In soils, instead of sodium, if the adsorbed ions are of divalent in nature eg -calcium or magnesium, the resulting dispersivity in clays would be minimized. This is because in non-sodic clays, the repulsion due to hydration of the ions (say, calcium) is not that great enough to completely dominate the attractive force. Thus, the clay may swell due to the penetration of water but need not necessarily cause dispersion (see Figure 1.2).

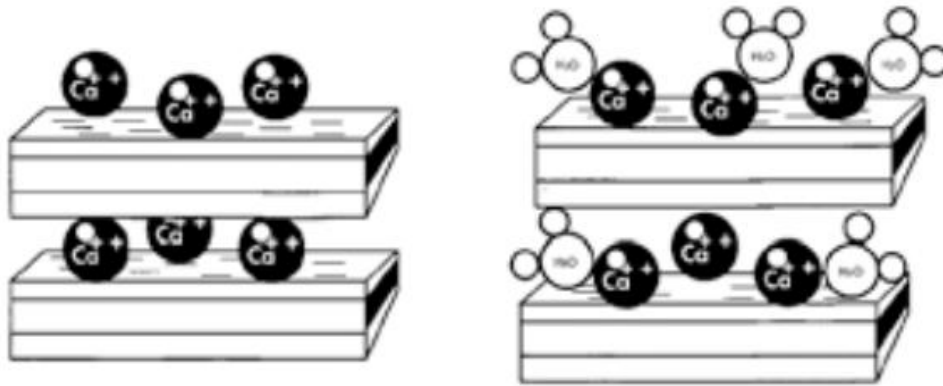


Figure 1.2 Behavior of non-sodic soils in water (Hardie 2009).

From the consideration of mechanisms of dispersion, it appears that the only major difference in the dispersivity in clayey soils is by repulsion between clay particles by the presence of sodium and silty soils is by loss of cohesion due to saturation breaking the binding of silty particles.

1.3 GEOTECHNICAL PROBLEMS FACED DUE TO DISPERSION

The significance of dispersion in soils is not limited to the field of construction and civil engineering. The property has implications for agriculture, mining, water quality, tunnelling activities etc. Problems associated with dispersive soils are reported in many parts of the world including United States, Australia, Greece, India, Latin America, South Africa

and Thailand. Damages in civil engineering infrastructures such as earth-filled dam, embankments, irrigation canals etc. can often be attributed to dispersive soils whose erosion may lead to failure of these structures. Piping failures occurs in embankment dams constructed with dispersive soils due to deflocculation where water travels through a concentrated leakage channel, such as a crack from its source. The erosion of the walls of the leakage channel then occurs along the entire length at the same time. Erosional damage in embankments constructed with dispersive clays generally occurs in areas of high crack potential, such as along conduits, in areas of large differences in compressibility of foundation materials, or in areas of desiccation. All failures were associated with the presence of water and cracking by shrinkage, differential settlement, or construction deficiencies. Some of the problems faced are explained in detail.

1.3.1 Internal erosion in soils

The internal erosion has been closely linked to the soil composition and identification of dispersive clays. The fundamental factor contributing to geotechnical problems such as piping phenomena in earth dam, loss in bearing capacity of road sub-base, the erosion of the compacted soil of landfill clay liner and the instability of soil slope can all be attributed to the natural clay in a dispersive state. The failure is initiated with the development of a tension crack due to the flowing water added with the washing away of soils. The inter-particle attraction and the density of the soil mass is the parameter which governs the erodability of the soil. The soil grains gradually detach from the soil mass when the fluid flow velocity is relatively large. Figure 1.3 illustrates the sequence of erosion taking place in Dispersive soils.

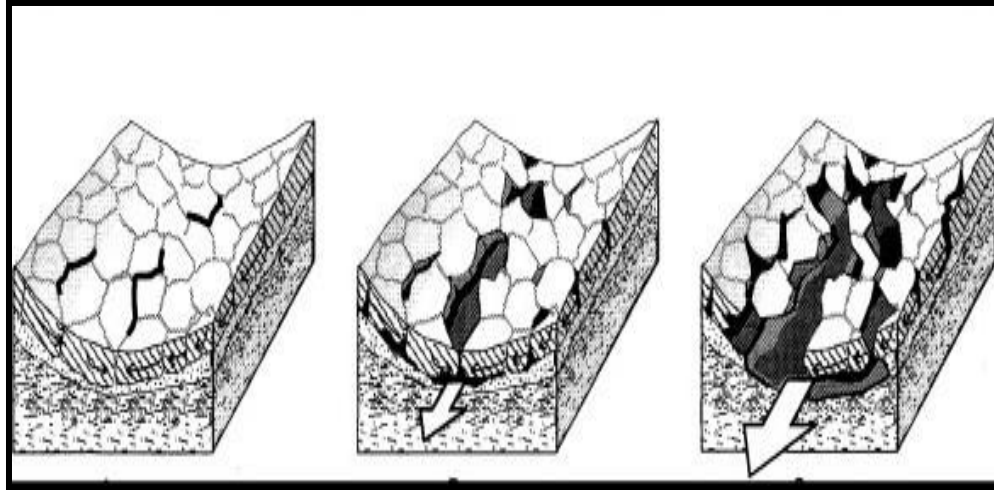


Figure 1.3 Erosion of Dispersive Soil (Faulkner 2012)

The effective stress approaches zero in the soil adjacent to a soil mass wherein a water-filled crack channel is developed. At this point the cohesion of the soil is the fundamental parameter which governs the strength of the soil mass. When the cohesion becomes negative due to the increase in pore pressure, the soil grains get dispersed in water. The individual soil particles gradually detach from the soil mass when the fluid flow velocity is relatively larger. The magnitude and the equilibrium states of the true cohesion in soil depend on the physicochemical properties of the soil grains, the pore water and the free water.

1.3.2 Piping failure in soils and dams

Figure 1.4 depicts piping failures in soils due to dispersion. The erosion in soils happens when the shearing stress offered by the flowing water on the surface is large enough to result particle removal from the surface.

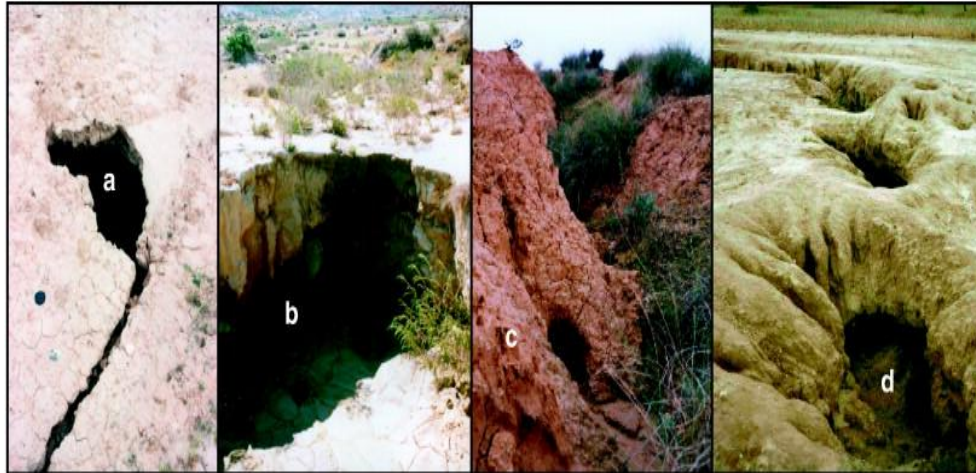


Figure 1.4 Piping failures in soils (Faulkner 2012)

- a) holes in surfaces; b) pipe outlets beneath head cuts; c) pipe outlets in side slopes
d) Gully development in bridges

Piping failure in an earthen embankment dam develops when water flows through the pores of the soil through a concentrated leak established at the downstream side of the dam. The erosion initiates at the discharge end of the leak, causing a local concentration of seepage and erosion forces. Erosion progresses upstream forming a tunnel-shaped passage until it reaches the water source, consequently a rapid catastrophic failure may result. Such erosion occurs mainly in cohesionless soils or soils with low cohesion which have little resistance to the plucking forces of seeping water. In dispersive clay, piping is due to a deflocculation process where water travels through a concentrated leakage channel, such as a crack (even a very small crack), from its source. The erosion of the walls of the leakage channel then occurs along the entire length at the same time. Unlike erosion in cohesionless soils, erosion in dispersive clay is not a result of seepage through the pores of clay mass. A concentrated leakage channel, even though it can be very small, must be present in order for erosion to start (Decker 1977). Erosion damage in embankments constructed with dispersive clays

generally occurs in areas of high crack potential, such as along conduits, in areas of large differences in compressibility of foundation materials, or in areas of desiccation (Sherard et al. 1972).

When a concentrated leak starts through an embankment constructed of dispersive clay, either of two actions can occur (1) if the velocity is sufficiently low, the clay surrounding the flow channel can swell and progressively seal off the leak, or (2) if the initial velocity is high enough, the dispersed clay particles are carried away, enlarging the flow channel at a faster rate than it is closed by swelling, leading to progressive piping failure. Figure 1.5 shows a typical piping failure occurred in a dam.



Figure 1.5 Piping failure of a dam. (Hardie 2009)

1.3.3 Top soil removal by rainfall

Removal of the top soil caused by sheet or surface erosion by rainfall may occur in cohesive soil masses, often in conjunction with dispersive erosion. Slaking of soil grains contributes to the sheet erodability of soil masses and may also be a factor in internal erosion occurring in a dispersive clay soil when a dry surface is present for water contact within the soil mass. Reaction by the surface of the soil mass to water is essentially that of soil crumbs,

and slaking is the breakup of soil crumbs into discrete fragments when immersed in water. This breakup may proceed to individual clay platelet size when the crumb particles are composed of dispersive clay. Two causes of slaking are replacement of entrapped air by water and internal shear stresses caused by swelling (Haliburton et al. 1975).

A study comparing laboratory behaviour to field situations (Emerson 1964) showed that when kaolinitic soil was wetted slowly from the surface, it did not slake to any depth, but when wetted quickly by a heavy rain it slaked to an appreciable depth. In the first case, vapour phase water entered the subsurface soil, allowing air to be dispersed. Water that was quickly introduced in liquid form caused slaking. Another study (Huddleston and Lynch 1975) described development of severe rill and tunnel erosion in non vegetated cut and fill slopes of dispersive clay when there was heavy rainfall following a drought. Vegetated fill slopes of dispersive clay showed severe tunnel erosion under certain climatic conditions, i.e., heavy rainfall following a drought. Natural slopes in non-dispersive soils normally covered with vegetation and containing organic matter in the topsoil in humid areas, usually exhibit little erosion.

Dispersive soils are usually not present in the topsoil of natural slopes due to the process of eluviation, which is the movement of clay particles and nutrients downward in the soil profile. One study of dispersive clays in the State of Mississippi showed that although severe rainfall erosion tunnels developed in many small dams, no rainfall damage was found in the undisturbed natural soil adjacent to the dams (Perry 1979). Figure 1.6 demonstrates a typical case of pitting and pocketing failure in soils due top soil removal.



Figure 1.6 Pitting and pocketing in soils. (Hardie 2009)

Knowing now that dispersive clays are found in widespread geographic areas, and that the process of dispersion causes serious engineering problems to geotechnical structures it should be assured that these soils are identified accurately and their degree of dispersion perfectly quantified so as to ensure the safety of a structure.

1.4 MEASUREMENT OF DISPERSION

Although a number of tests have been used to identify dispersive soils, no single test could be completely relied upon to quantify the amount of dispersion under all conditions (Bell and Maud 1994; Bell and Walker 2000). A review of analytical procedures for identifying dispersive behaviour in soils is presented by Bell and Maud (1994) as well as Bell and Walker (2000). There are various physical and chemical tests which are helpful in determining the dispersivity of the soil. Physical tests involve tests such as Emerson crumb test, pin hole test and double hydrometer test. Determination of chemical properties such as cation exchange capacity, exchangeable sodium percentage and sodium adsorption ratio is used for estimating the amounts of possible dispersion in soil. Recent studies show that laboratory tests such as unconfined compressive strength and shrinkage limit can also be

used to quantify dispersivity. Various tests estimate the amount of dispersion through the measurement of various aspects of dispersion. Detailed descriptions of the various tests used are given below.

1.4.1 Physical tests

Physical tests reveal the result of dispersivity of the soil which may or may not be quantified. Experiments such as Emerson crumb test, Double Hydrometer Test and Pin hole Tests rely on measuring and classifying soil dispersion in distilled water with or without the use of a dispersing agent. The relative efficiency and ranges of various laboratory procedures for the prediction of soil dispersion have been reported by various authors including; Sherard et al. (1976), Moore et al. (1985) and Elges (1985), Bell and Maud (1994), Bell and Walker (2000).

Emerson crumb test is a simple way of identifying dispersive soils. It provides a qualitative indication of the natural dispersive characteristics of clayey soils. The test was originally developed by Emerson (and hence the name) which was then later modified by Sherard. In this test, a cube of remolded soil having a diameter around 1mm is immersed in a beaker containing approximately 250ml distilled water and the subsequent reaction is observed for 5 minutes. A visual determination of the dispersion grade is then recorded. The soil is classified in one of the four levels of dispersion in accordance with ASTM-D6572 based on the formation, extent, and turbidity of a dense cloud or halo of colloidal sized particles extending from the soil crumb.

The following interpretation guide is used for assessing the dispersivity of the soil:

Grade 1: Except for possible slaking of the crumb, no indication of cloudiness caused by colloids in suspension.

Grade 2: A bare hint of cloudiness near the surface of the crumb.

Grade 3: Easily recognizable cloud of colloids in suspension, spreading out in thin streaks at the bottom of the beaker.

Grade 4: A considerable reaction with colloidal clouds completely covering the bottom of the beaker and also spreading to its upper regions.

The following figures from 1.7a to 1.7d illustrate the respective grades of dispersivity:

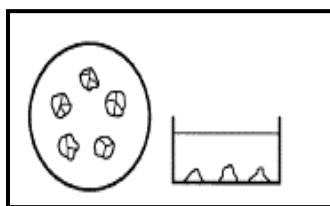


Figure 1.7a Grade 1 dispersivity (Water remains clear though particles may crumble)

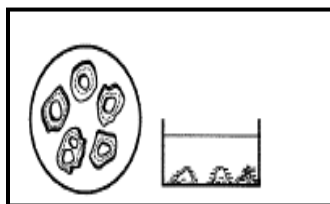


Figure 1.7b Grade 2 dispersivity (Discoloration surrounding particles or distinct cloudiness surrounding some particles)

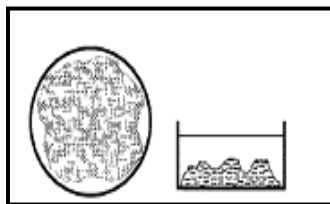


Figure 1.7c Grade 3 Dispersivity (Discoloration surrounding most or all particles)

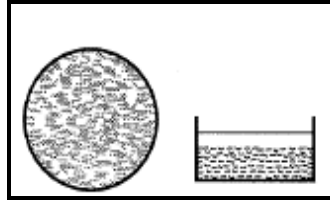


Figure 1.7d Grade 4 Dispersivity (Discoloration and cloudiness extending vertically throughout most or all water) (Hardie 2009)

Another test used to identify dispersive soils is the Pin hole test. The test records a qualitative measure of dispersivity by causing water to flow through a small hole punched in a soil sample. In Figure 1.8 the apparatus of Pinhole Test is depicted. The test begins by allowing distilled water to flow horizontally under a hydraulic head of 50 mm (2 in.) through a 1.0 mm (0.04 in.) diameter hole punched in the soil specimen. The differentiation between dispersive and non-dispersive clay is made by visually observing the solution emerging from the sample.

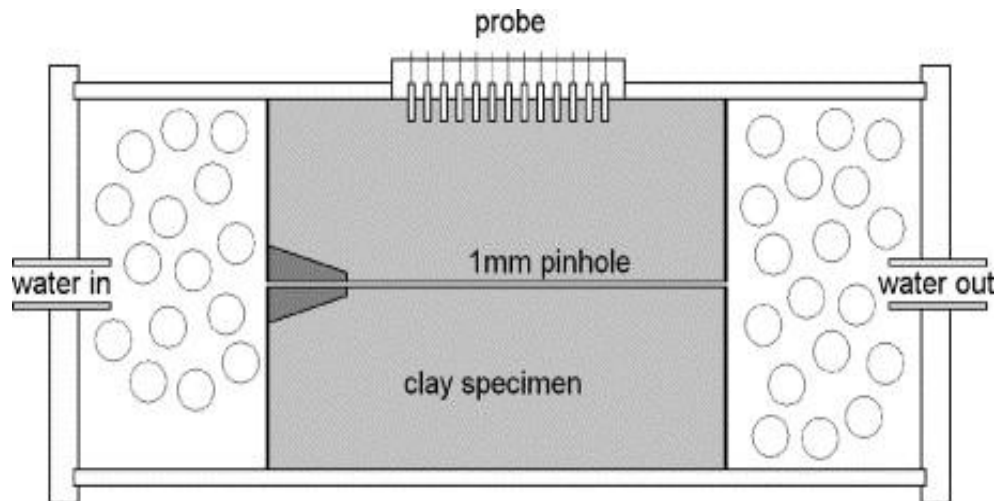


Figure 1.8 Pinhole test apparatus (Faulkner 2012)

The dispersivity of the soils is judged based on the appearance of the solution emerging from the specimen, the rate of flow, and the final size of the hole through the specimen. The solution coming out from dispersive clays will be distinctly dark; the hole enlarging rapidly,

with a resultant increase in the flow rate. Flow from slightly to moderately dispersive clays will be slightly dark with a constant hole size and flow rate. Flow from non-dispersive clays will be completely clear with no measurable increase in the hole size. This test method depicts the action of flowing water along a crack in an earth embankment. The most consistent results are produced when the natural water content of the sample is preserved during the sampling, storage and testing operations.

The third test, the double hydrometer test offers a mathematical value of dispersivity of the soil. The test involves the estimation of the particle size distribution using the standard hydrometer test in which the soil is dispersed in distilled water with a chemical dispersant (usually sodium hexametaphosphate). A parallel hydrometer test will be done on the same soil but without the addition of the dispersing agent. The percent dispersion is the ratio of the percentage mass of particles finer than 0.005 mm diameter of the test without dispersing agent to the test with dispersing agent expressed as a percentage. The degree of dispersion of the soil is classified using the below table given in ASTM D4221-standard double hydrometer test. Table 1.1 shows classification of the soil to various categories depending on the amount of dispersion.

Table 1.1 Degree of dispersion based on double hydrometer test

Percentage dispersion	Degree of dispersion
<30	Non-dispersive
30 to 50	Intermediate
>50	Highly Dispersive

1.4.2 Chemical tests

Chemical tests of estimating dispersivity involve the measurement of sodium ion and classifying dispersive soil based on the preponderance of sodium over other ions notably Calcium, Magnesium and Potassium. Parameters such as Exchangeable Sodium Percent (ESP) and Sodium Adsorption Ratio (SAR) are the conventionally used parameters. After measuring CEC of the soil, the proportion of exchangeable sodium relative to summation of exchangeable cations is calculated to provide the exchangeable sodium percentage (ESP) for the soil. This simple calculation (units of %) is used to indicate the likely effects that a soil may have with respect to structural stability, as Na^+ favors dispersion and Ca^{+2} and Mg^{+2} favor flocculation.

Exchangeable sodium percentage is defined as the concentration of sodium ions present in the soil with respect to the Cation exchange capacity of the soil. It is given by the below formula:

$$ESP = \frac{[Na^+]}{CEC} \times 100 \quad \dots\dots\dots(1.1)$$

Where,

$[Na^+]$ is the Sodium concentrations in meq/100 g of clay and

CEC is the Cation Exchange Capacity of the soil.

There is a threshold value for the dissolved salts in the pore water (for a given ESP), above which the soil remains flocculated. Nonetheless, a soil having a high ESP but initially in a flocculated state could be made dispersive by the leaching of salts from the pore water (Bell and Walker 2000). Soils that have more than 6% ESP are considered to have stability issues related to potential dispersion. A threshold value of 10% ESP has been recommended, above which the soils that have a potential for their free salts leached by the seepage of

relatively pure water are prone to dispersion (Elges 1985). Soils with ESP higher than 15%, according to Gerber and Harmse (1987), are highly dispersive. Those with low Cation exchange capacity (of 15 meq/100 g of clay) have been found to be completely non-dispersive at 6% or below.

The other chemical parameter used for the assessment of dispersivity as mentioned above is SAR. SAR gives an indication of the predominance of dissolved sodium in pore water compared to amounts of dissolved calcium and magnesium. It is the ratio of the amount of cationic charge offered by sodium ion to that by calcium and magnesium. SAR is defined as

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}} \times 100 \quad \dots\dots\dots(1.2)$$

Where,

[Na⁺], [Ca²⁺] and [Mg²⁺] are respectively Sodium, Calcium and Magnesium concentrations in meq/100 g of clay.

Sodium adsorption ratio is used to quantify the free salts present in the pore water. Gerber and Harmse (1987) considered soils having SAR greater than 10 as dispersive soils, 6 to 10 as intermediately dispersive soils and less than 6 as non-dispersive soils. Bell and Maud (1994) suggests that SAR should not be used for defining dispersive soils if free salts are absent.

An important point to be taken into account is that the threshold levels for dispersion are arbitrarily defined (Sumner 1993). The United States Salinity Laboratory (USSL) proposed one of the earlier models to predict soil Exchangeable Sodium Percentage (ESP) from soil Sodium Adsorption Ratio (SAR) as

$ESP = -0.0126 + 0.01475 \text{ SAR}$ for United States soils (Richards 1954).

Seilsepour and Rashidi (2008) modeled SAR from soil electrical conductivity as the measurement of SAR is tedious. They expressed SAR as,

$$\text{SAR} = 1.91 + 0.68 \text{ EC}.$$

1.4.3 Other laboratory tests

Even though historically the above mentioned tests are used for assessing dispersivity in soils, recent research shows that measurement of engineering properties of soils such as shrinkage limit and unconfined compressive strength could be used for the same. In earlier days, unconfined compressive strength and shrinkage limit were commonly used for the assessment of engineering and index properties of soils. Compression tests were used for acquiring knowledge about the strength properties, cohesion, load carrying capacity, stress-strain behaviour etc, while Atterberg's limit tests for understanding the consistency of soils, the volume change behaviour, water holding capacity, expansion and compressibility. These properties also give an indication about the structure of the soil. It is very well established that a dispersed structure gives low shrinkage limit and strength values. Umesh et al. (2011) explored the usage of these properties in understanding the structure of soils and thereby demonstrated their applicability for estimating dispersivity.

A soil may be in its natural dispersed or flocculated state. Addition of dispersing agent increases the amount of negative charge in the soil and hence the repulsion. The increased repulsion in the soil forces the soil to maintain a dispersed structure. Addition of an optimum amount of dispersing agent makes the soil completely dispersive. The strength and shrinkage properties are measured in the soil's natural state and after complete deflocculation. The rate of change of the property (UCC strength or shrinkage limit values) in percentage is expressed

as dispersivity. The tests calculate the dispersivity based on the changes happening to the structure of the soil. The potential of the soil to get dispersed due to the influence of dispersing agent is getting measured. Higher the induced dispersion, lesser is the state of being dispersed in its natural state.

Thus, it can be clearly seen that, there are a variety of methods that helps an engineer to identify dispersive soils or quantify the amount of dispersion in a soil. Bell and Maud (1994) state that no single test could be relied upon completely for the identification of dispersive soils. It is reported that the tests may give even contradicting results. Due to all these reasons a rating system is proposed for identifying potentially dispersive soils. Fan and Kong (2013) developed an empirical equation for evaluating the dispersivity of cohesive soil consisting physical and chemical indicators such as liquid limit, clay content, sodium percentage and pH. As a single test could not be able to identify dispersive soils with absolute certainty, often combinations of tests are used.

1.5 LIMITATIONS OF THE EXISTING THEORIES AND TECHNIQUES

When tests such as Emerson crumb test and pin hole test give qualitative results double hydrometer test, shrinkage limit test, unconfined compressive strength test and swell tests offer quantitative values of dispersivity. There are different perspectives through which dispersivity could be conceived. Various aspects of dispersivity get measured with various tests. The individual contribution of factors that affect dispersivity will be subject to the testing conditions and thus a self-contented value of dispersivity can't be achieved through the current experimental methods.

One of the main drawbacks of the existing studies is that the mechanism of dispersion is explained or the quantification of dispersivity is practiced merely on the basis of presence

of sodium. Soils are classified into dispersive and non-dispersive categories based on ESP or SAR. The role and influence of other factors such as cation exchange capacity, electrolyte concentration, pH, type of clay minerals, dissolved salts and other monovalent ions, if present are not well considered. The effect of monovalency and charge of cations in general, in dispersion of soils is not given sufficient importance and the mechanism of dispersivity in clayey soil is not explained sufficiently. The importance of factors other than the valency of exchangeable ion is not well brought out. Even though the methods prove to be useful they cannot be considered completely theoretical.

When it comes to the measurement of dispersivity, the commonly employed tests as mentioned above are double hydrometer, pin hole, Emerson crumb, shrinkage limit, and unconfined compressive strength apart from the chemical tests. Of these, shrinkage limit, and unconfined compressive strength tests calculate dispersivity of the soil based on just its structure. The influences of other factors are not taken into consideration and moreover the results are not standardized. Categorizing soils into various classes of dispersivity is also not done which makes the analysis of the results more difficult. Double hydrometer method compares the ratio of percentage finer than 5μ with and without the usage of a dispersing agent and get the dispersivity pertaining to these fractions only. As dispersion is the process of splitting of a soil mass into its individual soil grains it is not rational to limit the property just to these fractions only. Dispersion can occur in higher soil fractions also (example silts); and thus, even though the method proves to be useful in practical situations (as dispersion of clays is more of concern), it can't be claimed fully theoretical. Only a part of the total dispersion occurring is contributing to the dispersivity as measured. In addition, the dispersion as observed is the result of addition of a dispersing agent. The result changes if the

dispersing agent or its amount is altered and hence the tests may give a variable figure. Also, the underlying assumption in the test is that the addition of the dispersing agent ensures complete deflocculation for which is not a guaranty. Pin hole test and Emerson crumb test do not give a quantitative measure of dispersivity and methods such as shrinkage limit and UCC give variable dispersivity values. Another drawback existing with the current methods is that they are time consuming.

To summarize, the drawbacks associated with the existing theories, methods and procedures are,

1. Influence of factors other than exchangeable sodium is not well understood and the mechanism of dispersion is not explained sufficiently.
2. Double hydrometer test gives dispersivity pertaining to the clay fractions only. Dispersivity of higher sized fractions goes unnoticed.
3. Shrinkage limit and unconfined compressive strength tests assess dispersivity purely based on just its structure and their results are not standardized.
4. All the tests practiced commonly are more or less measuring just the effect of a chemical dispersing agent.
5. The underlying assumption for all the tests is that the addition of dispersing agent ensures complete deflocculation which can't be assured.
6. Pin hole test and Emerson crumb test give just a qualitative measure of dispersion.
7. Some of the methods consume time extensively.

Due to these reasons, an estimation of dispersivity from fundamental consideration is appropriate and is attempted in this study.

1.6 OBJECTIVE OF THE STUDY

It can be seen that there are various perspectives through which dispersivity could be conceived. Dispersivity could be related to the changes occurring to the structure of a soil, it may be understood as the loss of cohesion occurring in a soil mass or it may even be visualised as a process materializing when the repulsion in a soil overcomes the attraction in a soil mass. These ambiguous interpretations of dispersivity undoubtedly indicate the lack of clarity in the phenomenon of dispersion. Hence the primary objective of this study is to develop a complete philosophy of dispersion, which encompasses various issues such as effect of various factors affecting dispersion apart from exchangeable sodium, influence of attractive and repulsive forces and the manifestation of these forces contributing towards dispersion.

Another noticeable inference which could be taken from the existing methods of measuring dispersivity is that different aspects of dispersivity get measured with different tests. The individual contribution of factors that affect dispersivity will be subject to the testing conditions. A self-contented value of dispersivity is not possible to be achieved through the existing experimental methods. Hence, another objective is formulated which is to estimate dispersivity that contains the influence of all the factors that may possibly affect dispersion in soils. The method developed is to be able to bring all the factors that influence dispersivity into a single entity that help attain an absolute dispersivity of the soil.

Thus the main objectives of this thesis are to develop a complete philosophy of dispersion and estimate dispersivity incorporating the influence of all factors that affect dispersivity and to achieve an absolute dispersivity of soils.

CHAPTER 2

ANALYSIS OF FACTORS INFLUENCING DISPERSIVITY AND HYPOTHESIS FOR DISPERSIVITY OF SOILS

2.1 INTRODUCTION

Literature mainly attributes soil dispersivity to the presence of exchangeable sodium in the soil (eg- Bell and Maud 1994; Bell and Walker 2000; Bhuvaneshwari et al. 2007; Umesha et al. 2009). Further research on the topic led to the conclusion that several other factors such as soil pH, cation exchange capacity, structure of the soil, electrolyte concentration, clay minerals, presence of organic matter and dissolved salts also affect dispersivity. In addition, apart from the prevalent methods of measuring dispersivity, several geotechnical properties of soils could be used for determining the amount of dispersion present in the soil.

Generally, dispersive soils are known to have a high pH, high CEC, high amounts of sodium, and a dispersed structure (Bell and Maud 1994; Bell and Walker 2000; Ouhadi et al. 2007). Earlier literatures have mentioned these properties as just the properties that may have an effect on the dispersivity of the specific soil under study. The influence of these factors on the dispersivity of other soils (or generally in any soil) is not well explored. Research on the topic by understanding their mechanism of action led to the conclusion that these parameters could be generalized for any soil. Here an attempt is made to prepare a comprehensive list of factors affecting dispersivity in any soil.

2.2 CHEMICAL FACTORS INFLUENCING DISPERSIVITY

The factors or properties of soils that can affect the repulsion and attraction in soils and hence the dispersivity are listed as below.

2.2.1 Cation exchange capacity (CEC)/Exchangeable sodium

Cation exchange capacity is the maximum amount of cations a soil is capable of holding, at a given pH, available for exchange (Robertson et al. 1999). It is also a measure of the negative charge present per unit mass of a soil (Peverill et al. 1999). A soil with a high CEC will have more surface negative charge or negative sites and thus more positive ions will adsorb. If sodium ions are adsorbed onto the surface of the clay, water molecules get attracted to these sodium ions. The ions hydrate and force the clay plates to move apart. The binding force is overcome by the repulsive forces which cause the clay to swell and ultimately to get dispersed (Hardie 2009).

