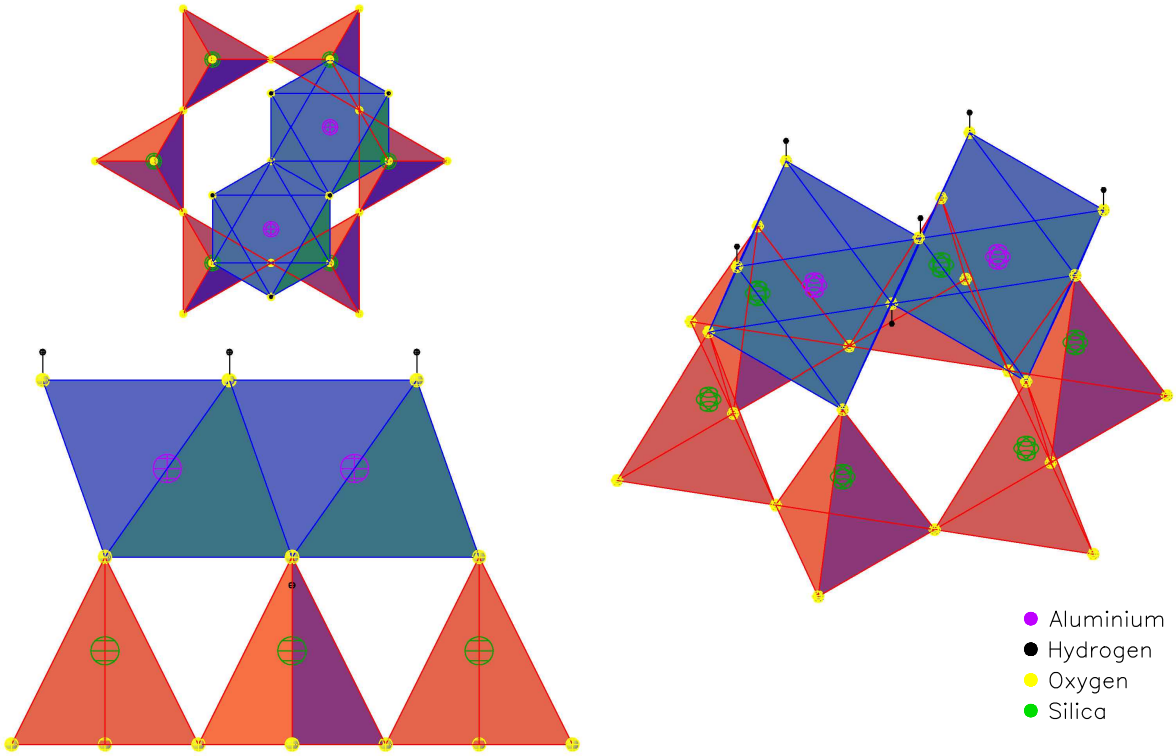
CHALMERS
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On the influence of ionic strength on the rheological properties of kaolin

Master's thesis in the Master Programme Infrastructure and Environmental Engineering

JULIO C. SERRANO ROMERO

Department of Architecture and Civil Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2019

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JULIO C. SERRANO ROMERO



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Department of Architecture and Civil Engineering
Division of Geotechnics
Chalmers University of Technology
Gothenburg, Sweden 2019

Experimental work on the influence of NaCl in pore fluid chemistry and kaoline's rheological properties
This work was performed to kaolinite reconstituted and slurry samples
JULIO C. SERRANO ROMERO

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Supervisor: Georgios Birmpilis, Division of Geology and Geotechnics
Jelke Dijkstra, Division of Geology and Geotechnics
Examiner: Jelke Dijkstra, Division of Geology and Geotechnics

Master's Thesis 2019:NN
Department of Architecture and Civil Engineering
Division of Geology and Geotechnics
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

Cover: Representation of kaolinite mineral structure, this picture shows the tethraedral and octahedral crystal structures that form this type of clay. Draw was made by Julio Serrano, based on the idealisation of kaolinite's crystal structure by Cora et al. (2014).

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Experimental work that studied the influence of NaCl concentration on both clay reconstituted samples and suspensions.
This work includes an experimental work of leaching salt from reconstituted samples with fresh water, emulating the formation of quick clay suggested by several author cited in this thesis.
JULIO SERRANO ROMERO
Department of Architecture and Civil Engineering
Chalmers University of Technology

Abstract

This Thesis presents an experimental study that investigates the effect water content and pore water chemistry on the emerging hydro-mechanical response of clay samples. In order to capture the basic strength and stiffness response as function of strain amplitude and rate, rheology experiments have been performed. As opposed to standard geotechnical tests rheology experiments are fast to execute, more consistent and only require small sample volumes. In order to properly benchmark the rheometer apparatus for testing soft soils kaolin was used. The latter reduces the complexity associated with natural materials at the expense of some saillant features (such as the high sensitivity in sensitive clays) and allows to control the initial conditions to the required degree. The samples consisted of kaolin slurries prepared at differnt void ratios and with different initial pore water salinities, one slurry with a water content equal to the liquid limit and another slurry with 1.5 times the liquid limit. Furthermore, a reconstituted sample was consolidated to 80 kPa. Two series of slurries were prepared, i.e. a reference slurry with distilled water and saline slurry where 0.2 M NaCl was added to the pore water. The results showed that the effect of NaCl is most pronounced for the slurries with water content equal to the liquid limit and 150% the liquid limit. In contrast the effect of NaCl in the reconstituted consolidated sample was less evident. Finally, a different series was performed that emulated leaching of the saline pore water composition to simulate some of the processes that occur during the formation of sensitive clay deposits. These initial tests show that the beneficial effects of a saline injection can be fully reversed by subsequent leaching with fresh water.

Keywords: kaolinite, reconstituted sample, slurry, ionic influence, NaCl, viscosity, leaching, quick clay, double layer, pH.

Acknowledgements

"Throughout the centuries there were men who took first steps down new roads armed with nothing but their vision."
-Ayn Rand, The Fountainhead

Foremost, my family is the greatest support I have ever had through my life. José, you inspired me to make such great things. Verónica, you taught me to never give up and work hard. Erika, thanks for being there to support me. Thank you family.

This work could not have been possible without the guidance of both Jelke Dijkstra and Georgios Birmpilis, your patience and helpful attention were invaluable for the fulfilment of this work.

Julio Serrano Romero, Gothenburg, June 2019

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1
Introduction

This chapter gives an general overview of the concepts of this work. The formation of some soft soils and some of its characteristics. Also is introduced the type of material studied and some of the methods used in the Geotechnical area that has given to some solutions of the problems related to soft soils.

1.1 Problem description

1.1.1 Soft soils

Soft soils are mainly composed of clay minerals and other fine-grained consituents, such as rock flour. Especially, the minerals easily adsorb water. Therefore in Geotechnics, the study of the clay constituents and water in the pores are an essential part for understanding this type of fine-grained geo-materials. Clay deposits are found in every part of the world, however the more challenging clay deposits are found in Scandinavia, East Canada and Russia (Brenner et al., 1981). After formation of these clay deposits from deposition of post-glacial material, a by-product from physical and chemical erosion on rock by glaciers, in both marine and brackish waters they raised to the surface following land upheaval (Andersson-Sköld et al., 2005). The puzzling behaviour of these sensitive clays, also called quick clays, are radically different from more common clay deposits that have been formed under more typical geological conditions.

In the case of the clay found on the West Coast of Sweden studies indicate that the composition of clay minerals are 40-60% of illite, 15-25% quartz and feldspar and the rest is a fraction between kaolinite, chlorite and some montmorillonite (Pusch, 1970; Lundström et al., 2009). This type of clay is usually of similar composition as found in Norway (Lundström et al., 2009).

Fundamental behaviour of clay The many physico-chemical factors involved in response of clayey soils makes it difficult to predict the hydro-mechanical response when starting from the micro-scale. Although some research has been performed in order to investigate the hydro-mechanical behaviour of clays and the role of its underlying physico-chemical properties at the particle scale, the majority of the research focused on understanding and predicting its behaviour on the engineering scale. Among the properties mentioned that govern the hydro-mechanical response of clay is the mineralogy of the clay platelets, the molecular interaction, the cation

exchange on the clay surface and electrochemical properties, such as pH and ion concentration of the pore fluid.

Some of the differences in composition are induced by the deposition history. As an example in East Canadian swelling minerals like montmorillonite are common (Lundström et al., 2009). The lacustrine deposits of Mexico City clay, on the other hand, contain microfossils, called diatoms, whose properties are changed in unexpected ways (Pusch, 1966). In contrast the clays found on the West Coast of Sweden and some of the Norwegian sensitive clay deposits have a large clay fraction of mainly Illite minerals. The large difference between the intact and remoulded shear strength have resulted in numerous landslides, as a small perturbation in the equilibrium state is sufficient to trigger an instability (Rankka et al., 2004).

Sensitive clay Sensitivity in clay is defined as the ratio of the undisturbed shear strength against the remoulded remoulded shear strength (Brenner et al., 1981). The most common technique used to measure sensitivity in the laboratory in Sweden is by using the Swedish fall-cone test. The term quick clay, from the Swedish term *kvicklera* is the term used to describe clay that changes from solid to viscous fluid after a perturbation, or in the lab, after remoulding (Söderblom, 1969). Several authors classify quick clay based on their degree of sensitivity as seen on 1.1. This type of clay is found in post-glacial clay deposits, like the ones found in Scandinavia. Please note that in this Thesis we follow the international qualification for sensitivity.

Table 1.1: Classification of clay sensitivity, S_t

Skempton and R.D. (1952)	Rosenqvist (1953)	Söderblom (1969)
1.0 : Insensitivity	1.0 : Insensitivity	$<$ 20 : Normal
1 - 2 : Low sensitivity	1 - 2 : Slightly sensitive	20 - 50 : Semi-quick
2 - 4 : Medium sensitivity	2 - 4 : Medium sensitive	$>$ 20 : Quick
4 - 8 : Sensitive	4 - 8 : Very sensitive	
8 - 16 : Extra-sensitive	8 - 16 : Slightly quick	
$>$ 16 : Quick	16 - 32 : Medium quick	
	32 - 64 : Very quick	
	$>$ 64 : Extra quick	

1.1.2 Methods for ground improvement

Several methods have been developed to improve the hydro-mechanical properties, that originate from the complex physico-chemical proceses at micro-scale, of sensitive clays around the world, e.g. (Bjerrum, 1969; Mitchell, 1981; Broms, 1979; Chu et al., 2009). These solutions include the construction of ancillary infrastructure or other special construction methods. However, chemical injections that manipulate the pore chemistry are of most interest, as they potentially provide an improvement in stability of the soil, hence the structure on top, by simply changing the

physico-chemical properties at the particle level. A possible approach for the latter is to inject a saline solution (salt) in the clay. Broms (1979) inject of KCl and $Ca(OH)_2$ to improve shear strength. Mitchell (1981) investigated other materials ranging from iron oxide based to silicate chemicals that stabilises soft soils. Recent investigations regarding monovalent and divalent salts effects on mechanical and rheological clay suspension properties have been performed Pedrotti and Tarantino (2017); Palomino and Santamarina (2005); Ibanez et al. (2014); Li et al. (2013); Au and Leong (2016). Those studies investigated the injection of materials as function of a ground improvement technique based on chemical stabilisation.

1.2 Aim and objectives

The aim of this research is to experimentally investigate the influence of ionic strength on the rheological properties of kaolin clay at different water content (suspension – consolidated specimens). The following objectives are formulated:

- to create a well controlled set of kaolin samples at different magnitude of water content and salinity of the pore fluid
- to perform injection and leaching experiments on consoldiated samples
- to characterise the rheological properties, rather than the use of classical geotechnical characterisation methods, this facilitates the short testing times required for the project and gathers fundamental insight in the response.

2

Fundamentals of clay behaviour

This chapter explains the fundamentals that has to do with the behaviour of the particle interaction and its effect in micro structure of clay. These concepts are the base of the methods used in this thesis work.

2.1 Composition of fine-grained soils

Typically, in geotechnical engineering fine-grained soils are classified following the grain size. Fine-grained soils pass the 63 μm sieve, whilst the grain size of the clay fraction falls below 2 μm. Due to the geological deposition history these soils are (partially) saturated. Hence, the composition comprise of silt (resulting from physical weathering), clay minerals (chemical weathering). The pores in this particulate system typically are filed with a pore fluid (water). Silt results from natural weathering actions such as e.g. wind, water and glaciers against rocks with particle sizes as small as the clay fraction (rock flour). In contrast the clay platelets are usually flat and elongated, the small size and high aspect ratio leads to more complex surface charge effects when compared to silt fraction. A further classification of the clay fraction has been made based on the following properties sensitivity, swelling potential.

