Titel: Investigation of Shear Yield Stress, Zeta Potential and Particle Size in Kaolinite and Bentonite Suspensions

Project Period: September 2008 – June 2009 Composed by: Joan Skadhauge Larsen

Abstract

An ideal circumstance would be to accurately determine the shear yield stress of several clay suspensions from the measurement of particle surface charge and particle size characteristics, or vice versa. This will improve investigation of the dewaterability of clay mineral tailings.

Shear yield stress, zeta potential and particle size, estimated with the vane technique by Nguyen and Boger [1985], with electro-acoustics and with light scattering, respectively, have been measured in kaolinite suspensions. It was not possible to determine the yield stress in bentonite suspension by the used sample preparation; hence the shear yield stress cannot be correlated to the zeta potential and particle size.

To correlate the measured parameters, the shear yield stress times the surface area weighted particle size was plotted as function of zeta potential squared. The shear yield stress times the surface area weighted particle size in a kaolinite suspension with a pH dependent surface charge is increasing as the zeta potential squared, i.e. the surface charge is decreasing. This is in agreement with the correlation, based on the mathematic model proposed by Scales *et al.*[1998]. The shear yield stress times particle size in a kaolinite suspension with a pH independent surface charge does not change as the surface charge decreases due to the minor change in zeta potential between pH 4-10.

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Titel: Undersøgelse af shear yield stress, zeta potentiale og partikelstørrelse i kaolin og bentonite suspensioner

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Resumé

I en ideel situation kan shear yield stress af en ler suspension bestemmes nøjagtigt ud fra målinger af partiklernes overfladeladning samt partikelstørrelse karakteristika, eller omvendt.

Shear yield stress, zeta potentiale og partikelstørrelse er blevet målt i forskellige kaolin suspensioner, målt med henholdsvist et fire-bladet "vane", metode udviklet af Nguyen og Boger [1985], elektro-akustik måling og lys spredning. Det var ikke muligt at bestemme shear yield stress for bentonite suspensioner med den anvendte prøveforberedelse, og dermed kan sammenhængen mellem shear yield stress, zeta potentiale og partikelstørrelse ikke bestemmes.

For at undersøge sammenhængen mellem de målte parametre er shear yield stress ganget den overfladeareal bestemt partikelstørrelse blevet plottet som funktion af zeta potentiale i anden. Shear yield stress gange den overfladearea bestemt partikelstørrelse i en kaolin suspension med en pH afhængig overfladladning stiger mens zeta potentialet i anden, dvs. overfladeladningen, falder. The stemmer overens med den matematiske model forslået af Scales *et al.* [1998]. Shear yield stress ganget den overflade areal bestemte partikelstørrelse i en kaolin suspension med pH uafhængig overfladeladning ændres ikke når zeta potentialet falder grundet den mindre ændring i zeta potentialet mellem pH 4-10.

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PREFACE

This master thesis "Investigation of Shear Yield Stress, Zeta Potential and Particle Size in Kaolinite and Bentonite Suspensions" was written in the period from September 2008 to June 2009, composed at Department of Chemistry & Biomolecular Engineering, University of Melbourne, Australia and at Section of Chemistry, Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Denmark.

The Harvard System [Holland 2005] is used for literature references throughout the report and appendices and the references are listed in alphabetical order under References. The report in separated in main sections and subsections, all numbered. Figures, tables and equations are numbered chronological. Raw data and a pdf version of the thesis are enclosed on the CD-ROM.

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1 INTRODUCTION

Mining and mineral processing in Australia and the rest of the world generates great amounts of mineral tailings, i.e. soil residues in aqueous suspension, which must be disposed in an economically and environmentally acceptable way [Nguyen and Boger 1998]. A high solid content in tailings is desirable as the waste water can be recycled, and the volume of tailings is reduced. Commonly, dewatering of tailings is achieved by flocculation and gravity settling in a thickener tank and subsequently in a tailings pond [Nguyen and Boger 1998], see Figure 1. However tailings can have a poor processability and dewaterability due to the high content of clay minerals [de Kretser 1995].



Figure 1: Tailings dam from a cobber-gold mine, Northparks Mines in New South Wales, Australia [Mineral Council of Australia, 2007]

The faces of kaolinite platelets are negative charged and the edges positive below pH 7, thus attraction between edges and faces can occur at pH 4-7 and form a "house of cards" formation [Johnson *et al.* 1998]. This edge-face interaction is also possible for bentonite in a lower pH range [van Olphen 1963]. The "house of cards" formation will increase the clay volume and reduce the dewaterability.

In bentonites and to some extent in kaolinites isomorphous substitution occurs, i.e. an atom of lower positive valence replaces an approx same-size atom of higher positive valence [van Olphen 1963]. The excess of negative lattice charges is compensated by adsorption of cations on the surface of the unit layer. These compensating cations can induce swelling in between the unit layers [van Olphen 1963] and increase the clay volume [McFarlane *et al.* 2006], thus reducing the dewaterability significantly [de Kretser 1995].

One of the initial steps to improve the dewaterability of mineral tailings is to investigate the interactions between clay platelets. As shear yield stress is an indication of interaction between the particles, it is used to study interactions between particles in clay suspensions and in metal oxides suspensions [Johnson et al. 1998; Johnson et al. 1999; Johnson et al. 2000; McFarlane et al. 2006]. A model proposed by Scales et al. [1998] describes a correlation between shear yield stress, solid concentration, particle size and zeta potential for flocculated suspensions. By using the distance between the particles as a fitting parameter the model is in reasonable agreement with experimental data for alumina suspension at different solid concentrations and different pH conditions. The model gives a qualitative assessment of the shear yield stress and hence an indication of the particle interactions in kaolinite suspensions [Johnson et al. 1998; Johnson et al. 1999]. The work is done on two different kaolinites at approx same solid concentration and electrolyte concentration; however there is a significant difference in shear yield stress partly due to the doubling of the surface area. An ideal circumstance would be to accurately determine the shear yield stress of several clay suspensions from the measurement of particle surface charge and particle size characteristics, or vice versa. This leads up to the problem statement of this thesis:

Is it possible to correlate the shear yield stress, the zeta potential and the particle size in kaolinite and bentonite suspensions based on the model proposed by Scales et al [1998]?

To comprehend the interactions between the clay platelets more theory about the composition of clay and the inter-particle interactions is necessary. The mathematic model proposed by Scales *et al.* [1998] is presented to understand the correlation between shear yield stress, zeta potential and particle size. This is given in the following chapter.

In this chapter basic theory about kaolinite and bentonite is introduced to get an understanding of the interactions between clay particles. The surface charge of clay is governed by many chemical and physical phenomena such as ion exchange, adsorption, swelling and colloidal stability. To understand these phenomena, theory about the surface charge of alumina and silica and the effect of pH and electrolyte concentration in an aqueous medium is presented. Some of the interaction theory is used to estimate shear yield stress of a particle suspension. This is clarified in the last part of this chapter.