2.2.2 pH

At low pH, H^+ ions concentration increase, which gets adsorbed on to the edges of the clay particles (Hillel 1980). This causes flocculation in soils and thus a reduction in the repulsive force leading to lesser dispersivity.

2.2.3 Structure

Soil structure describes the spatial arrangement of the soil particles and the pore space located between them (Marshall et al. 1979). A sudden movement of a liquid at the surface of a clay produces swelling on particle surface that may reduce the bonding between the particles (Bell and Maud 1994). More dispersed the structure; more will be the swelling which may ultimately lead to dispersion.

2.2.4 Electrolyte concentration/ Dissolved salts in the pore fluid

The mechanism of dispersion is dependent on structure of soil and the character of interaction between the pore fluids (Bell and Maud 1994). At lower electrolyte concentrations, or when the amount of dissolved salts is low, repulsive forces overcome the attractive forces to cause swelling and then dispersion (Tan 2010). Thus, higher the electrolyte concentration, lower will be the dispersivity.

2.2.5 Organic matter

Organic matter in the soil usually exists as negatively charged ions due to the presence of carboxyl or phenolic groups. Complex organic acids adsorbed on clay surface increase the negative charge on clays. Similarly, organic anions form complexes with metal ions and increase the negative charge on clay surfaces favoring the dispersion of clay particles (Oades 1984).

2.2.6 Temperature

pH of a soil is dependent on temperature. Oven drying process of dispersive samples may change the soil structure and pH value permanently, which results in a change in dispersivity (Yong and Thomas 2004). Hence it is suggested that oven dried soil shall not be used in dispersivity measurements.

2.2.7 Clay minerals

The behavior of a soil is largely dependent on the type of clay minerals present. When it comes to dispersivity of the soil, the CEC and ESP (along with other properties like swelling characteristics, pH, cohesion etc.) of a soil is largely affected by the nature of clay minerals present. Generally in soils, if smectitic (montmorillonite or other 2:1) minerals are present in large quantities, dispersivity will be more (Bell and Maud 1994).

The above mentioned are factors that are reported in various literatures, defined to be affecting dispersivity of a particular soil under consideration. As stated earlier, no earlier works have considered these factors in a more generic way as affecting dispersivity of any soil. Even though the extent to which these properties affect may be minimal, they certainly do affect dispersivity in any soil. The fact that these are factors affecting dispersivity does not mean that this is an exhaustive list of the same and there may be other factors as well which may have a similar co-relation with dispersivity.

2.3 USE OF GEOTECHNICAL CHARACTERS FOR ASSESSING DISPERSIVITY OF SOILS

Apart from widely used methods for estimation of dispersivity through tests by double hydrometer, pin hole test, Emerson crumb test, shrinkage limit and unconfined compressive strength, several geotechnical characteristics of soil could serve as good indicators of the amount of dispersion in soils. It is known that the structure of the soil particles has a significant bearing on many geotechnical properties of soil which also controls the dispersivity of soils. These include swell tests, liquid limit, plastic limit, compaction characteristics, and permeability. The amount of dispersion in a soil could also be qualitatively determined from the comparison of several properties such as shrinkage limit with liquid limit, plastic limit with OMC, plastic limit with shrinkage etc. The applicability of these tests and the principle behind their usage is described below.

2.3.1 Swell indices

Swell indices which may be estimated through various methods such as free swell, modified free swell or differential free swell indicates the amount of expansion in the soil. The test could give an indication about the amount of repulsion in soils which can be used to

estimate the amount of possible dispersion in soils. Swell indices also serve as a measure of compressibility of the soil. Higher the expansion, higher will be the compressibility and more dispersed the soil will be.

2.3.2 Compaction characteristics

It is very well established that a soil with a dispersed structure will have a lower OMC (Optimum moisture content) and a higher MDD (Maximum dry density). When the dispersivity in a soil is high, the water holding capacity increases which increases the OMC and due to which dry density will be reduced. Thus compaction characteristics could be used for understanding the dispersivity of soils.

2.3.3 Stress – strain relationships

The stress-strain curve for a flocculated soil will show a well pronounced peak at its maximum strength while that of a dispersed soil will be comparatively flatter showing no distinct peak.

2.3.4 Shear strength

Flocculated soils generally have a higher strength than dispersed soils which is primarily due to the presence of higher interparticle attraction and higher difficulty in displacing the particles even when they are arranged disorderly.

2.3.5 Permeability

Permeability of the soil could also give an indication of the structure it possesses. A clay with a flocculated structure will have a higher permeability than the same soil with a dispersed structure. This is due to the availability of larger channels for fluid flow. The resistance to flow through a dispersed soil structure will be higher when compared to a flocculated structure.

2.3.6 Atterberg's limits

Atterberg's limits also could also be used as an indication for assessing the structure of the soil. Soils with higher liquid limit would have expansive minerals such as montmorillonite which would have higher water holding capacity. The repulsion between the particles would be large enough to absorb and hold water in the pores which ultimately may lead to dispersion when the repulsion overcomes the attraction. These soils undergo high shrinkage and thus their shrinkage limit would be lower.

2.3.7 Comparative studies

Apart from the usage of various singular properties of soils as detailed above, comparison of several properties could also serve as an indicator of dispersion. For example, a dispersed structure will be associated with a higher liquid limit and lower shrinkage limit. Similarly, a lower OMC and a lower plastic limit indicate a flocculated structure. In a similar way shrinkage limit and MDD values could be used for identifying the structure etc.

Apart from all the above properties and characteristics of soils, it is proposed to examine another property which can take into account most of these factors and can facilitate to estimate the dispersivity of soils.

2.4 USE OF ZETA POTENTIAL TO ESTIMATE DISPERSIVITY

When an electric field is applied, some cations which are held close with the negatively charged clay particle move along with the clay while others shear away in the opposite direction. The potential difference between the slipping plane (plane dividing the ions into those migrating with the clay and those shearing away) and the solution is called zeta potential (Oswal 1983). The net charge at the particle surface affects the distribution of ions in the surrounding region. This may lead to an increased concentration of counter ions

close to the surface. An electrical double layer is formed around each particle. A brief description about the evolution of various theoretical aspects surrounding the double layer and hence the zeta potential is given below.

2.4.1 Theoretical aspects of zeta potential

All solids carry a negative charge once they are suspended in a fluid or water which is due to the high dielectric constant of water. The soil with low dielectric constant carries an anionic surface charge and as water contains ions of dissolved salts, these get attracted towards the anionic charges on the solid surface and form an immovable layer. These positive charges from water neutralize the surface charges but since particle is always surrounded by water, the cationic charges in first layer cannot completely neutralize the anionic charges and residual anionic charges still remain and these attract further cationic charges from the surroundings. Hence a second layer develops around the particle, which is further away from the particle surface. This formation of two layers around the particle is known as Electric Double Layer.

According to the double layer theory, all surface charges suspended in a fluid are covered by a diffuse layer of ions, which has the same charge but of opposite sign with respect to that of the surface charge. The electric field applied also exerts a force on the ions of the diffuse double layer which has direction opposite to that acting on the surface charge. The latter is applied to the ions in the diffuse layer located at some distance from the particle surface and not directly to the particle but even then, a part of it is transferred to the particle through viscous stress. The particle surface is usually surrounded by a liquid layer which commonly exists as two parts; an inner region where the ions are strongly bound and an outer, diffuse, region where they are less firmly attached. Within the diffuse layer there is a

notional boundary inside which the ions and particles form a stable entity. When a particle moves (e.g. due to gravity), ions within the boundary move with it, but any ions beyond the boundary do not travel with the particle. This boundary is called the surface of hydrodynamic shear or slipping plane. The potential that exists at this boundary is known as the Zeta potential (See Figure 2.1).

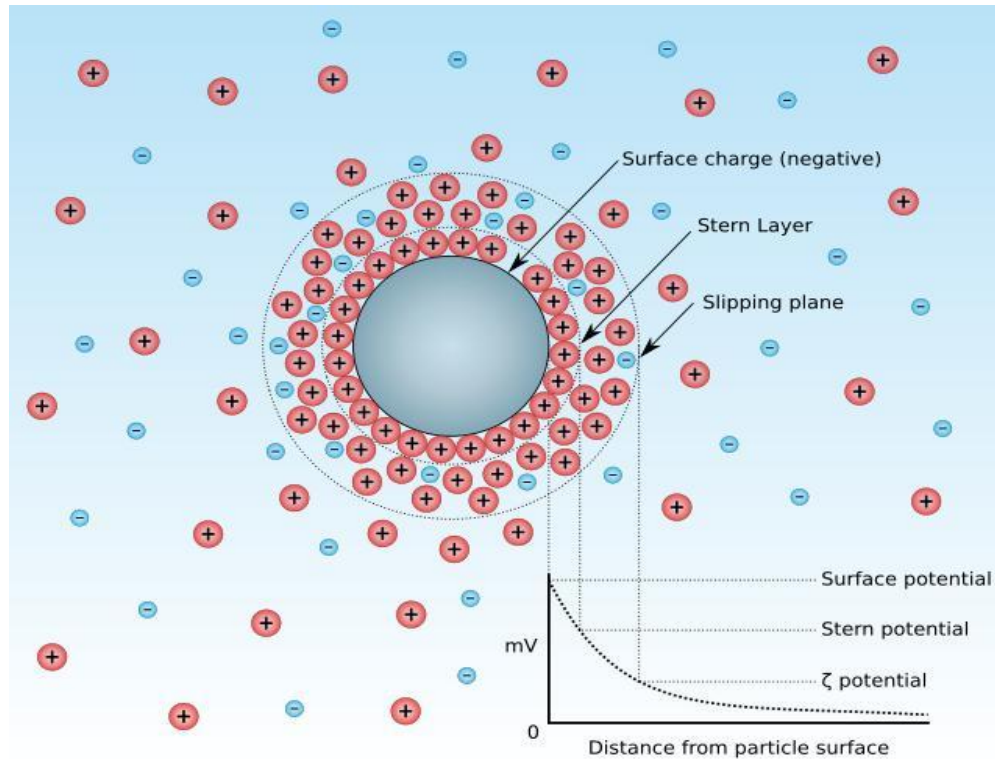


Figure 2.1 Zeta potential of soils (https://en.wikipedia.org/wiki/Zeta_potential)

Thus, it can be seen that there exists a very close relation between the electrical double layer and the zeta potential. The concept of electrical double layer has evolved highly over a period of time. A brief history of the various theories which conceived the various concepts surrounding the electrical/diffuse double layer are presented below.

2.4.1.1 *Parallel plate condenser theory: Helmholtz model*

This was the first type of model proposed for the structure of the double layer. Helmholtz considered the two layers of charge to be equivalent to a simple parallel plate condenser. Then, the potential difference across the plates was expressed as

$$\zeta = \frac{4\pi\epsilon d}{k} \dots\dots\dots(2.1)$$

Where,

ϵ = Charge density per unit area on one of the plates,

d = Separation of the two layers,

k = Dielectric constant of the water, and

ζ = Potential difference across the plates.

The condenser theory of Helmholtz failed to explain the observed electrical phenomena in a colloidal system. Then came the Guoy-Chapman diffused double layer theory.

2.4.1.2 *Diffused double layer theory: Guoy – Chapman model*

Gouy related the interfacial potential at the charged surface of a clay particle to the presence of a number of ions of given sign attached to the surface and to an equal number of opposite charge in a solid-liquid mixture. The counter ions try to diffuse into the liquid phase, until the counter potential set up restricts the diffusion. Gouy and Chapman proposed theoretical expression for electric potential in double layer by combining Boltzman equation and Poisson equation wherein, the Boltzman equation relates ion distribution to electric potential and Poisson equation relates electric potential and distance (Reddi and Inyang 2000). Gouy-Chapman theory gave that

$$\zeta^{-1} = \zeta e^{-pd} \dots\dots\dots(2.2)$$

Where,

ζ^{-1} is the potential at a distance d from the surface of potential ζ ,

p is a parameter of the system associated with concentration and valence of ions in the system, the dielectric constant and the temperature.

The model could be applied to the soils only if they had behaved like a true parallel particle system. The description of the potential immediately adjacent to the charged particle is not satisfactorily explained. This is mainly due to the mechanisms associated with chemical bonding and complexation. The ion-ion interaction which was becoming increasingly important at high concentrations was neglected completely.

2.4.1.3 Compact diffuse double layer model: Stern model

This model is a hybrid one combining the above two models. First, the ions were considered to have a finite size and were assumed to be located at a finite distance from the clay surface. Second, the charge distribution in the electrolyte was divided as

1. Charge immobilized close to the clay surface (Helmholtz model) and
2. Charge diffusely spread out in the solution (Guoy – Chapman model)

The total surface charge is counter balanced by Stern layer (inner region) charge and diffuse layer charge. The surface potential is expressed as a function of electrolyte concentration and surface charge (permanent and pH dependent). It decreases when the distance increases from surface of the clay to the outer boundary of the Stern layer. This model failed to take into account the role of the solvent as related to the hydration of the ions and its influence on the structure of the double layer.

2.4.1.4 DLVO theory

The DLVO theory named after Boris Derjaguin and Lev Landau, Evert Verwey and Theodoor Overbeek sums up all the forces between charged surfaces interacting in a liquid medium. It combines the effects of the Van der Waals attraction and the electrostatic repulsion due to the double layer of counterions. This is the most commonly used theory used for studying the stability of colloidal dispersions. Very few researches have been conducted which studies the applicability of DLVO theory for clay colloidal stability even which proved that the theory could not be applied for the prediction of clay colloidal stability (eg - Missana and Adell 2000). The primary drawbacks associated with the applicability were, inadequacy of the theory to accommodate pH dependent charge effects to the stability behavior of clay, discrepancies associated with approximating surface potential to the zeta potential and lack of explanation in the selection Hamkaer constants.

Even though the DLVO theory could not be used for assessing the stability of clay colloidal suspensions, it was found that when the factors affecting dispersivity are analyzed, the influences of these factors could be mapped into the various parameters which govern the zeta potential. The factors could be connected with zeta potential in one way or the other. Cation exchange capacity, pH, organic acids and temperature affects the charge density of clays, while presence of sodium ions, soil structure and electrolyte concentration affects the double layer thickness and thus, the zeta potentials. There can be other relations between the parameters as well. For example, electrolyte concentration can affect the di-electric constant, structure of the soil influences charge density, type of clay minerals present in the soil affects the charge density and double layer

thickness etc. To summarize, all the factors which are found to have an influence on dispersivity could be related with zeta potential of the soil.

Similarly, the above mentioned indicative geotechnical characteristics of soil such as shrinkage, strength or permeability can also be graphed into zeta potential in perspective of dispersivity. The fundamental concept behind the usage of such properties for the identification of the amount of dispersion in soils is that these properties extensively depend on the charge of clays. As zeta potential serves as the ideal method for identifying the surface characteristics of clays, properties such as liquid limit, OMC, strength and permeability could even be expressed as some function of the zeta potential.

2.4.2 Estimation of zeta potential

As the measurement of zeta potential forms a very important part in this thesis, the various theories related to the measurement of zeta potential also need to be addressed. Zeta potential is usually estimated from the electrokinetic properties of the soil. The measurement is based on the principles of electrophoresis wherein electrophoresis is the measurement of the movement of colloidal particles when they are placed in an electric field. When an electric field is applied across an electrolyte, charged particles suspended in the electrolyte are attracted towards the electrode of opposite charge. Viscous forces acting on the particles tend to oppose this movement. When equilibrium is reached between these two opposing forces, the particles move with constant velocity. The velocity of a particle in an electric field is commonly referred to as its Electrophoretic mobility. Zeta potential is calculated by estimating the electrophoretic mobility of the suspended clay colloids.

Numerous theories exist which explains the relationship between zeta potential and electrophoretic mobility. The relation between zeta potential (ζ) and electrophoretic mobility μ_E in general can be expressed as

$$\mu_E = \frac{k\zeta}{f\pi\eta} \text{ (Kissa 1999).....(2.3)}$$

Where,

μ_E is the electrophoretic mobility defined as $\mu_E = v/E$ wherein v is the velocity of a dispersed particle and E is the applied electric field,

k is the dielectric constant of the dispersion medium,

f is the shape factor varying from 4 to 6 and,

η is the solvent viscosity.

Various models have been proposed by various scientists who suggested various values for the shape factor according to the various assumptions made by them. The models along with their assumptions are discussed below.

2.4.2.1 Smoluchowski's model

This model was one of the first models developed. It is the most known and widely used theory for calculating zeta potential of dispersed systems containing spherical particles developed by Marian Smoluchowski in 1903. This model is primarily based upon the Helmholtz parallel plate condenser theory for the electric double layer. Smoluchowski assumed a shape factor of 4 and expressed the relation as,

$$\mu_E = \frac{k\zeta}{4\pi\eta} \text{(2.4)}$$

Smoluchowski assumed that the extent of the diffused double layer expressed as κ^{-1} is small relative to the particle radius (r) i.e. κr is large. The particle was assumed to be non conductive and the surface conductivity is sufficiently low to not disturb the external electric field (E). Due to these limitations or drawbacks the theory could be applied for only thin double layers thus came the need for a revised theory.

2.4.2.2 *Huckel's model*

In his model it was assumed that the particle doesn't disturb the electric field and the double layer, i.e. the particle size (r) is very small when compared to thickness of double layer (κ^{-1}). In mathematical terms, $r < \kappa^{-1}$ and κr is small. The external field acts on the charge of particle and causes particles to migrate. However, the electric field forces counter ions to migrate in the opposite direction resulting in a liquid flow opposite to that of the particle. Hence, the particle doesn't migrate in stationary liquid but in a liquid flow opposing and retarding the movement of particle. Thus, Huckel included frictional force and resulted in value of 6 for the shape factor f.

The Huckel's equation for zeta potential measurement is given as

$$\mu_E = \frac{k\zeta}{6\pi\eta} \dots\dots\dots(2.5)$$

The application of Huckel's theory was also limited to spherical particles.

2.4.2.3 *Henry's model*

It was Henry who took into consideration the deformation of electric field (E) by the particle and the retardation caused by the movement of counter ions in the opposite direction.

The Henry equation relating electrophoretic mobility and zeta potential is

$$\mu_E = \frac{k\zeta}{6\pi\eta} [1 + \lambda f(\kappa r)] \dots\dots\dots(2.6)$$

Where,

$$\lambda = \frac{\sigma_0 - \sigma}{2\sigma_0 - \sigma} \dots\dots\dots(2.7)$$

σ_0 is the electrical conductivity of the dispersion medium and

σ is the electrical conductivity of the particle.

$f(\kappa r)$ is Henry's function and it is depended on particle shape. The conductivity of particle can be neglected, as the particle becomes polarized in applied electric field and prevents any further charge transport and thus behaves as if it is non-conducting. With this approximation λ assumes value of 0.5 and thus,

$$\mu_E = \frac{k\zeta}{6\pi\eta} [1 + 0.5 f(\kappa r)] \dots\dots\dots(2.8)$$

Later it was observed that in the limit of a thick double layer (i.e. $\kappa r \ll 1$), $f(\kappa r)$ approaches unity and the Huckel equation is obtained. In the limit of a thin double layer, (i.e. $\kappa r \gg 1$), $f(\kappa r)$ tends to 1.5 and the Smoluchowski equation is obtained.

Thus it can be seen that, there are several theories present which are used for measuring zeta potential of soils. Even though all the theories estimate zeta potential from electrophoretic mobility values of soils, the relation between them is different in different theories. Henry's equation is the most commonly used theoretical procedure adopted for accurate assessment of the zeta potential of soils but the accuracy of the measurement depends largely on the characteristics of the soil water suspension. In order to study the relationship between the properties and to validate the proposed relation experimental investigations are carried out on soil samples. The materials used and the methodology adopted are discussed in the subsequent sections.

CHAPTER 3

MATERIALS AND METHODS

3.1 INTRODUCTION

The choices of soils, reasons for selecting the soils, and tests to be conducted to achieve the objectives of the study are explained in this chapter.

3.2 SOILS USED

Three different soils namely Suddha soil (as called by the locals, obtained from Tumkuru Karnataka, India), Red soil (local soil from Bangalore) and Black Cotton soil (from Belgaum, Karnataka, India) were chosen to propose a hypothesis and bring out the role of various factors controlling the dispersivity. The various reasons for identifying these soils are summarized here.

Many hydraulic structures such as earth dams and roadway embankments in the areas of Southern Karnataka have undergone serious problems of erosion due to the presence of this dispersive soil called “Suddha soil”. It is wide spread below a depth of 1.5 m from the ground level. Several failures in canal slopes, road bases, and foundation have occurred at stretches where Suddha soil is present. Ramesh (2012) has reported Suddha soil to be dispersive. This soil was selected as one of the soils for studying the dispersion characteristics. This soil is relatively low plastic in nature.

Black Cotton soil, found most commonly in central and western parts of India was another soil picked for the study. This soil is an expansive soil with very high plasticity. Further the behavior of soil is known to be influenced by physico-chemical characteristics of the pore fluid as it contains predominantly montmorillonite clay mineral. These soils are

residually derived from gneiss, volcanic ash, lime stones, calcareous alluvium and sedimentary rocks, slates and sand stones (Humad 1987). The soil used for the present study is obtained from Belgaum district of Karnataka state in India. The soil was collected from a depth of around 1-1.5m below ground by open excavation. Black Cotton soil was chosen as one of the soils so as to study the relation between expansion and dispersion.

The third soil used was Red soil which represents a group of soil formed by the weathering of the ancient crystalline and metamorphic rocks. They contain high amounts of iron oxide which gives them red/pink color. The soil is commonly found in regions of Tamil Nadu, Madhya Pradesh, Jharkhand, Karnataka and Maharashtra. Locally available Red soil collected from the campus of Indian Institute of Science was used for this study. This soil contains silt sized particles and the primary clay mineral is kaolinite. It is well known that the behavior of kaolinite is markedly different from montmorillonitic clay. The behavior of this type of clay is more controlled by shearing resistance at particle level rather than double layer thickness as it is also low in its plasticity.

The three soils selected are different in their plasticity, expansion characteristics, particle sizes and mineralogy. They have wide ranges of geotechnical properties and can form varying ranges of dispersivity.

The experimental program mentioned above is drawn to study the physico-chemical and geotechnical properties of soil. Details of experimental program are presented in relevant sections. The details of experimental set up, basic properties of the soils, the method of preparation of the specimens for conducting various tests pertaining to dispersivity, testing procedure are all elaborated in the subsequent sections.

3.3 BASIC CHARACTERIZATION

Basic characterization of the material very crucial as it serves as a measure of the fundamental soil behavior. The procedure involved finding index properties of soil such as specific gravity, consistency limits and particle size distribution. The tests done along with the procedure adopted are described below.

3.3.1 Specific gravity

Specific gravity of all the soils was determined as per the ASTM Code ASTM D854-14, Method B on oven dried samples. An average of three test values nearest to the 0.01 is reported as the specific gravity of soil solids.

3.3.2 Atterberg's limits

Atterberg's limits (liquid limit, plastic limit and shrinkage limit) for the soils were also determined. The liquid limit (cone penetration method) and plastic limit was determined as per IS 2720 (Part 5) (1985). Mercury method was used for measuring shrinkage limit (S.L) and the procedure as per ASTM D427-04 was followed. An average of three values rounded to the nearest integer is reported as the test result.

3.3.3 Particle size analysis

Particle size distribution of the soils was done so as to determine the amount of sand (4.75 – 0.075mm) content, silt (0.075-0.002mm) content and clay (<0.002mm) content. Single set sieving according to ASTM D6913-09 was adopted for particle size in between 4.75 – 0.075mm and hydrometer analysis for lesser sized fractions.

The results of these tests are summarized in Table 3.1.

Table 3.1 Index properties of soils

SI No	Index properties	Suddha soil	Black Cotton soil	Red soil
1	Specific Gravity	2.53	2.67	2.71
2	Liquid Limit (%)	60	72	36
3	Plastic Limit (%)	34	32	22
4	Shrinkage Limit (%)	23	14	20
5	Soil classification	MH	CH	CI
6	Sand (%)	30	6	46
7	Silt (%)	42	31	30
8	Clay (%)	28	63	24

3.3.4 XRD studies

X-ray diffraction is a powerful tool used for mineralogical analysis as mineralogy plays a vital role in the soil behavior. X-ray Diffraction (XRD) studies were done on powdered soil samples using “XRD BRUKER D8 Advance” (instrument) on soil passing 75 μ in the air dried state. XRD is carried out with CuK α radiation with a wavelength of 1.54Å at 1°/minute speed for Bragg’s angle range of 5 to 80°. Philips X`pert Highscore plus software was used to analyze the data obtained from the diffractometer by plotting the intensities against the 2 θ values. Analysis of the data and identification of the minerals by identifying the peaks was done by comparing the data sets of known minerals from the ICDD patterns. The diffraction patterns are as shown in Figures 3.1 to 3.3.

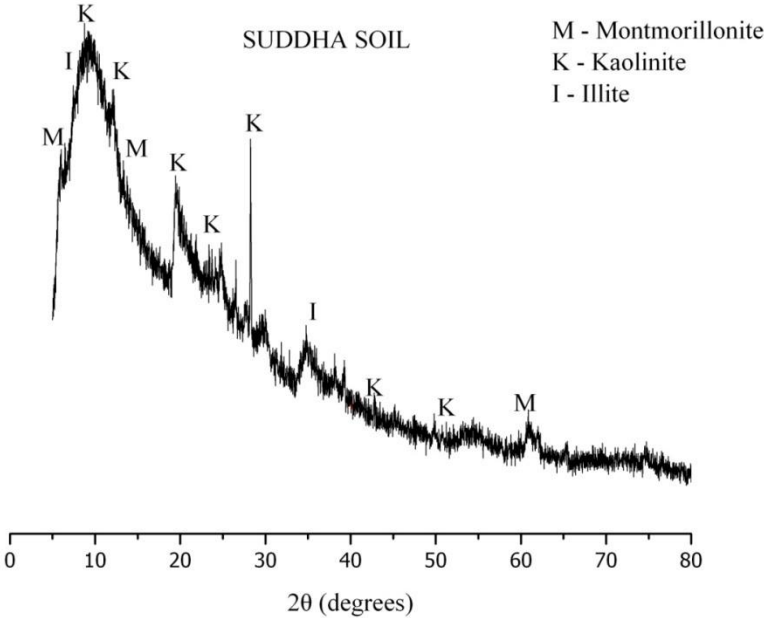


Figure 3.1 XRD pattern of Suddha soil

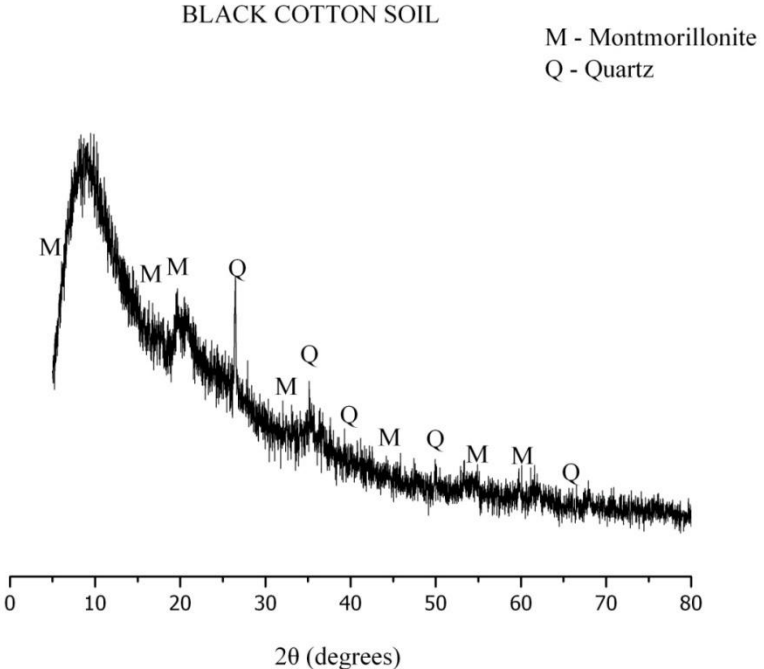


Figure 3.2 XRD pattern of Black Cotton soil

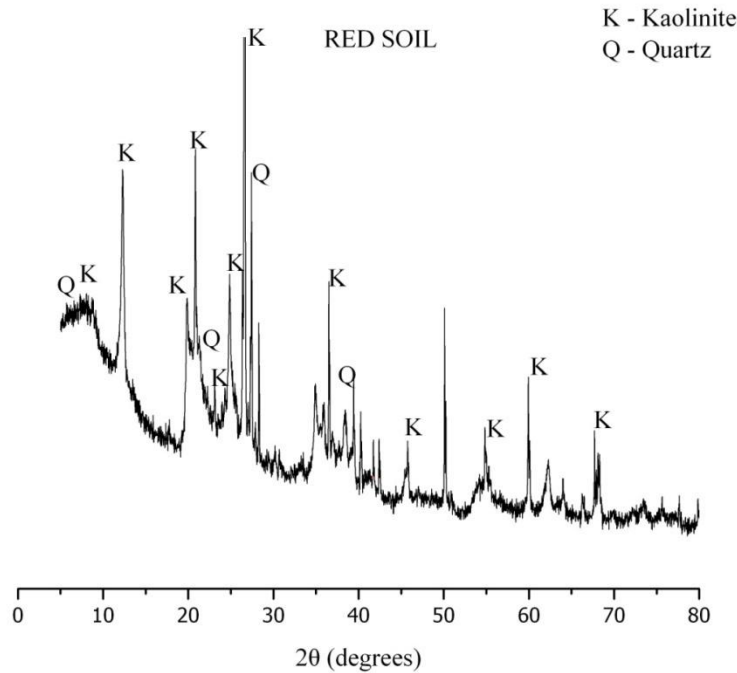


Figure 3.3 XRD pattern of Red soil

3.4 TESTS FOR THE DETERMINATION OF DISPERSIVE CHARACTERISTICS

Apart from the index properties, experiments indicative of the dispersive behavior of soils were also conducted on the samples. Soil finer than 75μ was selected as the sample size as the dispersive characteristics of finer fractions are more important and experiments such as swell tests, compaction behavior, strength tests, dispersivity measurements, pH tests and cation exchange capacity estimation were carried out.