2.1.1 Clay mineralogy

The structure of most clay minerals consist of alternating sheets of octahedral aluminium and a tethraedral silicate. Isomorphic substitution of Si for Al in the octahedral sheet and Mg for Si in the tethraedral sheet exposes oxygen anions in the surfaces of the clay plates, thus giving them negative charged surfaces. A 2:1 clay makes a sandwich of an octahedral aluminium mineral between two tethraedral silicate layers, montmorillonite and illite are 2:1 clays. On the other hand, a 1:1 clay has a layer of octaedral aluminium and other of tethraedral silicate layer, kaolinite is 1:1 clay. Kaolinite's structure is shown in Figure 2.1

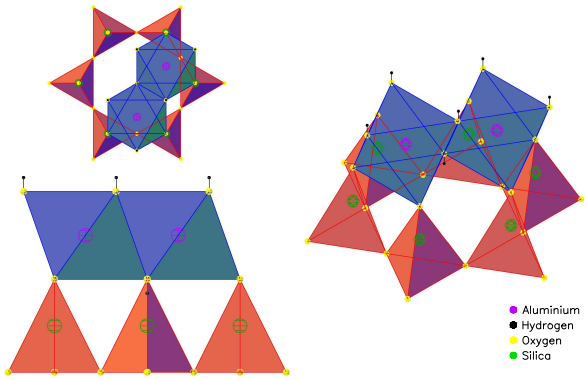


Figure 2.1: Representation of Kaolinite mineral structure. In blue is the aluminium octahedral structure and in light red is the tethraedral structure. Source: Cora et al. (2014)

2.1.2 Electronegativity of clay platelets

Isomorphic substitution leaves negatively charged molecules in the surface of the particle. This leads to negatively charged surface of most clay minerals (Mitchell et al., 2005)

The negative charged surfaces in the clay, due to molecular exchange, combined with the large surface of the clay, makes cations like K+, Mg+, Ca+ to be attached easily to clay surfaces. This capacity is the reason why plants grow better in soils whose capacity to retain this cations is large, also known as cation exchange capacity (CEC). Additionally, due to the dipolar nature of water, the hydrogen positive pole creates a hydrogen bond with clay. Alternatively at the same time the oxygen negative pole can attach more positive cations.

Depending on its mineral structure, every type of clays behave differently. Some clay allows more water molecules in between the clay plates, which increases the volume of the sample. The latter type of clay is called expansive clay, Montmorillonite and Bentonite are examples of this type of clay. Whereas, Illite is a type of non expansive clay, due to the potassium ion present in between the clay plates.

2.2 Aqueous clay systems

It is known that dry clay can adsorb water even from the atmosphere present as humid in the air. Properties of water adsorbed in water tend to change from bulk water, some of this properties will affect the way the bonds between the particles are formed.

2.2.1 Ion hydration

Both clay particles and ions interact in an aqueous medium. Particle of clay adsorbs water and ions get hydrated, especially the cations. Once the cations are hydrated, depending on the distance from the surface area water molecules in the surroundings have different behaviour. The model from Frank and Wen (1957) explains this behaviour, Figure 2.2. This model is characterised by three layers: first region, A, is a zone of immobilisation, in this layer water molecules are strongly bonded with the ion. Next layer, region B, the structure of water is broken down. Finally, region C, is practically out the influence from the ion being normally structured molecules.

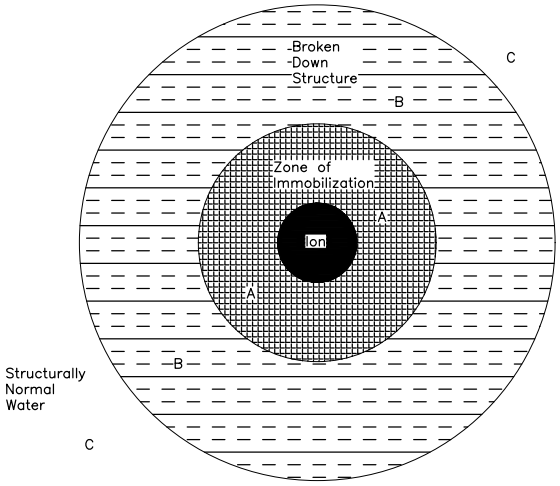


Figure 2.2: Ion model represented by Frank and Wen. Adapted from Mitchell et al. (2005)

2.2.2 Water–clay medium

Water present in the clay, especially the water closer to a clay molecules, forms a strong bond. Theories suggest that water and clay arrange can occur in different ways; a hydrogen bonding, formed with the negatively clay surface; hydrated cations attached to the surfaces of clay; concentration of ions balances the water in areas close to the clay via osmosis is an alternative way; and dipole bonding, due to the dipole nature of water, molecules will arrange water molecules as in a queue, arranging them in series of negative poles bonding with positive poles (Mitchell et al., 2005).

2.2.3 Double diffuse layer

Due to the large amount of specific surface from clay particles, authors (Mitchell et al., 2005) represent clay surface in a single layer, which emits dispersion forces from its molecules, see Figure 2.3. Cations and anions are influenced from the particle superficial charge, the latter is usually part of the dispersion forces in an aqueous medium. The gravity center of this concentration lies at certain distance from the

surface, this distance called the limit of the double diffuse layer. First layer is the so-called Stern layer. This double layer can be also recognised as the limit of the influence from the particle charge. Beyond this layer, effects of charge from clay are disregarded. Length of this diffusion layer can be expressed with next equation. Important influence in the length of the layer are the electrolyte concentration, cation valence, dielectric constant of the medium and the temperature.

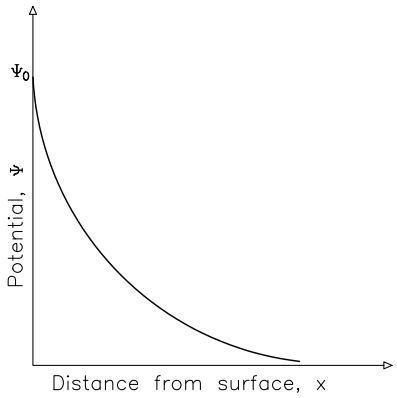


Figure 2.3: Idealization of Gouy-Chapman concentration of charges. Adapted from Mitchell et al. (2005)

From a force field at equilibrium, Equation 2.1, expresses the concentration of ions,

$$n_i = n_{i0} exp\left(\frac{E_{i0} - E_i}{kT}\right) \tag{2.1}$$

In an electric field the potential energy of an ion is expressed with Equation 2.2,

$$E_i = \nu_i e\psi \tag{2.2}$$

Assuming that $E_{io} = 0$ and $\psi = 0$ because are at a large distance, a simplified Boltzmann equation is found in Equation 2.3,

$$n_i = n_{i0} exp\left(\frac{-\nu e\psi}{kT}\right) \tag{2.3}$$

On the other hand, the Poisson equation, Equation 2.4, can express change of electrical potential with distance,

$$\frac{d^2\psi}{dx^2} = \frac{\rho}{\varepsilon} \tag{2.4}$$

Where ρ is the charge density,

$$\rho = e \sum \nu_i n_i \tag{2.5}$$

Substituting Equation 2.3 into Equation 2.5, then into Equation 2.4, yields,

$$\frac{d^2\psi}{dx^2} = \frac{e}{\varepsilon} \sum \nu_i n_0 exp \frac{-\nu_i e \psi}{kT} \tag{2.6}$$

Equation 2.6, is the differential equation for the electric double layer who lies next to a planar surface. Where x is the distance from the particle surface, in m, ρ is the charge density (C/m^3) and ϵ is the static permittivity of the medium (C^2J^{-1}).

A simplified version of Equation 2.6 is given for when existing cation and anion species of the same valence.

$$\frac{d^2\psi}{dx^2} = \frac{2n_0\nu e}{\varepsilon} sinh \frac{\nu e \psi}{kT} \tag{2.7}$$

In clay, the charge density is proportional to the cation exchange capacity divided by the specific surface. Ions in solutions will determine the amount of dissociation of alumina in octahedral sheets of clay minerals. These equations discussed here apply to colloidal systems with constant surface charge. Despite of not being representative to most of the clay systems, these equations are useful for understanding effects in changes in concentration of solution and molecular valence related to clay material.

The group of equations that solve Equations 2.7 are the following

$$Potential functions \begin{cases} y = \frac{\nu e \psi}{kT} \\ z = \frac{\nu e \psi_0}{kT} \end{cases} \tag{2.8}$$

$$\xi = Kx \tag{2.9}$$

From Equation 2.9,

$$K^2 = \frac{2\nu^2 e^2 n_0}{\varepsilon kT} \tag{2.10}$$

These solutions, Equations 2.8 and 2.9, are applied in cases where surface potential is less than 25 mV.The influence of the charge particle forces, or the so-called double layer thickness, is expressed: $x = 1/K$, Equation 2.11.

From 2.10, $1/K$ is,

$$1/K = \left(\frac{\varepsilon_0 DkT}{2n_0 e^2 \nu^2} \right)^{1/2} \tag{2.11}$$

The thickness of double layer expressed in Equation 2.10, is affected by electrolyte concentration n_o , cation valence ν_0, dielectric constant in the solution. Also in this case the pore water in clay D, temperature in soil T affects the equation, in soils these are usually constant. Purpose of this section is to demonstrate the influence of the electrolyte concentration and the valence of the salt in the clay particle interaction.

2.2.4 Molecular repulsion and attractive forces

Attractive forces, V_A, are result of the different ways of bonding of particles like, dipole attraction, hydrogen bonds, cation hydration or osmosis, see Figure 2.4.

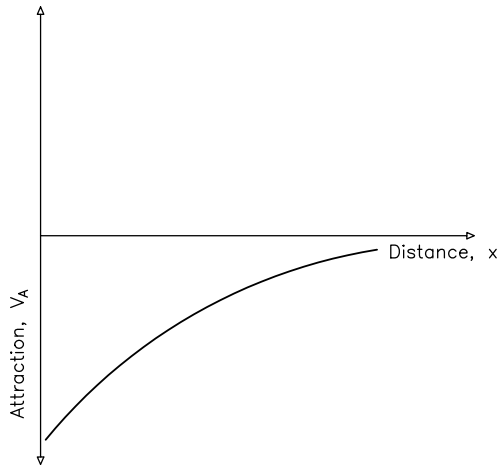


Figure 2.4: Energy of attraction in function of the surface length. Source: Mitchell et al. (2005)

Repulsive energy, V_R, is the result of the thickness of the double layer and the particle charge nature, see Figure 2.5.

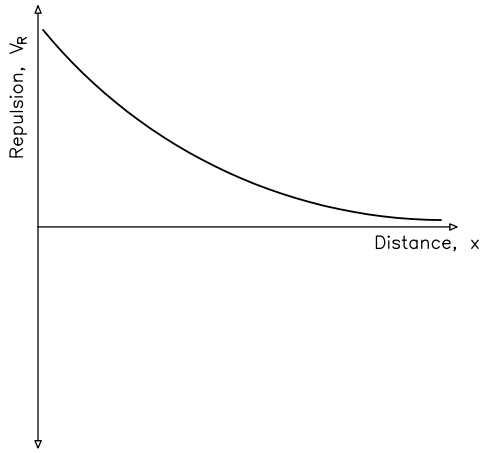


Figure 2.5: Energy of repulsion in function of the surface length. Source: Mitchell et al. (2005)

The superposition of both energies, V_R and V_A, show the interaction and of both repulsion and attraction effects, also known as Coulombic and van der Waals forces, shown in Figure 2.6. This is the principle of the DLVO (Derjaguin and Landau, 1993; Verwey et al., 1948) theory which can be suited for clay suspensions. However, in reality exist more than these two forces that drive the behaviour of the repulsive and attractive forces.