2.1 CLAY THEORY

2.1.1 MINERALOGY

Clay minerals have a layered structure consisting of unit layers of silica sheet(s) and an alumina/magnesia sheet. In a silica sheet a silicon atom is coordinated with four oxygen atoms forming a tetrahedron [van Olphen 1963]. Three of the four oxygen atoms are shared with other silica tetrahedrons forming hexagons where the fourth can be shared with another sheet. In the latter sheet an aluminium or a magnesium atom is coordinated in the centre of an octahedron with six oxygen atoms/hydroxyl groups in the corners [van Olphen 1963]. If the octahedron sheet is occupied with aluminium atoms 2/3 of the available octahedral sites are occupied whereas for magnesia sheet every octahedral is occupied. Three of the oxygen atoms and hydroxyl groups are placed "above" an aluminium/magnesium atom and the other three below. When combining a silica sheet and an alumina/magnesia sheet two of the three hydroxyl groups are "replaced" by two oxygen atoms from two silica tetrahedrons [van Olphen 1963]. Thus the alumina/magnesia sheet contains one hydroxyl group towards the silica sheet and three hydroxyl groups away from the alumina/magnesia sheet, see Figure 2.



Figure 2: An illustration of the atom arrangement in the unit cell of kaolinite. Modified from Grim [1968]

Kaolinite is a 1:1 layer mineral consisting of one silica sheet and one alumina sheet, see Figure 2, whereas *bentonite* is a 2:1 layer mineral consisting of two silica sheets with an alumina/magnesia sheet in between, see Figure 3. The unit layers are held together by van der Waals forces and hydrogen bonds which are comparable weak with respect to the primary valence forces between the tetrahedral and octahedral sheets [van Olphen 1963]. In dispersion in water with breakup into single clay platelets that have a flat sheet-like particle shape and a high aspect ratio [van Olphen 1963].



Figure 3: An illustration of the atom arrangement in the unit cell of bentonite. Exchangeable cations are situated in between the unit layers due to isomorphous substitution, which leads to swelling. Modified from Grim [1968]

The lattice of an ideal clay mineral is uncharged, however isomorphous substitution can occur, i.e. an atom of lower positive valence replaces an approx same-size atom of higher positive valence [van Olphen 1963]. If a silicon atom is substituted with an aluminium atom the net charge of the lattice becomes negative. In general, silicon is substituted with aluminium and aluminium with magnesium in the tetrahedral and the octahedral sheet, respectively. The excess of negative lattice charges is compensated by adsorption of cations, which are too large to penetrate into the lattice, on the surface of the unit layer. Some of the compensating cations may be exchanged with other cations in the presence of water, and this ability is called Cation Exchange Capacity (CEC) [van Olphen 1963]. The CEC of kaolinite is approx 1-10 meq per 100 gram dry clay while bentonite is approx 70 meq per 100 gram dry clay [van Olphen 1963].

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Isomorphous substitution is significantly propagated in bentonite and as the high CEC indicates it has many interlayer ions [van Olphen 1963]. In the presence of water two things can occur; hydration of the adsorbed and non-exchangeable compensating cations occurs, also called interlayer swelling, and osmotic swelling in between the unit layers due to the exchangeable cations [McFarlane *et al.* 2006]. Both can lead to a significant increase in the volume [McFarlane *et al.* 2006] and thus a significant reduction in the dewaterability.

Bentonites can be referred to as sodium exchanged bentonite or calcium exchanged bentonite. A sodium exchanged bentonite is a bentonite where all the exchangeable cations are sodium and like-wise for calcium exchangeable bentonite. This can be induced by repeating washes with sodium chloride. Calcium exchanged bentonite has reduced swelling compared to sodium exchanged, even after normalisation for its valence [de Kretser 1995]. This reducing swelling effect is used in improving dewaterability by "controlled dispersion" of bentonite [de Kretser 1995].

2.1.2 SURFACE CHARGE

Many researchers have studied the surface charge of clay particles [Duc et al. 2005]. This is a very complex study as many mechanisms can occur simultaneous at the

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surface, such as dissociation of hydroxyl groups, ion exchange, dissolution and precipitation of metal oxides and re-adsorption [Duc *et al.* 2005]. The mechanisms can take place at the faces and/or at the edges.

2.1.2.1 CHARGE OF FACES

Due to isomorphous substitution the lattice of clay minerals are negatively charged and hence cations are adsorbed to the surface. Some of these cations are strongly adsorbed and some are exchangeable, but both affect the surface charge [van Olphen 1963]. The surface potential can change due to electrolyte concentration, pH dependent adsorption/re-adsorption and precipitation of metal oxides.

As the electrolyte concentration increases the cations at the surface are compressed – the thickness of the electric double layer is reduced (this is explained in section 2.2.3.1 Repulsive Electrical Double Layer Force) [van Olphen 1963]. Thus the potential increases as the charge density increases. This is valid for bentonites with many exchangeable cations [van Olphen 1963]. Due to the small spacing between the layers in kaolinites, it is assumed that the few compensating cations are situated on the exterior surface of a platelet and not in between [van Olphen 1963]. Based on this observation, it is assumed that the surface charge of kaolinite can also be affected by electrolyte concentration as the exchangeable cations are situated in the exterior.

Franks [2002] describes pH dependent adsorption and re-adsorption of caesium, potassium, sodium and lithium on quartz particles. Depending on the specific cation the zeta potential differs. Lithium gives the numeric largest zeta potential, sodium the second largest and caesium gives the lowest. This is an example on how adsorption of different cations can change the surface charge of silica. Whether this adsorption is possible for the faces of silica sheet in kaolinite and bentonite is not verified. The adsorption is assumed to be valid for the edges of clay as lattice structure is interrupted.

According to Johnson *et al.* [1999] "precipitation" of metal oxides on the surface can alter the surface charge of the particle. The theory is based on an alumina surface but is

expected to be valid for kaolinite as well [Johnson *et al.* 1999] as they have an exposed alumina sheet in the unit layer. Metal ions dissolved in the medium can be hydrolysed as followed;

$$M^{n+} + xOH^{-} \to M(OH)_{x}^{(n-x)+}$$

$$M(OH)_{x}^{(n-x)+} + OH^{-} \to M(OH)_{x+1}^{(n-x+1)}$$

$$M(OH)_{x}^{(n-x)+} + H^{+} \to M(OH)_{x-1}^{(n-x+1)} + H_{2}O$$

 M^{n+} is not expected to adsorb strongly to the metal oxide surface, even though surface is strongly negative, whereas the lower charged hydrolysis product will adsorb to the surface [Johnson *et al.* 1999]. As pH increases, the adsorption of metal hydrolysis products increases until a layer of the metal hydroxide is "precipitated" on the surface [Johnson *et al.* 1999]. As bentonite has an alumina sheets in between two sheets of silica this kind of precipitation is not assumed to be possible. Furthermore will swelling work against this form for precipitation.

2.1.2.2 Charge of Broken Bond Atoms

The lattice structure is broken at the edges; hence some of the lattice atoms exposed to the surface are not completely compensated [van Olphen 1963]. These surfaces are called "broken-bond" surfaces. According to Felhi *et al.* [2008] a poor crystalline kaolinite can result in formation of small particles with broken edges. The poor crystalline may be poor due to the presence of impurities [Felhi *et al.* 2005].

The exposed atoms give rise to an electric charge at which dissociation-complexation reactions occur [Duc *et al.* 2005], see the above reaction.