3.4.1 Swell tests

Modified free swell test as per Sridharan and Prakash (2000) were conducted on soil specimens in order to characterize the swell behavior. Sridharan and Prakash (2000) defined modified free swell index (MFSI) as the ratio of equilibrium sediment volume (V_d) after 10 g

of oven dried soil is mixed with water to form a soil suspension of initial volume 100 ml in a 100ml measuring jar and allowed to settle, to the dry weight of the soil. Thus,

$$MFSI = \frac{V_d}{10} \dots\dots\dots(3.1)$$

3.4.2 pH measurements

pH serves as a measure to quantify the amount of alkalinity or acidity in a soil. The pH range normally found in soils varies from 3 to 9. The experiments were done on the soils as per ASTM D4972-13 using pH Meter. An average of three test values nearest to the 0.1 is reported as the pH of soils.

3.4.3 Compaction characteristics

The compaction behavior widely controls the engineering behavior of soils. The standard proctor test and modified proctor test are the conventionally used tests for establishing the dry density water content relationship for a soil under controlled conditions. Large quantities of soil (about 12 to 15 kg) are required for doing these tests. In addition, the tests involve lot of effort and time. In order to overcome these problems a mini compaction apparatus proposed by Sridharan and Sivapullaiah (2005) has been used. The method demands only 1/10th of the amount of material required for the standard proctor test thus reducing the time and effort. The average of the three measurements was recorded as the water content values from which OMC and MDD were reported.

3.4.4 Unconfined compression tests

Unconfined compressive strength (UCS) tests were done on all the soils passing 75 μ at their respective optimum moisture contents. The sample height was fixed as 76mm and diameter as 38mm. The tests were done as per ASTM D2166M-13 under a constant strain

rate of 1.2 mm/minute. The experiments were done on three samples for each soil and the average values corresponding to the peak stress were reported as the UCS value unless the peak stress varied by more than 10%.

3.4.5 Measurement of organic matter

Organic matter as mentioned earlier can affect the charges on the clay and hence the dispersivity. Thus the amount of organic matter needs to be quantified. The amounts of organic matter in the soils were determined as per ASTM D2974 – 14.

3.4.6 Cation exchange capacity (CEC) measurements

Clay minerals in fine grained soils possess a negative charge which is balanced by the bound cations near the surface of the clays. The bound cations usually exchange with the cations in the pore water. The CEC value could be used as an indicative measure for the identification of the clay minerals involved. Higher CEC is reported for 2:1 minerals such as the montmorillonite group while lower value indicates the presence of non expansive minerals such as kaolinite and illite. The CEC is measured for the soils using the ammonium acetate method. 5 g of oven dried sample was taken which is added to 100 ml of 1 N ammonium acetate solution (pH =7). The mixture was agitated for 24 hrs by keeping it in a mechanical shaker. The mixer was then centrifuged for 20 min at 14000 rpm. The supernatant was filtered and the pH was adjusted to 2 by adding 10% dilute nitric acid. The concentrations of the different adsorbed monovalent cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) in the filtrate were recorded using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) iCAP 6000 series.

In the ammonium acetate method, a common practice involves washing the soil with water first, drying it and then mixing the soil with 1 N Ammonium acetate solution. Washing

a soil with solvents like acetone or water results in the removal of soluble or free ions from the pore water and, further addition of ammonium acetate results in an exchange of the ammonium cations for the exchangeable cations present in the soil. In the current study the washing process is omitted as ions present in the pore water also contribute to the dispersive behavior of soil. Measurements were done on three samples for each soil and the average values of the three measurements were reported as the ion concentration. The sodium concentration in each soil was also found out from the experiments.

3.4.7 Dispersivity measurement through Emerson crumb test

A crumb of soil (about 1 cm in diameter) at natural water content was immersed in a beaker of distilled water (250 ml) and subsequent reaction was observed for ten minutes. The degree of dispersivity was assessed by the interpretation guide by Sherard et al. (1976).

3.4.8 Dispersivity measurement through double hydrometer (D.H) test

The Soil Conservation Service laboratory dispersion test, also known as the double hydrometer test is one of the first methods developed to assess dispersion of soils. The particle size distribution is initially determined by the standard hydrometer test in which the soil is dispersed in water with a chemical dispersant. A parallel hydrometer test is then made on a duplicate soil specimen, but without the application of the dispersing agent (D.A). The test was carried out according to ASTM D4221.

3.4.9 Dispersivity measurement through unconfined compressive strength and shrinkage limit

Dispersivity of the soils was also measured with UCS test and from shrinkage limit as per Umesh et al. (2011). Unconfined compressive strength test and shrinkage limit tests were determined as per the relevant codes. In addition, the tests were done on the same soil

samples after the addition of 10% dispersing agent (sodium hexametaphosphate). The chemical and the dosage were fixed as above so as to compare the dispersivity values obtained from UCS test and shrinkage limit with double hydrometer results.

3.5 ZETA POTENTIAL MEASUREMENT

As brought out an attempt is being made to explore the use of zeta potential of the soil as one of the major factors in understanding the dispersivity of soils. It is to be specified that, different researchers use different measurement procedures for estimating the zeta potential. As the accurate determination of zeta potential forms a major step in this thesis, the measurement procedure was standardized, the details of which are explained in **Chapter 6**.

Zeta potential was measured using Zetasizer nano series – Zen 3690 (Malvern Instruments). In order to get the zeta potential of clay particles and to make the mixture more or less homogeneous, the soil water mixture (1:25) was filtered through 0.45 μ filter paper (Millipore - Durapore HVLP 0.45 μ m) and the measurements were done on an aliquot of the filtrate. The average of three measurements was taken to represent the measured potential.

Atterberg's limits and specific gravity were estimated on these soil fractions also as per the codes mentioned earlier. In order to quantify dispersivity through shrinkage limit and unconfined compression tests, the tests were repeated on soil samples by adding 10% dispersing agent (Sodium hexametaphosphate) by weight. The results of the tests conducted are as reported in Table 3.2.

Table 3.2 Dispersive behavior of soils

SI No	Properties	Suddha soil	Black Cotton soil	Red soil
1	Specific Gravity	2.53	2.67	2.71
2	Liquid Limit (%)	69	74	30
3	Plastic Limit (%)	34	32	29
4	Shrinkage Limit (%)	22	12	28
5	Shrinkage limit with 10% D.A	18	10	20
6	MFSI	2.0	2.1	1.1
7	pH	6.3	5.7	7.0
8	Organic matter (%)	4.46	9.68	4.57
9	OMC (%)	28	32	13
10	MDD (kg/m ³)	1420	1365	1913
11	UCS (kPa)	256	285	258
12	UCS with 10% D.A	109	213	201
13	CEC (cmol/kg)	51.09	59.73	20.12
14	Sodium concentration (%)	1.68	0.43	0.40
15	Zeta potential (mV)	-7.11	-4.83	-3.50
16	Dispersivity			
	Emerson test	Grade 3	Grade 1	Grade 1
	S.L	18	17	29
	UCS	57	25	22
	D.H	21	14	9

3.6 SUMMARY OF THE TESTS RESULTS AND INFERENCES

From the results it can be seen that, Suddha soil is a silty soil as indicated from the particle size distribution and Atterberg's limits. Kaolinite, Montmorillonite and Illite are the predominant minerals in the soil; the swelling index is comparatively high which may be due to the predominance of montmorillonite mineral. The soil is slightly tending towards an acidic behavior and the amount of organic content is comparatively lesser. The soil shows reasonably a good amount of strength and the CEC of the soil is reasonably higher owing to the presence of montmorillonite mineral. The sodium concentration is also higher which may be the reason for the higher dispersivity compared to other soils.

Black Cotton soil on the other hand is more clayey, montmorillonite being the predominant mineral. The swelling index is the highest showing high expansion due to 2:1 minerals being present. The soil pH is more towards an acidic nature and the soil has higher amounts of organic matter. The CEC of the soil is also high but as the amount of sodium concentration is lower the soil shows less dispersion.

In the case of Red soil, it can be noted that the specific gravity of the soil is high which may be due to the presence of higher amounts of heavy metals such as iron oxide. The predominant minerals are kaolinite and quartz which are non expansive as reflected in the swelling index value. The soil pH is 7 which make it a neutral soil. The cation exchange capacity and the amount of sodium content is very less which makes it the least dispersive.

The basic characteristics and the properties relevant to the dispersive behavior of soils have been studied. It can be concluded that Suddha soil could be used to represent a class of dispersive soils while Black Cotton soil and Red soil a non dispersive category. The soil samples selected for testing is able to provide wide ranges of dispersivity and could serve as

good soil samples for the study. The study regarding the role of zeta potential in the dispersive behavior in any soil is dealt in the next chapter.

CHAPTER 4

ROLE OF ZETA POTENTIAL

4.1 INTRODUCTION

In **Chapter 2**, it was concluded that all the factors which are found to have an influence on dispersivity could be connected to the zeta potential of the soil and, all the indicative properties related to the dispersivity of soil could be expressed as some function of zeta potential. Earlier studies so far have not considered the individual factor mapping and the approach taken in this study takes a fresh look at how zeta potential and dispersivity are related. In order to study the relation of zeta potential with various parameters affecting dispersivity experiments were conducted on Suddha soil, Black Cotton soil and Red soil. The determination of the role of various factors in controlling the dispersivity of soils is conducted in their natural state and after enhancing their dispersivity. Methods for enhancement of dispersivity of soil include enhancing the clay content of soil, treating the soil with alkali solutions, increasing organic matter of soil or addition of known concentrations of monovalent cations to the soil. Addition of dispersing agent such as sodium hexametaphosphate to determine dispersivity of soil by hydrometer method is in vogue. However, its use in determining the dispersivity with other common laboratory tests has not been much popularized. Thus hydrometer method as well as other methods with the application of dispersing agent (sodium hexametaphosphate) for the identification of factors controlling the dispersivity of soils by the enhancement of dispersivity is being attempted. The methodologies and the experimental procedures adopted for the study are discussed below.

4.2 EXPERIMENTAL INVESTIGATION

Soil samples (Suddha soil, Black Cotton soil and Red soil) finer than $75\ \mu$ was selected. The soil samples were treated with 0.5 M and 1 M urea solution and sodium hydroxide solution by maintaining a solid liquid ratio of 1:2.5. The samples were treated with urea solution in order to understand the influence of organic matter on dispersivity and the treatment with sodium hydroxide was carried out so as to study the effect of exchangeable ions on dispersivity. Sodium hydroxide was chosen as the chemical as hydroxyl ions present can alter the pH and increase dispersivity. The samples were subjected to air drying for two weeks and a part of the samples were taken for oven drying after which dispersivity and factors affecting dispersivity were measured with appropriate tests. The dispersivity was assessed through double hydrometer, shrinkage limit and UCS test by adopting 10% dispersing agent (sodium hexametaphosphate) by weight. The measurements were taken on air dried and oven dried samples to study the influence of oven drying on dispersivity. As it is proposed that zeta potential of soil may have a profound influence on the dispersivity, the role of various factors that influence the dispersivity and the sensitivity of zeta potential to monitor the influence of them are examined.

4.3 RESULTS

The influence of various parameters on dispersivity and zeta potential are discussed in the following sections.

4.3.1 Influence of sodium/monovalent ions

The total ion concentration and the corresponding sodium percentages of the untreated and sodium hydroxide treated soils along with the dispersivity values measured using double hydrometer experiment are as given in Table 4.1.

Table 4.1 Zeta potentials and dispersivity values of sodium hydroxide treated soils

Properties	Sodium hydroxide treated soils								
	Suddha soil			Black cotton soil			Red soil		
	0M	0.5M	1M	0M	0.5M	1M	0M	0.5M	1M
Total ion concentration (cmol/kg)	51.09	92.68	136.00	59.73	165.34	253.81	20.12	97.76	171.22
Sodium concentration (%)	1.7	34.3	66.9	0.4	43.6	82.6	0.4	44.4	90.3
Zeta potential (mV)	-7.11	-16.98	-19.05	-4.83	12.05	-17.98	-3.50	-15.89	-20.85
D.H dispersivity	21	35	52	14	29	42	9	52	60
S.L dispersivity	18	19	19	17	25	30	29	6	-20
UCS dispersivity	57	58	60	25	35	42	22	3	-17

It can be seen from Table 4.1 the sodium concentration increases due to the treatment and the dispersivity increases when the sodium concentration increases. Figure 4.1 shows the variation of sodium concentration with dispersivity measured through double hydrometer.

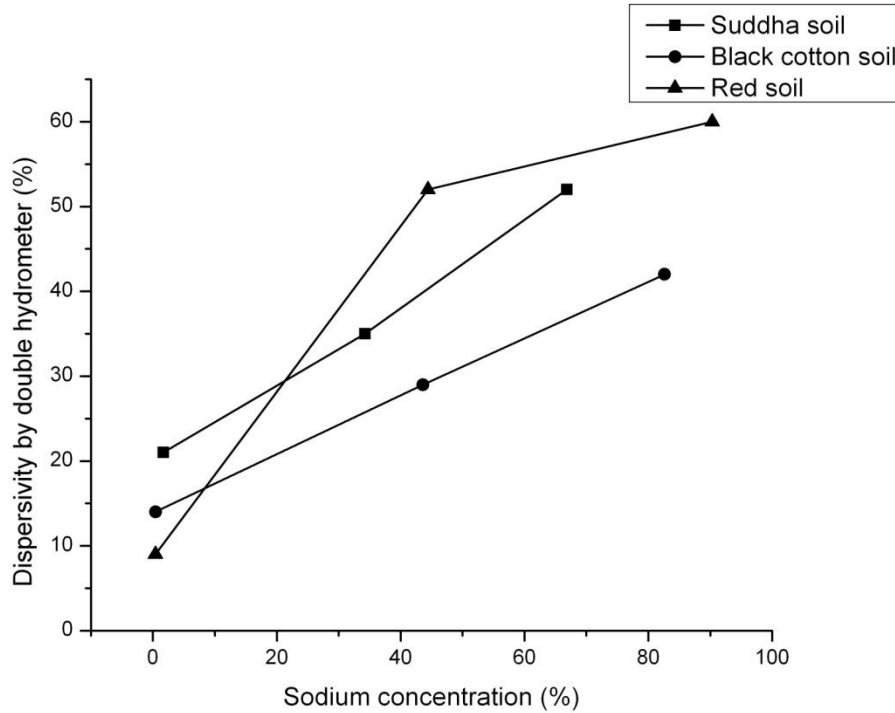


Figure 4.1 Dispersivity vs sodium concentration

It can be seen from the graph that as sodium concentration in the soil, be it in an exchangeable site or in dissolved state, is increasing the dispersivity of soils. This is due to the higher repulsion offered by the sodium ions due to hydration. When the concentration of sodium ion increases more repulsive force is produced due to hydration and hence the dispersion. Similar observation could be made through plotting graphs with dispersivity measured through shrinkage limit and unconfined compressive strength.

Another observation that could be made is the negative values of dispersivity obtained from shrinkage limit and unconfined compressive strength tests. This can be attributed to the negative influence of the dispersing agent. When soils are treated with sodium hydroxide they become highly dispersive such that the addition of a dispersing agent is causing a flocculation hence making the dispersivity value negative. Figure 4.2 shows the variation of zeta potential with the sodium ion concentration.

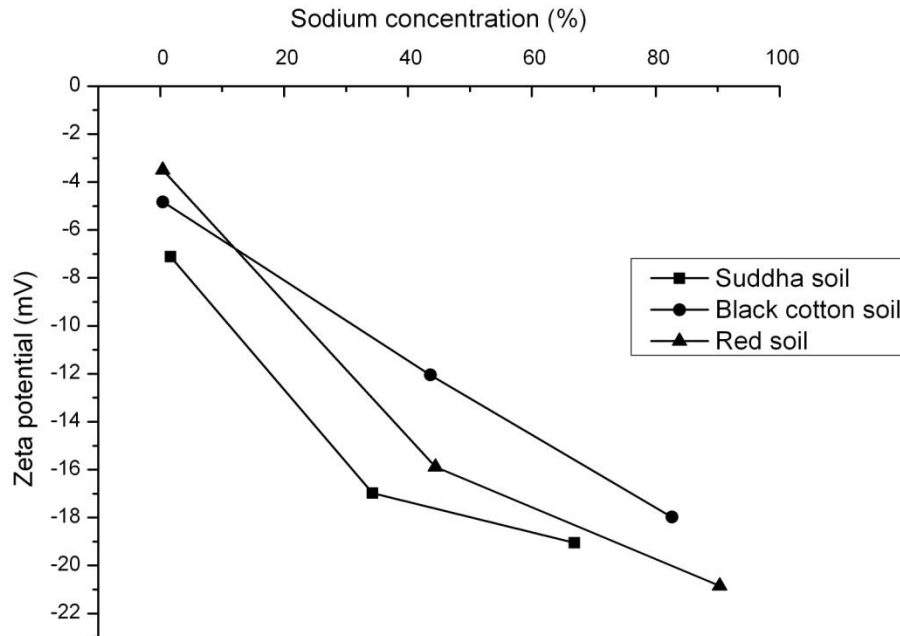


Figure 4.2 Zeta potential vs sodium concentration

From Figure 4.2 it is clearly visible that soils with higher amount of sodium are associated with higher zeta potential values. Ions in solution have a larger effective radius than in a crystal because of the water hull present around the ion. Sodium is a monovalent cation which has a small ionic radius. As smaller ions attract larger number of water molecules, the hydrated sodium cations in the outer layer increase the distance of the double layer or the separation between the plates and cause high zeta potentials. From Figure 4.2 it can be inferred that the increase in dispersivity due to higher sodium concentration is well reflected in the values of zeta potential also. Therefore, increase in sodium concentration causes increase in zeta potential or the presence of monovalent ions in the soil could be related to zeta potential of the soil in view of dispersivity.

4.3.2 Effect of organic matter

As mentioned earlier, organic matter present in the soil increase the repulsion between the particles and causes dispersivity. The amount of organic matter present in the three soils in the untreated state, urea treated state (0.5 M and 1 M treated) along with the corresponding dispersivity values and zeta potentials are as shown in Table 4.2. The plot between dispersivity and organic matter is as shown in Figure 4.3.

Table 4.2 Zeta potentials and dispersivity values of urea treated soils

Properties	Urea treated soils								
	Suddha soil			Black cotton soil			Red soil		
	0M	0.5M	1M	0M	0.5M	1M	0M	0.5M	1M
Organic matter (%)	4.5	5.2	5.9	9.7	13.5	16.5	4.6	5.7	6.8
Zeta potential (mV)	-7.11	-11.64	-16.13	-4.83	-7.23	-9.63	-3.50	-8.00	-12.60
D.H dispersivity	21	25	27	14	18	24	9	28	44
S.L dispersivity	18	18	18	17	19	22	29	10	-4
UCS dispersivity	57	57	58	25	27	32	22	7	-5

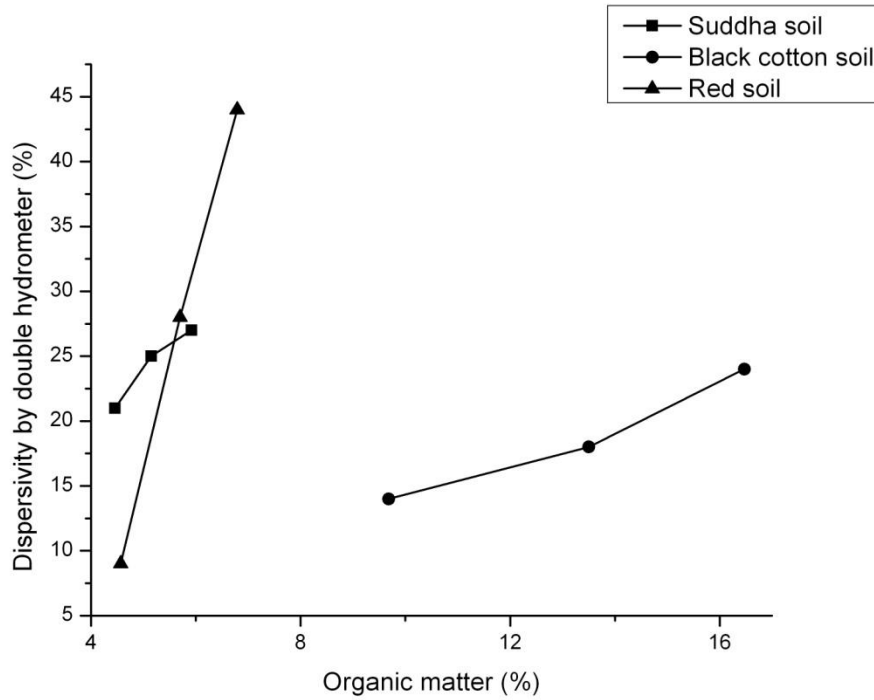


Figure 4.3 Dispersivity vs organic matter

With urea treatment of soils, the amount of organic matter increases as visible from the organic matter data. The presence of organic matter also affects the dispersivity value even though the effect may be minimal. Thus, it can be confirmed that presence of organic matter is also a factor that contributes to dispersivity. Figure 4.4 shows the variation of zeta potential with organic matter.

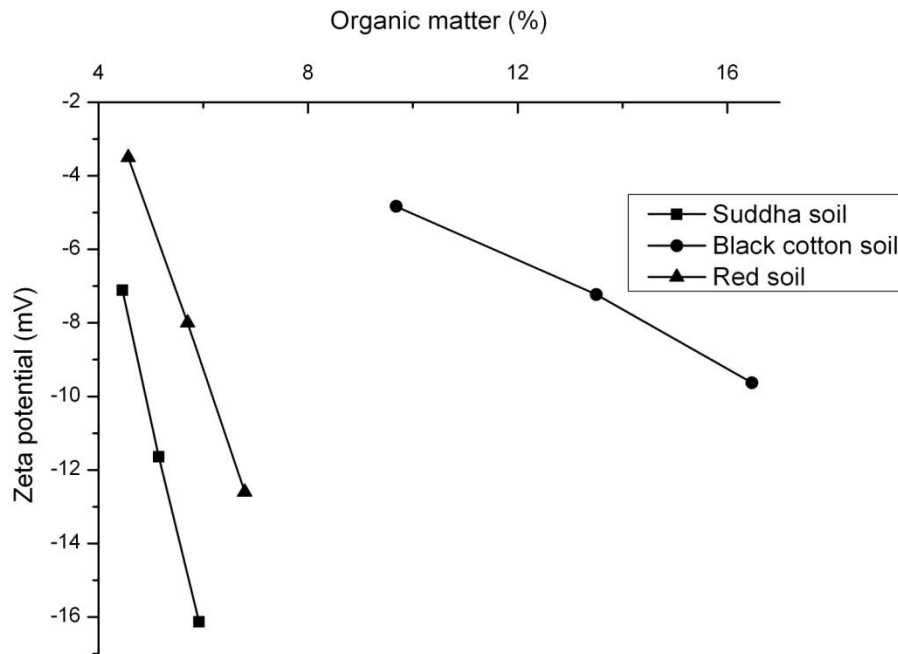


Figure 4.4 Zeta potential vs organic matter

When the concentration of organic matter in the soil increases, the charge density per unit area of a clay plate increases causing an increase in the zeta potential. Changes in dispersivity due to increase in organic matter is well reflected in the values of zeta potential also.

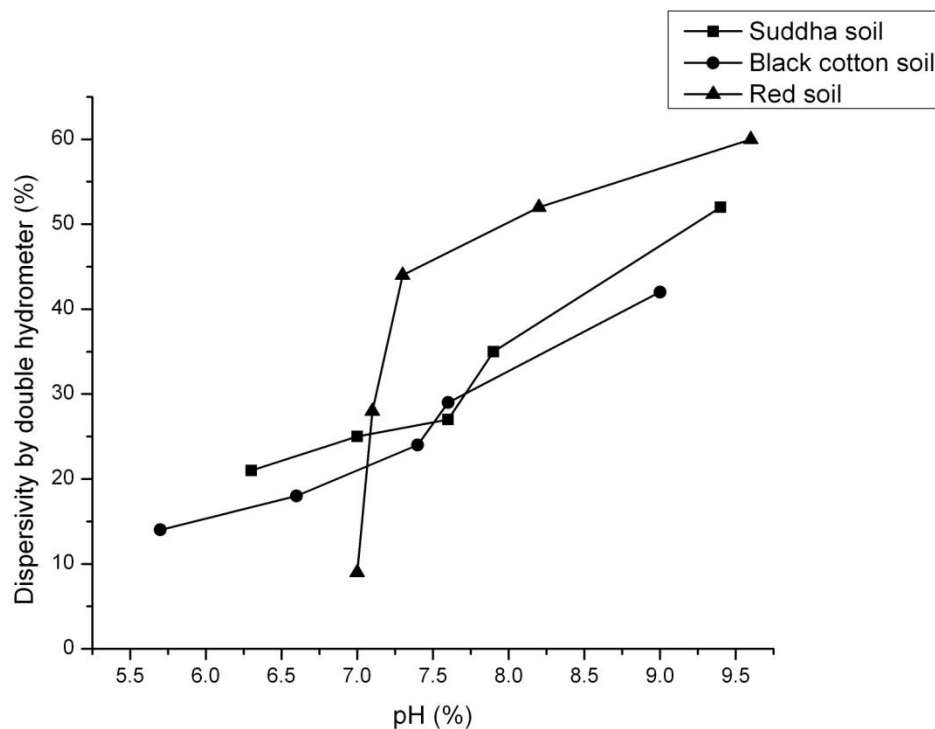
4.3.3 Role of pH

As mentioned in **Chapter 2**, presence of H^+ ions or OH^- ions affect the dispersivity of soils. To understand the effect of pH, the pH values of the three soils subjected to the various treatments were noted. The observations are as summarized in Table 4.3.

Table 4.3 pH values of sodium hydroxide treated and urea treated soils

Properties	pH values								
	Suddha soil			Black Cotton soil			Red soil		
	0M	0.5M	1M	0M	0.5M	1M	0M	0.5M	1M
Sodium	6.3	7.9	9.4	5.7	7.6	9.0	7.0	8.2	9.6
Urea treatment	6.3	7.0	7.6	5.7	6.6	7.4	7.0	7.1	7.3

The variation of dispersivity with pH is as shown in Figure 4.5. As changes in the pH is a resultant of the various treatments, pH values of both urea treated soils and sodium treated soils are used for plotting the graph. This enables to identify the contribution of pH towards dispersivity irrespective of the treatments done.

**Figure 4.5** Dispersivity vs pH for all treatments

It can be clearly observed that, soils with high pH correspond to high dispersivity values measured as per double hydrometer. Whenever the pH of the soil is increased due to any reason, the dispersivity is also increased or in other words increase in pH causes increase in dispersivity irrespective of the soil type. The variation of zeta potential with the pH of the soil is as shown in Figure 4.6.

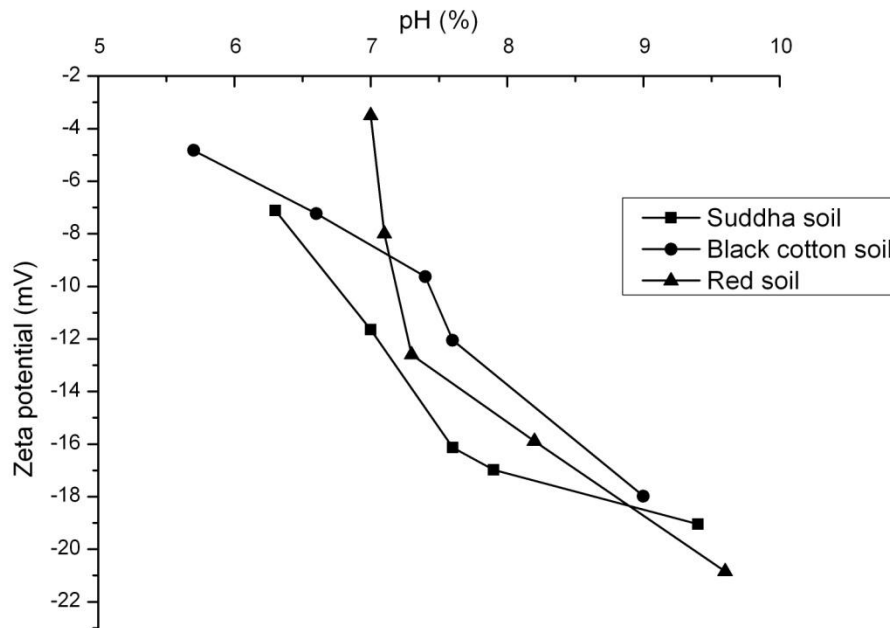


Figure 4.6 Zeta potential vs pH for all treatments

It can be noted from the graph that higher values of pH are related with higher values of zeta potential for treated and untreated soils irrespective of the soil type. When pH of a soil is high, there would be more OH^- ions adsorbed on the clay edges. This leads to an increase in the charge density causing an increase in the zeta potential. When soil pH increases the zeta potential associated with the soil also increases. Thus it can be said that changes in soil pH will be reflected in the values of zeta potential.

4.3.4 Impact of the structure

As mentioned in **Chapter 2**, there are several indicators of structure of the soil. Here shrinkage limit and UCS are used as the properties that define the structure. The shrinkage limit and unconfined compressive strength values corresponding to the urea treatment and sodium hydroxide treatment measured as per the various codes are as reported below in Table 4.4 and 4.5.

Table 4.4 Shrinkage limit and UCS values for sodium hydroxide treated soils

Properties	Sodium hydroxide treated soils								
	Suddha soil			Black cotton soil			Red soil		
	0M	0.5M	1M	0M	0.5M	1M	0M	0.5M	1M
S.L (%)	18	17	16	11	10	10	26	21	15
UCS (kPa)	256	212	171	285	257	233	258	211	159

Table 4.5 Shrinkage limit and UCS values for urea treated soils

Properties	Urea treated soils								
	Suddha soil			Black cotton soil			Red soil		
	0M	0.5M	1M	0M	0.5M	1M	0M	0.5M	1M
S.L (%)	18	32	45	11	18	25	26	36	49
UCS (kPa)	256	289	312	285	323	335	258	271	342

In the case of sodium hydroxide treated soils it can be seen that there is a steady decrease in the shrinkage limit and the UCS values indicating that the soil becomes more dispersed due to the addition of sodium ions and an increase in pH. At the same time when it

comes to the urea treated soils a reverse trend is seen. The shrinkage limit and UCS values have increased with the concentration of the organic matter. This may be due to the reduction in the swell-shrink potential caused due to the formation of complexes by the organic matter with the clay minerals. The relations between shrinkage limit and UCS with dispersivity for various soils are as plotted in Figure 4.7 and 4.8.