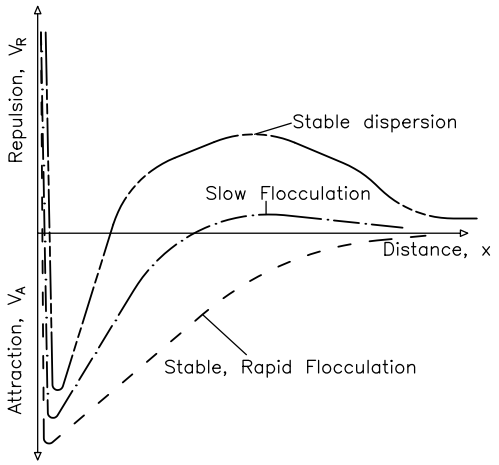


Figure 2.6: Superposition of both energies of repulsion and attraction with different cases of flocculation. Source: Mitchell et al. (2005)

2.3 Electrochemical clay behaviour

Changes in pH and electrolyte concentration (Palomino and Santamarina, 2005), electric permittivity (Mitchell et al., 2005) and electrolyte valence Ibanez et al. (2014) in clay can the mechanical properties of clay. Changes on pH has to do with the concentration of hydroxyl, OH^-, and hydron, H^+ in the medium. High concentration of H^+, can cause weathering of the mineral composition of the clay itself releasing cations. A documented case in Drammen, Norway (Bjerrum, 1967) where quick clay is abundant, an region with clay with shear strength increased was

identified and attributed by the reduction of pH due to percolation of rainwater with high CO^2 content, airing with CO^2 is a method used in mines to lower pH. The acidity does not affect the stiffness of clay, what the acid environment affects to the clay is the liberation of cation from the clay minerals of higher valence than Na^+, in this case Bjerrum concluded that the abundance of potassium cations in the Norwegian clay replaced the sodium cations giving the soil a higher shear strength.

An acidic environment tend to charge positively the edges of the clay particles. This phenomenon brings more open spaces between the clay. A more alkaline environment reduces the volumetric change and the spaces between clay platelets.

2.3.1 Clay negatively charged

Due to cation exchange and exposure of negative molecules clay particle is asusmed to be negatively charged (Mitchell et al., 2005). Negatively charged surfaces in clay combined with a large specific surface area, give appeal attraction to cations like K^+, Mg^2+, Ca^+ to attach to surface clay. As an example, by absorbing these cations available in soft soils, give plants to ability to grow. Additionally, water possesses a dipolar nature, meaning that it can be attracted easily by ions despite its charge. For clay, the negative charged surface of the clay particles attract the positive pole of the hydrogen molecules of the water. Shown in Figure 2.6, attraction and repulsion forces interact in clay when in suspension.

Some clay allows more water molecules in between the clay plates, which increases the volume of the sample. The latter type of clay is called expansive clay, montmorillonite and bentonite are examples of this type of clay. Whereas, illite is a type of non expansive clay, due to the potassium ion present in between the clay plates,(Rankka et al., 2004).

DLVO limitations Application of DLVO theory in soft soils has given authors like Guven (1992) cite number of limitations that are ignored by the such theory for this specific case: ions are points and the size is neglected, dielectric constant of clay water is assumed to be the same as bulk water, charge of particle is uniformly charged, which is not the case in reality since the clay structure does not allow this to happen, hydration from clay and ions is ignored. Changes in pH affect the amount of H+ available in the medium, therefore a change in negative charge is experienced as well. The higher the pH, the more hydroxyls are available, therefore the more alkaline the solution which leads to an increase of a negative charge in the particle. Also, in high pH solutions, exists a higher tendency and rate ion exchange. At low pH, clays tend to present positively charged edges.

2.3.2 Ion exchange

Repulsion force explained in previous chapters, is also the potential force from the clay surface. This force is a negative electrical force expressed in electric potential. Thus, clay surface attracts positive ions, also called cations.

Cations of higher valence develop stronger bonds to the clay surface than those of lower valence. In a similar way, smaller cations are more difficult to replace than those of higher size. Nevertheless, other factors can affect this interchange, as cations of lower replacing power can replace cations of higher replacing power simply by mass balance due to high concentration of the lower power cation.

Mitchell (2005), represents a typical series of replaceability as follows:

$$Na^{+} < Li^{+} < K^{+} < Rb^{+} < Cs^{+} < Mg^{2+} < Ca^{2+} < Ba^{2+} < Cu^{2+} < Al^{3+} < Fe^{3+}$$

The speed of this process depends on the type of clay, solution concentrations, pH and dielectric constant value in the solution.

2.3.3 Other inter-particle behaviour

In this thesis is assumed that only repulsion and attraction forces are the main responsible factors in the interparticle interaction of clay, based on the DLVO theory. Santamarina (2003) adds a more aspects explanation about forces governing the microstructure of a particle, in his research he cites normal and tangencial forces between particles under effective stresses. Tensile forces from effects of cementation and capillary forces have a degree of interaction in soft soils. Changes in the hydrodynamics of pore fluid by movement and buoyancy forces in particles have a role in the clay-water system.

2.4 Macro properties as a result if particle interaction

Previous chapters had explained interaction of individual particles, this dictates ultimately the shape of the macrostructure of clay. Arrangement between particles influences volumetric changes and mechanical properties(Mitchell et al., 2005).

2.4.1 Zeta potential

This concept is usually linked when the application of a colloidal theory of DLVO, due to use of common concepts. Zeta potential is a theoretical electric potential charge at the burden of the double layer influence, also known as slipping plane. Along with the zeta potential in colloidal sciences, exist the surface potential and the Stern potential, measurements in different planes of the double layer. Usually, high zeta potential in absolute values is associated with high colloidal stability, near

the zero potential charge the interaction between anions and cations tend to disturb the ability of formation of colloids.

The charge of the zeta potential plays a role in the flocculation ability of a particle. The charge of the zeta potential determines if the particle is negatively or positively charged. In aqueous system of flocculation the pH influences the nature of this charge. Authors like (Ibanez et al., 2014) and (Au and Leong, 2016) have studied the influence of ionic forces on zeta potential, finding that valence and ionic concentration affect also zeta potential value.

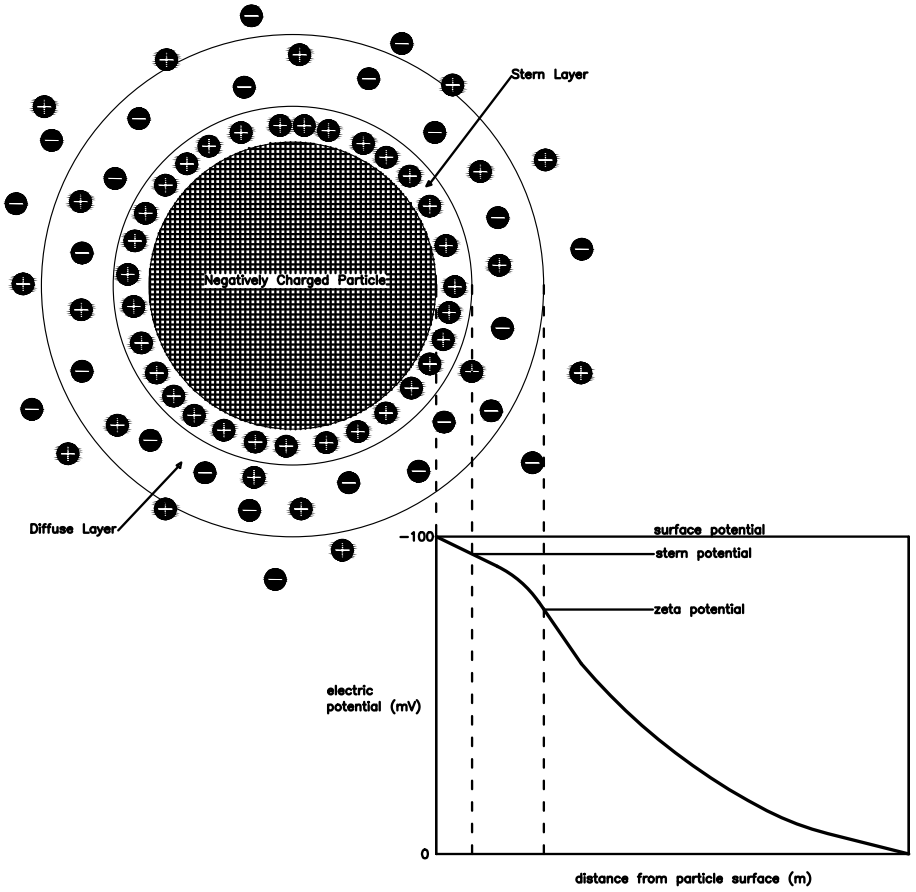


Figure 2.7: Energy of attraction in function of the surface length. Source: Birdi and S (2002)

Change of zeta potential from negative to positive means that in one point along this change of charges zeta potential can experience a value of zero. This point, pH dependant, is called the point of zero charge (pzc), when the particle is found in this point is assumed that the particle will not have any flocculation interaction with both anion and cations.

Electrophoresis is the common method used in experiments to measure the charge

of the zeta potential. At zero ionic concentration the point of zero charge is known for kaolinite from several authors.

A related concept called point of zero net proton charge (pznpc) is related in which the density of the both cation and anions is equal. In other words, the sum of negative and positive charges in the slipping plane is zero. At this point the electrical mobility is the lowest. Several authors had defined different values. Schroth and Sposito (Schroth and Sposito, 1997) found a value of 3.5 - 3.6 of pzc and 5 - 5.4 of pznpc in kaolin.

2.4.2 Clay fabric

Charge in faces and the edges of the particles are subjected by pH in the medium. This relationship is related to the influence of free hydroxyl, OH^-, and hydron, H^+ concentration, who interact with the mineral structure of the clay particle. Several authors that have studied the influence of ionic strength in the clay also monitor the variation of the pH, thus the role in the clay fabric and the so-called point of zero charge mentioned above. The pH in part, affects the relationship between clay particles. Palomino and Santamarina (2005) found the influence of the concentration of NaCl and the pH level and their influence upon the flocculation of the clay particles. They also detected the combination of ionic strength and pH in solutions so the flocculation changes from edge to edge (EE) to face to edge (FE).

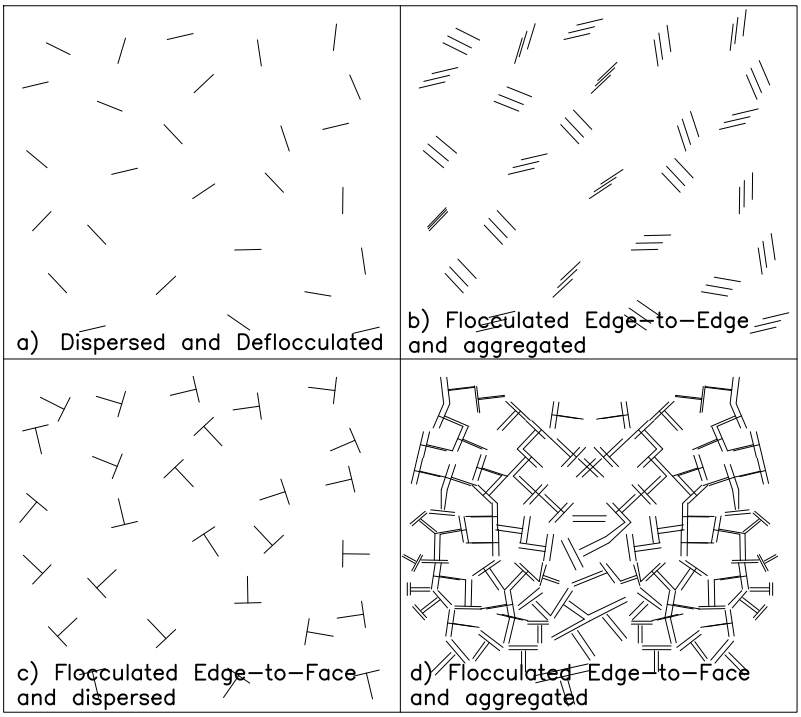


Figure 2.8: Fabric clay interactions. Source: Mitchell et al. (2005)

In a) from Figure 2.8, is clear that dispersed and deflocculated clay fabric is a consequence from a particle who is completely charged on faces and edges. This type of fabric is usually found at very acidic or very alkaline pore medium. In b), an adhesion between face to face (FF) exists but a repulsion between particles keeps. When the particles start to have some degree of attraction between edges and faces (EF) particles can start a perpendicular dispersed shape like in c). Usually a more stable flocculation and a shape that is expected to have a better mechanical properties is when the fabric is found with both EE and EF interactions as seen in c).