The possibility of aluminium atoms at the edges greater as some of the silicon atoms are replaced by aluminium atoms in the silica sheet. Depending on the availability of Al³⁺ and OH⁻ the surface of the edge becomes either positive or negative [van Olphen 1963]. In acidic environment Al³⁺ ions are hydrolysed and the edge becomes positive. In alkaline environment both OH⁻ and complex aluminate ions are present and the edge becomes negative. Accurate acid-base constants of clays are difficult to obtain

experimentally as numerous mechanisms can occur at the surface of a clay platelet, it gets even more complicated in the presence of other minerals [Duc *et al.* 2005].

When measuring the surface charge of clay minerals the net charge is measured. As the clay particles are negatively charged and the area of the faces is significantly larger than the edges the faces is assumed to be negatively charged. Williams and Williams [1978] estimated the edge charge of kaolinite particles to be positive below pH 7, see Figure 4. This corresponds to the structure of the edges, which is half silica and half alumina in an ideal kaolinite, as alumina is positively charged in acidic environments [Johnson *et al.* 1998] and crystalline silica is negatively charged above pH 2 [Franks 2002]. Due to the positively charged edges attraction between edges and faces can occur below pH7 and thus form a "house of card" formation [Johnson *et al.* 1997]. This is also verified by measuring shear yield stress as function of pH on a kaolinite. The maximum shear yield stress is around pH 5-6 which is interpreted as an indication of the "house of cards" formation [Johnson *et al.* 1998].



Figure 4: The estimated zeta potential of edges and faces of kaolinite based on results from Williams and Williams [1978] and Johnson *et al.* [1998] plotted as function of pH

The edges of bentonites consists of two layers of silica and one of alumina, it is still assumed that the edges are positively charged at low pH and low electrolyte concentration [van Olphen 1963], hence bentonite can form "house of cards" formation.

2.2 INTER-PARTICLE INTERACTION FORCES IN A SUSPENSION

Clay consists of fine particles, thus colloid chemistry is used to understand the interparticle interactions. The rheological properties of a colloid suspension are affected by the particle structure and interaction forces such as hydrodynamic, Brownian and colloidal forces [Hunter 1993]. The former force arises from the relative motion of particles to the surrounding bulk, the Brownian force from the thermal randomised motion of the particles and the colloid force from interaction between the particles. As the aim of this project is to study the magnitude of interaction in clay suspensions hydrodynamic forces and Brownian forces are only introduced briefly whereas a broader review of colloid forces is given.

2.2.1 HYDRODYNAMIC FORCES

Hydrodynamic forces arise from interactions between particles and the flowing medium as the particles disturb the flowing medium and leads to an increase in the viscosity [Hunter 1993]. Particle concentration, size distribution and shape influence the hydrodynamic forces as well as the viscosity of the flowing medium [Hunter 1993].

2.2.2 BROWNIAN FORCE

Brownian force is a diffusive force and arises from thermal randomising motion of the particles to maintain equilibrium distribution of particles in a suspension [Hunter 1993]. The equilibrium distribution is disturbed when shear is induced in the suspension. Brownian forces are trying to restore the equilibrium distribution, but the shear rate and the hydrodynamic forces can prevent this if they are dominating in the flowing suspension.

2.2.3 THE COLLOID FORCE

Colloid forces in mineral suspensions are governed by the sum of different forces. In simple cases only the forces, defined by the well-known DLVO theory, i.e. attractive van der Waals and repulsive electrical double layer forces, are taken into account. Furthermore, attractive forces such as hydrophobic, bridging and depletion forces and repulsive forces such as structural (hydration) and steric forces can also influence particle interactions in mineral suspensions [Johnsen *et al.* 2000]. However, in clay mineral suspensions without flocculants and surfactants the interactions are dominated by van der Waals and repulsive double layer forces and to some extended structural forces [Johnson *et al.* 2000; Israelachvili and Pashley 1983]. These three are presented in this section.

2.2.3.1 REPULSIVE ELECTRICAL DOUBLE LAYER FORCE

In the presence of water, the compensating cations on the surface of clay particles have a tendency to diffuse away from the clay surface due to Brownian motions. However, they are also electrically attracted to the negatively charged clay particles [van Olphen 1963]. This results in an electrical double layer around the clay particle, where the concentration of positive counter-ions increases close to the surface of the particle whereas the concentration of negative co-ion decreases as they are repelled [Hunter 1993], see Figure 5. The result is an ionic neutralisation of the surface charge over a short distance.



Figure 5: A schematic illustration of the double layer consisting of the Stern layer and the diffuse layer at the negative lattice surface. The potential is plotted as function of distance from the surface. The zeta potential, ζ , the potential at the surface of shear is also plotted. Inspired by van Olphen [1963]

The electrical double layer consists of two regions; an inner region of surface-adsorbed counter-ions, called the Stern layer, and a diffuse region of counter-ions and co-ions, called the diffuse layer, see Figure 5. The thickness of the electrical double layer is expressed by the Debye length, κ^{-1} [Hunter 1993] as in equation 1.

$$\kappa^{-1} = \left(\frac{\varepsilon_0 \varepsilon k_B T}{e^2 I}\right)^{0.5}$$
 Eq. 1

where ε and ε_0 is the dielectric constant of the bulk solution and vacuum, respectively, k_B is Boltzmann constant, T is the absolute temperature, e is the elemental charge and I is the ionic strength defined as in equation 2.

$$I = 0.5 \sum (n_i z_i^2)$$
 Eq. 2

where n_i is the number concentration of ions, i, in the bulk solution and z_i is the valence of the ion, i.

As equation 1 states the thickness and hence magnitude of the electrical double layer can be reduced by increasing the ionic strength and/or decreasing the temperature.

The surface potential of the particle may not predict the interaction characteristics as counter-ions are adsorbed in the Stern layer and hence the potential changes outwards in the bulk. The potential at the surface of the Stern layer is a more proper potential when predicting the particle interactions, and it is called zeta potential, ζ -potential, or electro-kinetic potential [Hunter 1993]. The surface of the Stern layer is also the shear plane, i.e. the ions in the diffuse layer are affected by the shear and set into motion contrary the adsorbed ions, see Figure 5.

As two particles approach each other, the electrical double layers overlap and the concentration of ions between the particles increases. The difference in concentration between the double layer overlap and the bulk leads to an osmotic pressure, which pushes the two particles apart. The repulsive force between two identical spherical particles can be expressed in terms of the corresponding potential energy, V_R , in equation 3 [Hunter 1993].

$$V_R = 2\pi \varepsilon \varepsilon_0 r \xi^2 e^{-\kappa D} \qquad \text{Eq. 3}$$

where ε and ε_0 is the dielectric constant of the bulk solution and vacuum, respectively, r is the radius of the particles, ζ is the zeta potential, κ is the inverse Debye length, see equation 1 and *D* is the shortest distance between the two spheres.

Equation 3 states that the repulsive potential between two similar spherical particles can be reduced by reducing the thickness of the electrical double layer (Debye thickness) and/or by changing the pH (altering the zeta potential). At the isoelectric point, IEP, corresponding to the pH where the zeta potential is zero, the repulsive electrical double forces are non-exciting.

2.2.3.2 VAN DER WAALS FORCES

The force of attraction between colloidal particles occurs between all particles in any suspension medium [Hunter 1993]. Except from opposite charged particles attractive interactions arise from either permanent or induced dipoles in molecules. Interactions between two permanent dipoles, between a permanent and an induced dipole and between two induced dipoles are called Keesom, Debye and London interactions, respectively [Hiemenz and Rajagopalan 1997]. These interactions generate the van der Waals forces. Even though the interactions are weak the forces are long-range as a dipole molecule moment of the molecule affects the molecule next to it ect.