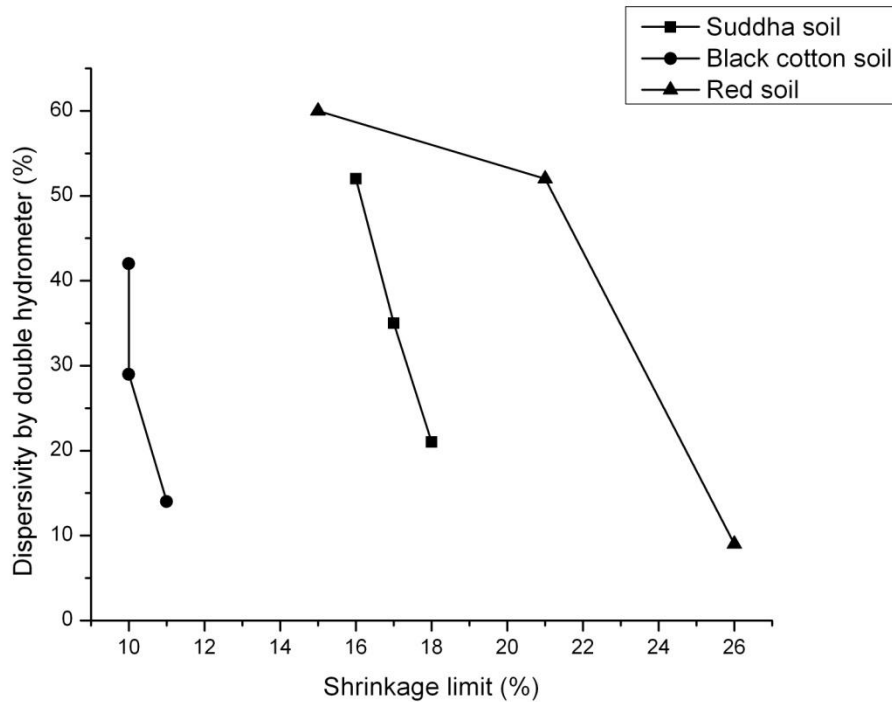


Figure 4.7 Dispersivity vs shrinkage limit

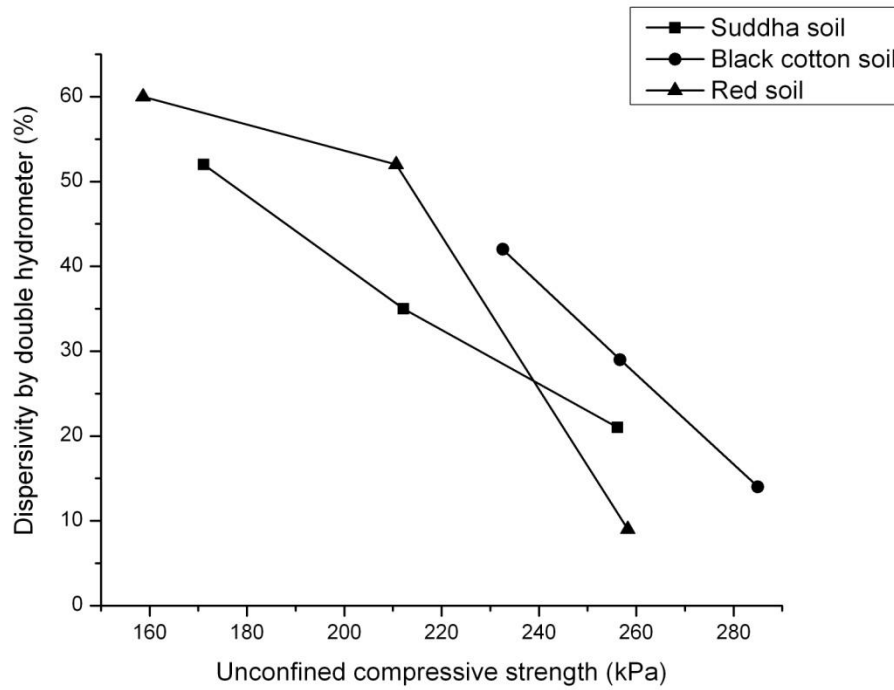


Figure 4.8 Dispersivity vs UCS

It can be seen that the dispersivity increases as the structure of the soil becomes more dispersed as indicated by the decrease of UCS value and shrinkage limit. The relation of shrinkage limit and UCS values with zeta potential of the soil is as shown in Figures 4.9 and 4.10.

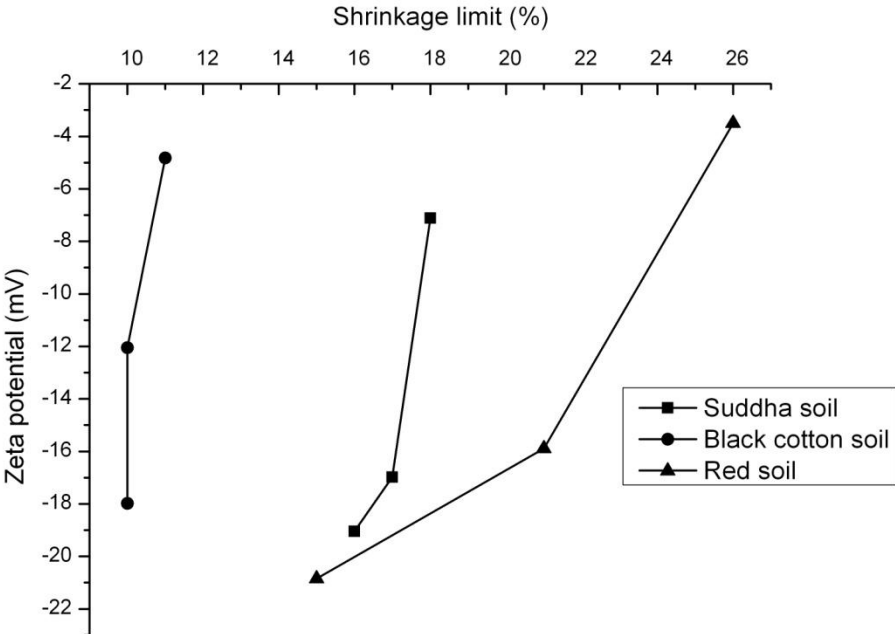


Figure 4.9 Zeta potential vs shrinkage limit

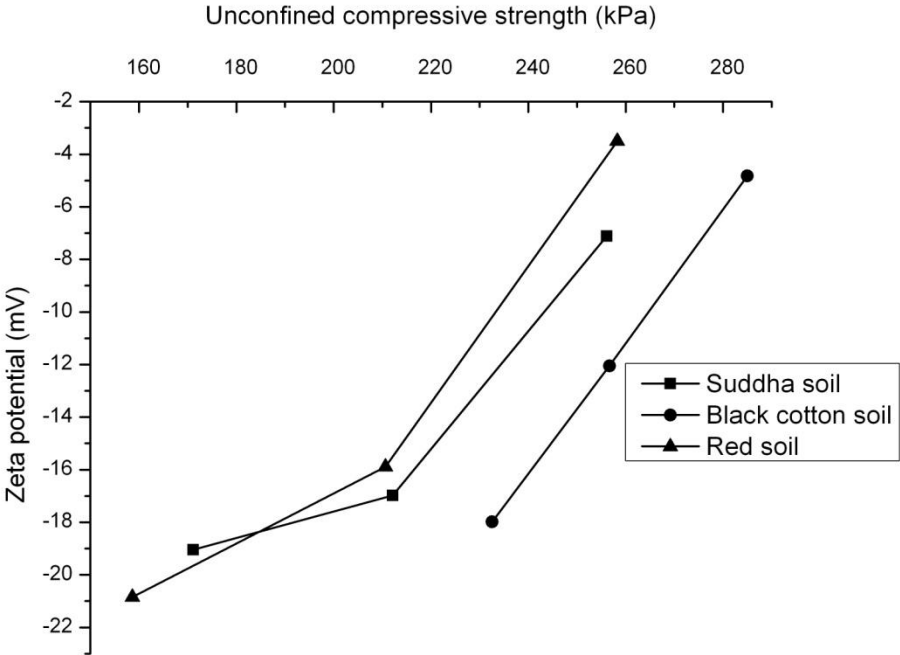


Figure 4.10 Zeta potential vs UCS

The decrease in unconfined compressive strength and shrinkage limit with the increase in sodium concentration shows the structure of the soil becoming more and more dispersive. From the graphs it is obvious that zeta potential increases as the structure becomes more dispersed.

In a similar way, the relation between dispersivity and structure could be established through other indicative tests such as liquid limit, plasticity characteristics, swelling indices, compaction behavior, permeability values etc.

It is interesting to note that even though complexes may be formed due to the addition of organic matter into the soil the charge on the clays has been increased as indicated by the dispersivity values and the zeta potential. Thus even if indicative tests such as shrinkage limit and unconfined compressive strength could not be used for identifying dispersivity, zeta potential could still be used to quantify dispersivity.

4.3.5 Effect of drying

Several studies report that oven drying of dispersive samples causes permanent changes in the soil causing an alteration in the dispersivity. To study that effect, dispersivity measurements through double hydrometer and estimation of zeta potential was done on oven dried and air dried soil samples. The tests were done on untreated, sodium hydroxide treated and urea treated soils. The results of the experiments are as recorded in Table 4.6.

Table 4.6 Zeta potential and dispersivity values for air dried and oven dried soils

Soil	Zeta potential (mV)	Dispersivity (%)
Suddha soil (oven dry)	-7.11	21
Suddha soil (air dry)	-11.11	23
Suddha soil + 0.5 M Urea (oven dry)	-11.64	25
Suddha soil + 0.5 M Urea (air dry)	-12.04	26
Suddha soil + 1M Urea (oven dry)	-16.13	27
Suddha soil + 1M Urea (air dry)	-18.25	32
Suddha soil + 0.5M NaOH (oven dry)	-16.98	35
Suddha soil + 0.5M NaOH (air dry)	-17.56	42
Suddha soil + 1M NaOH (oven dry)	-19.05	52
Suddha soil + 1M NaOH (air dry)	-20.59	60
Black cotton soil (oven dry)	-4.83	14
Black cotton soil (air dry)	-5.51	20
Black cotton soil + 0.5M Urea (oven dry)	-7.23	18
Black cotton soil + 0.5M Urea (air dry)	-8.15	21
Black cotton soil + 1M Urea (oven dry)	-9.63	24
Black cotton soil + 1M Urea (air dry)	-14.19	29
Black cotton soil + 0.5M NaOH (oven dry)	-12.05	29

Black cotton soil + 0.5M NaOH (air dry)	-16.35	35
Black cotton soil + 1M NaOH (oven dry)	-17.98	42
Black cotton soil + 1M NaOH (air dry)	-18.91	51
Red soil (oven dry)	-3.50	9
Red soil (air dry)	-5.23	15
Red soil + 0.5M Urea (oven dry)	-8.00	28
Red soil + 0.5M Urea (air dry)	-10.00	30
Red soil + 1M Urea (oven dry)	-12.60	44
Red soil + 1M Urea (air dry)	-20.23	50
Red soil + 0.5M NaOH (oven dry)	-15.89	52
Red soil + 0.5M NaOH (air dry)	-20.56	56
Red soil + 1M NaOH (oven dry)	-20.85	60
Red soil + 1M NaOH (air dry)	-21.58	64

It can be seen from Table 4.7 that there is a very small change occurring to the dispersivity and zeta potential of the soil due to the drying process. Air dried samples show higher values of dispersivity and zeta potential for all types of soils. This is due to the permanent changes occurring to the soil due to the temperature effect. Oven drying might cause volatilization of organic compounds present in the soil which might be affecting the dispersivity and zeta potential. Since there is no drastic or considerable change occurring to

the dispersivity due to drying, the effect of temperature could be conveniently neglected.

Figure 4.11 shows the relation between zeta potential and dispersivity of soils.

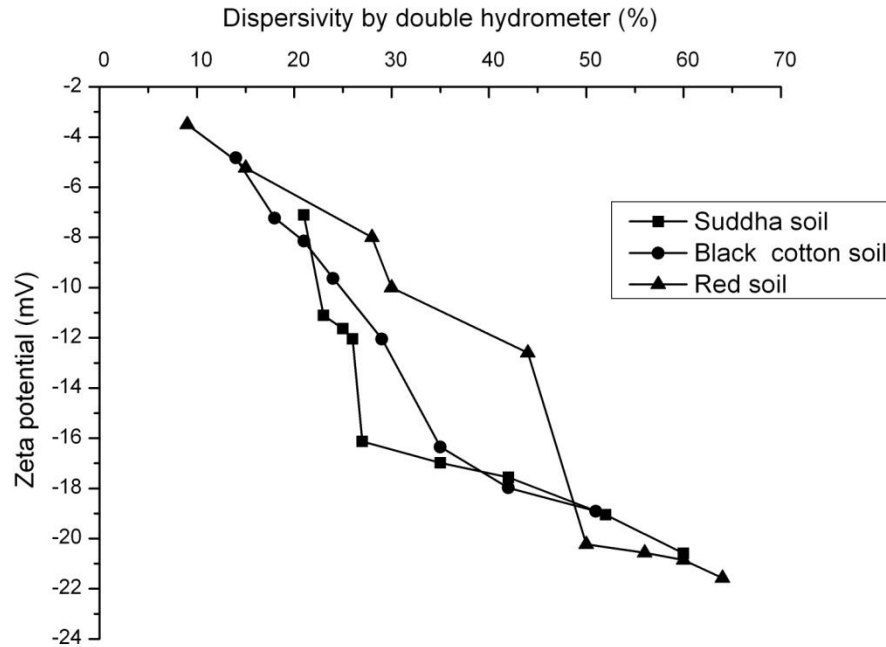


Figure 4.11 Zeta potential vs double hydrometer for all treatments

From Figure 4.11 it could be easily inferred that when the dispersivity of the soil is altered in any way there is a corresponding change in the zeta potential value. It can be confirmed that zeta potential serves as an ideal measure of estimating dispersivity irrespective of the soil type. The property can be also conceived as the best geotechnical indicative property of potential dispersion in soils.

4.4 SUMMARY

1. It is generally found that zeta potential of soil is found to relate with dispersivity of soil for any treatment or conditions. The zeta potential is found to have a correlation with dispersivity measured through double hydrometer, shrinkage limit or UCS test.

2. The influence of factors such as pH, cation exchange capacity, organic matter, and sodium concentration on the dispersivity of soils has been established confirming that these are prime factors influencing the dispersivity of soils. Even then, presence of monovalent ions such as sodium has greater influence on dispersivity than organic matter concentration. All these properties which have an influence on dispersivity are all well related with zeta potential of the soil.

3. The main reason for the observed relationship between the dispersivity under different conditions and zeta potential is because the factors controlling these properties are in way or other related to zeta potential. From the results it can be concluded that out of all the various geotechnical properties such as strength, shrinkage or CEC, zeta potential is the parameter which represents best the dispersivity of soils and thus hence could be used for estimating dispersivity of soils.

4. Drying of the soil does not have significant effect on the dispersivity of soils and also on the zeta potential.

5. There is however a singular exception to the above general observation in the case of urea treated soil because of the complexation of urea with the soil altering its behavior which may not be well reflected in the shrinkage limit and UCS test of measuring dispersivity.

CHAPTER 5

ESTIMATION OF DISPERSIVITY FROM ZETA POTENTIAL AND ATTRACTIVE FORCES

5.1 INTRODUCTION

From previous chapter it was evident that zeta potential is related to various factors that cause repulsion in soils, leading to dispersion. This chapter deals with the estimation of dispersivity of soil using zeta potential. Dispersivity has been interpreted as a phenomenon occurring when the repulsive forces in a soil exceeds the attractive forces. As dispersion is a phenomenon occurring in a soil water suspension the primary repulsive force to be considered is the electrostatic repulsion between soil particles. Attractive force can be estimated as the van der Waal's force of attraction. Thus, it could be conceived that dispersion occurs when the electrostatic repulsion dominates over the van der Waal's forces of attraction. Several theories are available in *Soft Matter Physics* which can be used to estimate the attractive and repulsive forces the most popular being classical DLVO theory.

5.2 DLVO THEORY AND STABILITY RATIO

As mentioned in **Chapter 2**, the DLVO theory is the most extensively used theory for studying the interactions between particles suspended in a liquid. The theory takes into account both the electrostatic repulsion and van der Waal's attraction for estimating the stability of a suspension. The theory has been primarily developed for colloidal dispersions which maintain their homogeneity throughout the suspension; or in other words for particles suspended in solution which follow more or less a uniform size distribution.

The theory established the van der Waal's forces for two particles by initially considering the basic microscopic interactions between two Bohr atoms. The interaction energy between two Bohr atoms was derived by equating the Coloumb's energy and the first ionization potential. The interaction energy between Bohr atoms were then extended to macroscopic bodies by simply summing up the interactions between all pairs of atoms in each of the bodies. In a similar way, the molecular interaction energy was defined which was then extended to a particle level through the use of a parameter called number density of molecules. The concept of surface potential and electrolyte concentration was then introduced which at the end helped in conceiving the idea of electrostatic repulsion between particles. The total interaction energy between two particles was then expressed as the arithmetic sum of the electrostatic repulsion and van der Waal's attraction (wherein the attractive part was given a negative sign). It is to be specifically noted that the presence of a third atom/molecule was assumed to be not affecting the interactions between the first and the second. The theory also provides the usage of a parameter called Stability ratio (a function of surface potential) which tells whether the particles suspended in a solution has the ability to remain in the state of a colloidal dispersion or not. Only a handful of studies have been conducted on the applicability of the DLVO theory and stability ratio for clay colloidal suspensions. The researchers finally reached the conclusion that the theory could not be used for estimating the stability of clay colloids. As mentioned in **Chapter 2**, the setbacks associated with the suitability of the theory for clay colloids is not connected with the zeta potential and as from **Chapter 4**, the zeta potential correlates well with dispersivity, an attempt is made in this chapter to formulate the attractive and repulsive interaction energies in a soil mass by adopting a similar approach as taken by the DLVO.

5.3 ESTIMATION OF ATTRACTION AND REPULSION THROUGH INFINITESIMAL PARTICLE APPROACH

The dispersivity as proposed in this study is the release of energy that occurs when the repulsive force overcomes the force of attraction. The repulsive energy is calculated from zeta potential and the attraction from van der Waal's forces. The repulsive energy and attractive energy for a defined soil mass is calculated and the difference between them is expressed as dispersivity in terms of release of energy (as in the case of DLVO).

5.3.1 Estimation of attraction

The attractive force in the soil mass is principally contributed by the van der Waal's attraction (Lambe and Whitman 2008). The van der Waal's interaction energy between two spherical particles when the inter-particle distance is sufficiently small when compared to the size of the particle is given by

$$U = \frac{-Ar_1r_2}{6d(r_1 + r_2)} \quad (\text{Israelachvili 2011}) \dots\dots\dots (5.1)$$

Where,

A is the Hamaker constant,

r_1 and r_2 are the radii of the particles,

d is the distance between the surfaces.

The soil particles are conceived as spheres rather than flat plates because a spherical shape is more reasonable due to the irregularities arising due to building up of the clay particles (Garcia Garcia et al. 2007). The total van der Waal's energy in a soil mass needs to be obtained to get the dispersivity of the soil.

In the above equation it can be seen that the energy for a two particle system is well defined. By extension the total interaction energy for a three particle system could also be

found if the particle-particle interaction is known. When an “n” particle system (where n is potentially large) is considered, computing energy of the system by judging all the possible interactions is cumbersome.

To find the total van der Waal's energy of such a system of particles, the ideal procedure is to integrate the van der Waal's energy contributed by each pair of particles to a soil mass. Since, there are only a finite number of particles; a direct integration (without further making some simplifying approximations) is not possible. This is because integration is inherently an infinitesimal concept and can roughly be thought of as adding up of infinite number of infinitesimal particles. Hence some simplifying approximations were made and the energy was found out via the method indicated.

Assume that a clay particle is an infinitesimal particle of radius dr. It can be proposed that, any clay particle with some radius “r”, can be thought of as formed by the combination of infinite number of these infinitesimal particles. Van der Waal's energy between two infinitesimal particles can be defined in the same way as in the two particle system. This allows computing the van der Waal's energy of a two infinitesimal particle system which are separated from each other by a distance “d”. With this setting, the van der Waal's energy of any clay mass can be computed without really bothering about what exact particles constitute a clay mass. The exact method is described below.

Let ΔU be the increase in van der Waal’s energy due to an increase in radius Δr. As energy is a function of radius r let us represent it as U(r). Then the total van der Waal’s energy of a clay mass of radius R can be written as

$$\int_{r=0}^R dU(r) = \int_{r=0}^R \frac{dU(r)}{dr} \times dr \dots\dots\dots(5.2)$$

U(r) can be written as $U(r) = - Ar/12d$. Thus we get, $dU(r)/dr = - A/12d$

Total van der Waal's energy of attraction,

$$T.A.E = \frac{-AR}{24d} \dots\dots\dots(5.3)$$

As there are several practical limitations to report a radius of a purely spherical soil mass, the radius may be substituted with the Mass (M) of the soil as,

$$R = \sqrt[3]{3M / 4\pi\rho} \dots\dots\dots(5.4)$$

Where ρ may be the field dry density.

The inter-particle separation d may be found out as

$$d = 2e / A_s G \rho_w \text{ (Fam and Santamarina 1996) ..(5.5)}$$

Where, e is the void ratio, A_s is the specific surface area, ρ_w is the density of water, G is the specific gravity. As specific surface area is the surface area per unit mass of a soil, it can be written,

$$A_s = \frac{4\pi r^2}{\frac{4}{3}\pi r^3 \rho} = \frac{3}{\rho_s r} = \frac{3}{G\rho_w r} \text{ ; Thus d becomes } d = 2er/3 \dots(5.6)$$

Thus the total attraction energy becomes

$$T.A.E = - \frac{A}{16er} \times \left(\frac{3M}{4\pi\rho} \right)^{1/3} \dots\dots\dots(5.7)$$

5.3.2 Estimation of repulsion

The surface potential of a particle, ψ_0 is given by the Coulomb potential (Somasundaran 2006),

$$\psi_0 = \frac{Q}{4\pi\epsilon_0\epsilon_r r} \dots\dots\dots(5.8)$$

Where,

Q is the total charge,

ϵ_0 is the permittivity of the free space

ϵ_r is the relative permittivity of the medium

r is the particle radius

Thus,
$$Q = \psi_0 \times 4\pi\epsilon_0\epsilon_r r \dots\dots\dots(5.9)$$

If ψ_0 is identified as ζ , zeta potential, ψ_0 could be replaced by ζ in the above equation. The underlying assumption taken here is that the distance from the surface to the slipping plane “d” is far less than the particle radius “r”. i.e. $d \ll r$

Hence, it is written
$$Q = \zeta \times 4\pi\epsilon_0\epsilon_r r \dots\dots\dots(5.10)$$

The Coloumb’s interaction force, F between two charged bodies is given by (eg - Blinder 2012),

$$F = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{Q_1 Q_2}{d^2} \dots\dots\dots(5.11)$$

Where, Q_1 and Q_2 are point charges and d is the separation distance

Soil particles could be considered as spheres over which the charge is distributed (Garcia Garcia et al. 2007; Ida 2000).

Using, Equation 5.9, it can be written,

$$F = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{\zeta_1 \zeta_2}{d^2} \times (4\pi\epsilon_0\epsilon_r)^2 r_1 r_2 \dots\dots\dots(5.12)$$

If the soil is conceived as particles of uniform size, $r_1 = r_2$, and $\zeta_1 = \zeta_2$ may be assumed.

Then the repulsive energy between two clay particles could be expressed as,

$$R.E = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{\zeta^2}{d} \times (4\pi\epsilon_0\epsilon_r)^2 r^2 = \frac{4\pi\epsilon_0\zeta^2\epsilon_r r^2}{d} \dots\dots\dots(5.13)$$

It can be seen from the above equation, the repulsion between two particles is dependent on the particle radius, their separation distance and the zeta potential. Similar to the approach taken above, let $\Delta R.E$ be the increase in the repulsive energy due to an increase in radius Δr .

Then the total repulsive energy in a soil mass could be expressed as,

$$\int_{r=0}^R dR.E(r) = \int_{r=0}^R \frac{dR.E(r)}{dr} \times dr \dots\dots\dots(5.14)$$

Differentiating (5.13) we get

$$\frac{dR.E(r)}{dr} = \frac{8\pi\epsilon_0\zeta^2\epsilon_r r}{d} \dots\dots\dots(5.15)$$

Thus the total repulsive energy is $T.R.E = \frac{4\pi\epsilon_0\zeta^2\epsilon_r R^2}{d} \dots\dots\dots(5.16)$

Substituting for R and d from Equations (5.4) and (5.6), we get

$$T.R.E = \frac{\pi\epsilon_0\epsilon_r\zeta^2}{er} \times \left(\frac{9M}{2\pi\rho}\right)^{2/3} \dots\dots\dots(5.17)$$

Thus the total dispersion could be expressed as

$$D = \frac{\pi\epsilon_0\epsilon_r\zeta^2}{er} \times \left(\frac{9M}{2\pi\rho}\right)^{2/3} - \frac{A}{16er} \times \left(\frac{3M}{4\pi\rho}\right)^{1/3} \dots\dots\dots(5.18)$$

Substituting $\epsilon_0 = 8.85418782 \times 10^{-12} \text{ C}^2 \text{ N}^{-1}\text{m}^{-2}$, $\epsilon_r = 77$ for water, the equation could be simplified and re-written as,

$$D = 2.14 \times 10^{-9} \frac{\zeta^2}{er} \times \left(\frac{9M}{2\pi\rho} \right)^{2/3} - \frac{A}{16er} \times \left(\frac{3M}{4\pi\rho} \right)^{1/3} \dots\dots\dots(5.19)$$

The above expression gives the dispersivity pertaining to a specific condition of the soil.

5.4 EXPERIMENTAL INVESTIGATION

In order to verify the proposed expression, experiments were carried out on three soils viz., Suddha soil, Black Cotton soil and Red soil after enhancing their dispersivity by enhancing the monoionic cations (in exchangeable sites and/or in pore fluid). Since in **Chapter 4** it was observed that dispersivity increased when treated with salts of monovalent cations, for fractions of soils passing 75 μ , a similar treatment approach is taken here. Soil passing 75 μ was selected and treatments were done with potassium hydroxide, sodium hydroxide and lithium hydroxide. 1 M solution of the chemicals was prepared and was mixed with the three soils by maintaining a solid liquid ratio of 1:2.5. The samples were allowed to air dry for two weeks after which they were oven dried before testing. Dispersivity was measured using double hydrometer, shrinkage limit, UCS test and with zeta potential.

5.5 RESULTS

The results of the various tests done on the soil samples are discussed in the subsequent sections.

5.5.1 Characterization of the test samples

Atterberg's limits of the test samples along with their UCS strengths, maximum dry density (from compaction characteristics) and corresponding void ratio values before and after treatments are as shown in Table 5.1.

Table 5.1 Basic characteristics of the test samples

Soil	Treatment	L.L (%)	P.L (%)	S.L (%)	Density (kg/m³)	Void ratio	UCS (kPa)
Suddha soil	Untreated	69	34	22	1420.00	0.65	256
	KOH treated	76	39	21	1361.52	0.73	214
	NaOH treated	80	42	16	1303.46	0.80	171
	LiOH treated	94	44	10	1048.20	1.59	84
Black cotton soil	Untreated	74	32	12	1365.00	0.96	285
	KOH treated	79	35	10	1330.00	1.01	260
	NaOH treated	85	37	10	1295.00	1.06	233
	LiOH treated	92	42	9	1187.00	1.25	180
Red soil	Untreated	30	29	28	1913.00	0.42	258
	KOH treated	32	30	19	1652.29	0.64	209
	NaOH treated	36	31	15	1475.25	0.86	159
	LiOH treated	40	32	11	1048.20	1.59	58

It should be noted that the samples are with soil fractions finer than 75 μ which may be the reason for the change in Atterberg's limits due to increased clay content compared to the original soil (Table 3.1). When treated with salts of monovalent cations, the soil becomes more dispersive as indicated by increase in their Atterberg's limits and reduction in strength values. The water holding capacity owing to higher repulsion between the particles has increased as indicated by the increased liquid limit and plastic limit along with decrease in shrinkage limit. The increased repulsion between the particles has made the soil more

dispersive thus reducing the strength. It could also be noted that the dispersivity of any soil increases when the size of the treated monovalent cation decreases. The shrinkage limit of soils is more sensitive to fabric changes; Figure 5.1 shows the variation of shrinkage limit of soils with their UCS strength values.

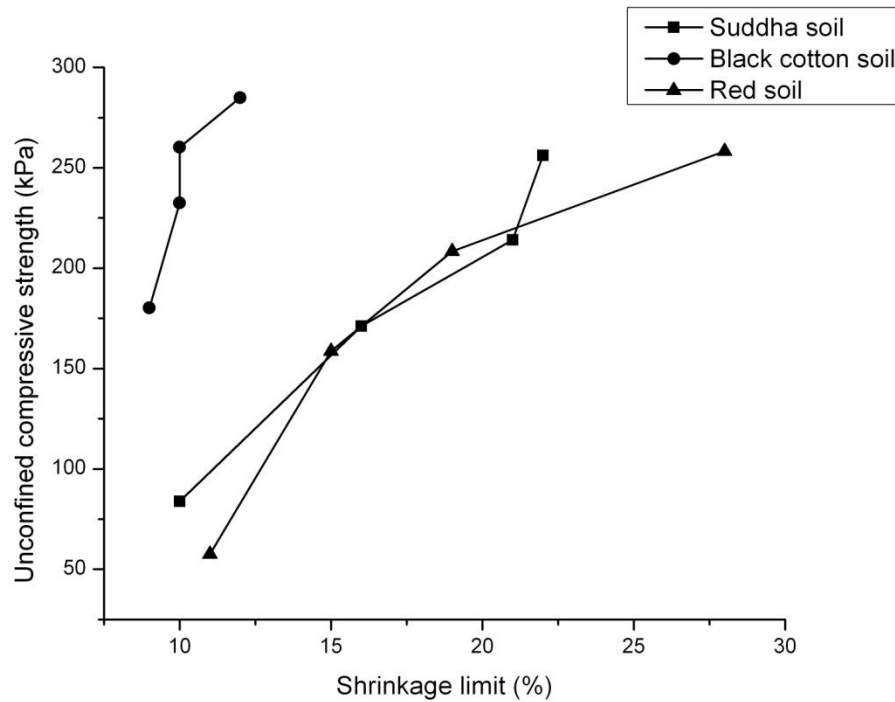


Figure 5.1 Variation of UCS with shrinkage limit after treatment with different hydroxides

From the plot above it can be seen that by the treatment of the soil with hydroxides the soils show a reduction in the shrinkage limit and compressive strength. The reduction is more when the ionic size of the monovalent cation is less. The replacement of exchangeable ions together with the increase in the charge density increases the repulsive pressure. Figure 5.2 shows the variation of the void ratio with shrinkage index.