2.5 Effect of ionic concentration in clay

Early attempts to study ionic influence in clay include the one made by Bjerrum (1967), who found threshold values of salinity in quick clay resulted from water leaching. Palomino and Santamarina (2005) worked with kaolin suspensions at different concentrations and they found a range of salinity concentration where NaCl's ionic influence affects the clay fabric, below this range kaolinite particles charges are mostly governed by pH. Other authors (Au and Leong, 2016; Ibanez et al., 2014; Li et al., 2013; Rand and Melton, 1977; Michaels and Bolger, 1964) have made other studies on the influence of cations on Kaolinite suspensions. Remarks on their work are resumed in Table 2.1.

Table 2.1: Values of ionic forces in kaolinite documented by several authors

Author	Substance	Value	Observations
Andersson-Sköld et al. (2005)	Na^+	< 35 mM	Quick clay in Sweden is usually found with this level of Na cation concentration
Bjerrum (1967)	Salinity*	< 17 mM	Found that extreme sensitivity in marine clays is when leaching from 600 mM (sea water) to below 17 mM
Ibanez et al. (2014)	NaCl	> 10 mM	Above this value is defined as high ionic strength, kaolinite particles are expected to flocculate despite pH of adsorbed water
Li et al. (2013)	$CaCl_2$	> 2 mM	Floculation from face to face to edge to face is expected above this value
Michaels and Bolger (1964)	NaCl	>0.01 mM	Rheological properties changed to a kaolinite with high density above this value
Palomino and Santamarina (2005)	NaCl	100-150 mM	Mapped a fabric clay map with different pH and NaCl concentrations, above these threshold value kaolinite is expected to flocculate
Rand and Melton (1977)	NaCl	120 mM	Yield stress was constant independently of pH of absorbed solution
Wang and Siu (2006)	NaCl	50-150 mM	Changed from face to face fabric to edge to face fabric

Palomino and Santamarina (2005) found a threshold value of 100-150 mM NaCl where the ionic influence affects the fabric of the clay. Wang and Liu (2006) found a value of 50-150 mM NaCl. What they found is that over these threshold values of ionic concentration clay fabric is driven to be edge to face flocculation, shown in d) from Figure 2.8

The studies from Bjerrum (1969), Söderblom (1969) and Lundström et al. (2009) suggest that the change of the chemical influence from a pore water environment

with salinity from the sea water to a desalinisation due to watering of fresh water along with diffusion of the material was one of the reasons that can lead to sensitive clay, in some cases finding quick clay in Sweden and Norway.

2.6 Salinity in soft soils

One of the biggest causes that relates salinity effects in clayey soil has to do with formation of quick clay. This type of clay represents the most common source of slides in Sweden, Norway and Canada. Under disturbance quick clay turns from competent firm soil to a liquid matter, this material is a potential threat that lead to problems to existent infrastructure that can cause enormous amounts of money in terms of reconstruction, rehabilitation and reparation. (Söderblom, 1969).

2.6.1 Quick clay

Most of the quick clays around the world are usually found in areas where erosion of rock was produced by glaciers and subsequently deposited on the bottom of marine or brackish waters. Upon clay deposition in an environment with high ionic strength, where double layer becomes thinner flocculation of particles is accomplished in a long period of time. Salinity in water content that surrounds the clay material may contain different type of ions, who ultimately affect in different ways structure in soil (Andersson-Sköld et al., 2005). The ratio between specific ions content may affect the sensitivity of the soil.

Bjerrum (1967) found, in the case of Norwegian quick clay, was usually a result from leaching marine clay with fresh water from 35 gr/mL to below 1 gr/mL. This supports the theory that a decrease of salinity increases the sensitivity of clayey soil. However, leaching does not only lead to a loss of stiffness in the soil, some cases of cementing had been documented, like the case of a marine Canadian clay with low value of salinity and high content of ion cations gave the soil a competent strength despite the loss of volume due to loss of water (Kenney, 1966).
Söderblom (1969) research in salt content in Swedish clay found that is not usually to found clay with pore water content that has the same salt concentration than the marine water content, 35 gr/L. In Sweden, sensitive clays are usually found in a range between 0.2 and 25 gr/L and that usually most of salty clays are found in the middle of clay deposits. This is a product of the different diffusion values present in different parts of the clay deposit and the leaching process of fresh water on the bottom of the deposit and the runoff from surface water. In a study on clay from Göta River found that sodium was the dominant cation in pore water from salty clay.

The most common method tets to detect quick clay is by cone ponetration test (CPT), measured to an undisturbed sample compared to a remoulded sample. Lundström et al. (2009) tried to map quick clay by detecting it by different methods. A different method used was by measuring electrical resistivity, despite Söderblom (1969) found a relationship between quick clay existence and electrical resistivity, other studies have to be done in order to confirm quick clay. Detection of quick clay

by sonar device can be a more effective method.

These studies correlates the link between change pore fluid chemistry and the ocurrence of quick clay in soft soils.

2.7 Fundamentals of rheology in soils

Rheology is the science that studies the mechanical properties of fluids and plastic bodies when are under external stresses. This chapter shows basic rheological properties that explains the behaviuor of a body under shear stress. Some theoretical fundamentals studied by rheology are not completely used by soil mechanics. One of the few attempts to investigate soils with rheology is made by Markgraf and Horn (2005). She investigated the change in micro structure induced by certain salt concentrations, and mentions that different methods and investigation can give practical information to soil mechanics.

Both rheology and soil mechanics study shear stress which can be either by steady state or oscillation. Formula for shear stress τ is defined by Equation 2.12

$$\tau = F/A \tag{2.12}$$

where τ is the shear strength, F the force and A is the area.

Newton's law of ideal liquids recognises shear strength proportional to the flow velocity. Naming a factor of proportionality as the "lack of slipperiness", today known as viscosity. A modern definition of viscosity is the resistance of a fluid against the movement. Although fundamentally, this concept has to do with the velocity of a fluid as a result of a stress applied (Rudolph and Osswald, 2014). The formula is given as follows

$$\tau = \eta \times \dot{\gamma} \tag{2.13}$$

where η is the shear viscosity and is a constant and gamma dot is the shear rate and can be expressed as

$$\dot{\gamma} = v/h \tag{2.14}$$

where v is the velocity of deformation and h is the gap height as seen in Figure 2.10

The viscosity curve of a material describes its behaviour when is submitted to an increment on shear rate. A shear thickening fluid increases its viscosity with the increment of shear rate, whereas a shear-thinning fluid gradually decreases with increasing shear rate (Markgraf, 2011). Figure 2.9. shows the type of fluid depending of their viscosity flow.

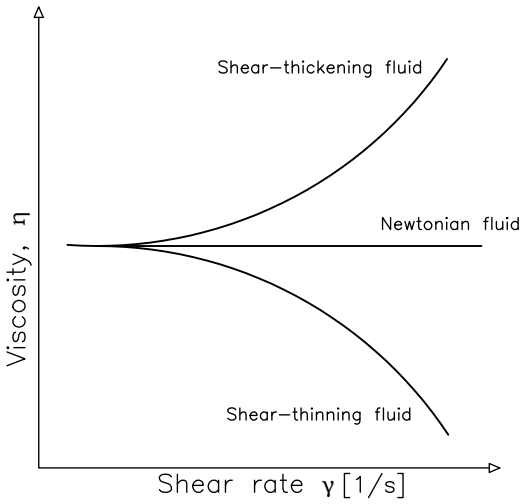


Figure 2.9: Viscosity curve of different materials fluid

Viscosity, η, from Equation 2.13, is usually referred as dynamic viscosity, a parameter under external forces. Whereas under no external forces, is assumed gravity is the only pressure acting on the material, this parameter is called kinematic viscosity, ν. This is the ratio between the dynamic viscosity and the material density ρ

$$\nu = \eta/\rho \tag{2.15}$$

Hooke's law describes the ideal elastic behaviour. Robert Hooke made his research testing deformation of beams and springs, concluding that this deformation is proportional to the acting force (Markgraf et al., 2006). Similarly to the liquid case in Newton's law of ideal liquids, for this case of ideal elastic materials the constant of proportionality is called Young's modulus E

$$\sigma = E\varepsilon \tag{2.16}$$

where σ is the stress applied to the material and ε is the elastic strain (%) or (1). Leaving Young's modulus as

$$E = \sigma/\varepsilon \tag{2.17}$$

Alternatively, a shear modulus G can be defined based with this formula

$$G = \tau/\gamma \tag{2.18}$$

where G is the shear modulus, τ is the shear stress and γ is the shear deformation, which is also expressed as

$$\gamma = s/h \tag{2.19}$$

and

$$s/h = tan(\varphi) \tag{2.20}$$

where s is the deflection, and h is the distance between surfaces and φ is the deflection angle.

As soft soils content water, this can categorise it as a viscoelastic material, meaning that both states of liquid viscosity and solid elasticity are present in the material against shearing. Two types of modulii can also be present under this effect: The storage modulus *G'* associated with the elastic component and *G"* represents the elastic behaviour.

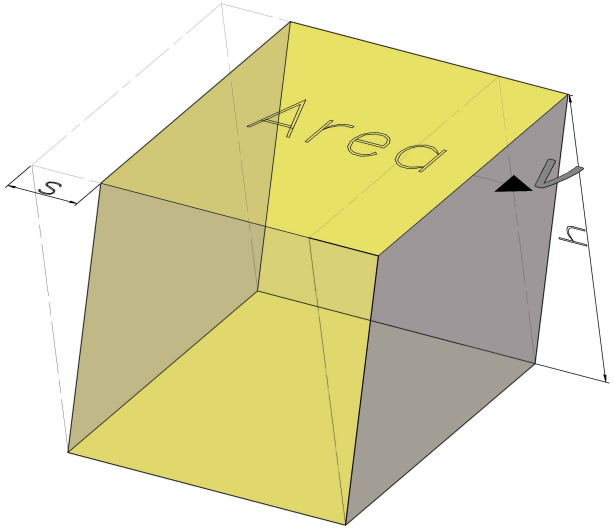


Figure 2.10: Deformation of material under shear stress. Source: Birdi and S (2002)

Proportionality of the elastic behaviour and the viscous will dictate the behaviour of the material: when $G' < G''$ the viscous prevails making the substance turning like a fluid, whereas when $G' > G''$ the elastic one dominates in the material structure.

$$tan(\delta) = G''/G' \tag{2.21}$$

When tan δ equals zero ideally plastic behaviour is assumed, meaning that G"= 0 hence, no viscous effect. When tan δ equals 90 degrees G'= 0, thus no elastic portion.

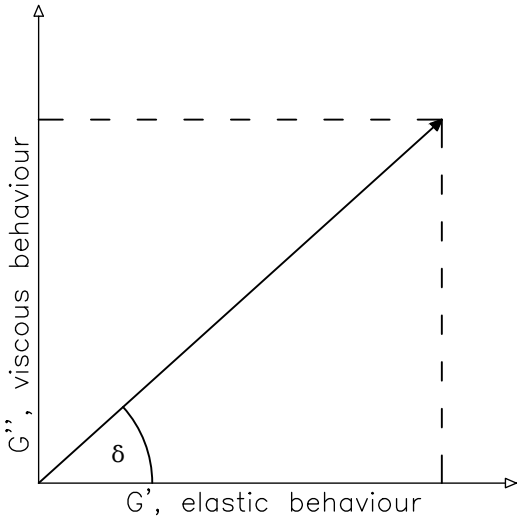


Figure 2.11: Visualisation of G' and G". Source: Alas and Ali (2019)

Markgraf (2006; 2011) uses amplitude tests with a parallel-plate measuring rheometer to give information regarding parameters showed in Figure 2.11, by doing this is common to observe the behaviour between *G'* and *G"* and their transition. She also notes that this test can give some useful information, as the yield point, linear viscoelastic (LVE) deformation range, deformation limit and yield point.