The interactions between two identical spherical particles where the distance between the particles is significantly smaller than the radius of the particles (r>D) can be expressed in terms of a corresponding potential energy, V_A , in equation 4 [Johnson *et al.* 2000].

$$V_A = -\frac{A_H \cdot r}{12D^2} \qquad \qquad \text{Eq. 4}$$

where A_H is the Hamaker constant, r the radius of the particle and D is the shortest distance between the two spheres. The Hamaker constant depends on the properties of the material and the solvent, such as the dielectric constant and refractive indices [Johnson *et al.* 2000].

2.2.3.3 Hydration Forces

According to Israelachvili and Pashley [1983] a repulsive short-range force can be observed at interaction between two clay particles in an aqueous medium due to a strongly surface-associated layer of water on each particle. The dissemination of the repulsive hydration force between two mica surfaces, which has similar lattice construction as bentonites though with a limited isomorphous substitution, is up to 1.5 nm [Israelachvili and Pashley 1983].

The strongly surface-associated layer of water can arise from hydrogen bonds between water molecules and the hydroxyl groups on the clay surface [Israejachvili 1992]. According to the lattice structure kaolinite has some "available" hydroxyl groups on the 14

surface of the alumina sheet. Based on this it is assumed that the kaolinite is cable of making hydrogen bonds with water and thus have a repulsive hydration layer of water on the surface. In bentonite isomorphous substitution is higher and hence bentonite has adsorbed cations on the surface which can be hydrated in aqueous medium and lead to a repulsive hydration layer.

2.2.3.4 Summation of Repulsive and Attractive Forces

The stability of the suspension is determined by the particle interactions as reviewed above. An approach to understand the stability of a suspension is developed independently by Derjaguin and Landau, Verwey and Overbeek, called the DLVO theory [Hunter 1993]. The DLVO theory is based on the attractive van der Waal forces and the repulsive double layer forces. The short range repulsive hydration force is also included in the understanding of the potential distribution in this thesis.

The total potential energy of the interaction between two similar particles, V_T , is the sum of repulsive, V_R , and attractive interactions, V_{A_r} as in equation 5 [Hunter 1993]

$$V_T = V_R + V_A$$
 Eq. 5

The total potential energy together with repulsive double layer potential, attractive van der Waals potential and the short-range repulsive hydration can be depictured as function of distance from the particle surface, see Figure 6.



Figure 6: The interaction energy as function of distance from the particle surface. V_A and V_R are the attractive and repulsive energy, respectively, and V_T is the total energy. The repulsive force close to the particle is the repulsive hydration. In the lower right corner the total energy is depictured as function of ionic strength where "a" is the lowest and "e" the highest ionic strength. Inspired by van Olphen [1963]

The magnitude of the repulsive double layer forces is dependent on the ionic strength and pH as it changes the Debye length and particle surface potential, respectively. A low ionic strength the repulsive double layer forces are strong and will be dominating and constitute an energy barrier where the suspension is stable, see Figure 6, graph a. This energy barrier is called the secondary minima. As the ionic strength increases the energy barrier is reduced until the repulsive double layer forces are non-exciting, see Figure 6, graph a-e. This will give an un-stable suspension where coagulation can occur. This effect can also be caused by pH regulation. At the isoelectric point the repulsive

double layer forces are zero. As the pH is changed the repulsive double layer forces are increased and will dominate more and more.

Based on the DLVO-theory one can control a colloid system by changing the ionic strength, the zeta potential, or the solvent. As the clay particles are suspended in water the latter manipulation parameter is not pertinent.

2.3 CORRELATION BETWEEN YIELD STRESS, SURFACE CHARGE AND PARTICLE SIZE

A model proposed by Kapur *et al.* [1997] based on knowledge from many former studies estimates the yield stress of a flocculated suspension as function of solid concentration and particle size distribution at the isoelectric point (IEP). The model is reasonable consistent with experimental data for zirconia and titania suspensions with the inter-particle spacing between particles in the flocculated state as a fitting parameter. Scales *et al.* [1998] extended the model to include the effect of particle-particle repulsion, i.e. particles with a numeric zeta potential larger than zero, by using the DVLO theory. Thus the model can be used in a broader pH range instead of only at the isoelectric point. This model is consistent with measurements made on alumina suspensions at different pH, particle size and concentrations [Scales *et al.* 1998].

The model is estimating the shear yield stress for size distributed spherical particles and hence a complex particle size expression is incorporated. As the model proposed by Scales *et al.* [1998] is only able to give a qualitative assessment of the shear yield stress and zeta potential of kaolinite suspensions [Johnson *et al.* 1998; Johnson *et al.* 1999] a simplified version deduced by Zhou *et al.* [2001] is presented. The shear yield stress, τ_y , for mono-distributed spherical particles is expressed in equation 6.

$$\tau_{y} = \frac{\phi K(\phi)}{24\pi d} \left[\frac{A_{H}}{D^{2}} - \frac{24\pi \varepsilon \varepsilon_{0} \kappa \zeta^{2}}{\left(1 + e^{\kappa D}\right)} \right] \qquad \text{Eq. 6}$$

where ϕ is the solid concentration, $K(\phi)$ is the mean coordination number as function of solid concentration, d is the surface area weighted particle radius, D is the distance between the particles, A_H the Hamaker constant, ε and ε_0 is the dielectric constant of the bulk solution and vacuum, respectively, ζ is the zeta potential and κ is the inverse Debye length.

By comparing equation 3, equation 4 and equation 5 with equation 6 it is obvious that equation 6 is based on the DLVO theory, thus structural forces is not taken into account. However Kapur *et al.* [1997] have suggested a correction of the particle size by one water molecules due to an adsorbed layer of water. The coordination number is based on spherical particles and is function of solid concentration. A broad size distribution can increase the coordination number as small particles can be situated in between the larger particles [Scales *et al.* 1998]. Furthermore finer particles will have a larger coordination number and thus a larger shear yield stress.

If the parameters except from yield stress, particle size and zeta potential in equation 6 is constant it must be possible to find a linear correlation between yield stress, particle size and zeta potential. This means the Hamaker constant and dielectric constant have to be similar for different kaolinites and bentonites, the thickness of the double layer and the distance between the particles have to be constant for suspensions with same solid concentration.

By assuming that the maximum yield stress is at the isoelectric point due to the nonexisting repulsive double layer forces a normalisation of shear yield stress is possible, as stated in equation 7.

$$\frac{\tau_{y}}{\tau_{y \max}} = 1 - \frac{24\pi\varepsilon\kappa\zeta^{2}D^{2}}{A(1+e^{\kappa D})}$$
 Eq. 7

This normalisation of shear yield stress can only be done if shear yield stress reaches a maximum. By normalising the shear yield stress one does not have to take the effect of coordination number or particle size into account. This normalisation is used in many studies of metal oxides and some kaolinites [Zhou *et al.* 2001; Johnson *et al.* 1998].

The correlations between yield stress, zeta potential and particle size from equation 6 and equation 7 is used in this thesis if possible.

3 EXPERIMENTAL APPROACH

In this section considerations regarding the different analysis are presented to give a more thorough insight in the planning of the experimental procedure. The experiments are arranged in four sections; sample preparation, particle size analysis, surface charge analysis and shear rheology.