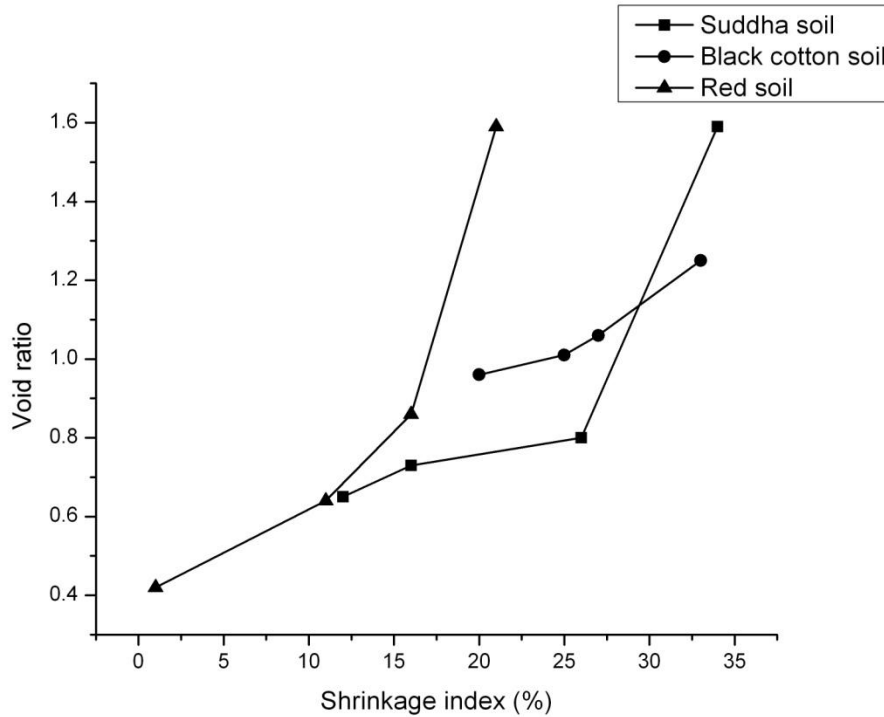


Figure 5.2 Variation of void ratio with shrinkage index

Sridharan and Nagaraj (2000) showed that shrinkage index correlates well with compressibility behavior of soils. As in this case as both void ratio and shrinkage index is increasing due to the treatments it can be inferred that the soil becomes more compressible and expansive owing to the fabric changes. The soils have become more dispersed and hence offer higher repulsive pressure between particles.

5.5.2 Zeta potential measurements

The concentrations of the various monovalent cations along with the zeta potential values and the associated particle radius for the various treated soils are summarized in Table 5.2.

Table 5.2 Total ion concentrations and zeta potential of soils

Soil	Treatment	Ion concentration (cmol/kg)					Z.P (V)
		Li	Na	K	Ca	Mg	
Suddha soil	Untreated	0.36	0.86	0.70	33.77	15.76	-7.11
	KOH treated	0.21	2.44	50.36	34.09	13.25	-14.02
	NaOH treated	0.07	90.93	0.54	34.48	10.05	-19.05
	LiOH treated	169.17	4.02	1.41	35.07	3.32	-32.05
Black cotton soil	Untreated	0.02	0.26	0.39	47.13	11.95	-4.83
	KOH treated	0.02	1.56	153.68	41.23	8.25	-12.86
	NaOH treated	0.02	209.70	0.64	36.35	7.12	-17.98
	LiOH treated	417.98	2.93	0.87	27.94	2.79	-32.25
Red soil	Untreated	0.07	0.08	0.93	18.20	0.91	-3.50
	KOH treated	0.05	1.16	87.43	15.38	1.01	-16.54
	NaOH treated	0.06	154.68	1.15	14.28	1.11	-20.85
	LiOH treated	309.00	2.23	1.24	11.53	1.14	-34.00

As it can be seen, the concentrations of the monovalent cations have increased after their respective treatments with the monovalent salts. The zeta potential of the soil also has increased when treated with monovalent cations. This is due to the influence of the hydrated monovalent cations present in the soil (dissolved and adsorbed). Hydrated monovalent ions (as their radius is higher), can't approach the negative inner layer or the crystal lattice of the particle as closely as non-hydrated ions. Hence, ions with the small crystal-lattice radii become hydrated, increase the thickness of the double layer and produce high zeta potentials.

It can also be noted that the zeta potential increases as the size of the monovalent cation decreases. This is because; zeta potential is also related to valence, size, energy of adsorption and release of ions. Smaller the ion, lesser will be the energy of adsorption and higher will be the zeta potential. At higher negative zeta potential values, the soil becomes more dispersive because larger electric potential near the soil surface generates electric repulsive force among soil particles. Figure 5.3 shows the variation of zeta potential with liquid limit.

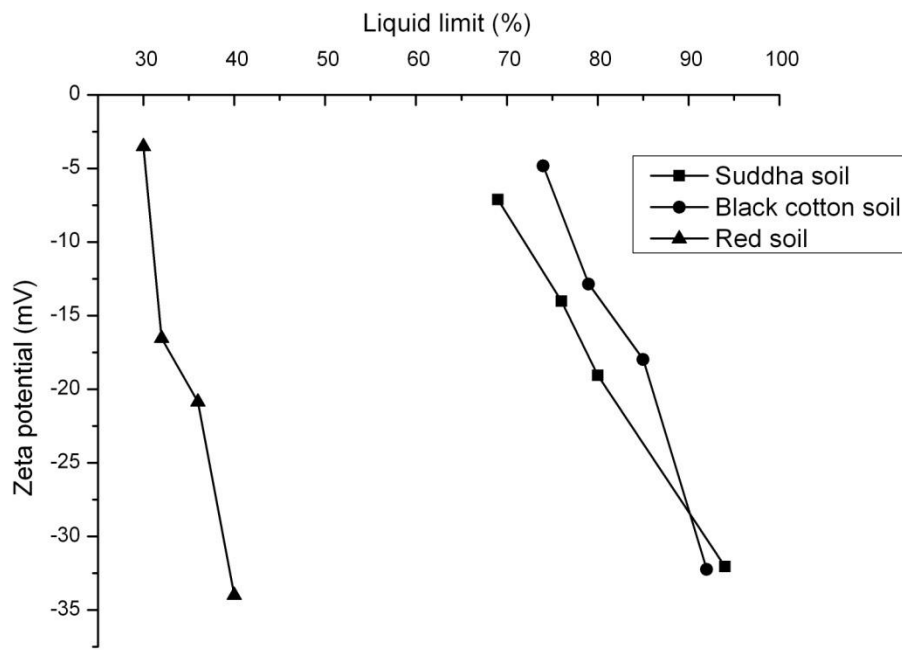


Figure 5.3 Zeta potential vs liquid limit of soils

From Figure 5.3 it can be seen that liquid limit is proportional to the zeta potential. Higher liquid limit in soils indicate higher repulsion between the particles as indicated by a higher zeta potential. Similar plots of zeta potential could be made with the compressive strength, plastic limit, compaction characteristics or swell indices and a similar inference could be made.

5.5.3 Effect of dispersing agent

In the double hydrometer method, UCS test or shrinkage limit experiment of measuring dispersivity, an optimum amount of dispersing agent (commonly fixed as 10% by weight) is added to the soil and the property is measured. The values of the shrinkage limit and UCS after the addition of dispersing agent are as shown in Table 5.3.

Table 5.3 Effect of dispersing agent on soils

Soil	Treatment	S.L With D.A (%)	UCS With D.A (kPa)
Suddha soil	Untreated	18	110
	KOH treated	17	89
	NaOH treated	13	68
	LiOH treated	8	30
Black cotton soil	Untreated	10	214
	KOH treated	8	174
	NaOH treated	7	134
	LiOH treated	6	58
Red soil	Untreated	20	201
	KOH treated	20	194
	NaOH treated	18	186
	LiOH treated	16	110

When dispersing agent (sodium hexametaphosphate) is added, complex phosphates plate the clay particle and yields maximum deflocculation owing to the repulsion of clay particles which have like charges. It is well known that reduction in viscosity is the measure

of deflocculation achieved (Tchillingarian 1952). As in sodium hexametaphosphate the number of phosphate radicals is high, it produces a rapid reduction in viscosity causing high dispersion. This results in higher shrinkage and lesser strength as shown in Table 5.3.

5.5.4 Dispersivity measurements

The dispersivity for the various soils before and after various treatments is estimated using double hydrometer, shrinkage limit, UCC test and finally the proposed expression. The dispersivity obtained from the derived expression reports dispersion as a measure of release of energy and hence, the values are reported in Joules. In order to estimate the dispersivity using the proposed equation, D_{50} value (from hydrometer analysis) was chosen as the mean particle diameter (r). The D_{50} values for Suddha soil, Black Cotton soil and Red soil were found as 3.6μ , 0.0087μ and 0.64μ respectively. The Hamaker constant for all the soils were fixed as 6×10^{-20} J (Missana and Adell 2000). Maximum dry density values obtained from compaction studies and the corresponding values of void ratios were chosen for estimating the repulsion and attraction. The mass of the soil was fixed as 40 g so as to compare with double hydrometer dispersivity. S.I units have been used for all the parameters involved and the results are as summarized in Table 5.4.

Table 5.4 Dispersivity values of soils

Soils	Treatment	D.H (%)	S.L (%)	UCS (%)	R-A values (J)		
					T.R.E (J)	T.A.E (J)	Dispersivity (J)
Suddha soil	Untreated	21	18	57	5.45×10^{-11}	3.01×10^{-17}	5.45×10^{-11}
	KOH treated	33	19	58	1.94×10^{-10}	2.74×10^{-17}	1.94×10^{-10}
	NaOH treated	52	19	60	3.36×10^{-10}	2.52×10^{-17}	3.36×10^{-10}
	LiOH treated	69	20	64	5.54×10^{-10}	2.13×10^{-17}	5.54×10^{-10}
Black cotton soil	Untreated	14	17	25	7.23×10^{-8}	8.53×10^{-17}	7.23×10^{-8}
	KOH treated	29	25	33	4.96×10^{-7}	8.16×10^{-17}	4.96×10^{-7}
	NaOH treated	42	30	42	9.40×10^{-7}	7.81×10^{-17}	9.40×10^{-7}
	LiOH treated	72	33	68	2.72×10^{-6}	6.84×10^{-17}	2.72×10^{-6}
Red soil	Untreated	9	29	22	9.42×10^{-12}	2.40×10^{-16}	9.42×10^{-12}
	KOH treated	36	-5	7	1.52×10^{-12}	1.64×10^{-16}	1.52×10^{-10}
	NaOH treated	60	-20	-17	1.94×10^{-10}	1.27×10^{-16}	1.94×10^{-10}
	LiOH treated	110	-45	-91	3.51×10^{-10}	7.72×10^{-17}	3.51×10^{-10}

Table 5.4 gives the values of dispersivity along with the corresponding repulsion and attraction in various soils under the defined conditions. A plot between liquid limit of the soils with the repulsion obtained is as shown in Figure 5.4.

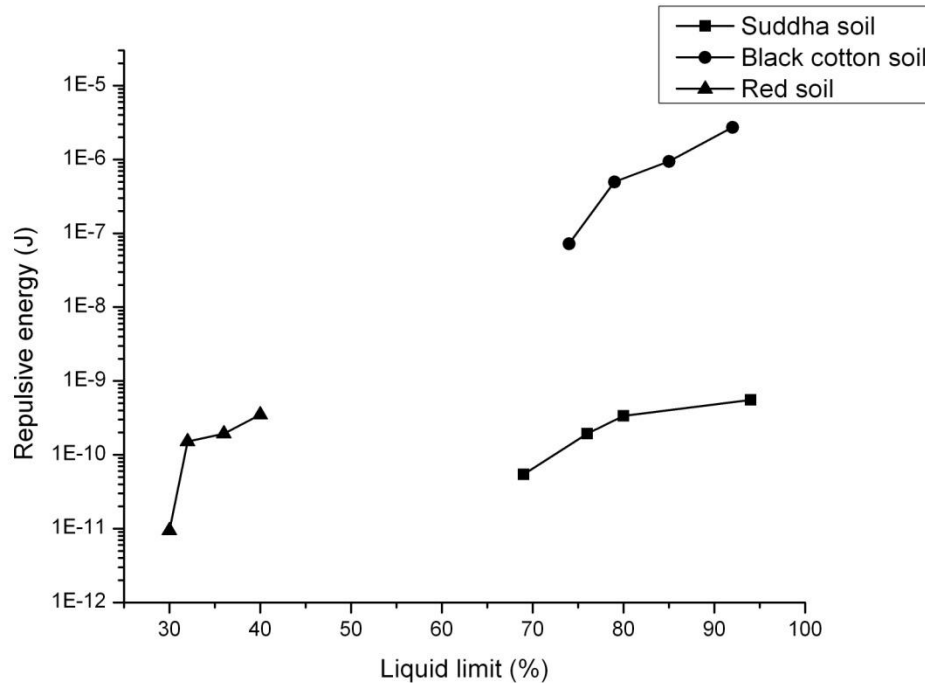


Figure 5.4 Variation of repulsive energy with liquid limit through infinite particle approach

The increase in liquid limit in a soil can be attributed to the increase in repulsion between the particles in a soil. From Figure 5.3, it can be seen that the repulsion in the soil mass is proportional to the liquid limit. Due to increased repulsion water molecules are able to enter the microstructure leading to higher water holding capacity and thus the liquid limit.

It may also be noted from Table 5.4 that the dispersivity increases when the concentration of monovalent cation increases. The dispersivity increase is higher when the size of the adsorbed monovalent cation is lesser. It can be seen that the dispersivity increase due to the treatment with various monovalent cations is well reflected in the dispersivity values measured by double hydrometer, UCS and shrinkage limit. The dispersivity measured

from the R-A values also follow a similar trend. Figure 5.5 shows the variation of dispersivity measured from R-A value with the double hydrometer values. Since the values vary highly, a semi-log plot is drawn.

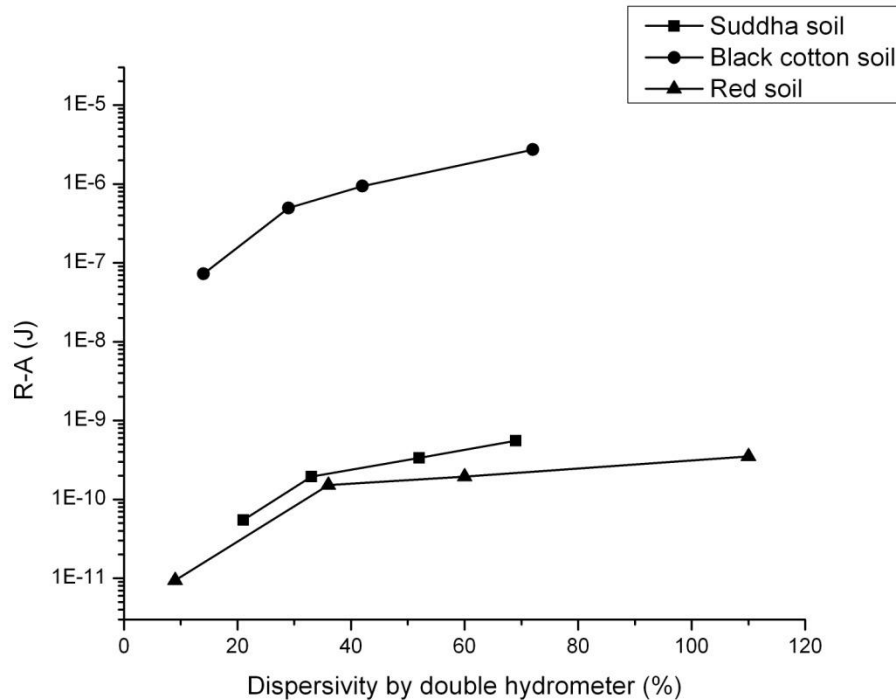


Figure 5.5 Comparison of the dispersivity values through infinitesimal particle approach

From the graph it can be seen that the dispersivity obtained from the derived expression is more or less proportional to the double hydrometer dispersivity. The similarity in the trend of the dispersivity values obtained from the derived expression with that assessed by the double hydrometer test confirms the suitability of the expression for estimating dispersivity for practical purposes.

5.6 ESTIMATION OF ATTRACTION AND REPULSION THROUGH FINITE PARTICLE APPROACH

In the above mentioned method (infinitesimal particle approach) of calculating the attraction and repulsion of a soil mass, it was assumed that the total number of particles in a

soil mass is potentially very large to calculate the total forces. Hence, in order to find the total energy, each soil particle was assumed to be composed of combinations of an infinitely small particle radius “dr”. Thus any clay particle of radius “r” could be defined as an infinite combination of infinitesimal radius “dr”. The method gives a dispersivity value for a soil if the conditions of the soil are defined; i.e. when information regarding the physical properties of the soil such as density, void ratio and mean particle diameter are provided with. In common practices, the environment of the soil may not be well defined and there would be a need of determining dispersivity of the soil. To cater such requirements, an alternate method of estimating dispersivity is proposed here.

5.6.1 Estimation of attraction

As mentioned above,

$U(r) = - Ar/12d$, if particle radii are assumed to be similar where, $U(r)$ is the attractive energy between two soil particles.

Now, the total attractive energy in a soil mass could be expressed as

$$T.A.E = \sum_{i=1}^{N_{C_2}} \frac{-Ar}{12d_i} \dots\dots\dots(5.20)$$

Wherein,

N denotes the total number of particles in the mass which could be expressed as

$$N = \frac{\frac{4}{3}\pi R^3}{\frac{4}{3}\pi r^3} = \frac{R^3}{r^3} \dots\dots\dots(5.21)$$

approximated to the nearest integer.

Then, the total number of particle pairs in the soil mass can be expressed as ${}^N C_2$ and corresponding to each pair “ P_i ”, there is an inter particle separation d_i . If a summation over the energies of all particle pairs (${}^N C_2$) is performed, it could reasonably serve as an estimate of the total attractive energy of a soil mass.

In the above equation, the inter particle separation d_i for the i^{th} pair P_i could very well be replaced by an average separation distance d_{avg} . Thus the total attractive energy in a soil mass could be expressed as

$$T.A.E = \sum_{i=1}^{N C_2} \frac{-Ar}{12d_{\text{avg}}} = \frac{-Ar}{12d_{\text{avg}}} \times {}^N C_2 \quad \dots\dots\dots(5.22)$$

If soil particles are assumed to be spherical and randomly distributed over a sphere the average distance could be expressed as,

$$d_{\text{avg}} = 36R/35 \quad (\text{Lund et al. 1997})\dots\dots\dots(5.23)$$

Substituting in (5.22) the total attractive energy becomes,

$$T.A.E = \frac{-35Ar}{432R} \times {}^N C_2 \quad \dots\dots\dots(5.24)$$

5.6.2 Estimation of repulsion

From Equation 5.13, the repulsive energy between two soil particles is given by,

$$R.E = \frac{4\pi\epsilon_0\zeta^2\epsilon_r r^2}{d} \quad \dots\dots\dots(5.25)$$

In a similar way, the total repulsive energy in a soil mass could be expressed as

$$T.R.E = \sum_{i=1}^{N C_2} \frac{4\pi\epsilon_0\zeta^2\epsilon_r r^2}{d_i} = \sum_{i=1}^{N C_2} \frac{4\pi\epsilon_0\zeta^2\epsilon_r r^2}{d_{\text{avg}}} = \frac{4\pi\epsilon_0\zeta^2\epsilon_r r^2}{36R/35} \times {}^N C_2 \quad \dots\dots\dots(5.26)$$

Substituting $\epsilon_0 = 8.85418782 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$, $\epsilon_r = 77$ for water, the equation could be simplified and re-written as,

$$T.R.E = 8.33 \times 10^{-9} \frac{\zeta^2 r^2}{R} \times^N C_2 \dots\dots\dots(5.27)$$

The total dispersion in a soil mass could be expressed as a combination of Equations (5.24) and (5.27).

$$D = 8.33 \times 10^{-9} \frac{\zeta^2 r^2}{R} \times^N C_2 - \frac{35Ar}{432R} \times^N C_2 \dots\dots\dots(5.28)$$

It should be specifically made clear that the above equation is derived on the assumption that the soil mass is assumed to be very dense such that the possible voids in a soil mass is completely neglected. The expression primarily serves as an estimate of the total dispersion occurring to a defined soil mass.

To verify the proposed equation, the same treatment sets along with their corresponding zeta potentials and Hamaker constant values are being used here. In order to make comparison regarding the dispersivity characteristics of various soils much more rational, the dispersion occurring to a soil mass of radius 1 cm comprised of 5 μ particles are being studied. Table 5.5 shows the values of dispersivity along with their attraction and repulsion values for various treated soils.

Table 5.5 Dispersion characteristics of soils.

Soils	Treatment	D.H (%)	R-A values (J)		
			T.R.E (J)	T.A.E (J)	Dispersivity (J)
Suddha soil	Untreated	21	3.37×10^{-2}	7.78×10^{-5}	3.36×10^{-2}
	KOH treated	33	1.31×10^{-1}	7.78×10^{-5}	1.31×10^{-1}
	NaOH treated	52	2.42×10^{-1}	7.78×10^{-5}	2.42×10^{-1}
	LiOH treated	69	6.85×10^{-1}	7.78×10^{-5}	6.85×10^{-1}
Black cotton soil	Untreated	14	1.55×10^{-2}	7.78×10^{-5}	1.55×10^{-2}
	KOH treated	29	1.10×10^{-1}	7.78×10^{-5}	1.10×10^{-1}
	NaOH treated	42	2.15×10^{-1}	7.78×10^{-5}	2.15×10^{-1}
	LiOH treated	72	6.93×10^{-1}	7.78×10^{-5}	6.93×10^{-1}
Red soil	Untreated	9	8.16×10^{-3}	7.78×10^{-5}	8.09×10^{-3}
	KOH treated	36	1.82×10^{-1}	7.78×10^{-5}	1.82×10^{-1}
	NaOH treated	60	2.90×10^{-1}	7.78×10^{-5}	2.90×10^{-1}
	LiOH treated	110	7.70×10^{-1}	7.78×10^{-5}	7.70×10^{-1}

A similar graph between liquid limit and repulsion is as shown in Figure 5.6

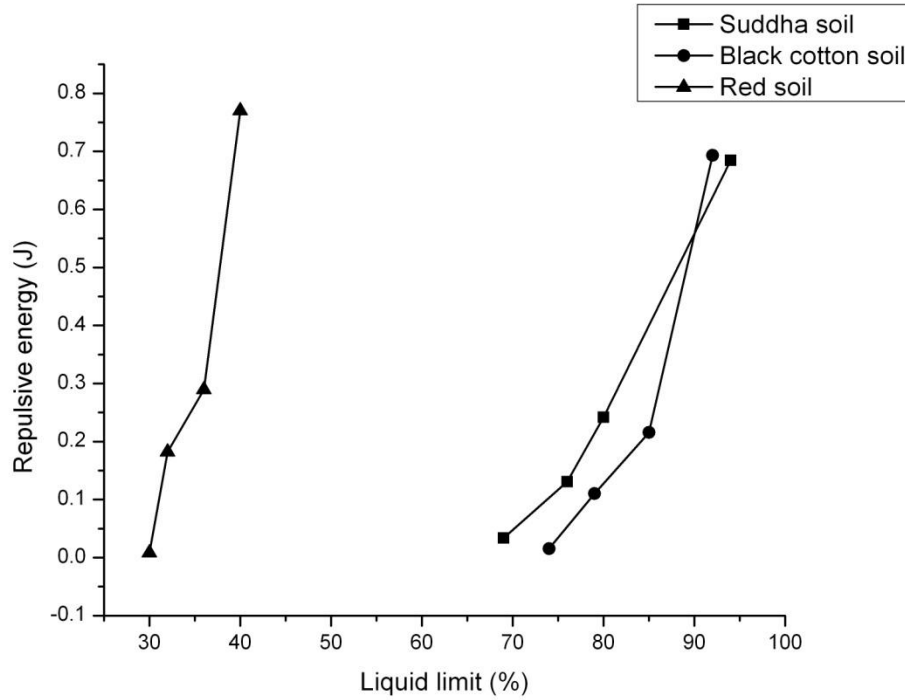


Figure 5.6 Variation of repulsion with liquid limit through finite particle approach

It can be observed that even though the trend is different the repulsion in soils is proportional to the liquid limit. The difference in the values may be due to the difference in the settings for the estimation of repulsion between the infinitesimal particle approach and finite particle approach. As earlier, the comparison of the dispersivities observed from the R-A values with the double hydrometer test results are presented in Figure 5.7.

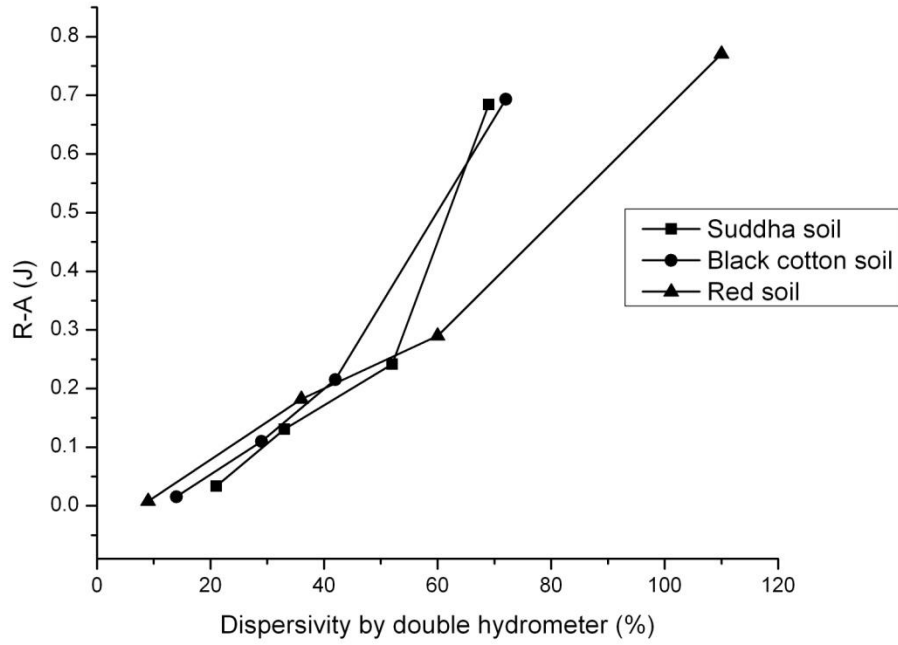


Figure 5.7 Comparison of the dispersivity values through finite particle approach

It can be seen that the proposed dispersivity values follow a similar pattern as the double hydrometer dispersivity as earlier in the infinitesimal particle approach. Figure 5.8 shows the variation of dispersivity values with the R-A values combining all the soils.

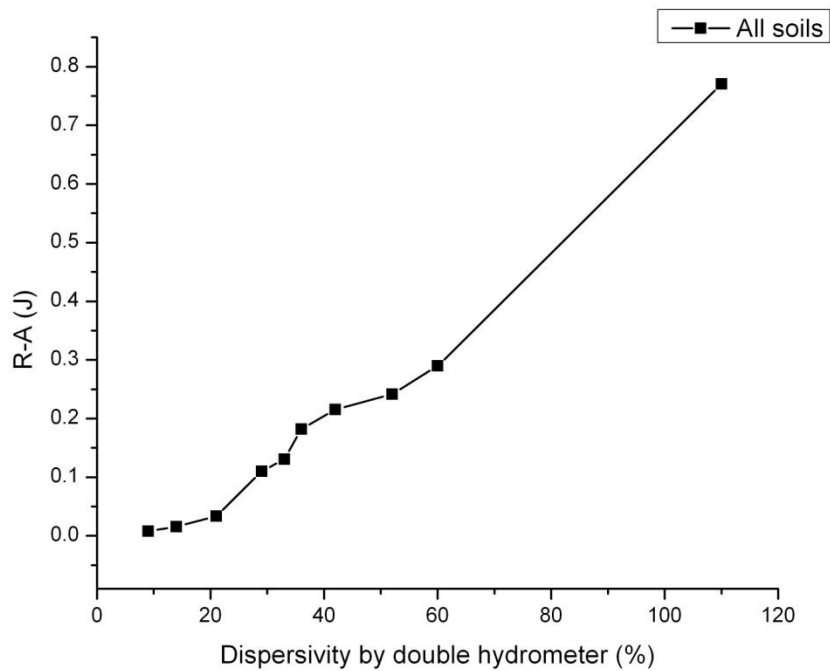


Figure 5.8 Comparison of the dispersivity values for all soils combined through finite particle approach.

It can be seen that the proposed measure of dispersivity obtained through the finite particle approach is proportional to the double hydrometer test results immaterial of the soil type or the type of treatment. The dispersivity calculated through the finite particle approach serves as an ideal measure of estimating dispersivity. The issues associated with conventional methods such as the effect of a dispersing agent, absence of the effects of other parameters influencing dispersivity, time and effort with other methods etc. are completely solved. The zeta potential method is able to

1. Incorporate the effects of all parameters affecting dispersivity,
2. Avoid the application of a dispersing agent

3. Provide a quantitative measure of dispersivity
4. Save time and effort to a great extent.

5.7 SUMMARY

Estimation of dispersivity from the repulsion and attraction values through the usage of zeta potential is being presented in this chapter. The estimation was carried out by adopting two different approaches namely the infinitesimal particle approach and the finite particle approach. It is clearly visible that the dispersivity values obtained from both the approaches correlates well with the dispersivity obtained from other conventional methods. The finite particle approach could be used for assessing dispersivity if the physical conditions of the soil are given; i.e. when the physical properties governing the attraction and repulsion such as density, void ratio and mean particle diameter are given. When such information is not provided the finite particle approach could be used.

It is also noticed that the dispersivity obtained from the finite particle approach is immaterial of the soil type. The dispersivity solely depends upon the zeta potential values of the soils. Thus the method could serve as the ideal method for assessing dispersivity if just the zeta potential values are known. It is interesting to note that, the attractive energy in a soil mass from infinitesimal particle approach is of the order of 10^{-16} - 10^{-17} J; while repulsive energies are of far greater magnitudes. This means that even in soils having lesser monovalent ion concentration, repulsion dominates over attraction and causes dispersion. This can be considered as the reason why all soils can be considered dispersive even though the degree varies considerably. Also, as the repulsive energy is the least affected by the attraction (with respect to dispersion), it is sufficient to calculate just the repulsive force

in the soil which makes the estimation even easier. Another common problem associated when dealing with the stability of clay colloidal suspension is the selection of a proper Hamaker constant. Various authors use different Hamaker constant values without a proper justification for their choice (Missana and Adell 2000) which makes the results not comparable. As repulsive forces are far more dominant, the choice of a Hamaker constant is less significant.