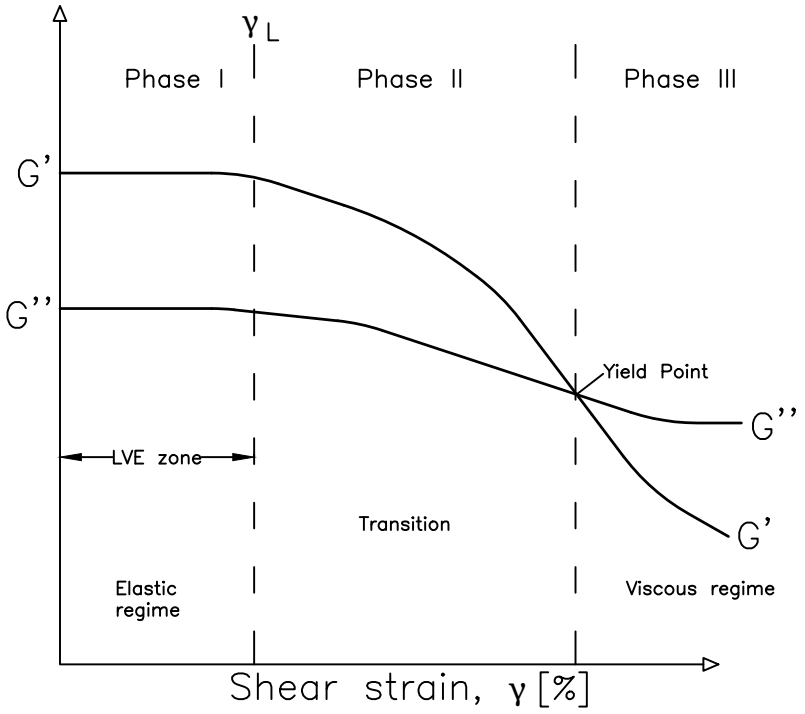


Figure 2.12: Sweep Amplitude Results. Source: Markgraf (2011)

Phase I, characterised by a plateau value and is defined by a quasi elastic behaviour, an ideal elastic material is expected to behave like this. LVE range in also localised in this phase. Phase II, a value of strain id called deformation limit, after this limit soil particles are reorienting and micro structure is given but gradually decreasing. When it is closer to the yeild point a stage of pre-yielding is identified, this stage when tan δ =1 indicates a complete loss of stiffness and rigidity of the mircro structure. When $G' = G''$, also know as the yield point, a complete loss of stiffness and rigidity of micro structure is assumed after reaching this point and the regime if completely viscous. In this phase substance is creeping. (Markgraf, 2011).

3

Materials and method

Rheological properties measured selected were viscosity and storage/loss modulii, gauged via viscosity flow test and amplitude sweep tests respectively. These tests were perfromed with a rheometer manufactured by the company Anton Paar and model MCR-302. Sample material consisted of two types: suspension and reconstituted. Suspension material was divided into two different water content magnitudes: one at water limit and the second at 1.5 times water limit.

3.1 Materials

3.1.1 Clay mineral

Kaolin was the mineral clay used to perform the tests in this paper. Kaolin used was provided by the company Acros Organics N.V. with specific density of 2.6 and whose chemical formula is $H_2Al_2Si_2O_8$-H_2O and CAS 1322-58-7. Liquid limit, w_L, chosen in this work was set to 0.64 (Pedrotti and Tarantino, 2017).

3.1.2 Pore fluid

Water used for all the samples fabricated in this work was purified via Milli-Q system. Additionally, pure water was submitted to vacuum, this way ensuring pore fluid with no air content. See Figure 3.1. Samples with ionic strength were elaborated adding a salt, and for this work, sodium chloride was chosen as the saline agent. Sodium chloride used was provided by the company Fisher Chemical, with CAS number 7647-14-5. Molecular weight of 54.88 g/mol, a density of 1.199 g/mL at 20 C° and NaCl as chemical formula.



Figure 3.1: Distilled water being placed in vacuum.

3.2 Methods

3.2.1 Suspension samples

Material tested in this work began with the preparation of clay with suspension at different water content: a first equivalent to 100% liquid limit (0.64) and a second equivalent to 150% liquid limit (1.00). From each of these two slurries two additional mixtures were produced: one with pure water and a second adding saline solution. According to Palomino and Santamarina (2005) and Wang and Siu (2006) a concentration above 0.05 - 0.15 M of NaCl changes the interparticle forces between kaolinite particles. See Table 2.1 in Chapter 2.5. Therefore, in this work a value of 0.2 M NaCl was selected for the saline solution, this is 11 grams of sodium chloride per liter of water and higher to the threshold value mentioned. As a reference, 0.2 M lays below the average value of salinity of sea water, around 0.5 or 30 grams per liter (Söderblom, 1969). Mixing of this mixture was done in a blender sealed in vacuum, this was done in order to have a well mixed and homogeneous material with no air content. See Figures 3.2 and 3.3. Figure 3.5 shows this part under "Mixture".



Figure 3.2: Sample material being mixed by the vacuum blender

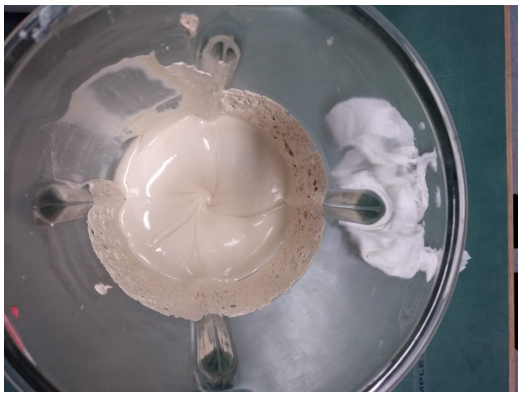


Figure 3.3: Reconstituted material with apparent no air content

3.2.2 Reconstituted samples

Reconstituted material was obtained after a vertical stress in tubes of slurries with pure water as pore fluid at water content equivalent to liquid limit (0.64). A vertical pressure of 80 kPa was determined for this material. Material was placed in consolidation tubes and subsequently compressed. Process of loading followed a double load method: starting with 1 kg until no deformation of sampled was measured, followed with 2 kg, 4 kg, 8 kg and so forth until reaching a stress of 80 kPa. Figure 3.4. This stage is shown in Figure 3.5 under "Oedometer".



Figure 3.4: Reconstituted material loaded in tubes

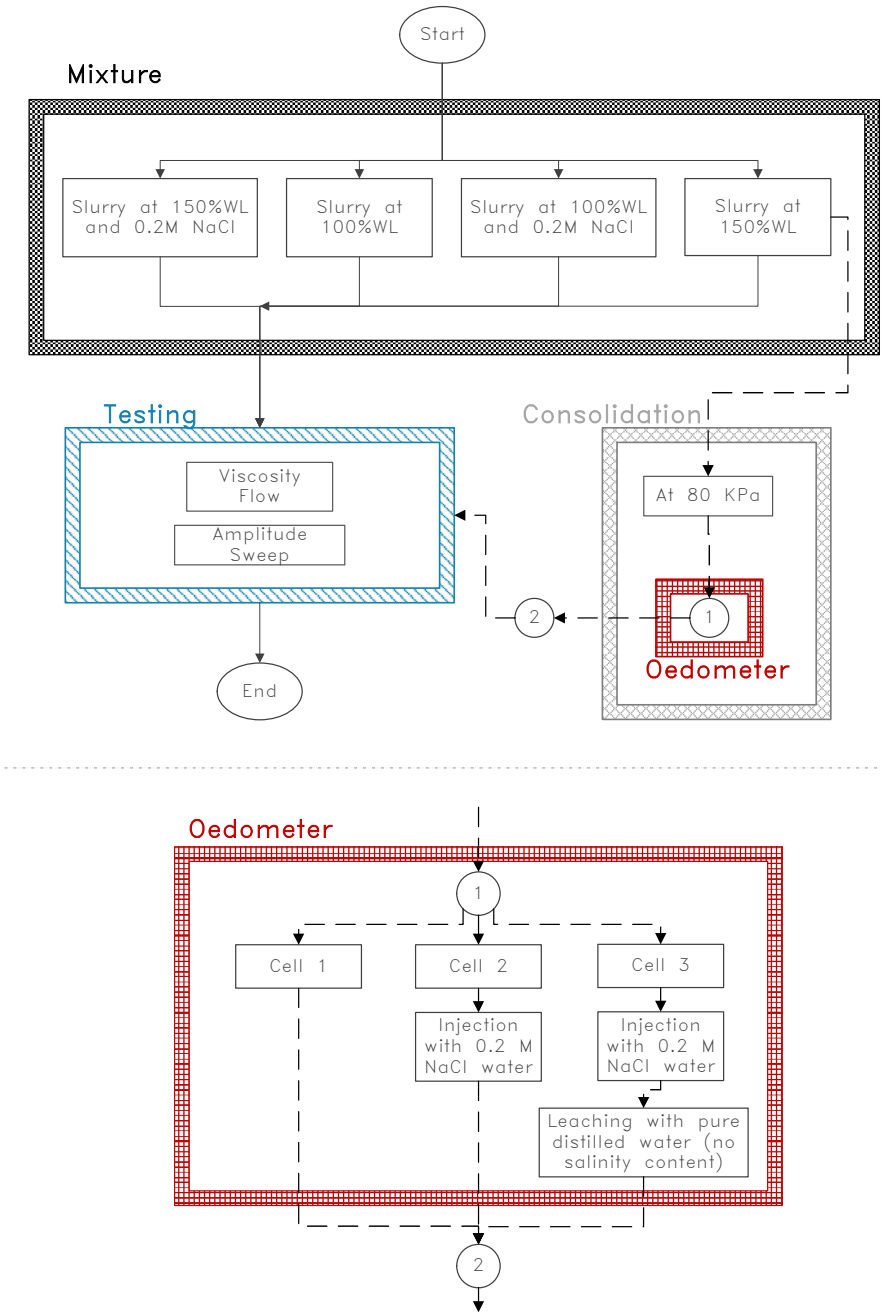


Figure 3.5: The general overview of the work method of this thesis

3.2.3 Saline injection in Oedometer

Three cells filled with reconstituted material were set in parallel and compressed at the same time up to 80 kPa, see Figure 3.6. Each of the three cell had a different treatment: first one was a control sample and was not altered; a second one was injected with saline solution at 0.2 M NaCl via back pressure from the bottom of

the cell; a third one had injection with saline solution followed by a leaching process with pure water. The time for injection and leaching was function on the decrease of liquid level injected in the cells. When the volume of saline solution or pure water introduced equalised the volume inside the cells, complete saturation of the material was assumed.



Figure 3.6: From left to right: Cell 1, 2 and 3 mounted in the test apparatus

Both effects of slow injection and leaching were of interest. This process emulates in a much smaller scale leaching of saline pore fluid in clay in nature, which is one of the main causes of sensitive clay (Söderblom, 1969; Bjerrum, 1969; Rankka et al., 2004).

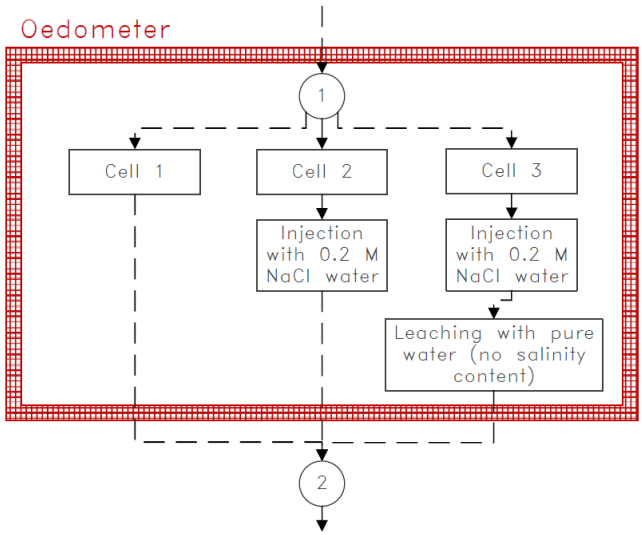


Figure 3.7: Material treated in oedometer apparatus. Extract from Figure 3.5

Additionally, values of pH were measured with a soil pH testers at the end of the consolidation in the tubes. Registered values oscillated between of 5.4 - 5.6, which are far form the 3.5 - 3.6 of point of zero charge reported by Schroth and Sposito (1997).

3.3 Rheometer Testing

The tests were performed on a rheometer model MC-302 manufactured by the company Anton Paar. The tests performed aimed to measure dynamic viscosity and shear modulii of the material under shear deformation. Two different tests were performed: viscosity flow and sweep amplitude. Results of these tests gave information required to analyse effects of ionic influence on clay.

From Equation 2.11 in Chapter 2.2.3, thickness of double layer is influenced by electrolyte concentration and cation valence. Alteration of pore water chemistry affects thickness of this layer, reducing the size of double layer thus reducing dispersion forces among platelets. Mitchell et al. (2005) mentioned that kaolinite has instantaneous exchange reactions, therefore alteration on this double layer is also instantaneous due to adsorption of ions. Additionally, alteration on clay fabric is also expected to be instant.