3.1 SAMPLE PREPARATION

The Run Of Mine Clays, a kaolinite and a bentonite, are not processed by any means after mining. The clays are delivered as big stones, and thus it is necessary to grind it. To get the highest content of clay particles it is sieved, pebbles under 425 nm are used for further analysis.

The moisture content for all the clays must be determined as it can have a great impact on the solid concentration in the suspensions.

Due to impurities in the clays the specific gravity is determined for all the clays. As the clay suspension is poured into a pycnometer the viscosity of the suspension must not be too high, however a high solid content is desirable to limit errors. Calcium chloride is added to suppress the swelling behaviour of clays.

3.2 PARTICLE SIZE ANALYSIS

The particle size of suspended clay is measured with light scattering and the shape of dry particles is analysed with microscopy. Particle size of dry clay is estimated from the BET isotherm fitted to experimental results from gas adsorption.

When measuring the particle size in suspensions, a dispersed suspension is desirable. Thus a dispersant, sodium polyphosphate, is added. Polyphosphate is negative charged and can interact with the possible positive charged edges of clay. Thus the edges become negatively charged, see Figure 7, and the clay particles cannot form edge-face interactions.



Figure 7: An illustration of polyphosphate at the positive clay edges, hence the edges are negatively charged

The dispersant was used when preparing suspensions for light scattering analyses and microscopic analyses to avoid tactoids.

Particle size of dry clay is estimated from the BET isotherm fitted to experimental results from gas adsorption. BET surface area is the surface area pr. gram clay and by dividing surface area of a sphere $(4\pi r^2)$ with the mass of a sphere $(\frac{4}{3}\pi r^3 \rho)$, the particle size can be calculated from equation 8.

surface area pr.mass =
$$\frac{6}{d\rho}$$
 Eq. 8

where d is diameter and ρ is the specific gravity. Based on this calculation an under estimated particle size can be determine as the porosity of the clay particles are not taken into account.

3.3 SURFACE CHARGE ANALYSIS

To determine the zeta potential of all the kaolinites, the measurements for the clays are made from pH 10 to pH 4 to get a more dispersed sample.

A background electrolyte was added to the samples to avoid a large conductivity changes from impurities in the clay sample or when acid and base is added.

Bentonites have many exchangeable ions and hence a swelling behaviour. The latter affects the viscosity and can make it difficult to mix properly when measuring on the acoustosizer. Hence the zeta potential is also measured with electrophoresis where the solid concentration has to be much lower compared to the electro-acoustic measurement. These measurements are only used to verify the zeta potential level of the zeta potential from the electro-acoustic measurement.

3.4 Shear Rheology Analyses

The vane technique by Nguyen and Boger [1985] is used to estimate the shear yield stress as it is a fast and simple method. The background electrolyte concentration used at the electro-acoustic is also used at shear yield stress measurements.

4 EXPERIMENTAL

Eight different kaolinites and four different bentonites from Australia were studied in this thesis. The mineral content in each clay sample was determined with x-ray diffraction by the University of Melbourne, Australia, see Table 1 and Table 2 for kaolinites and bentonites, respectively. The names of the clays are the name given by the manufactures. The signature "ROM" refers to Run Of Mine, the clays are not processed after mining. The clay suppliers are listed in Table 3.

Table 1: X-ray diffraction of the kaolinite clays, measured by University of Melbourne, Australia

Clay Sample	Quartz	Kaolinite	Anatase	Dolomite	Muscovite	Orthoclase
	[wt %]	[wt %]	[wt %]	[wt %]	[wt %]	[wt %]
Acid Washed	0.9	93	-	-	4.5	1.7
K15GM	1.4	97.5	1.1	-	-	-
P523A	3	95.6	1	-	0.5	-
Q38	5.9	87.5	0.7	5.9	-	-
ROM Skardon River¹	23	65	0.9	-	6	-
Snobrite 55 ²	5.2	92.3	<0.5	1	-	-
Snobrite 80	0.9	98.6	0.5	-	-	-
SPS	1.2	90.7	-	-	5.9	2.3

¹ contains also 3 wt % Biotite and some loss of ignition (LOI) residuals, ² contains also 2.1 wt % Calcite

Table 2: X-ray diffraction of bentonite clays, measured by University of Melbourne, Australia

Clay Sample	Quartz	Na- Bentonite	Ca- Bentonite	Albite/ Anorthite	Cristobalite	Heulandite
	[wt %]	[wt %]	[wt %]	[wt %]	[wt %]	[wt %]
Active Gel 50	16	84	-	< 0.5	-	-
Active Gel 53	18.3	80.7	-	1	-	-
Bentonite 150	12.3	85.2	-	2.5	-	-
ROM Volclay	10.5	33.9	33.2	4	13.8	4.7

Quartz consist of SiO₂, *anatase* of TiO₂, *biotite* of K(Mg,Fe)₃(Si₃Al)O₁₀(OH,F)₂, *calcite* of CaCO₃, *dolomite* of CaMg(CO₃)₂, *muscovite* of KAl₂(Si₃Al)O₁₀(OH,F)₂ and *orthoclase* of KAlSi₃O₈.

Albite/anorthite consists of $CaAl_2Si_2O_8$, cristobalite of SiO_2 and heulandite of calcium, sodium, alumina and silica.

Clay	Supplier
Acid Washed	APS Chemicals
K15GM	APS Chemicals
P523A	APS Chemicals
Q38	Unimin
ROM Skardon River	N/A
Snobrite 55	Unimin
Snobrite 80	Unimin
SPS	APS Chemicals
Active Gel 50	N/A
Active Gel 53	N/A
Bentonite 150	N/A
ROM Volclay	Volclay

Table 3: A list of the Australian clay suppliers

N/A means not available

During the measurements, a background electrolyte was added to the solutions. $CaCl_2$ (Merck, purity > 98.0%) was used as a background electrolyte in measurements of specific gravity and 0.01M KCl (AnalaR, purity: 99.8%) in zeta potential and shear yield stress analysis. 1 wt % sodium polymetaphosphate, $(NaPO_3)_nNaO_2$, (Ajax Finechem) was used as a dispersant in the particle size measurement. All pH adjustments was made with 1M and 5M HCl and KOH or 1M Ca(OH)₂.

4.1 SAMPLE PREPARATION

4.1.1 PROCESSING OF RUN OF MINE CLAYS

The Run Of Mine bentonite and kaolinite, ROM Volclay and ROM Skardon, respectively, were in big clots, thus the clays were ground with a ring mill (LM2 Laboratory Pulverising, The Labtechnics, Australia) and sieved with grainsize <425 μ m.

4.1.2 MOISTURE CONTENT TEST

To determine the moisture content in the clays a plastic tray was dried in a 100 degrees oven for one hour, cooled in a desiccator and weighted. Approx 2 grams of clay sample was added, dried for two days at 100 degrees, cooled in a desiccator and weighted. From the difference of the dried and the undried sample the moisture content in the clays was calculated. Two repetitions were made for every sample.