The DLVO theory suggests the usage of a parameter called Stability ratio for assessing the stability of colloids. The stability ratio (W) is given by

$$W = 2r \int_{2r}^{\infty} \exp\left(\frac{\Delta G}{kT}\right) \frac{dh}{h^2} \dots\dots\dots(5.29)$$

Where, ΔG is the total interaction energy between two particles, k is the Boltzmann constant, T is the temperature and h is the separation distance between the particles.

The stability ratio varies with the square of zeta potential. Often it is approximated that, for a stable colloidal dispersion,

$$\zeta^2 \geq \frac{10^3}{Dr} \text{ With } \zeta \text{ in mV and } r \text{ in } \mu\text{m} \dots\dots\dots(5.30)$$

It is interesting to note that the derived expression of total repulsive energy in a soil mass for calculating the dispersivity of soils also varies with the square of the zeta potential making a resemblance with the stability ratio.

CHAPTER 6

APPROPRIATE CONDITIONS FOR THE MEASUREMENT OF ZETA POTENTIAL

6.1 INTRODUCTION

As discussed in **Chapters 4 and 5**, zeta potential plays a very important role in the dispersive characteristics of soils and thus a precise measurement of the same is very trivial in determining the dispersivity. As described in **Chapter 2**, zeta potential is usually calculated using Henry's equation, Smoluchowski's equation and Huckel's equation which gives the relation between electrophoretic mobility and zeta potential. Henry's model is the most accepted and commonly adopted method for zeta potential measurements. Several procedures have been reported for measuring the zeta potential of soils. Akbult and Arasan (2010) allowed the soil samples to tend for 5 min to let larger particles settle and measured the zeta potential on the supernatant. Decker (1977) conducted the experiments on 1:10 clay-water ratio by agitating the mixture in a mechanical shaker for half an hour and then subsequently centrifuging them for 5 min at 3000 rpm. Sajjan et al. (2012) took 1g of sample, passed through 75 μ IS sieve in 100 mL distilled water, added in beaker and rinsed for 24 hrs at room temperature. The samples were stirred and allowed to tend for 5 min to let larger particles settle. Zeta potential measurements were then conducted on the supernatant.

Thus it can be seen that various researchers use various measurement procedure for estimating the zeta potential. The procedures adopted lack theoretical backgrounds and hence the results obtained have very less reproducibility. It is clearly visible that several ambiguities exist surrounding the zeta potential measurement. Numerous aspects such as the

amount of soil, size of the soil fractions, solid: liquid ratio, shaking time or the requirement of the application of any filtering/centrifuging techniques are not well established. The procedure for materializing an ideal soil-water suspension for zeta potential measurement is highly speculative. Due to these reasons and to quantify dispersivity more accurately from zeta potential values, the experiment procedure is normalized. The present chapter deals with the standardization of the measurement procedure of zeta potential test pertaining to dispersivity.

6.2 IDEAL CONDITIONS FOR ZETA POTENTIAL MEASUREMENTS

From the analysis of the various theories of zeta potential measurements as described in **Chapter 2** it could be inferred that even though there are factors such as viscosity, or dielectric constant of the medium which affect the zeta potential values, the fundamental property governing the zeta potential is the electrokinetic property of the soil solute which is primarily the electrophoretic mobility. Thus a non erroneous estimation of the electrophoretic mobility of soils is very essential to obtain an accurate value of zeta potential.

The electrophoretic mobility (μ_E) of the soil solute is the ratio of velocity of the soil particle (v) to the applied electric field (E) which is causing the movement of the clay particle.

$$\mu_E = \frac{v}{E} \dots\dots\dots(6.1)$$

When an electric field is applied on a soil water suspension, clay particles as they are negatively charged, will move towards the positive electrode. The velocities with which the clay particles move are recorded from which electrophoretic mobility and hence the zeta potential is calculated. It should be noted that the velocity of a suspended particle is the resultant of a combined effect of the surface charge density (which is causing the movement)

and the resistance offered by viscous forces in the liquid. The viscous force acting on the solute depends on the particle size and hence can have an effect on the electrophoretic mobility. Thus, the particle size for zeta potential measurement needs to be carefully chosen as the zeta potential is a function of primarily the surface charge density as from theoretical backgrounds and as the value sufficiently represents the zeta potential of the soil.

In practical situations a soil can have wide ranges of particle sizes and hence may display various electrophoretic mobility values. In such cases, an average value of the electrophoretic mobility is adopted for zeta potential calculations which may lead to high standard deviation values and hence the accuracy of the value could be seriously questioned. Thus, an ideal test suspension is the one that is in a homogeneous state which is practically difficult. More homogeneous the mixture more will be the accuracy of the calculated zeta potential.

In perspective of the stability of a soil water suspension, the optimal condition for finding the electrophoretic mobility is the condition wherein the particles suspended in a liquid exist in Brownian motion as such a condition would offer an easier and precise measurement of the velocity values. Several studies report the requirement of Brownian motion to exist for accurate zeta potential measurements. Palanisami and Miller (2010) reported that the size resolution increases as the particles size decreases due to the increased Brownian motion. The particle interactions in a fluid base can lead to formation of aggregates or clusters which can have a significant effect on the flow behavior and the transport properties of the particles and thus the electrophoretic mobility values (Michaelides 2014). The Brownian motion of particles is the property that doesn't allow the particles to

settle and thus helps in the measurement of electrophoretic mobility. If particles do not undergo Brownian motion they would settle down leading to erroneous results.

6.3 ESTABLISHMENT OF THE OPTIMAL CONDITIONS FOR ZETA POTENTIAL MEASUREMENTS

6.3.1 Forces deciding the stability of a solute particle

The fundamental forces which affect the stability of a solute particle in a colloidal suspension are the Brownian forces and Gravitational forces. If particles are denser than suspending liquid, they would settle as they are acted upon by the gravitational forces. The Brownian forces act opposite to gravity due to which the particles try to diffuse away from the sediment layer at bottom of a container. These forces are responsible for maintaining the dispersion of soil particles in suspension. The ratio of gravitational forces to Brownian forces acting on a solute particle is the commonly used parameter for deciding whether the solute has the ability to remain in the state of suspension or not. The ratio is given by

$$\frac{4\pi r^4 \Delta\rho g}{3k_B T} \quad (\text{McKetta 1976}) \dots\dots\dots(6.2)$$

Where,

$\Delta\rho$ is the difference in densities of the particle and the fluid (kg/m^3)

g is acceleration due to gravity (9.81m/s^2),

k_B is Boltzmann constant ($1.38 \times 10^{-23} \text{m}^2 \text{kg s}^{-2} \text{K}^{-1}$)

T is absolute temperature of suspending fluid (in K).

If the Brownian forces are dominant and larger than Gravitational forces then the soil particles will remain dispersed. That is when the ratio is less than unity.

Assigning a temperature of 300 K (27°C) and a density of water as 1000 kg/m³, the radius values are obtained as,

$$r < 0.5009\mu\text{m for Suddha soil,}$$

$$r < 0.4964\mu\text{m for Black Cotton soil and,}$$

$$r < 0.5041\mu\text{m for Red soil.}$$

To summarize, the particle size of Suddha soil, Black Cotton soil and Red soil must be less than 0.5009 μm , 0.4964 μm and 0.5041 μm respectively for a stable suspension ensuring Brownian motion for accurate zeta potential measurement.

It is also to be made clear that the particles should not be finer than the order of a few nanometers as it would be difficult to identify and resolve particles of different electrophoretic mobility values.

6.3.2 Role of other parameters

Factors such as amount of soil, solid liquid ratio and shaking time could be fixed as per the double hydrometer standards so that the verification of the values could be done by comparing it with the double hydrometer test results. Even otherwise, these parameters could be conveniently neglected as properties such as electrophoretic mobility or zeta potential basically are the characteristics of a single clay particle and thus is not dependent on the amount of soil or the ratio at which they are present in the test sample.

6.4 EXPERIMENTAL DESIGN

In order to study the relevance or the role of Brownian motion in zeta potential measurements, soil-water suspensions using Suddha soil, Black Cotton soil and Red soil were prepared. Potassium hydroxide treated, sodium hydroxide treated, lithium hydroxide treated and untreated soils (as prepared in **Chapter 5**) were used for the measurements. In

order to co-relate with double hydrometer test results, the solid liquid ratio for the test suspensions were fixed as 1:25. 4 g of soil was added to 100 ml water and were kept for shaking for 90 minutes replicating the conditions as in double hydrometer. Soil water suspensions passing 0.45 μ , 2.5 μ and without any filtering were prepared as above for zeta potential measurement. Millipore (Durapore HVLP 0.45 μ m) filter paper was used for filtering the soil suspension and the filtering was done through vacuum suction. As the particle sizes obtained above for various soils were higher than 0.45 μ , these samples could sufficiently be used for studying the influence of Brownian motion. Whatman 42 filter paper was used for obtaining a soil water suspension finer than 2.5 μ . This size was fixed so as to provide an intermediate range of particle sizes. In order to study the accuracy of measurement in the natural state, a soil water suspension without any screening or filtering was also used. Zeta potential of the various soil suspensions were measured using Zetasizer nano series – Zen 3690 (Malvern Instruments) which uses Henry's model for evaluating the zeta potential. The measurements were carried out by performing 300 iterations in each of the 3 cycles.

6.5 ANALYSES OF RESULTS

Researchers employ the usage of a parameter called “zeta deviation” which indicates the accuracy or the acceptability of the zeta potential distribution. The value takes into account the variations in the electrophoretic mobility measurements, dielectric constant, viscosity values, Henry's function etc. It should be specifically noted that zeta deviation is not the deviation from the mean values of the distribution. The parameter could be perceived as a function of the higher moments of the zeta potential distribution. A lower value of the deviation indicates a higher uniformity in the zeta potential values in the distribution. The

zeta potentials of the soils along with the observed zeta deviations (Z.D) during the measurements for various filtered samples are as shown in Table 6.1, 6.2 and 6.3.

Table 6.1 Zeta potential values of unfiltered samples

Soil	Treatment	Zeta potential values without filtering (mV)			Average (mV)	Z.D (mV)
		Cycle 1	Cycle 2	Cycle 3		
Suddha soil	Untreated	-5.69	-6.98	-7.69	-6.79	95.61
	KOH treated	-14.12	-11.87	-13.55	-13.18	94.25
	NaOH treated	-18.67	-16.56	-20.68	-18.64	92.33
	LiOH treated	-26.20	-29.70	-31.80	-29.23	86.65
Black cotton soil	Untreated	-4.46	-11.30	-9.14	-8.30	97.27
	KOH treated	-13.64	-10.58	-11.11	-11.78	87.78
	NaOH treated	-18.98	-17.98	-18.67	-18.54	79.40
	LiOH treated	-30.90	-28.40	-34.69	-31.33	88.88
Red soil	Untreated	-2.41	-5.04	-7.00	-4.82	96.16
	KOH treated	-18.54	-17.96	-16.13	-17.54	79.63
	NaOH treated	-17.55	-22.85	-15.69	-18.70	83.94
	LiOH treated	-31.60	-35.10	-29.30	-32.00	74.12

Table 6.2 Zeta potential values of 2.5 μ filtered samples

Soil	Treatment	Zeta potential values by 2.5 μ filtering (mV)			Average (mV)	Z.D (mV)
		Cycle 1	Cycle 2	Cycle 3		
Suddha soil	Untreated	-7.12	-7.23	-7.64	-7.33	43.57
	KOH treated	-14.51	-14.83	-14.31	-14.55	34.68
	NaOH treated	-19.44	-19.00	-19.05	-19.16	33.54
	LiOH treated	-32.55	-32.26	-32.05	-32.29	51.27
Black cotton soil	Untreated	-4.54	-4.18	-4.15	-4.29	43.54
	KOH treated	-12.97	-12.13	-12.57	-12.56	41.05
	NaOH treated	-17.62	-17.18	-17.99	-17.60	39.97
	LiOH treated	-32.42	-32.64	-32.33	-32.46	33.33
Red soil	Untreated	-3.15	-3.57	-3.00	-3.24	37.74
	KOH treated	-16.87	-16.08	-16.96	-16.64	35.55
	NaOH treated	-20.19	-20.77	-20.88	-20.61	44.44
	LiOH treated	-34.00	-34.55	-33.16	-33.90	48.84

Table 6.3 Zeta potential values of 0.45 μ filtered samples

Soil	Treatment	Zeta potential values by			Average (mV)	Z.D (mV)
		0.45 μ filtering (mV)				
		Cycle 1	Cycle 2	Cycle 3		
Suddha soil	Untreated	-7.12	-7.11	-7.11	-7.11	1.65
	KOH treated	-14.02	-14.01	-14.02	-14.02	1.45
	NaOH treated	-19.06	-19.04	-19.05	-19.05	2.68
	LiOH treated	-32.05	-32.06	-32.05	-32.05	1.68
Black cotton soil	Untreated	-4.85	-4.81	-4.82	-4.83	3.61
	KOH treated	-12.86	-12.86	-12.86	-12.86	1.04
	NaOH treated	-17.97	-17.98	-17.98	-17.98	3.01
	LiOH treated	-32.24	-32.25	-32.26	-32.25	2.54
Red soil	Untreated	-3.51	-3.50	-3.50	-3.50	2.11
	KOH treated	-16.55	-16.53	-16.54	-16.54	3.67
	NaOH treated	-20.84	-20.85	-20.86	-20.85	1.74
	LiOH treated	-34.02	-34.00	-33.98	-34.00	1.98

From Table 6.1, it is clearly visible that the zeta deviation values are very high for unfiltered samples. There is a high variation in the values obtained in the various cycles of zeta potential measurement. This can be attributed to the variations in the electrophoretic mobility measurements due to the differences in the particle size. When the samples undergo no filtration, the heterogeneity in the samples would be high as there would be varying

particle sizes in the mixture. This can cause huge variations in the electrophoretic mobility values and hence the zeta potentials.

When the samples are filtered through 2.5 μ pore sized filter paper it can be seen that the variation is reduced greatly due to the higher uniformity in the distribution. The zeta deviation in the values is more than around 30 mV which still makes the values unacceptable.

In Table 6.3, it can be noted that the variation in the zeta potential values are very less. The zeta deviations of the samples are less than 4 % which is acceptable. The reason for this low variation in the distribution could be assigned to the presence of Brownian motion in the samples. As the particles, are finer than the size required for exhibiting Brownian motion, they do not undergo settling and hence make the estimation of the electrophoretic mobility accurate. The particles neither rise nor fall out of the stationary level under the influence of gravity while the measurements are being done. A zeta deviation less than 5 mV is generally considered good and acceptable. Table 6.4 shows the zeta potential values and dispersivity values obtained through double hydrometer test for various soils.

Table 6.4 Zeta potential and dispersivity values

Soil	Treatment	Zeta potential (mV)	Dispersivity by D.H (%)
Suddha soil	Untreated	-7.11	21
	KOH treated	-14.02	33
	NaOH treated	-19.05	52
	LiOH treated	-32.05	69
Black cotton soil	Untreated	-4.83	14
	KOH treated	-12.86	29
	NaOH treated	-17.98	42
	LiOH treated	-32.25	72
Red soil	Untreated	-3.50	9
	KOH treated	-16.54	36
	NaOH treated	-20.85	60
	LiOH treated	-34.00	110

Figure 6.1 shows the plot between the zeta potential values and dispersivity values obtained by double hydrometer test.

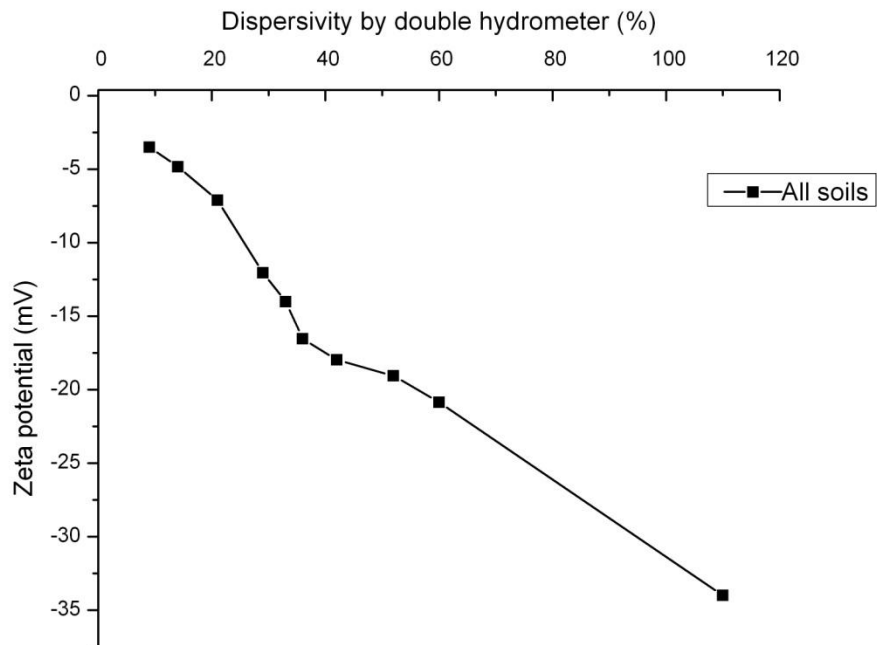


Figure 6.1 Zeta potential vs double hydrometer dispersivity.

From Figure 6.1, it can be seen that the zeta potential obtained for samples finer than 0.45μ matches well with the double hydrometer dispersivity. The zeta potential values correlates well with double hydrometer test results irrespective of the soil type. In **Chapter 5**, it was revealed that dispersivity could be estimated from zeta potentials by calculating the repulsion caused, offering a new method of assessing dispersivity. Since zeta potential of the soil is independent of particle size the potential dispersion in the soils could even be estimated from zeta potential by correlating it to double hydrometer test results. The process of estimating dispersivity by calculating the repulsion between the particles could be avoided if the drawbacks associated with the double hydrometer test are conveniently neglected. The value of zeta potential sufficiently could quantify the amount of dispersion in soils.

6.6 SUMMARY

The experimental procedure of estimating zeta potential from the perspective of measuring dispersivity of soils has been standardized. The soil samples finer than 0.45μ show acceptable values of zeta deviation and hence could be used as a standard procedure for estimating zeta potentials. It can also be concluded that the presence of Brownian motion makes the assessment of zeta potential through electrophoretic measurements easier and accurate. The variation in the values would be lesser as the particles do not settle under the influence of gravity. It is also proposed from fundamental theoretical considerations that parameters such as solid liquid ratio, amount of soils, shaking time does not play a major role in zeta potential measurements. The measurements would still be accurate if any reasonable and sensible values of the same are adopted.

CHAPTER 7

ROLE OF MONOVALENT CATIONS IN DISPERSIVITY OF SOILS

7.1 INTRODUCTION

In previous chapters the relationship between zeta potential with dispersivity of soils along with estimation of dispersivity from the zeta potential of soils has been presented. This chapter presents emphatic role played by monovalent cations present in the soil on the dispersivity. Existing literatures highlights the dependency of primarily the sodium ion on dispersivity of soils. Various factors such as cation exchange capacity, electrolyte concentration, pH, type of clay minerals, dissolved salts and other monovalent ions, if present on the dispersivity of soils have been elaborated in **Chapter 2**. The role of monovalent cations in general, in dispersion of soils has not been specifically brought out. The mechanism of dispersivity vis a vis the role of monovalent cations has been not explicitly established. This chapter offers an explanation of how other factors influence the dispersivity of soils as well as their relationship with the type of monovalent cations on the soil. The role of ionic size (within the monovalent cations) on dispersivity of clayey soils is also brought out here. Apart from the cations it is known that anionic part also plays a role on the dispersivity of soils. Since hydroxide ions aid dispersion, while considering the effects of cations, the influence of the hydroxyl ions is also considered here.

7.2 EXPERIMENTAL DESIGN

To understand the relationship of these factors with the repulsive pressure as well as their role in the dispersivity of soils within the same valency, dispersivity measurements made on untreated, potassium hydroxide treated, sodium hydroxide treated and lithium hydroxide treated

samples of Suddha soil, Black cotton soil and Red soil are analyzed from the perspectives of monovalent cations, pH and electrolyte/dissolved salts effects. In addition, in order to study the applicability of common geotechnical characteristics of soil in assessing the dispersive behavior of soils, studies are also made by comparing the various geotechnical properties of soils.

7.3 RESULTS

7.3.1 Physico chemical and index properties of the soils

Table 7.1 Physico chemical and index properties of soils

Soil	Treatment	L.L (%)	P.L (%)	S.L (%)	MFSI	pH	TIC (cmol/kg)
Suddha soil	Untreated	69	34	22	2	6.3	51.45
	KOH treated	76	39	21	2.2	7.9	100.35
	NaOH treated	80	42	16	2.5	9.4	136.00
	LiOH treated	94	44	10	2.9	10.9	325.14
Black cotton soil	Untreated	74	32	12	2.1	5.7	59.75
	KOH treated	79	35	10	2.3	7.5	204.74
	NaOH treated	85	37	10	2.7	9.0	253.83
	LiOH treated	92	42	9	3.0	10.8	452.51
Red soil	Untreated	30	29	28	1.1	7.0	20.19
	KOH treated	32	30	19	1.9	8.2	105.03
	NaOH treated	36	31	15	2.3	9.6	171.28
	LiOH treated	40	32	11	2.8	10.0	325.14

Table 7.1 shows the values of Atterberg limits, Swell indices pH and total ion concentration of untreated natural soil, potassium, sodium and lithium treated soils. The total ion concentration expressed is the sum of the total sodium, potassium, calcium, magnesium and lithium ions in this chapter unlike in **Chapter 4**.

It can be seen that with the increase of sodium or lithium concentration the geotechnical properties of the soil are significantly altered. The liquid limit and plastic limit of the soil have increased and the shrinkage limit has decreased. These changes suggest an increase in the repulsive pressure of the soil particles. The soils have become more alkaline as noted by an increase in pH which is due to the presence of alkaline hydroxyl ions. In the untreated soil the amounts of sodium and potassium is very less with lithium being almost negligible. The amounts of sodium, potassium and lithium in the untreated soils are considered in total whether present as exchangeable ions or present in pore fluid. With the treatment of the soil with potassium hydroxide solution, both the potassium content and total ion concentration increase. Similarly, with the treatment of the soil with sodium hydroxide and lithium hydroxide, concentration of sodium and lithium ion concentrations increase respectively along with increase in the total ion concentration (Table 7.1). Though all soils treated with monovalent ions shown higher dispersivity as seen in **Chapter 5** the increase is more for lithium soils. This can be attributed to the replacement of other exchangeable ions by lithium due to its lower ionic size compared to other cations. The exchangeable lithium in soil increases the pressure even with an increase in the total ionic concentration. This is due to predominant role played by exchangeable ion compared to the effect of pore fluid electrolyte concentration. Whenever a soil is treated with hydroxide salts of monovalent cations such as potassium sodium or lithium, there occurs an increase in the electrolyte concentration of the pore fluid along with increase in pH. It is well

understood that with increase in the amount of hydroxyl ions there will be an increase in the cation exchange capacity of clays itself slightly. The replacement of exchangeable ions together with the increase in the cation exchange capacity dominates over the effect of increase in electrolyte concentration and thus the net repulsive pressure increases. This in turn increases the water holding capacity, as indicated by the increase in liquid limit. The increase in pH and replacement of exchangeable ions by potassium/sodium/lithium dominates over the effect of increase in electrolyte concentration. This is further supported by the increase in the liquid limit of the various treated soils compared to the untreated. The effect of monovalent ionic size is seen even at higher electrolyte concentration for all soils. The variations in liquid limit in different soils treated soil is support of this mechanism. It is known that the higher sized hydrated lithium ion (10.03 Å) can increase the repulsive pressure more than a hydrated sodium ion (7.90 Å) or potassium ion (5.32 Å). The lower repulsive pressure and reduction in water holding capacity indicated by liquid limit with potassium treated soil when compared with sodium/lithium treated soils may also be due to potassium fixation in the soil. In Black Cotton soil, as montmorillonite is the principal clay mineral, potassium ions bridge the 2:1 layers of montmorillonite more effectively. Thus the liquid limit of Suddha soil and Black Cotton soil treated with potassium are almost similar.

7.3.2 Dispersivity assessment from fabric chart using geotechnical properties

The nature of the fabric can be estimated by comparing the liquid limit of a soil with its shrinkage limit (Sivapullaiah et al. 2000). In a flocculated soil the liquid limit and the shrinkage limit will be generally high whereas an aggregated soil is characterized by a higher shrinkage limit and a lower liquid limit. When a soil possesses a dispersive fabric, the soil would exhibit a high liquid limit and a low shrinkage limit. Using these information Sivapullaiah et al. (2000)

developed a fabric chart for identification of fabric of soil particles. Figures 7.1 to 7.3 show fabric charts, as developed for Suddha soil, Black Cotton soil and Red soil respectively.

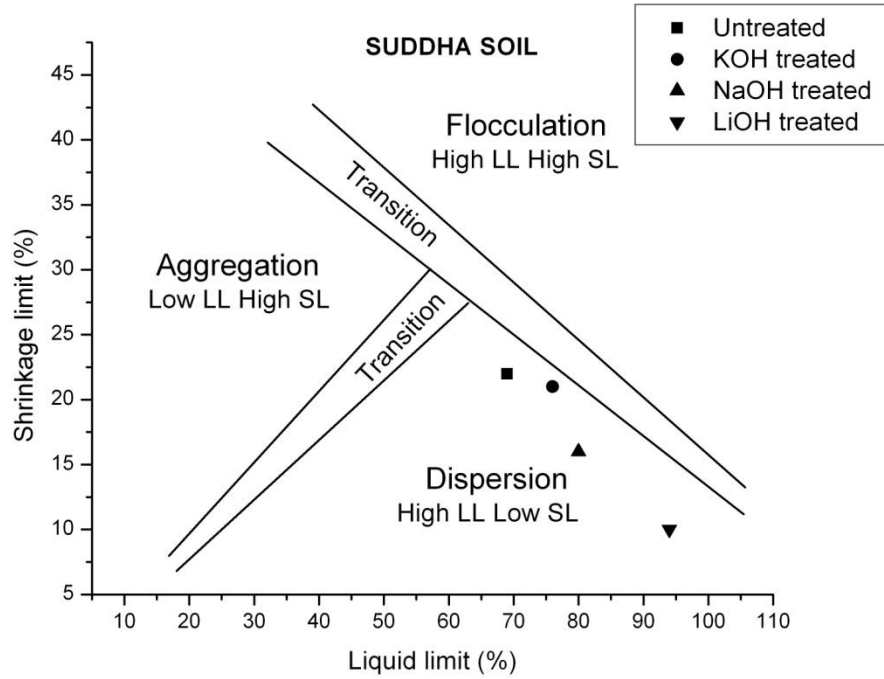


Figure 7.1 Fabric chart of Suddha soil

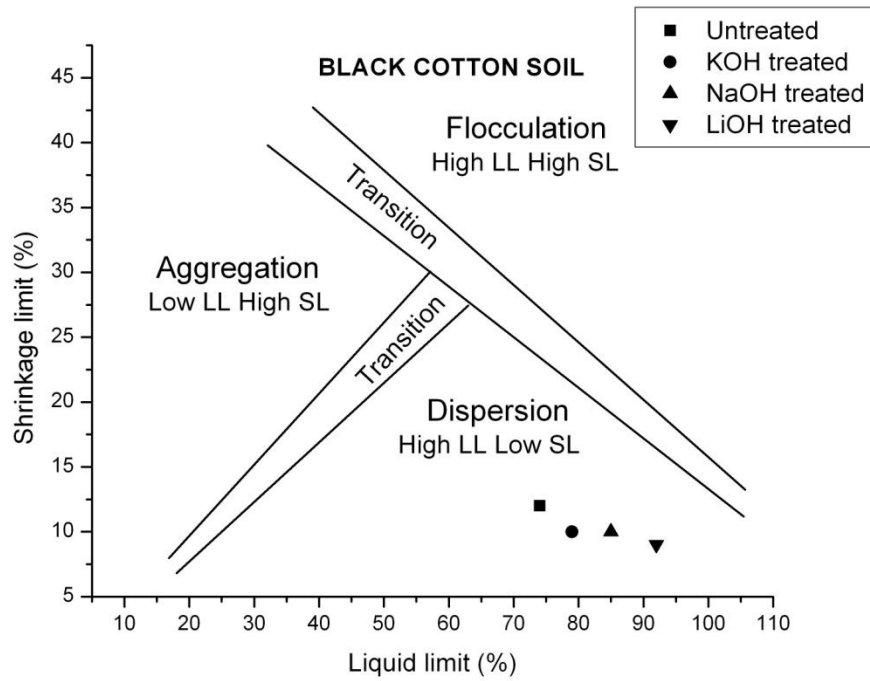


Figure 7.2 Fabric chart of Black Cotton soil

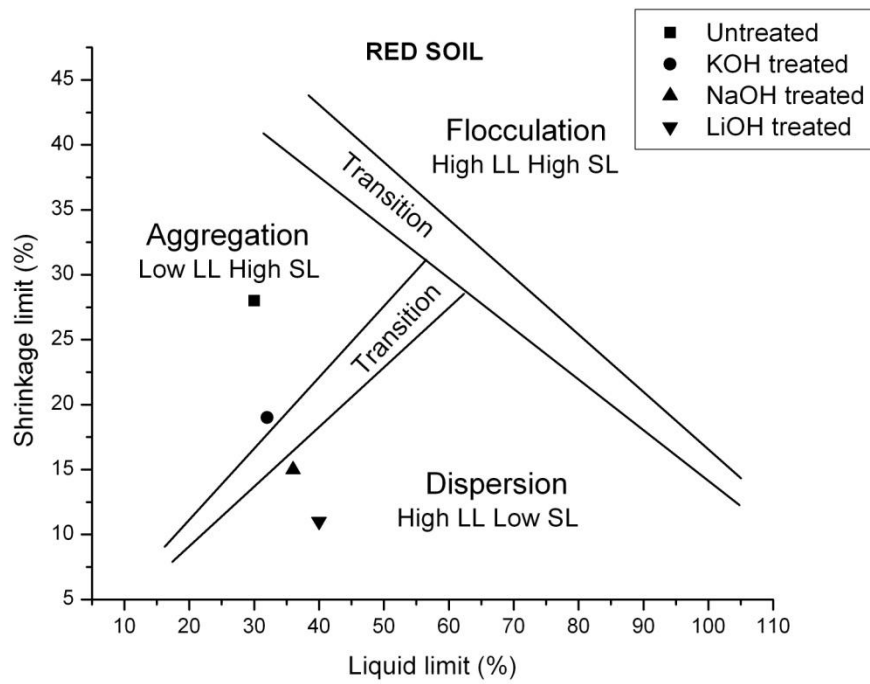


Figure 7.3 Fabric chart of Red soil

From the analysis of the fabric charts it can be seen clearly that even for an untreated soil which falls in the non - dispersion zone, when treated with monovalent cations of smaller radii, the soils becomes more and more dispersive due to the increase in the repulsive pressure. Suddha soil and Black Cotton soil which were in the dispersion zone tend to be even more dispersive by the addition of the monovalent cations. The soils are characterized by an increased liquid limit and decreased shrinkage limit. In the case of Red soil, the soil treated with sodium and lithium clearly moves toward dispersion zone where soil treated with potassium is near the zone between dispersion and aggregation. Thus potassium hydroxide treated Red soil is at the border line of the dispersion zone and aggregation zone. When treated with sodium or lithium hydroxide, the soil becomes more dispersed and completely falls into the dispersion zone. This clearly indicates that even for soils possessing an aggregated or flocculated structure, the fabric changes to a dispersed structure when the concentration of monovalent cations is increased. The changes occurring to the structure would be higher if the size of the monovalent cation is lesser.