Viscosity or dynamic viscosity, as shown in Equation 2.13 from Chapter 2.7, is known as the "response of the material" against external shear stress. Thus, material with high viscosity results in much slower shear rate than material with low viscosity value. Viscoelastic properties were tested by sweep amplitude tests showing modulii relationship, as seen in Figure 2.11. Below are shown the details of the experiments of all the tests run in this work.

Table 3.1 shows technical details on rheometer tests performed in this work.

Table 3.1: Experiment details

Viscosity Flow	Amplitude Sweep
Duration: 150 seconds Initial shear rate: 0.0001 [1/s] Final shear rate: 10 [1/s] Points: 300 Initial point recording: 0.001 s Final point recording: 1 s Ramp Linear increment point recording	Duration: 156.5 seconds Initial shear strain: 0.01 % Final shear strain: 10% Points: 2000 Initial point recording: 0.1 s

3.3.1 Sample classification and naming

Next table shows details and name code use in this thesis. Given the different type of samples a resume of name tests, gives the reader opportunity to identify different material in this work.

Appendix includes additional figures from complement procedures realised in this chapter, as a photographic record. Figures A.1, A.3, A.4, A.5, A.6 are part of the procedure of placing material in between the rheometer plates to perform tests. This way reader can consult them if an insight of this work is needed.

Table 3.2: Sample details

Suspension	**Oedometer**
100% liquid limit 64% of water content and distilled water *Name:* `LPU`	Oedometer cell 1 at 80 kPa Cell with no injection nor leaching *Name:* `OE1`
100% liquid limit and Saline Solution 64% water content and 0.2 M NaCl pore fluid *Name:* `LSA`	Cell 2 at 80 kPa Cell with 0.2 M NaCl pore fluid injection *Name:* `OE2`
150% liquid limit 100% water content and distilled water *Name:* `1.5LPU`	Cell 3 at 80 kPa Cell with 0.2 M NaCl fluid injection and fresh water leaching *Name:* `OE3`
150% liquid limit and Saline Solution 100% water content and 0.2M NaCl pore fluid *Name:* `1.5LSA`	

4

Results

Once all data was gathered from tests, these were plotted in one single curve interpolating the median on every point plotted by rheometer. Details of the code that plotted the curves can be found in the Appendix under Chapters A.2.1 and A.2.2. Curves showed in this chapter include all representative tests to each type of material and pore fluid.

4.1 Effect of water content

Water content had the most sensitive parameter in these tests. Suspensions at liquid limit (LSA and LPU) showed higher results in viscosity and amplitude sweep than suspensions at 1.5 times liquid limit (1.5LSA and 1.5LPU) .

4.1.1 Viscosity

Lower fluid content gives clay more stiffness, giving material decrease in velocity of particles movement under shear strain, as shown in Figure 2.10. As seen in Figures 4.1 and 4.2 LSA and LPU suspensions, at 100% liquid limit (0.64 water content), show higher values of viscosity that 1.5LSA and 1.5LPU, with 150% liquid limit (1.00 water content).

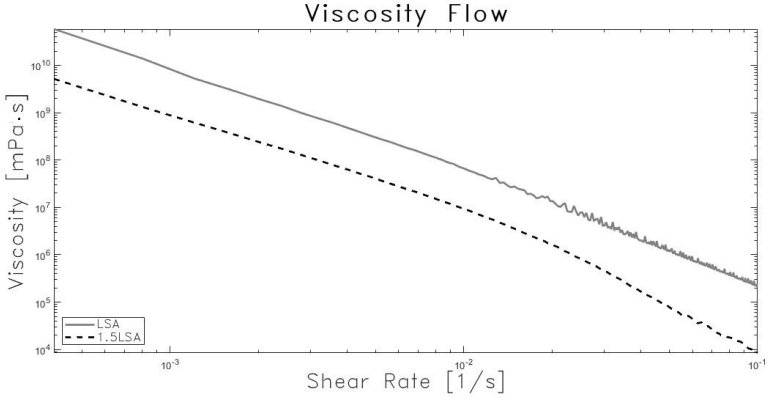


Figure 4.1: Viscosity flow for suspensions and saline solution (LSA, 1.5LSA)

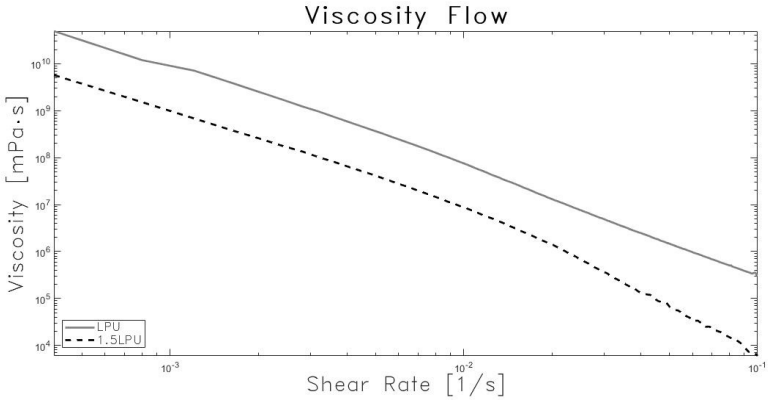


Figure 4.2: Viscosity flow for suspensions and distilled water (LPU, 1.5LPU)

4.1.2 Shear modulii

Trend from amplitude tests follow the same path in Figures 4.3 and 4.4. Increase in both modulii in the range of ten times higher for the LSA and LPU over 1.5LSA and 1.5LPU. Both figures show that both 1.5LPU and 1.5LSA had the same value of G' and G", being almost viscous. Whereas from $10^{-}6$ and $10^{-}3$ a clear dominance from G' is seen. LSA and LPU shows drop of viscous component, G", before 0.002 shear strain before it starts turning into a liquid f.

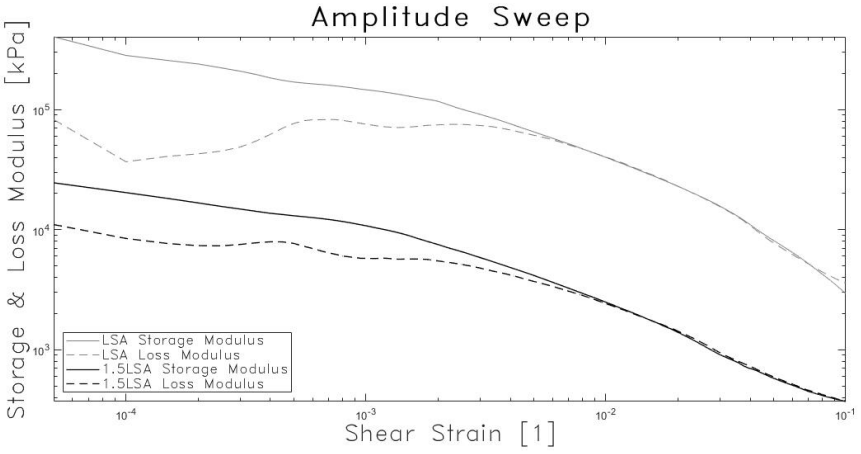


Figure 4.3: Amplitude sweep for suspensions and saline solution (LSA, 1.5LSA)

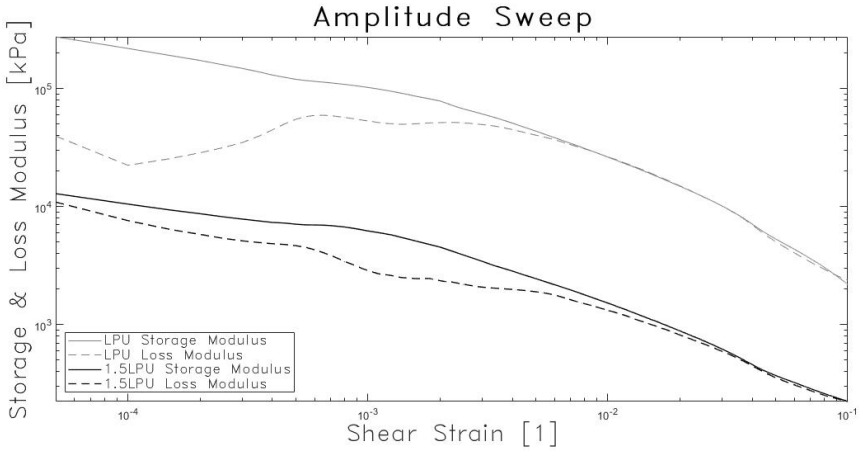


Figure 4.4: Amplitude sweep for suspensions and distilled water (LPU, 1.5LPU)

4.2 Effect of saline solution

Behaviour from saline solution had different behaviour in different tests, not so much change in the viscosity flow of material response. However, greater effects are visible in amplitude tests.

4.2.1 Viscosity

Figures 4.5 and 4.6 showed only an increase of viscosity of the saline samples during the smallest shear rate at the start of the test, showed with the black line.

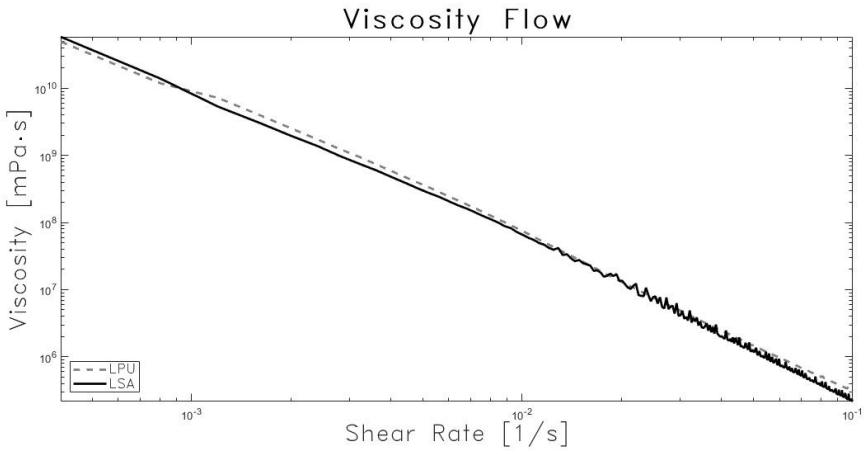


Figure 4.5: Viscosity flow of suspension clay at liquid limit (LPU, LSA)

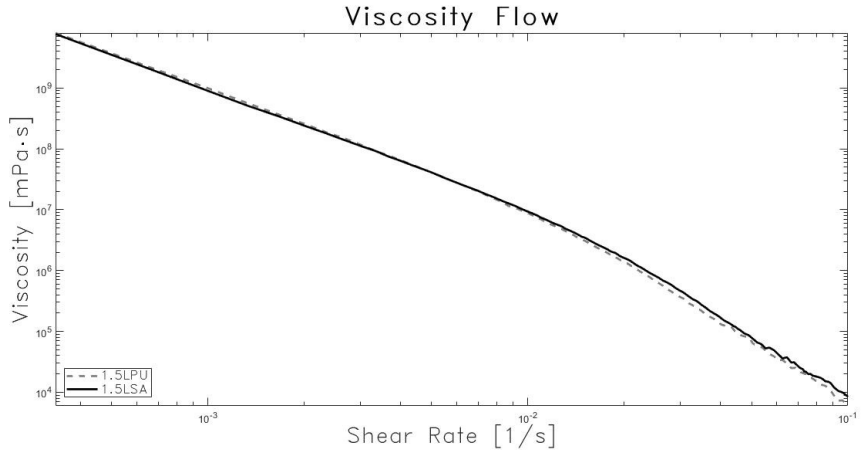


Figure 4.6: Viscosity flow of suspension at 1.5 times liquid limit (1.5LPU, 1.5LSA)

At small shear rate undisrupted material (OE1) showed higher values of viscosity, after a shear rate of 6 x $10_{(} - 3$) injected material showed a greater increment in viscosity values. On the other hand, leached material (OE3) showed the lowest values, thus indicating a decrease of viscosity after saline pore fluid injection. Any increment or constant conditions on viscosity were regressed by the effect of fresh water leach. See Figure 4.7.