4.1.3 MEASUREMENT OF SPECIFIC GRAVITY

The pycnometer (Duran, 100 mL at 20°C) was calibrated with reverse osmosis water. The clay samples were dispersed in 0.1 M CaCl₂, thus the pycnometer filled with 0.1 M CaCl₂ solution was weighted to determine the specific gravity of CaCl₂. An amount of clay between 10.0-15.5 g and 7.3-15.2 g for kaolinites and bentonites, respectively, was added to a container with approx 60 mL of 0.1 M CaCl₂ solution and sonicated for 5 min with a Sonicator 3000 (Novusolution, USA) which operated at a frequency of 20 kHz and a power output maintained at the maximum power of 600 W with a puls on/off time of 5 sec. Afterwards the sample was shaken minimum over night and poured into the pycnometer, filled up with 0.1 M CaCl₂ solution and weighted. The temperature of the different solutions and suspensions was measured. Two repetitions were made for every sample.

4.2 PARTICLE SIZE ANALYSIS

Different sample preparation methods were investigated and the following was the most stable one during measuring, see "Particle Size Method Analyses", page 61 for choice of sample preparation. 1 vol% clay sample was dispersed with sodium polymetaphosphate, and pH (pHM92, Radiometer Analytical, Denmark) was adjusted to approx 9. The sample was sonicated for 5 min (see method specifications under "Measurement of Specific Gravity"). The pH was adjusted to approx 9 after sonication, and the sample was minimum shaken overnight to establish thermal and chemical equilibrium.

4.2.1 PARTICLE SIZE ANALYSES WITH LIGHT SCATTERING

The Mastersizer 2000 (Malvern Instruments, United Kingdom) was auto aligned, and a background measurement of tap water, Melbourne, Victoria, Australia, (conductivity 0.6 μ S/cm, pH 6.8) was measured. The sample was loaded to the dispersion unit with the stirrer at 200 rpm and pump speed of 1500 rpm until the obscuration was between 10-20 %. A measurement time and a background time of 30 and 20 sec, respectively, was used. The measurement was started right after loading. The laser was a He-Ne gas laser with a wavelength on 632.8 nm.

The particle size was measured three times and ten times for kaolinite ans bentonite, respectively at one sample load and averaged by the Mastersizer 2000 program (Malvern, United Kingdom). The three measurements after loading were used for kaolinites whereas the three measurements 7 min (7-10th sample measurement) after loading was used for bentonites, see "Particle Size Method Analyses", page 61 for further clarification. A sample was loaded two times to verify if the loaded sample was representative for the prepared amount of sample. The two measurements were averaged and used as the particle size for the given clay type.
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4.2.2 PARTICLE SIZE ANALYSES WITH SCANNING ELECTRON MICROSCOPY

The kaolinites were air dried on stubs and gold coated (Dynavac Mini Gold Sputter Coater) prior to measurement. An Environmental Scanning Electron Microscope (FEI Quanta, USA) with a high vacuum Everhart Tornley Detector, called ETD (FEI Quanta, USA) was used to take images of the clay particles. The Images were taken with a voltage of 5.00 kV, spot size of 2.0, a magnitude of 20,000x and the highest resolution.

The image of an air dried bentonite Active Gel 50 was also analysed with SEM.

4.2.3 PARTICLE SIZE ANALYSIS WITH GAS ADSORPTION

The analysis was performed by the University of Melbourne. Approx 0.2 g dry clay sample was degassed with nitrogen for 7 hours before the measurement. Measurement and calculation were performed by Micromeritics ASAP 2000 (Micromeritics[®], USA).

4.3 SURFACE CHARGE ANALYSES

250 mL 2 vol% kaolinite and 1 vol% bentonite clay was dispersed in 0.01M KCl with a pH adjusted to approx 9. The sample was sonicated for 5 min (see method specifications under "Measurement of Specific Gravity"). The pH was adjusted to approx 9 after sonication, and the sample was minimum shaken overnight.

4.3.1 Electro-Acoustic Measurement

Calibration with a KSiW standard was performed prior to a new clay sample. A background measurement of 0.01M KCl was made prior to a new clay sample and used for background correction. A water bath was used to stabilise the temperature of the clay suspension to around 25°C, and 1M HCl and 1M KOH were used for titration/pH adjustment of the clay suspension during measurement on Acoustosizer II (Colloidal Dynamics, Australia). The appertaining software AZR2 (Colloidal Dynamics, Australia)

calculated the zeta potential for bimodal distributed particles (bi-distributed), see "Zeta Potential Analysis", page 67 for further information. The measurement was repeated once.

Depending on the state or flow behaviour of the bentonite clays stirring rates between 200 and 1000 rpm were used.

To determine the concentration of clay in the suspension the dry matter was determined by drying >20 g of clay suspension. The data was reanalysed regarding the dry matter content. Only the data with a particle size fit error less than 5 % is assumed valid.

4.3.2 Electrophoresis Measurement on Bentonite

300 mL 0.1 vol% bentonite clay was dispersed in 0.01M KCl (J.T. Baker) with a pH adjusted (pHM220, Radiometer Analytical, Denmark) to approx 9 with 0.5 M HCl. The sample was sonicated for 2.5 min (Bandelin Sonoplus Electronic UW2200, Germany) which operated at a frequency of 20 kHz and a power output maintained at the maximum power of 200 W with 90% sonication pr. sec. The pH was adjusted to approx 9 after sonication, and the sample was minimum shaken overnight.

The sample was diluted 5 times with 0.01 M KCl (J.T. Baker). Before and after every measurement a pH reading was made. The Zetamaster (Malvern Instruments, United Kingdom) was rinsed with 0.1 M HCl and calibrated with min-U-sil. Approx 10 mL sample was loaded and an average of five measurements was made by the software Zeta Master S (Advanced) (Malvern Instruments, United Kingdom). Measurements were made from approx pH 9 to 4.

4.4 SHEAR RHEOLOGY ANALYSES

20 vol% or 5 vol% suspension of kaolinite or bentonite, respectively was mixed with 0.01 M KCl and mixed for min. 2 hour. pH was adjusted (pHM92, Radiometer Analytical, Denmark) to approx 9, sonicated (see method specifications under "Measurement of

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Specific Gravity") in maximum amounts of 500 mL at the time. The sample was shaken over night.

The shear yield stress was measured using the vane technique developed by Nguyen and Boger (1985), see "Shear Yield Stress", page 70. A four bladed vane with a diameter of 1.5 cm and a height of 2 cm was slowly immersed in the suspension and rotated at a shear rate of 0.2 rpm. Torque was plotted as function of time, and from the maximum torque shear yield stress was calculated by the software (Haake Rheowin 3 Job Manager, Thermo Scientific, Germany), see "Shear Yield Stress", page 70. The measurement was repeated three times, an average value was used as the final result. Between the three successive measurements the sample was stirred with a spatula and tapped to get air bubbles out of the sample. The rheometer was a Haake (VT550, Thermo Scientific, Germany). pH readings were made before and after every measurement. After a shear yield stress measurement acid is added and the sample was stirred until the pH reading was stable for at least 5 min. Only kaolinite Snobrite 80 was repeated once. AALBORG UNIVERSITY

5 RESULTS

The results of the analysis are presented in this chapter. Each result will be presented and discussed afterwards whereas the final discussion of the results compared with each other is in Discussion.

5.1 SAMPLE PREPARATION

5.1.1 MOISTURE CONTENT TEST

The moisture content in the clay with approximately 2 months in between is presented in Table 4.