7.3.3 Compaction characteristics

Several factors such as density, structure of the soil, strength and water holding capacity may possibly affect the dispersivity of soils. The dispersion properties of the soil can be gauged from the compaction characteristics of the soil. A more dispersed structure will exhibit higher optimum moisture content (OMC) and a reduced maximum dry density (MDD). The OMC and MDD values obtained from compaction curves (Figures 7.4 to 7.6) along with their plasticity index values for the various treated soils are given in Table 7.2.

Table 7.2 Compaction characteristics and plasticity indices of soils

Soil	Treatment	OMC (%)	MDD (kg/m³)	Plasticity index (%)
Suddha soil	Untreated	28	1420.00	35
	KOH treated	33	1361.52	37
	NaOH treated	37	1303.46	38
	LiOH treated	40	1048.20	50
Black cotton soil	Untreated	32	1365.00	40
	KOH treated	35	1330.00	44
	NaOH treated	38	1295.00	48
	LiOH treated	43	1187.00	50
Red soil	Untreated	13	1913.00	1
	KOH treated	15	1652.29	2
	NaOH treated	17	1475.25	5
	LiOH treated	21	1048.20	8

Figure 7.4 to 7.6 shows the compaction curve of various treated soils.

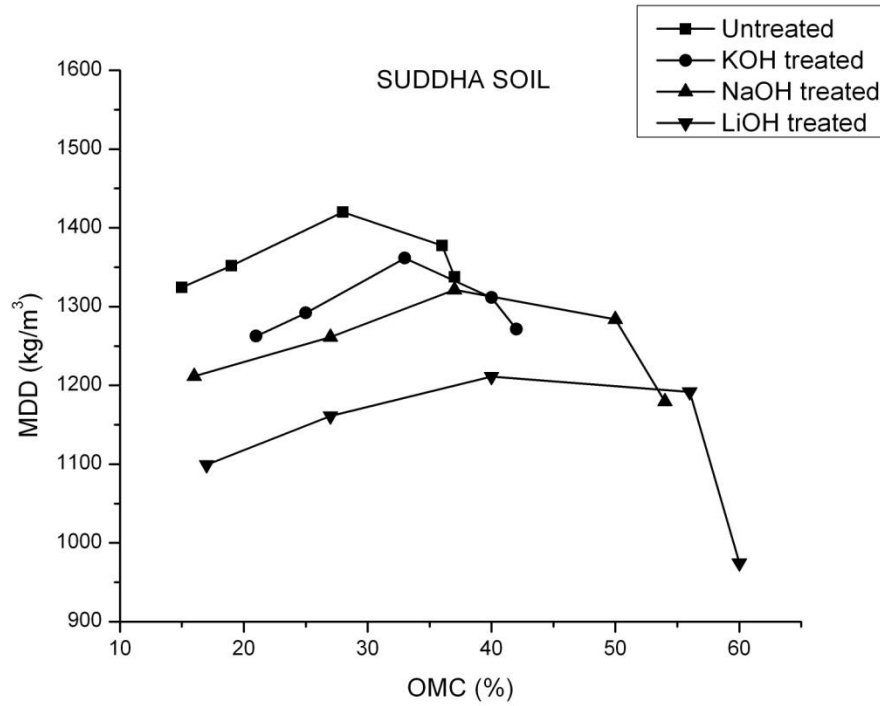


Figure 7.4 Compaction curves of Suddha soil

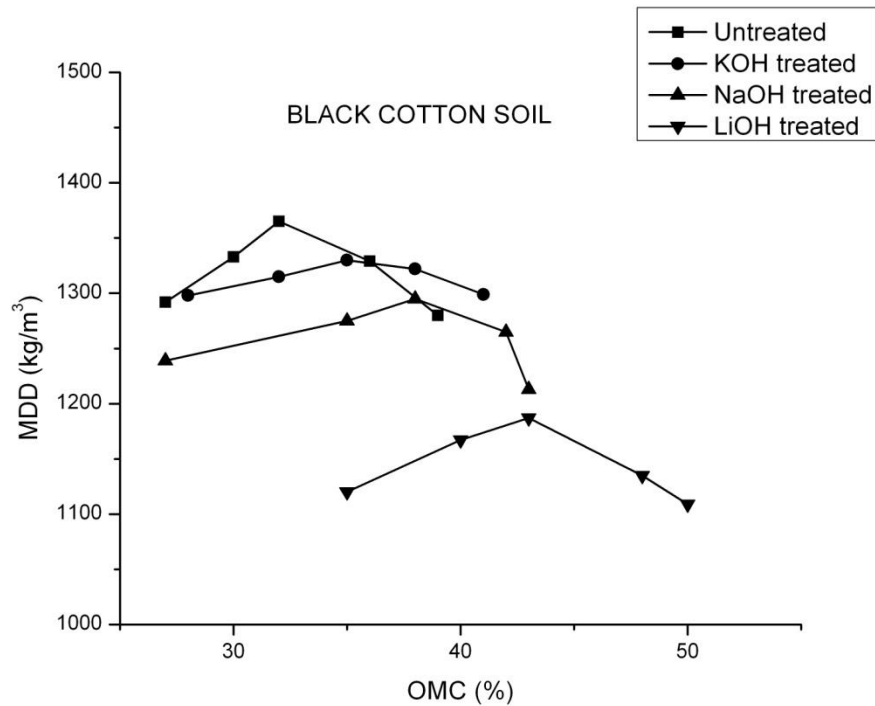


Figure 7.5 Compaction curves of Black Cotton soil

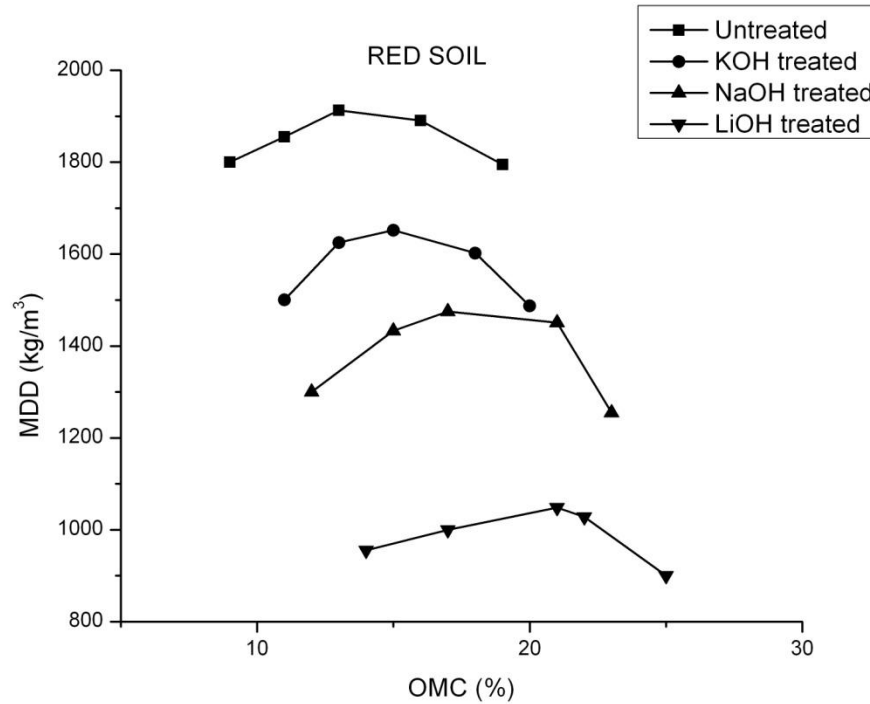


Figure 7.6 Compaction curves of Red soil

It can be observed that when the soil is treated with potassium, sodium or lithium hydroxide the soil becomes more deflocculated as indicated by an increased OMC and decreased MDD. The repulsive pressure generated as a result of increased surface charge on the clay surfaces and higher hydration of the monovalent cations makes the soil more dispersive. The increased repulsive pressure resists the compactive effort and increases the water holding capacity as indicated by the increased liquid limit. As the difference between the hydrated and unhydrated radius is higher for lithium (9.25 Å) than for sodium (6.92 Å) or potassium (3.99 Å), (Baver 1956) the repulsive pressure generated will be higher for lithium treated soils.

7.3.4 Role of plasticity in dispersivity

Several attempts have been made to correlate the index properties with compaction characteristics. However, recently Sridharan and Nagaraj (2005) have found that there is a good

correlation only with plastic limit. It was shown that the optimum moisture content is 0.92 times the plastic limit of the soil for flocculated soils. It is evident that addition of sodium or lithium hydroxide changes the fabric of the soil. When a well dispersed soil possesses high OMC and high plastic limit, a flocculated soil is associated with high plastic limit and a low OMC. The relationship between plastic limit and OMC for the treated and untreated soils along with their possible structure is shown in Figures 7.7, 7.8 and 7.9.

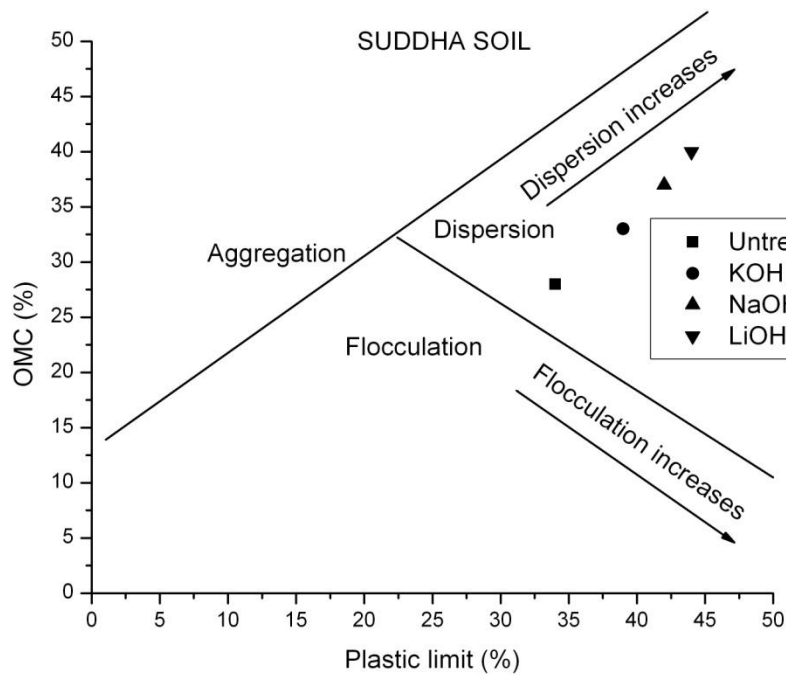


Figure 7.7 OMC vs plastic limit for Suddha soil

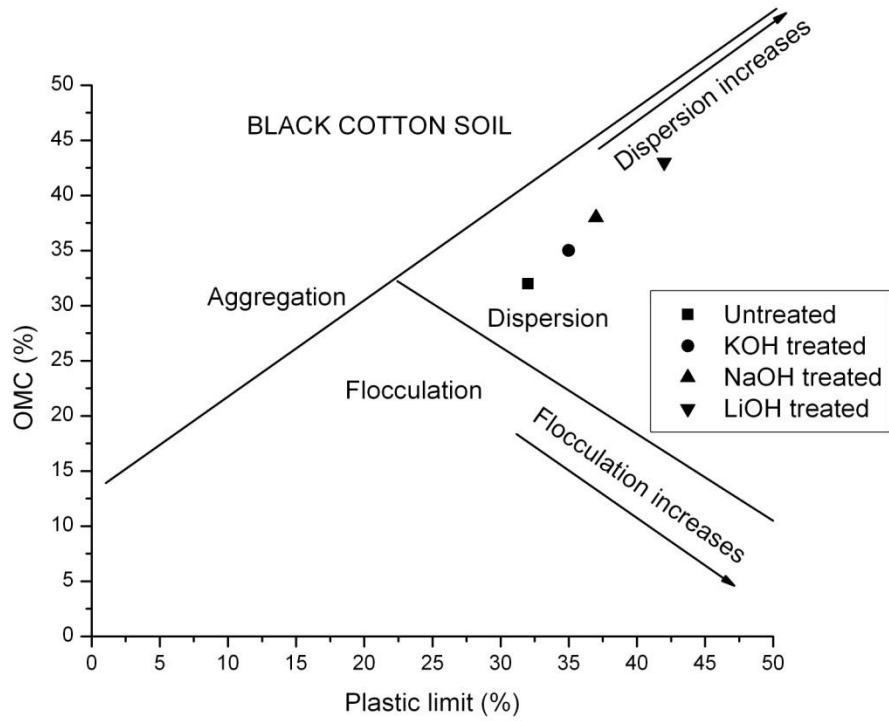


Figure 7.8 OMC vs plastic limit for Black Cotton soil

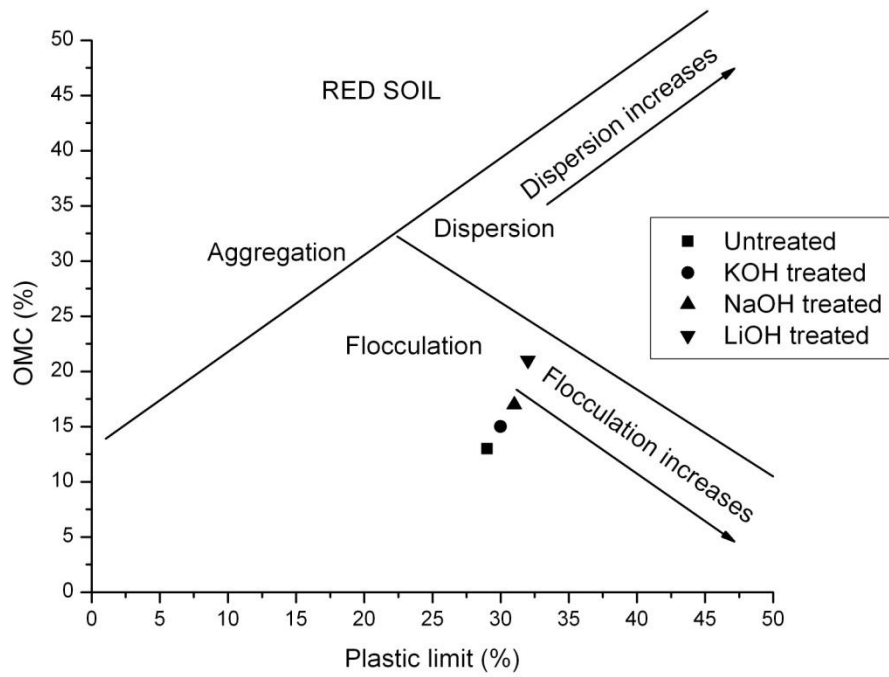


Figure 7.9 OMC vs plastic limit for Red soil

It can be noticed that the untreated soil is characterized by a lower plastic limit and a lower OMC. When the soil is treated with potassium, sodium or lithium hydroxide, the plasticity increases which in turn increases the OMC. Soils with higher plasticity exhibit more dispersivity. The addition of sodium or potassium hydroxide increases the amount of dispersion which is even higher when the treatment is done with lithium hydroxide. When the different soils are compared on the basis of this plasticity charts, it can be observed that Suddha soil and Black Cotton soil which were initially in the dispersion zone as per the chart become more and more dispersive due to the treatments. Red soil which is highly flocculated due to interlayer hydrogen bonding between kaolinitic clay minerals do not move into the dispersion zone even after the treatment with monovalent cation hydroxides. Thus unlike in the case of fabric chart presented in the previous section, the chart developed with plastic limit and OMC considerations may not be much sensitive to the dispersion characteristics of soils linked with hydrogen bonding particularly when the associated water contents are low (i.e. when soils are compacted at a defined water content).

Another attempt is made by relating the plasticity with shrinkage characteristics of the soil. Figures 7.10 to 7.12 show the relation between plasticity and shrinkage characteristics of different soils.

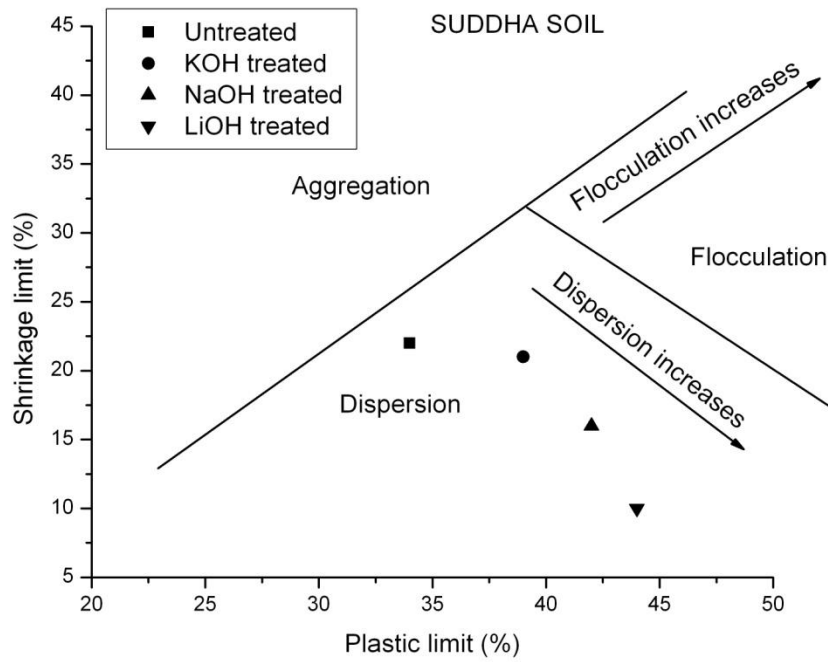


Figure 7.10 Shrinkage limit vs plastic limit for Suddha soil

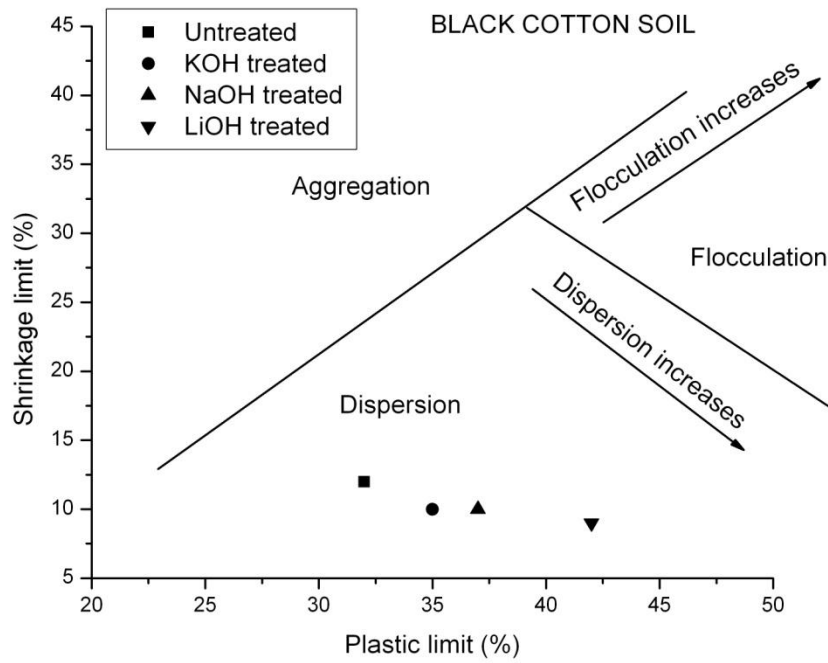


Figure 7.11 Shrinkage limit vs plastic limit for Black Cotton soil

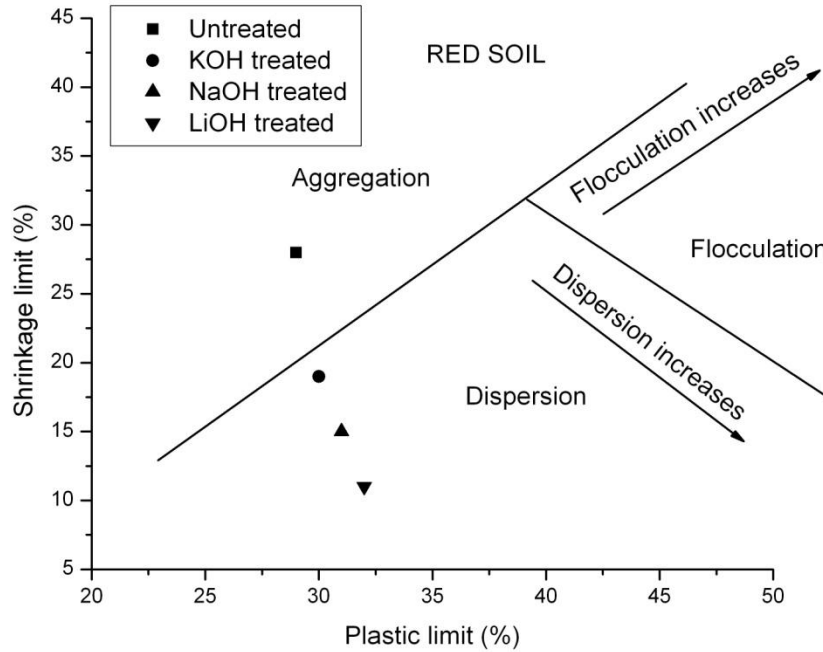


Figure 7.12 Shrinkage limit vs plastic limit for Red soil

From Figures 7.10, 7.11 and 7.12 it is evident that dispersivity is coupled with high plasticity and high shrinkage (low shrinkage limit). When the dispersivity increases the related plasticity and shrinkage of the soil also increases. It can be observed that the soils become more and more dispersive when treated with monovalent cations in their order of decreasing size. Another inference that could be made is that the plasticity chart based on shrinkage limit is able to represent the dispersivity of the soils better than that related with the OMC. This is primarily because of the higher sensitivity of the shrinkage limit to fabric changes than the compaction characteristics.

Most of the expansive soils contain minerals such as montmorillonite that are highly plastic which in the absence of any electrolyte will be dispersive due to an increased repulsive pressure between clay particles. On the other hand, non expansive soils such as those containing kaolinite having lesser plasticity will be naturally flocculated. In such soils if the plasticity is

increased, they also tend to be more dispersive. Also, plastic soils show lower shrinkage limit than non dispersive soils. This can be supported from the shrinkage limit considerations for the soil under study as shrinkage limit decreases with increase in dispersivity. Increase in liquid limit and decrease in shrinkage limit can occur due to the increase in plasticity and increase dispersion. The soil becomes more clayey and plastic as the ionic size of the adsorbed monovalent cation decreases as visible from Table 7.2.

7.3.5 Sensitivity of dispersivity measurements using different methods

As it can be seen, there are several methods or indicative geotechnical properties that could be used to define the state of dispersion in the soil. From Tables 5.4 and 5.5, and from the considerations of the various charts developed, it can be observed that the variation in the dispersivity values (measured for different samples) from the tests is the highest for tests such as double hydrometer and zeta potential. That is, the sensitivity of the test would be high when the associated water contents in the tests during measurements are high. As dispersivity is related with the behavior of a soil when it comes in contact with water, the effective behavior as the result of the interaction will not be fully reflected in a test if the water content is less. In tests such as double hydrometer or zeta potential the change in property is measured in a soil water suspension wherein the solid liquid ratio is very high. This ensures a complete interaction enabling the test to encompass even the slightest variations in properties.

7.4 ATTRACTIVE AND REPULSIVE FORCES AFFECTING DISPERSITY

In the untreated soil, the amounts of monovalent cations are less and hence the repulsive force they offer when hydrated is not so high. This can be observed from the values of Atterberg limits, pH, swell tests, compaction characteristics and dispersivity measurements by double hydrometer, zeta potential, UCS and shrinkage limit.

When soil is treated with potassium hydroxide, potassium ions get adsorbed on the clay surface making it more dispersive. The hydroxide ions also get adsorbed increasing the negative charge density of the clay which causes more repulsion between the particles. The effect of increased electrolyte concentration is dominated by the pH effect and by the increase in the monovalent ions. The presence of excess monovalent salts in the soil also contributes to the dispersivity of the soil. The plasticity of the soil is also increased which indicates the increase in repulsive pressure. The values given by double hydrometer, UCS and shrinkage limit confirm the higher amount of dispersion than of in the untreated soil.

When sodium hydroxide is added, the concentration of the sodium ions increases which causes an increase in the repulsion due to the higher hydrated size of the sodium ion. The negative charge density is also increased as in the case of potassium hydroxide. The contribution of pH and monovalency is higher than the influence of the electrolyte sodium hydroxide. The presence of exchangeable sodium along with dissolved sodium enhances the dispersivity of the soil as indicated by the results of conventional measurement of dispersivity.

Similarly, in the case of lithium hydroxide treatment, lithium ions and the adsorbed hydroxyl ions increase the dispersivity of the soil. As the dissociation of the salts into their corresponding anions and cations is more in this case, the changes in the properties will be even higher. In addition, as the difference between the unhydrated and hydrated ion radius is higher in the case of lithium than that of sodium the repulsive force offered towards dispersion will be more in lithium treated soils. The dispersivity values obtained from the tests are the highest for lithium treated soils. The soil becomes highly plastic and dispersed. The soil is completely dispersed as given by the various inter-relations.

When the concentration of dissolved salts or electrolyte concentration in the pore fluid increases, it leads to flocculation. On the contrary, increase in the amount of hydroxyl ions and exchangeable monovalent ions increases the repulsive pressure causing dispersion. In the present study, the soil is treated with potassium hydroxide, sodium hydroxide and lithium hydroxide. Thus the effect of electrolyte, pH, dissolved salts and monovalent ions come into action. It will be the net effect that decides the amount of dispersion in the soil. In order to obtain a complete picture, the conventional diffused double layer theory is used. The thickness of the diffused double layer is the key factor that controls the amount of dispersion and flocculation in a soil. When electrolyte concentration in the pore fluid and excess salts in the soil suppresses the diffused double layer, hydroxyl ions and monovalent cations causes an increase in the thickness. Properties such as water holding capacity, structure, plasticity and density can also be identified as some function of the diffused double layer thickness. The thickness of the electric double layer depends primarily on the type and concentration of ions in solution. If monovalent ions are present in the soil irrespective of the form in which they are present, this leads to increased swelling due to increase in repulsion compared to the divalent or higher ions. Thus the key factor controlling dispersion which incorporates the effects of all the above mentioned parameters can be concluded as the presence of monovalent cations in soil.

7.5 PHILOSOPHY OF DISPERSION

Soils are composed of both clay and a non clay fraction. Dispersion occurs in silty soils due to loss of cohesion upon saturation and the dispersivity of the non clayey fraction remains a constant irrespective of the treatment while the dispersivity of the clay fraction changes considerably due to the addition of ions in the soil. The conclusions from the study related with the dispersivity of clays are summarized below.

1. Even though there are several chemical factors such as CEC, pH, electrolyte concentration, type of clay minerals, dissolved salts etc. and physical factors such as plasticity, water holding capacity, density and structure which influence dispersion in soils, these factors affect either directly forces between the particles or the surface charge of clays which again affect the forces. The two phenomena can be combined through the hydration behavior of the adsorbed cations on the clay surface in view of dispersivity as- higher is the charge, higher will be the number of cations in the soil.
2. The hydration of an ion depends on the electrostatic attraction of water molecules to that ion. The hydration increases directly with the charge of an ion and inversely with its radius squared. Thus, the hydration is higher for ions of higher valency and smaller size. Such ions have a better ability to hold more number of water molecules close to them. The ions will have a thicker water hull and a larger outer hydration shell. In the case of monovalent ions, the ions are loosely held to the clay surfaces due to lower charge. Due to the lower charge, these ions do not have the ability to hold the water molecules close to them. Thus, the radius of the inner hydration shell will be higher for monovalent cations than those of higher valency ions and hence the difference between unhydrated radius and hydrated ionic radius will be greater for monovalent cations. This force due to hydration acts as the principal reason to separate the clay particles apart. The repulsion which dominates over the binding force (primarily the Van der waal's force) between the clay platelets causes the clay to swell and then to disperse.
3. The monovalent ions, whether present in the exchangeable complex or in the dissolved form contribute to dispersion through hydration as the solid liquid ratio is more. As per diffused double layer theory, the adsorbed cations are held strongly on the negatively

charged surface of dry fine-grained soil or clays and those cations in excess of those needed to neutralize electronegativity of clay particles and associated anions are present as salt precipitates. When dry clays come in contact with water, the precipitates go into solution and the adsorbed cations would try to diffuse away from the clay surface and tries to equalize the concentration throughout pore water. Water being a bipolar liquid, its molecules orient themselves and the positive part gets attracted to the negatively charged clay surfaces while the cations present in the soil get attracted to the negative end of the water molecules. As the ions get hydrated they get bigger in size and exert pressure on the system.

4. In the present study, lithium treated soil emerges out to be more dispersive than the sodium treated or potassium treated soil. This is due to the higher hydration of smaller ionic sized lithium ion. The repulsive pressure generated within the clay particles increases when the ionic size of the adsorbed monovalent cation decreases.
5. Out of the monovalent cations, sodium and potassium exist more common in soils than lithium. As the contribution of potassium ions towards dispersivity is of lesser magnitude, field practices involve measurement of dispersivity based on the amount of sodium. Even though the methods prove to be useful they cannot be considered theoretical. It is not the mere presence of sodium but the monovalent nature of sodium and lithium that causes the dispersivity as one can clearly see from the above discussion.
6. Dispersivity measurements for soils with different treatment are only to understand the mechanism. Dispersivity of the soil is best represented when the measurement is carried out in a soil water solution. Even though other tests/properties such as shrinkage, plasticity, compaction characteristics and compressive strength could give an indication

of dispersivity, the tests may not be able to replicate smaller variations in their values and hence double hydrometer or zeta potential method may be used.