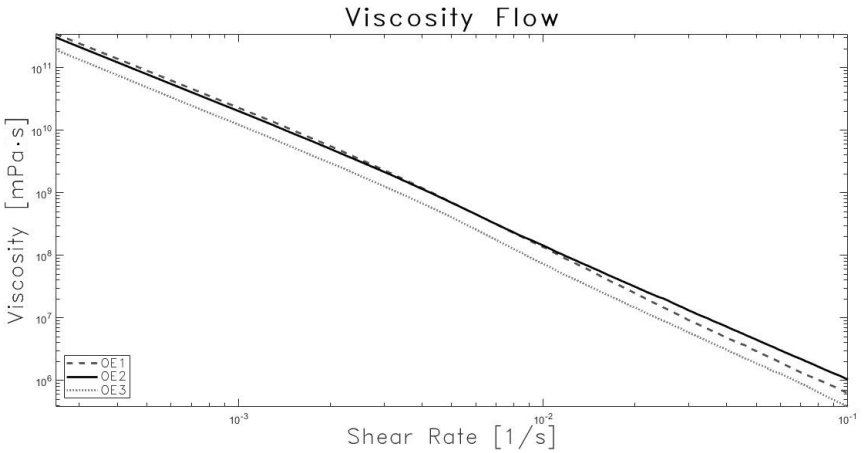


Figure 4.7: Viscosity flow of oedometer consolidated material (OE1, OE2, OE3)

4.2.2 Shear modulii

Increment in shear modulii is greater for saline material, see in Figures 4.8 and 4.9. Slurries with saline pore fluid, LSA and 1.5LSA respectively, showed higher values than pure water pore fluid, LPU and 1.5LPU. Indicating a improvement in material of the shear modulus component derived from the effects of ionic strength of salt.

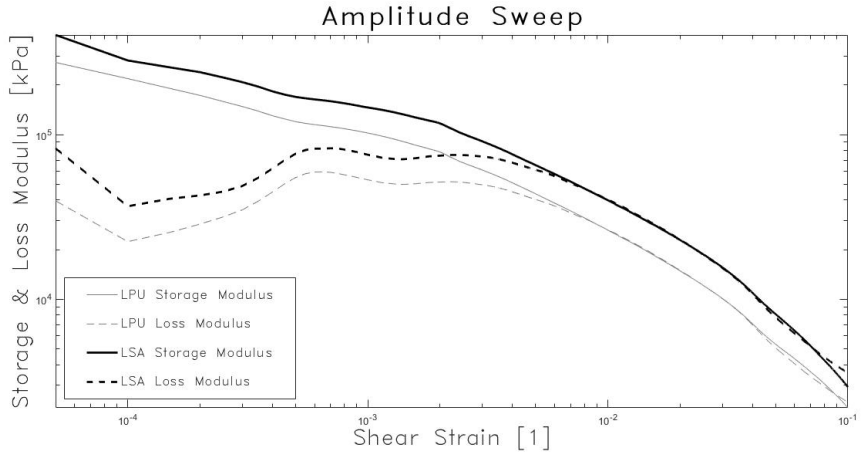


Figure 4.8: Amplitude sweep of suspension clay at liquid limit (LPU, LSA)

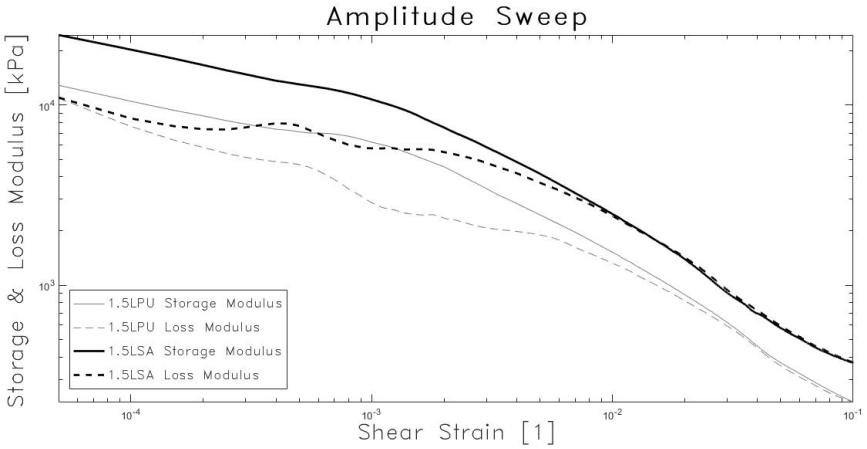


Figure 4.9: Amplitude sweep of suspension at 1.5 times liquid limit (1.5LPU, 1.5LSA)

Salinity in material injected during the oedometer (OE2) back pressure increased materials storage modulus and loss modulus, shown in Figure 4.10. From this figure the solid line in black shows material undisrupted (OE1) and, on the other hand leached material (OE3) had the lowest storage modulus and low loss of modulus compared with the saline sample (OE2). Leached sample results show a recovery of the material original rheological parameters, based on results from results retrieved by OE1.

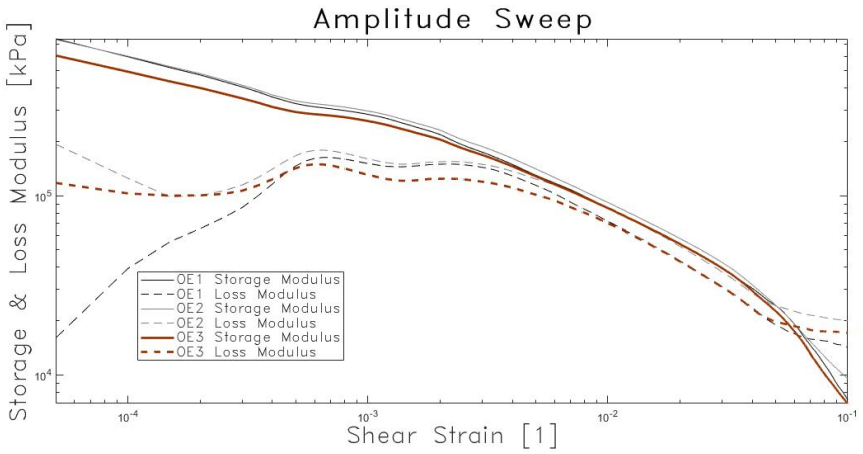


Figure 4.10: Amplitude sweep of oedometer consolidated material (OE1, OE2, OE3)

5

Discussion

Even though viscosity and shear modulus are not common parameters of stiffness used in geotechnics. Increase in viscosity and shear modulus showed in this work can show indirectly improvement of the classical parameters of strength used in soil mechanics. Effects of different ionic concentration and higher valence salts can be of interest.

Back pressure injection to oedometer cell was completed when a volume of water equal to the volume inside cell was introduced, and same methodology was followed when leaching with fresh water. This process lasted one month approximately. This improvement method can be paired with a faster method introducing material to clay.

6
Conclusions

This research has demonstrated that the rheometer is a feasible apparatus for testing small sample volumes of soft clays in slurry and consolidated form. In addition of more familiar rheological properties such as viscosity (ratio of shear strength and shear rate) it also allows to investigate the storage and loss modulus in the material (in terms of strain energy). The interpretation of the yield-point, remains a further topic for studies, as the interpretation from rheology tests differs from the conventional geotechnical interpretation.

In almost all tests the viscosity and shear modulus showed higher values in the kaolin samples that had saline pore fluid. The viscosity data further indicates that all the samples showed a shear thinning behaviour.

Viscosity of reconstituted consolidated clay sample that was initially prepared with distilled water improved after injection of saline fluid via back pressure line after consolidation to 80 kPa in an oedometer cell. Furthermore, the opposite effect, i.e. a loss of strength was noted after subsequent leaching with fresh water.

Not only the viscosity increased after injection of the saline solution, also the shear modulus increased with an apparent elastic behaviour over a large range of strain rate amplitude. Subsequent leaching of fresh water after saline injections changed the material response, as the viscosity and shear modulus reduced.

Curves retrieved from the amplitude tests shows that in the case of reconstituted samples consolidated to an effective stress level of 80 kPa showed more elasto-plastic behaviour, whereas the slurries with at 100% liquid limit and 150% times liquid limit behaved more like a viscous fluid.

Bibliography

Alas, M. and Ali, S. (2019). Prediction of the high-temperature performance of a geopolymer modified asphalt binder using artificial neural networks. *International Journal of Technology*, 10:417.

Andersson-Sköld, Y., Torrance, J. K., Lind, B., Odén, K., Stevens, R. L., and Rankka, K. (2005). Quick clay—a case study of chemical perspective in southwest sweden. *Engineering Geology*, 82(2):107–118.

Au, P.-I. and Leong, Y.-K. (2016). Surface chemistry and rheology of slurries of kaolinite and montmorillonite from different sources. *KONA Powder and Particle Journal*, page 2016007.

Birdi, K. and S (2002). *Handbook of surface and colloid chemistry*. CRC press.

Bjerrum, L. (1967). Engineering geology of norwegian normally-consolidated marine clays as related to settlements of buildings. *Geotechnique*, 17(2):83–118.

Bjerrum, L. (1969). A field study of factors responsible for quick clay slides. In *Proc. Int. Conf. on Soil Mechanics and Fundation Engineering, 1969*, pages B31–B40.

Brenner, R. P., Nutalaya, P., Chiligarian, G. V., and Robertson JR, J. O. (1981). Engineering geology of soft clay.

Broms, B. (1979). Problems and solutions to constructions in soft clay. In *Proc. 6th Asian Regional Conference SMFE, Singapore*, volume 2, pages 3–38.

Chu, J., Varaksin, S., Klotz, U., and Mengé, P. (2009). Construction processes. In *Proceedings of the International Conference on Soil Mechanics and Geotechnical Engineering, Alexandria, Egypt*.

Cora, I., Dódony, I., and Pekker, P. (2014). Electron crystallographic study of a kaolinite single crystal. *Applied Clay Science*, 90:6–10.

Derjaguin, B. v. and Landau, L. (1993). Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. *Progress in Surface Science*, 43(1-4):30–59.

Frank, H. S. and Wen, W.-Y. (1957). Ion-solvent interaction. structural aspects of ion-solvent interaction in aqueous solutions: a suggested picture of water structure. *Discussions of the Faraday Society*, 24:133–140.

Guven, N. (1992). Molecular aspects of clay-water interactions. *Clay-water interface and its rheological implications*, pages 2–79.

Ibanez, M., Wijdeveld, A., and Chassagne, C. (2014). The role of mono-and divalent ions in the stability of kaolinite suspensions and fine tailings. *Clays and Clay minerals*, 62(5):374–385.

Kenney, T. C. (1966). Shearing resistance of natural quick clays.

Li, Z., Katsumi, T., Inui, T., and Takai, A. (2013). Fabric effect on hydraulic conductivity of kaolin under different chemical and biochemical conditions. *Soils and Foundations*, 53(5):680–691.

Lundström, K., Larsson, R., and Dahlin, T. (2009). Mapping of quick clay formations using geotechnical and geophysical methods. *Landslides*, 6(1):1–15.

Markgraf, W. (2011). Rheology in soils. *Encyclopedia of Agrophysics*, pages 700–705.

Markgraf, W. and Horn, R. (2005). Rheology in soil mechanics-structural changes in soils depending on salt-and water content. *Annual Transactions of the Nordic Rheology Society*, 13:149–154.

Markgraf, W., Horn, R., and Peth, S. (2006). An approach to rheometry in soil mechanics—structural changes in bentonite, clayey and silty soils. *Soil and Tillage Research*, 91(1-2):1–14.

Michaels, A. S. and Bolger, J. C. (1964). Particle interactions in aqueous kaolinite dispersions. *Industrial & Engineering Chemistry Fundamentals*, 3(1):14–20.

Mitchell, J. K. (1981). Soil improvement-state of the art report. In *Proc., 11th Int. Conf. on SMFE*, volume 4, pages 509–565.

Mitchell, J. K., Soga, K., et al. (2005). *Fundamentals of soil behavior*, volume 3. John Wiley & Sons New York.

Palomino, A. M. and Santamarina, J. C. (2005). Fabric map for kaolinite: effects of ph and ionic concentration on behavior. *Clays and Clay minerals*, 53(3):211–223.

Pedrotti, M. and Tarantino, A. (2017). An experimental investigation into the micromechanics of non-active clays. *Géotechnique*, 68(8):666–683.

Pusch, R. (1966). Quick-clay microstructure. *Engineering Geology*, 1(6):433–443.

Pusch, R. (1970). *Clay microstructure. A study of the microstructure of soft clays with special reference to their physical properties.*

Rand, B. and Melton, I. E. (1977). Particle interactions in aqueous kaolinite suspensions: I. effect of ph and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions. *Journal of Colloid and Interface Science*, 60(2):308–320.

Rankka, K., Andersson-Sköld, Y., Hultén, C., Larsson, R., Leroux, V., and Dahlin, T. (2004). Quick clay in sweden.