Table 4: The moisture content of kaolinite (\blacksquare) and bentonite (\Box). The percentage standard deviation is calculated from three repetitions

Clay Sample	Moisture Content ¹	Std. Dev. ¹	Moisture Content ²	Std. Dev. ²	Moisture Content ³	Std. Dev. ³	
	[wt %]	[%]	[wt %]	[%]	[wt %]	[%]	
Acid Washed	0.8	7.8	1.2	7.9	0.9	9.3	
K15GM	2.4	1.4	2.3	1.7	2.2	3.9	
P523A	1.1	14.4	1.5	2.6	1.3	4.5	
Q38	1.8	0.7	2.1	11.2	1.6	7.8	
ROM Skardon River	1.6	3.4	1.5	7.5	1.6	3.5	
Snobrite 55	1.3	7.3	1.3	16.8	1.2	3.3	
Snobrite 80	0.8	5.0	1.2	17.2	0.9	14.6	
SPS	7.6	0.2	7.1	4.3	7.0	0.8	
Active Gel 50	9.1	0.9	9.8	0.6	9.6	1.5	
Active Gel 53	8.4	0.7	8.7	0.8	8.5	0.8	
Bentonite 150	9.8	0.2	9.8	0.9	9.7	0.4	
ROM Volclay	6.9	9.3	N/A	N/A	7.9	1.1	

Moisture content¹ is made in beginning for the experiments, moisture content² and moisture content³ 2 and 4.5 months after the former. N/A means not available

Within the standard deviations the moisture content does not change over a time of 4.5 months. The maximum standard deviation is however at 17.2 % of the moisture content. The high standard deviation is ascribed to errors introduced during

measurements or to the small amount of clay analysed. Hence the moisture content does not vary over time.

By comparing the moisture content of kaolinites and bentonites, it is observed that it is significantly higher for bentonites due water adsorbed to the compensating cations. One of the kaolinite SPS has high moisture content compared with the rest of the kaolinites. This deviation can be due to the handling of the clay by the supplier.

Though, standard deviation of some moisture content measurements is high, the moisture content measurements are still used for sample preparations.

5.1.2 MEASUREMENT OF SPECIFIC GRAVITY

The specific gravity of kaolinite and bentonite is presented in Table 5.

Table 5: the specific gravity of kaolinite (\blacksquare) and bentonite (\Box).Three repetitions are made, and a percentage wise standard deviation is calculated. Specific gravity does not have a unit as it is the density of clay divided by the density of water at 20 °C.

Clay Sample	Specific Gravity	Std. Dev.
	[-]	[%]
Acid Washed	2.60	0.9
K15GM	2.58	0.9
P523A	2.60	1.1
Q38	2.63	1.4
ROM Skardon River	2.65	0.4
Snobrite 55	2.65	0.3
Snobrite 80	2.58	0.7
SPS	2.58	0.7
Active Gel 50	2.69	2.0
Active Gel 53	2.78	0.6
Bentonite 150	2.77	0.8
ROM Volclay	2.49	1.3

The maximum standard deviation of the measurements is 2.0 %, hence the measurements are repeated well. The specific gravity does not have a unit as it is the clay density divided by density of water at 20 $^{\circ}$ C, 0.99823 g/mL [Lide *et al.* 2008-2009]

The specific gravity of kaolinites is between 2.58-2.65, which is consistence with specific gravity of 2.60 found for kaolinites in the literature [McFarlane *et al.* 2006; Mpofu *et al.* 32

2004]. According to Table 6 the kaolinites with most impurities should have the highest specific gravity as the specific gravity for most of the impurities is higher than pure kaolinite. This can to some extent be verified by comparing the measured specific gravity for the kaolinite samples (Table 5), mineral content (Table 1) and specific gravity for the minerals (Table 6). But no clearly correlation is found.

By comparing the kaolinites with bentonites, the latter is found to have a higher specific gravity. This is consistent with the specific gravity of 2.68 and 2.50 found for Active Gel 23 [Mpofu *et al.* 2005] and ROM Volclay [Volclay 2006]. ROM Volclay contains many impurities with a lower specific gravity, see Table 6, and therefore the low specific gravity.

The measured specific gravities are found valid, and thus they are used in the rest of the thesis when calculating solid concentrations.

Mineral	Specific Gravity				
	[-]				
Anatase [*]	3.8-4.0				
Biotite ^{**}	2.7-3.3				
Calcite ^{**}	2.7				
Dolomite ^{**}	2.8-2.9				
Muscovite ^{**}	2.8-2.9				
Orthoclase ^{**}	2.5-2.6				
Quartz ^{**}	2.6-2.7				
Albite/anorthite ^{**}	2.61				
Cristobalite ^{***}	2.32				
Heulandite ^{***}	2.2				

Table 6: the specific gravity of different minerals in the clay samples.

data from Alibaba.com [1999-2009], ** data from Geology.com [1995-2009] and *** data from Amethyst Galleries Inc. [1995-2009]

5.2 PARTICLE SIZE ANALYSIS

5.2.1 PARTICLE SIZE ANALYSES WITH LIGHT SCATTERING

The sample was prepared with a dispersant as this sample preparation gave the most stable sample during the experiment, see "Particle Size Method Analyses", page 6110.1 for choice of sample preparation.

The particle size in this section is volume weighted as this software used for analysing the data only give the distribution volume weighted or number weighted. However the particle size used in equation 6 is the surface area weighted and the mean surface area particle size is calculated by the software, hence this value is also stated in this section.

The graphic of all eight kaolinites are displayed in Figure 8 and in Figure 9. The mean volume weighted particle size, d[4.3], the mean surface area weighted particle size, d[3,2] and the volume weighted standard percentage readings, d(0.1), d(0.5) and d(0.9), are shown in the Table 7.



Figure 8: The average differential volume weighted particle size of kaolinites; Acid Washed, K15GM, P532A and Q38. Note that the abscissa is logarithmic



Figure 9: The average differential volume weighted particle size of kaolinites; ROM Skardon River, Snobrite 55, Snobrite 80 and SPS. Note that the abscissa is logarithmic

The standard deviations of the two repetitions are under 0.137 % for the kaolinite clays thus the data is reproducible. The standard deviation is not indicated graphically on Figure 8 and Figure 9.

The kaolinites are bimodal distributed on a logarithmic scale, except from ROM Skardon River which is log normal distributed. As the ROM Skardon River has been ground a log normal distribution was expected [Tasdemir 2008]. The rest of the kaolinites must have been ground by the suppliers, and thus is it surprising that these are not lognormal distributed.

According to van Olphen [1963] the particle size is around 1 μ m. However, it is difficult to compare this value with Figure 8 and Figure 9 as van Olphen does not mention whether it is volume weighted or number weighted particle size. When the particle distribution is volume weighted, the diameter is calculated from the volume of the particle and the large particles have a big impact on the distribution as seen in Figure 8 and Figure 9. If the particle distribution is number weighted, the diameter is based on the amount of particles and a large peak around 1 μ m would be displayed. Thus if the number of van Olphen [1963] is number based, it is consistence with the particle size measured by light scattering.