CHAPTER 8

ESTIMATION OF DISPERSIVITY FROM MONOVALENT ION CONCENTRATION

8.1 INTRODUCTION

From **Chapter 7** it is clear that the hydration behavior of monovalent cations largely affects the dispersion in soils. The present chapter deals with the estimation of dispersivity from the concentration of monovalent cations in the soil. The swelling pressure resulting due to the hydration of monovalent cations is formulated from the osmotic pressure difference between the ion concentration within the soil and the external solution created by water. From the swell pressure values, the total repulsive energy in a soil mass is derived from fundamental theoretical considerations. The difference between the repulsive energy liberated through the hydration of ions and attractive energy is expressed as dispersivity. The derivations of the various expressions are described in detail in the following sections. The calculation of attractive energy has already been presented **Chapter 5**.

8.2 ESTIMATION OF REPULSION FROM MONOVALENT ION CONCENTRATION

The dispersivity proposed in this thesis is the release of energy that occurs when the repulsive force overcomes the force of attraction. In this chapter, an alternate perspective is taken wherein the repulsive force that causes dispersion in soils is attributed to the hydration of the monovalent cations adsorbed on the surface unlike in **Chapter 5**. When soils rich in monovalent cations come in contact with water, these ions hydrate and when the hydrated size of the ions become higher than the inter particle separation, the attractive force reduces;

the clay swells and ultimately leads to dispersion. The reason for swelling is attributed to the osmotic differences only because, swelling due to interlamellar hydration of minerals in clays is attributed to matric suction (Rao et al. 2013) which is insignificant at higher water contents (Fredlund and Rahardjo 1993). Also, since dispersion deals with soil particles in a colloidal suspension, the particle separation would be greater than 7 nm where the surface hydration is no longer important (Rengasamy and Naidu 1995). In addition, it is the presence of monovalent cations (salts) that causes the double-layer repulsion/swelling (Marchuk and Rengasamy 2012) and cause dispersion in soils as it is the only or by far the dominant force between the plates.

In a soil water suspension, the swelling pressure (P) existing can be calculated as the difference between osmotic pressure of the solution and the osmotic pressure of its equilibrium dialyzate (Sparks 1999; Lal 2006).

i.e.
$$P = R_g T (C_c - 2C_0) \dots\dots\dots(8.1)$$

Where,

C_c is the molar concentration of cations midway between the plates,

C_0 represents the local molar concentration of the solution,

R_g is the universal gas constant and T is the temperature in Kelvin.

In the case of dispersion, the solution under consideration can be taken as pure water; where in the salt concentration is negligible. Thus C_0 can be approximated to zero. The pressure developed will be those contributed by the adsorbed ions in the soil. This pressure acts over the entire surface area of clay. As it is difficult to get the total surface area of a clay mass, an approximation is made that the total surface area of the clay mass is equal to the

total surface area of the hydrated cations. This assumption holds good as a hydrated cation exerts force in all the directions.

Thus the repulsive force can be written as

$$R.F = C_c R_g T \times N_M \times 4\pi r_h^2 \dots\dots\dots(8.2)$$

Where, N_M is the total number of monovalent cations in the soil and r_h is the hydrated radius of the monovalent cation.

Since divalent or higher valency ions inhibit dispersion, the factor N_M should correspond to a relative number of monovalent cations that contributes to dispersion.

N_M can be expressed as

$$N_M = c \times 0.01 \times A_v \times M \dots\dots\dots(8.3)$$

Where, c is the equivalent concentration of monovalent cations contributing to dispersivity in cmol/kg, A_v is the Avogadro's number and M is the mass of the soil (kg).

$$c = \{ [MONOVALENT] / [DIVALENT] \} \times TIC \dots\dots\dots(8.4)$$

Where, [MONOVALENT] and [DIVALENT] represent the concentration of monovalent and divalent cations respectively; TIC corresponds to the total ion concentration in cmol/kg.

The repulsive energy is calculated as the repulsive force multiplied by the hydrated ion radius of the monovalent cation, r_h . The total repulsive energy will be the sum of energies of all the equivalent monovalent cations.

Now, as the swelling pressure leading to dispersion of soils is being dealt, C_c should correspond to an equivalent monovalent cation concentration in the soil mass per litre of the solution.

C_c could be found out as

$$C_c = \{[MONOVALENT]/[DIVALENT]\} \times TIC \times 0.01 \times M \quad \dots\dots\dots(8.5)$$

Substituting $R_g = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ the equation could be simplified as rewritten as

$$R.E = 6.29 \times 10^{21} \times [TIC]^2 \times M^2 \times F^2 \times r_h^3 \times T \quad \dots\dots\dots(8.6)$$

Where, F can be considered as a dominance factor equal to the ratio of monovalent cation concentration to the divalent.

The repulsive energy for a soil mass from monovalent ion concentration is as shown in Equation 8.6. The succeeding section narrates the mathematical calculation of the repulsive energies for various treated soils.

8.3 ESTIMATING REPULSIVE ENERGIES OF SOILS

The repulsive energy values of potassium hydroxide treated, sodium hydroxide treated, lithium hydroxide treated as well as that of untreated soil samples of Suddha soil, Black Cotton soil and Red soil are estimated here. The concentrations of various monovalent cations as reported in Table 5.2 are used here. Since the contribution of various monovalent cations towards dispersion is of different magnitudes, and since the concentration of each monovalent cation is different in each soil, the total repulsion is expressed as a sum of contributions of all the individual monovalent cation. The mass of soil is again kept as 40 g as in **Chapter 5** and a temperature of 300 K is taken. The hydrated radius of lithium ion (10.03 Å) sodium (7.90 Å) and potassium (5.32 Å) is used for the calculations (Baver 1956). Table 8.1 shows the values of Total repulsive energy values for various treated soils.

Table 8.1 Repulsive energies of soils

Soil	Treatment	T.R.E
Suddha soil	Untreated	1.86×10^{-6}
	KOH treated	5.22×10^{-3}
	NaOH treated	1.15×10^{-1}
	LiOH treated	2.68
Black cotton soil	Untreated	1.76×10^{-7}
	KOH treated	0.18
	NaOH treated	2.23
	LiOH treated	115.35
Red soil	Untreated	4.59×10^{-7}
	KOH treated	0.14
	NaOH treated	4.41
	LiOH treated	191.64

When treatments with hydroxide salts of monovalent cations are done on a soil, the concentrations of the monovalent cations increase. Thus there would result a higher repulsion in the soils as visible from Table 8.1. The variation with the repulsive energies obtained from this approach and liquid limit is as shown in Figure 8.1.

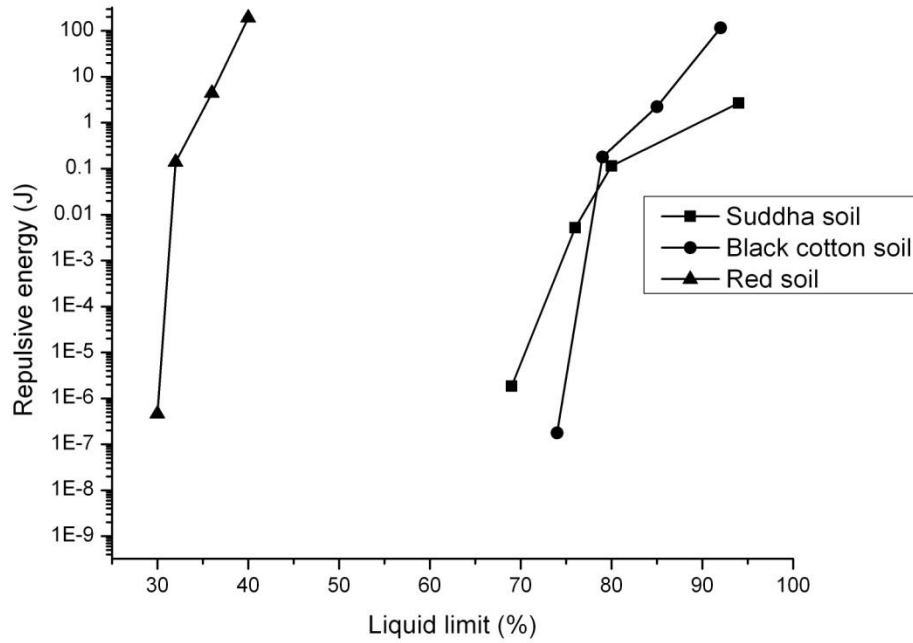


Figure 8.1 Variation of repulsive energy (from monovalent cations) with liquid limit.

Similar to **Chapter 5** it can be observed from Figure 8.1 that there is a good relation between the repulsive energy values obtained from the derived expression and with the liquid limit. The repulsive energy increases with the liquid limit of the various treated soils.

The expression derived for total attractive energy using infinitesimal particle approach (Equation 5.7) shall be used for estimating dispersivity (Table 5.4) as it is more reasonable.

Table 8.2 shows the values of dispersivity for the various treated soils.

Table 8.2 Dispersivity values from monovalent cation concentration

Soils	Treatment	D.H (%)	R-A values (J)		
			T.R.E (J)	T.A.E (J)	Dispersivity(J)
Suddha soil	Untreated	21	1.86×10^{-6}	3.01×10^{-17}	1.86×10^{-6}
	KOH treated	33	5.22×10^{-3}	2.74×10^{-17}	5.22×10^{-3}
	NaOH treated	52	1.15×10^{-1}	2.52×10^{-17}	1.15×10^{-1}
	LiOH treated	69	2.68	2.13×10^{-17}	2.68
Black cotton soil	Untreated	14	1.76×10^{-7}	8.53×10^{-17}	1.76×10^{-7}
	KOH treated	29	0.18	8.16×10^{-17}	0.18
	NaOH treated	42	2.23	7.81×10^{-17}	2.23
	LiOH treated	72	115.35	6.84×10^{-17}	115.35
Red soil	Untreated	9	4.59×10^{-7}	2.40×10^{-16}	4.59×10^{-7}
	KOH treated	36	0.14	1.64×10^{-16}	0.14
	NaOH treated	60	4.41	1.27×10^{-16}	4.41
	LiOH treated	110	191.64	7.72×10^{-17}	191.64

From Table 8.2, it can be seen that the total attractive energies are of far lesser magnitude when compared to the repulsive energies. Thus a similar conclusion as in **Chapter 5** could be made that only repulsive energy estimation is required for assessing dispersivity.

The plot between dispersivity estimated from monovalent cation concentration and double hydrometer dispersivity is as shown in Figure 8.2.

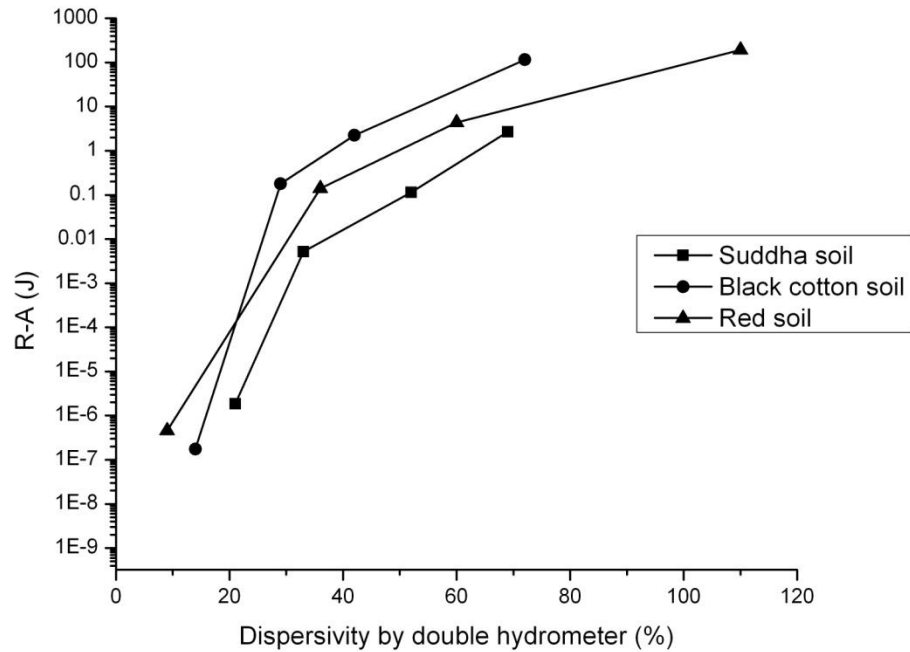


Figure 8.2 Comparison of dispersivity measured through double hydrometer and monovalent cations.

From Figure 8.2, it is evident that increase in dispersivity recorded from the conventional tests is well reflected in the derived expression also. There is an analogous increase in dispersivity obtained from the expression corresponding to the increase in dispersivity recorded from the standard tests for all the soils. This similarity in the trend between dispersivity values obtained from the derived expression and the conventional tests confirms the truthfulness of the expression. Similar plots could be made with dispersivity estimated through UCS or shrinkage limit tests and identical inferences could be made.

It can also be noted from the values that the sensitivity of the dispersivity measurement obtained from the proposed expression towards the variation in dispersivity is higher than all the other tests. The expression is able to incorporate even the slightest change in the dispersivity value. This is thanks to the better accuracy offered by the total ion concentration

measurement test and hence the expression will be able to report more precise values of dispersivity for soils. Figure 8.3 shows the variation of dispersivity obtained from double hydrometer method with derived expression.

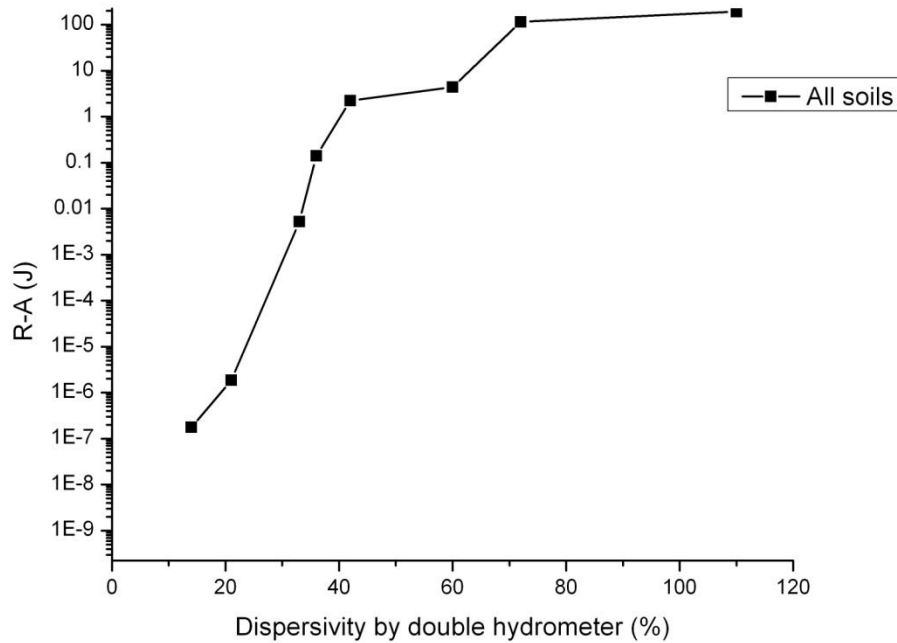


Figure 8.3 Comparison of dispersivity for all soils.

From Figure 8.3, it can be noted that there is a reasonably good relation of dispersivity estimated through monovalent cation concentration and dispersivity estimated from double hydrometer irrespective of the soil type or the nature of treatment. The dispersivity values calculated through the concentration of monovalent cations are in good relation with the double hydrometer test results. This means that the method could be used for estimating dispersivity for all soils.

8.4 SUMMARY

The repulsive energy in a soil mass is computed from the concentration of monovalent cations and the difference between repulsive and attractive energies, in terms of release of energy, is expressed as dispersivity. The repulsive energy obtained through the current approach is well related with the liquid limit of the soil. The dispersivity value obtained bears a very good relation with the double hydrometer test results for all soils under consideration. As presented earlier, the measurements of dispersivity would be accurate if the associated water content is high. The present method since is based on the results of cation exchange capacity experiments, the related water content is high and hence is able to incorporate even slight variations in the dispersivity. Even when the soils are combined for comparing the dispersivity, it is seen that the dispersivity obtained from the monovalent cation concentration is reasonably well related with the conventional methods such as double hydrometer. Thus the method could serve as a good measurement of the dispersion in any soil and similar to **Chapter 5**, as the dispersivity in soils is the least affected by the van der Waal's attraction, it is sufficient to calculate just the repulsive force in the soil which makes the estimation much easier. The same can be attributed to the fact that all soils are dispersive the degree may vary from soil to soil.

CHAPTER 9

COMPARATIVE STUDY OF THE METHODS & GENERAL CONCLUSIONS

9.1 INTRODUCTION

The main scope of the study has been to develop various approaches that could be adopted for the estimating the dispersivity of soils which are more realistic and could be connected to various geotechnical properties. A fairly unknown method of estimation of dispersivity through measuring the zeta potential and monovalent cation concentrations was developed which is very well correlated with the dispersivity estimated through the standard methods. This chapter presents a comparative study of the two methods in light of the electrical double layer theory and the applicability of the two methods for practical situations.

9.2 ANALOGY BETWEEN THE METHODS

Dispersivity in soil is considered as a process of manifestation when the repulsion in a soil mass dominates over the attraction. The various methods discussed earlier primarily bring out the various possible ways that could be adopted to calculate the total repulsive energy and total attractive energy in a soil mass. The attractive energy in a soil mass was computed by extending the van der Waal's interaction energy between two particles to a soil mass. The repulsive energy at the same time could be computed either from the zeta potential values or from the concentration of monovalent cations in the soil. In the zeta potential method of estimating dispersivity both the infinitesimal particle approach and the finite particle approach was introduced.

In the infinitesimal particle approach concepts such as void ratio, density or mean particle diameter (D_{50}) were introduced which essentially define the physical state of the soil. This method of serves a much more realistic estimate of the dispersion occurring as the physical state of the soil also has an influence on the total dispersion. In this approach, the total energy is found out by mathematically integrating the change in the energy due to a change in the particle radius. In practical situations, the particle-particle interaction plays a very important role in the assessment of the total energy of a system. The radius of a particle, total number of particles adjacent to it, number of particles any random particle could have a possible interaction with etc. largely decides the energy of the system. As here, the change occurring to the energy is integrated it enables an effortless computation of the estimate of the total energy without really bothering about the possibilities of all the various individual particle-particle interactions.

In the finite particle approach, the soil particles were treated as of finite radii and the total energy was computed by summing up all the possible particle combinations. The method ideally gives an overestimate of the actual energies because any random particle in a soil mass would not be interacting with all the other particles in the system. In addition, the total number of the particles was found out as the ratio of volumes of the soil mass to the volume of an individual soil particle in the mass. Here the effect of void ratios is neglected. This is a hypothetical concept as no soil would ever exist in a zero air void condition. Even then the method could be used for estimating dispersivity if information regarding the physical state of the soil is unavailable. If one wishes to incorporate such effects, the total number of particles, N could be replaced in Equation (5.1) as

$$N = \frac{R^3}{r^3(1+e)} \dots\dots\dots(9.1)$$

Where, e is the void ratio.

Another comment that could be made regarding the infinitesimal particle approach and the finite particle approach is about the huge variation in the attractive and repulsive energy values obtained from the different approaches. It can be seen that the difference in the attractive energies of the soil mass between the two methodologies is of the order of 10^{-11} to 10^{-12} Joules. This variation can also be attributed to the approximation in finding the number of particles in the soil mass in the finite particle approach through the assumption that the soil mass is highly dense without the presence of any air voids. The same inference can also be made from the differences in the repulsive energies also. As the order of difference is of a similar magnitude the above explanation stands well justified.

In the finite particle approach, the interparticle separation “d” was replaced by an average separation distance “ d_{avg} ” which was replaced by $36R/35$ as expressed in Equation (5.23) whereas the separation distance was expressed in terms of void ratio and average particle diameter in the infinitesimal particle approach as in Equation (5.6). These two substitutions should be recognized as just two different approaches in finding the interparticle distance. Any of the substitutions could be used for finding the dispersivity. I.e. the separation distance “d” could be related with void ratio and mean particle diameter in the finite particle approach provided, the number of particles is found out as per Equation (9.1). Similar is the case with the tradeoff between soil mass radius R with mass and density.

In field conditions, a soil may exist in a defined density and void ratio but when water comes in contact with the soil in large quantities, the structure of the soil is lost and concepts

such as density or void ratio are no longer valid. High erosion can take place due to dispersion in soils. In such situations, in order to simulate the field conditions, even combinations of the methods could be used. That is the domination of repulsive energy of the soil mass estimated through the finite particle approach over the attractive energy formulated through the infinitesimal particle approach could be studied. Here, the number of particles may be found out from Equation (9.1) so as to achieve a more realistic field condition.

9.3 RELATION BETWEEN ZETA POTENTIAL METHOD AND MONOVALENT CATION CONCENTRATION METHOD

In sections 4.3.1 and 5.5.2 it was well established that the amount of monovalent cations are well related to the zeta potential of the soil. Similarly, it was well established from **Chapters 5 and 8** that both zeta potential and monovalent cation concentrations serve good estimates of the total dispersion in a soil. The fundamental principle behind their measurements is that both serve as two different paths for assessing the charge on the clay. Figure 9.1 shows the variation of zeta potential dispersivity with monovalent cation dispersivity. In the monovalent cation approach of estimating dispersivity, the total repulsive energy of the soil mass is found through the measurement of the chemical properties of the soil irrespective of the physical conditions of the soil and hence for better comparison, the dispersivity of the soil estimated by adopting the finite particle approach is used to plot the graph.

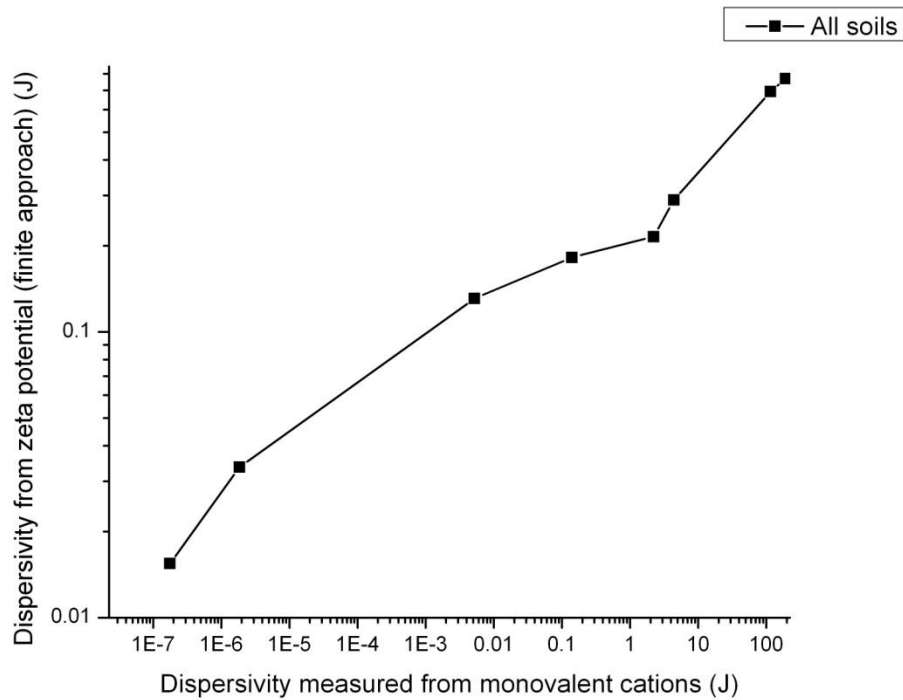


Figure 9.1 Comparison of dispersivity estimated through different measurements

It can be seen that, the dispersivity obtained through the monovalent cation approach is reasonably well related with the dispersivity obtained from zeta potential measurements. The similarity in the trends could be attributed to the relation between zeta potential and monovalent cations. This means that either of the methods could be used for estimating dispersivity of soils.

As per the electric double layer theory, positive cations will try to get adsorbed on the negatively charged clay particles. In equilibrium, the electrical neutrality in the interfacial region would be maintained and thus the concentration of the cations would sufficiently represent the charge on clays. When soils are treated with salt solutions of monovalent cations, the clay surface would be saturated with the respective monovalent cation and thus the concentration of the corresponding monovalent cation would be equivalent to the charge (permanent and pH dependent) on clays. In such cases, measurement of the monovalent

cations or the zeta potential could represent the repulsive forces in the soil and hence the dispersivity. The selection of the method of estimating dispersivity depends only on the choice of the parameter that could be measured.

9.4 MAJOR CONCLUSIONS DRAWN

Since, the existing definition of dispersivity fails to address the conditions at which dispersivity is recorded and the mechanism by which it occurs, a better definition is proposed. Dispersivity is defined as that property of soil by virtue of which particles detach from each other when electrostatic force of repulsion dominates over the van der Waal's force of attraction in presence of a liquid without the presence of any external force. The present study primarily focuses on the dispersivity of the soils with the proposition of several methods for estimating dispersivity of soils.

The important conclusions drawn from the study are as listed below.

1. Apart from exchangeable sodium, several chemical factors such as pH, cation exchange capacity, organic matter, and electrolyte concentration as well as various physical factors such as density, void ratio and particle size influence on the attractive and repulsive forces on the soils and hence can affect dispersivity of soils under the specified conditions.
2. Even though the above mentioned factors can influence dispersivity of the soil, the effects of all these parameters could be mapped into the hydration behavior of the monovalent cations adsorbed or to the zeta potential of the soil. Since dispersion is a phenomenon occurring at higher water contents, even though the above mentioned factors can have an influence, only the role of monovalent cations need to be studied to assess dispersion, which is also well related with zeta potential values. Role of

- monovalent cations only needs to be identified as the radius of the inner hydration shell is higher for monovalent cations than those of higher valency ions.
3. It is not the mere presence of sodium but the monovalent nature of these ions that causes the dispersivity and hence even though field practices involve measurement of sodium for estimating dispersivity, the methods, even though may prove useful, can't be claimed completely fundamental.
 4. Zeta potential could be identified as the ideal parameter of the soil which represents best the dispersivity of the soil. The property is related well with the chemical factors influencing dispersivity and with the test results of double hydrometer, shrinkage limit and unconfined compression tests methods of assessing dispersivity.
 5. Dispersivity could be conceived as the release of energy occurring when the repulsion dominates over the attraction. The study brings out the estimation of dispersivity through the measurement of zeta potential and monovalent cation concentration. Within the zeta potential measurement, two different approaches namely the infinitesimal particle approach and the finite particle approach are presented. It was seen that the methods co-relate well with the existing methods of estimating dispersivity. The choice of the method could be decided based on the selection of the measurement parameter.
 6. Various methods of determining dispersivity of soils through geotechnical properties depend on the variation in any given property with and without the addition of a dispersing agent. The use of the proposed methods based on measurement of zeta potential or monovalent cations do not require any dispersing agent. Also the method

- is quantitative in nature unlike pin hole test or Emerson crumb test. The methods also save time and effort to a great extent.
7. Since repulsive energies estimated through any method are of far higher magnitudes compared to attractive energies, it is sufficient enough to calculate only the total repulsion to estimate the dispersivity. The same could be stated as the reason why all soils are dispersive, though the degree varies from soil to soil.
 8. The drawbacks associated with the application of DLVO theory for clay colloidal stability were overcome by the usage of zeta potential instead of surface potential. The methods proposed for estimating dispersivity through zeta potential are able to quantify better the total dispersion than by the practice of various conventional theories existing in *Soft Matter Physics*.
 9. Several geotechnical tests could be used for assessing the dispersive characteristics of soils. Tests which involve higher water contents should be used so that a complete interaction is involved between the clay and the water. Tests such as zeta potential, double hydrometer and CEC are more sensitive towards dispersivity variations and are able to incorporate even the slightest variations in the dispersivity values due to the same. Estimations through shrinkage limit, plastic limit or strength behavior even though may give an indication about the dispersivity the usage of these properties for estimating the total dispersivity of the soil may not be very realistic in practice.
 10. The optimal conditions for accurate zeta potential measurements are established. It was observed that presence of Brownian motion enables accurate measurements of electrophoretic mobility values and thus zeta potential values with good amounts of reproducibility are obtained. Soil water suspensions passing 0.45μ gives acceptable

values of zeta deviations and hence could be idealized as a standard procedure for estimating zeta potentials.

11. A complete philosophy of dispersion is established by incorporating the effects of all known parameters influencing dispersivity.

9.5 SCOPE FOR FUTURE WORK

Dispersion in soil occurs when the monovalent cations hydrate and cause repulsion between the soil particles. In the soil, the monovalent cations may be present either in the exchangeable form or in the dissolved form. In this study, the total number of cations is taken for estimating the dispersivity. However, the influence of an exchangeable ion and a dissolved ion would be different. The exchangeable ions can contribute more to dispersivity than the dissolved ions. Thus, the separate effects of exchangeable ions and dissolved ions could be studied. For this purpose, the soil may be washed repeatedly so that the dissolved ions are lost in the process. Cation exchange capacity and dispersivity measurements on the washed soil samples could give the influence of purely the exchangeable ions.

When any soil is treated with hydroxide salts of monovalent cations, there would occur an increase in the electrolyte concentration along with the increase of pH and monovalent cations. The increase in the electrolyte concentration would cause a suppression of the diffused double layer thickness due to the reduction in the concentration gradient of the cations in the diffused layer. In the present study the monovalent cation effect along with the increase in pH lead to an increase in dispersion in spite of the increase in electrolyte concentration. However, there would be a threshold concentration beyond which the electrolyte effect would start dominating. Estimation of the threshold level would help in understanding dispersivity more along with the contribution of the exchangeable ions.

In *Statistical Mechanics*, the energy of a single particle (atom/molecule/particle) would be defined from which the total interaction energy of a system of the particle could be derived with the help of several theories. This approach would offer a much more scientific

way of estimating the energy of a system such as a clay mass which would help in better estimations of dispersivity.

Sposito (1972) defined the thermodynamics of the clay-water systems and derived an expression for the swelling pressure of the soil through the measurement of the change in chemical potential of the water. This theory could be extended to dispersion by defining various state variables that could be measured easily. In other words, the dispersion of a soil could be estimated by adopting a thermodynamic approach also.

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