Rosenqvist, I. T. (1953). Considerations on the sensitivity of norwegian quick-clays. *Geotechnique*, 3(5):195–200.

Rudolph, N. and Osswald, T. A. (2014). *Polymer rheology: fundamentals and applications*. Carl Hanser Verlag GmbH Co KG.

Santamarina, J. C. (2003). Soil behavior at the microscale: particle forces. *Geotechnical Special Publication*, pages 25–56.

Schroth, B. K. and Sposito, G. (1997). Surface charge properties of kaolinite. *Clays and Clay minerals*, 45(1):85–91.

Skempton, A. and R.D., N. (1952). "the sensitivity of clays,". *Géotechnique*.

Söderblom, R. (1969). *Salt in Swedish clays and its importance for quick clay formation. Results from some field and laboratory studies*.

Verwey, E. J. W., Overbeek, J. T. G., and Van Nes, K. (1948). *Theory of the stability of lyophobic colloids: the interaction of sol particles having an electric double layer*. Elsevier Publishing Company.

Wang, Y.-H. and Siu, W.-K. (2006). Structure characteristics and mechanical properties of kaolinite soils. i. surface charges and structural characterizations. *Canadian Geotechnical Journal*, 43(6):587–600.

A

Appendix 1

A.1 Photographic Record

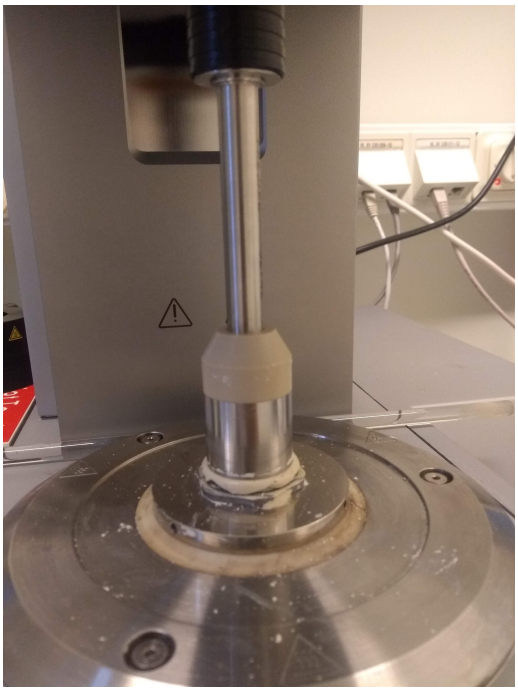


Figure A.1: Slurry material in between the plates of the rheometer. This figure shows a test made in between a 24mm plate

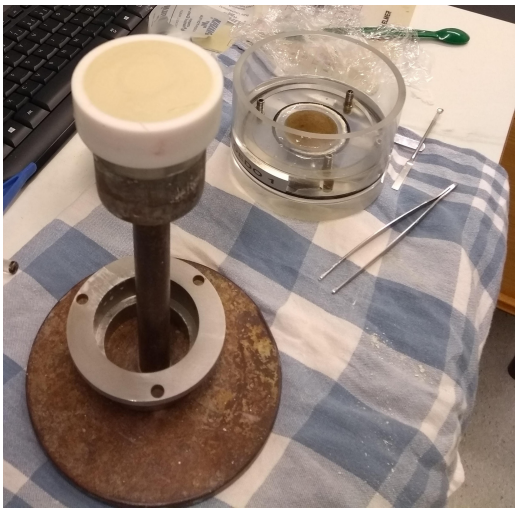


Figure A.2: Set cells ready to layer samples



Figure A.3: Process of handling layers from the one of the cells from oedometer

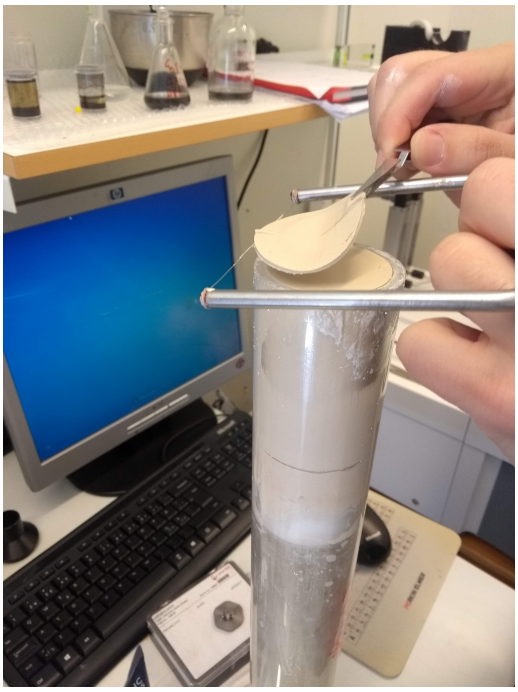


Figure A.4: Handling of layer samples from the reconstituted material

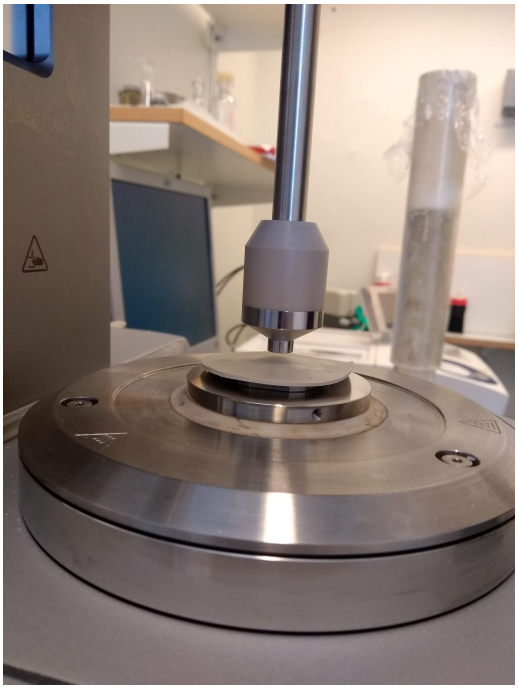


Figure A.5: Layer of material in the apparatus lower plate

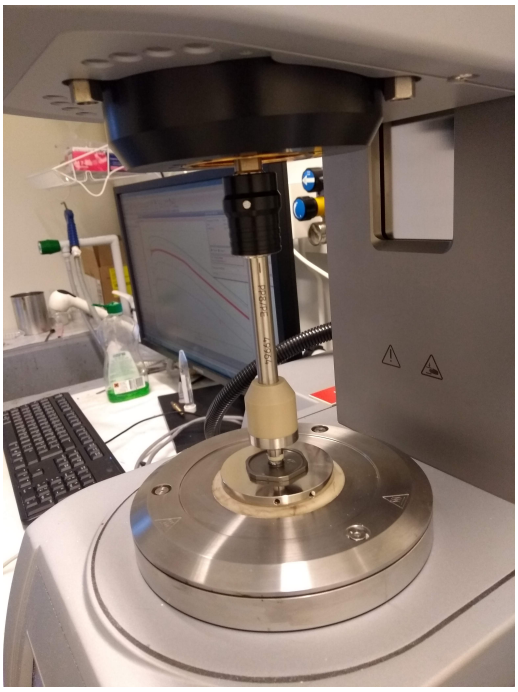


Figure A.6: Cleaned slurry material in between the plates of the rheometer during a test. This figure shows a test made with a 8mm plate

A.2 Plotting language code

A.2.1 Amplitude test plotting

```
    % load data
filename='C:\Users\Julio\OneDrive - Chalmers tekniska hogskola\AMPLITUDE_TEST (1).t
%filename='C:\Users\Julio\Documents\data_fit.txt';
data = importdata(filename);
test = data.data;

%%
info=data.textdata;
titles={info{1,:}}; %name of columns

info=info(2:end,:); %remove name of columns

% by codes
[codes,~,rowcode]=unique({info{:,10}});

%% fill empty with NaN
empties = cellfun('isempty',info(:,5));
fx = @(x)any(isempty(x));
ind=cellfun(fx,info);
info(ind)={NaN};
```

```
%%
xpoints=2000;
x1=linspace(0,.1,xpoints); %create the x points
ycode=zeros(length(codes),xpoints);

clrs = distinguishable_colors(20);


%select the codes (order in codes)
disp('Codes: ')
disp(codes)

%write it in brackets
selectCode=input('Choose codes to plot [#,#] :  ');
%selectCode=[3,4];

%how to write the namelegends
%newcodes={'a','b','c'};

%text in legend, repelem repeat element twice
namelegend=repelem(codes(selectCode),2);

for j= 1:length(selectCode)

    %how many different test you have with code j
    [diftest,~,codetest]=unique(test(rowcode==selectCode(j)));
    interpcode5=zeros(length(diftest),xpoints); %new y
    interpcode6=interpcode5;
    for itest = 1:length(diftest) %loop for test
        ix=(rowcode==selectCode(j) & test==itest);
        x = (str2double({info{ix,3}}));
        y5 =str2double({info{ix,5}});
        y6 =str2double({info{ix,6}});
        [~,b] = unique(x,'first');
        ii = sort(b);
        interpcode5(itest,:)=interp1(x(ii),y5(ii),x1); %interpolate to find more x
        interpcode6(itest,:)=interp1(x(ii),y6(ii),x1);
        % plot tests
        %loglog(x1,interpcode(itest,:))
        % hold on
        ycode5(j,:)=median(interpcode5,1,'omitnan');
        ycode6(j,:)=median(interpcode6,1,'omitnan');
    end
%    loglog(x1,ycode(j,:),'r','linewidth',2)
    loglog(x1,ycode5(j,:),'color',clrs(j,:))
    hold on
```

```
    loglog(x1,ycode6(j,:),'--','color',clrs(j,:))

end

legend(namelegend,'location','southwest')
title('Amplitude Sweep')
xlabel(titles{3})
ylabel('Storage & Loss Modulus [kPa]')
axis tight
```

A.2.2 Viscosity flow plotting

```
    % load data
filename='C:\Users\Julio\OneDrive - Chalmers tekniska hogskola\VISCOSITY_FLOW.txt';
%filename='C:\Users\Julio\Documents\data_fit.txt';
data = importdata(filename);
test = data.data;

%%
info=data.textdata;
titles={info{1,:}}; %name of columns

info=info(2:end,:); %remove name of columns

% by codes
[codes,~,rowcode]=unique({info{:,10}});

%% fill empty with NaN
empties = cellfun('isempty',info(:,7));
fx = @(x)any(isempty(x));
ind=cellfun(fx,info);
info(ind)={NaN};

%%
xpoints=250;
x1=linspace(0,.1,xpoints); %create the x points
ycode=zeros(length(codes),xpoints);

clrs = distinguishable_colors(20);


%select the codes (order in codes)
disp('Codes: ')
```

```
disp(codes)

%write it in brackets
selectCode=input('Choose codes to plot [#,#] :  ');
%selectCode=[3,4];

%how to write the namelegends
%newcodes={'a','b','c'};

%text in legend, repelem repeat element twice
namelegend=codes(selectCode);

for j= 1:length(selectCode)

    %how many different test you have with code j
    [diftest,~,codetest]=unique(test(rowcode==selectCode(j)));
    interpcode=zeros(length(diftest),xpoints); %new y
    %interpcode6=interpcode;
    for itest = 1:length(diftest) %loop for test
        ix=(rowcode==selectCode(j) & test==itest);
        x = (str2double({info{ix,3}}));
        y =str2double({info{ix,7}});
        %y6 =str2double({info{ix,6}});
        [~,b] = unique(x,'first');
        ii = sort(b);
        interpcode(itest,:)=interp1(x(ii),y(ii),x1); %interpolate to find more x po
        %interpcode6(itest,:)=interp1(x(ii),y6(ii),x1);
        % plot tests
        %loglog(x1,interpcode(itest,:))
        % hold on
        ycode(j,:)=median(interpcode,1,'omitnan');
        %ycode6(j,:)=median(interpcode6,1,'omitnan');
    end
%    loglog(x1,ycode(j,:),'r','linewidth',2)
    loglog(x1,ycode(j,:),'color',clrs(j,:),'linewidth',2)
    hold on

    %loglog(x1,ycode6(j,:),'--','color',clrs(j,:))

end
%legend
legend(namelegend,'location','southwest','FontSize',12,'FontName','RomanD')
title('\fontsize{24}Viscosity Flow','FontName','RomanD')
xlabel(titles{3},'FontSize',20,'FontName','RomanD')
ylabel('\fontsize{20}Viscosity [mPa·s]','FontName','RomanD')
axis tight
```