Table 7: Summery table of the particle size for all eight kaolinites with dispersant. All the data is an average of three measurements on each two loadings. The d[4,3] and d[3,2] are the volume and the surface area mean diameter in μ m, respectively. d(0.1), d(0.5) and the d(0.9) are the volume weighted standard percentile readings of 10%, 50% and 90 %, respectively

Sample	d[4,3]	d[3,2]	d(0.1)	d(0.5)	d(0.9)
	[µm]	[µm]	[µm]	[µm]	[µm]
Acid Washed	3.4	1.4	0.6	2.2	7.6
K15GM	6.4	1.7	0.6	4.1	15.1
P532A	7.9	2.0	0.7	4.7	19.5
Q38	7.1	2.7	1.1	4.9	15.5
ROM Skardon River	4.1	1.9	0.9	2.9	8.6
Snobrite 55	6.7	2.4	1.0	4.1	14.4
Snobrite 80	5.7	2.3	0.9	4.2	12.3
SPS	4.2	2.1	0.9	3.4	8.4

The mean volume weighted particle size for kaolinites is between 3.4 μ m and 7.9 μ m and is ranged in the following order; Acid Washed < ROM Skardon River < SPS < Snobrite 80 < K15GM < Snobrite 55 < Q38 < P532A. The mean volume weighted particle size does not give a complete presentation of the particle size distribution, as it is bimodal but it is still used as an indication of the particle size when looking at the correlation between shear yield stress, zeta potential and particle size.

The Mie theory assumes the particles to be spherical, see "Light Scattering", page 71. This is not the case with clay particles. The scattered light is converted to a volume of the spherical particle and volume weighted particle size is calculated. As the height of a clay platelet is very small, and hence undetectable with light scattering, it is only the faces which will be detected. The size of the detected particle will depend to the angle of the face compared to the laser beam. But due to the small volume of the clay platelet, the volume weighted particle size measured will be overestimated. Thus the particle sizes in Table 7 are only an approximation.

Beside the mean volume weighted particle size, the mean surface area weighted particle size is displayed in Table 7. This is the particle size used in the equation 6 and it is between 1.4 μ m and 2.7 μ m and in the same order as for the mean volume weighted particle size.

The volume weighted particle size distribution of bentonite is displayed in Figure 10 and the mean particle sizes in Table 7.



Figure 10: the average differential volume weighted particle size of bentonites; Active Gel 50, Active Gel 53, Bentonite 150 and ROM Volclay. Note that the abscissa is logarithmic.

The logarithm volume weighted particle size distribution is poly-modal. The ground ROM Volclay does not show a lognormal distribution as for the ROM Skardon River, this can be due to the propagated swelling behaviour in bentonites.

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Table 8: summery table of all four Bentonite Clays with dispersant. The d[4,3] and d[3,2] are the volume and the surface area mean diameter in μ m, respectively. d(0.1), d(0.5) and the d(0.9) are the volume weighted standard percentile readings of 10%, 50% and 90 %, respectively

Sample	d[4,3]	d[3,2]	d(0.1)	d(0.5)	d(0.9)
	[µm]	[µm]	[µm]	[µm]	[µm]
Active Gel 50	26.5	2.3	0.8	5.0	52.3
Active Gel 53	8.6	2.9	1.0	6.1	17.3
Bentonite 150	11.5	2.3	0.8	4.7	30.8
ROM Volclay	26.7	3.1	1.2	5.4	49.2

The mean volume weighted particle size is between 8.6 μ m and 26.7 μ m and the mean surface area weighted particle size is between 2.3 μ m and 3.1 μ m. The order of the mean volume weighted particle size and the mean surface area weighted particle size is different as ROM Volclay have some large particles compared with the rest of the bentonites, see Figure 10 between 100-1000 μ m.

When comparing the particles size of bentonite with the ones for kaolinites it is obvious that the bentonites are larger due to swelling.

The Mie theory predicts the intensity, a value predicted from the refractive difference between the particle and water, see "Light Scattering", page 71 for further clarifications. This value is compared the measured value and these are suppose to be similar. It is recommended by Malvern Instruments Ldt. [2009] to change the refractive index and adsorption until the predicted intensity and the measured intensity is similar. The particle distribution will alter when the refractive index is changed. This fitting of the predicted and the measured intensity is a subjective evaluation and hence this can introduce an error in the data. The clay samples studied in this thesis contain some impurities which can change the optical properties of the particles. But as the fitting of the predicted and measured intensity is subjective evaluation, it is not done in this thesis.

5.2.2 PARTICLE SIZE ANALYSES WITH SCANNING ELECTRON MICROSCOPY

The images taken with SEM are shown in "Scanning Electron Microscopy Images", page 73.

When comparing the images of kaolinite with each other, the order of the mean particle size is as following: K15GM = P532A < Q38 = Snobrite 55 < ROM Skardon River < Snobrite 80 < SPS. The order is based on subjective analyses of the images and can only be used as an indication.

It was not possible to reproduce an image of Bentonite Active Gel 50 as the surface of the sample is non-uniform and hence the rest of the bentonites were not analysed with SEM.

5.2.3 PARTICLE SIZE ANALYSES WITH GAS ADSORPTION

The measured BET surface area and the calculated particle from the BET surface area size are displayed in Table 9.

Table	9:	The	BET	surface	area	measured	by	University	of	Melbourne,	Australia	and	the
partic	le s	ize ca	alcula	ited from	n the I	BET surface	are	a					

Sample Name	BET Surface Area	Particle Size		
	[m2/g]	[µm]		
Acid Washed	13.765	0.17		
K15GM	28.504	0.08		
P532A	26.103	0.09		
Q38	22.057	0.10		
ROM Skardon River	-	-		
Snobrite 55	16.359	0.14		
Snobrite 80	16.285	0.14		
SPS	14.877	0.16		
Active Gel 50	33.565	0.07		
Active Gel 53	29.641	0.07		
Bentonite 150	44.562	0.05		
ROM Volclay	-	-		

The particle size calculated from the BET surface area is between 0.08 μ m to 0.17 μ m and 0.05 μ m and 0.07 μ m for kaolinites and bentonites, respectively. The order of the kaolinites is as following: K15GM < P532A <Q38 < Snobrite 55 = Snobrite 80 < SPS < Acid Washed.

Due to the propagated swelling behaviour for bentonites the particle size does not resemble the particle size in an aqueous suspension, and thus this particle size cannot be used as an indication of the particle size in a suspension. The particle size calculated from BET surface area is significantly smaller as the porosity of the bentonites is not taken into account. The data will not be used further in this thesis.

As the porosity of the kaolinite particles is unknown, the particle size calculated from the BET surface area is underestimated. This must be taken into account when comparing with other particle size measurements.

5.3 SURFACE CHARGE ANALYSIS

5.3.1 Electro-Acoustic Analyses

The zeta potential for all kaolinites is displayed in Figure 11.





Figure 11: zeta potential of the kaolinites as function of pH.

The acoustosizer adjust the pH automatically, which can result in some abrupt jumps in pH. Due to this it is not possible to calculate a standard deviation from the two repetitions.

The zeta potential of the kaolinites is between -28 to -72 mV at pH 10 and between -9 to -41 mV at pH 4, thus the kaolinites are negatively charged from pH 10 to pH 4 as excepted. When looking at the progress of zeta potential between pH 4-10 K15GM, P532A, Snobrite 55 and ROM Skardon River are similar. K15GM and P532A have the lowest numeric zeta potential whereas Snobrite 55 has a higher numeric zeta potential and ROM Skardon River the highest in the investigated pH range. The zeta potential of

kaolinite Q38 and Snobrite 80 does not change significantly between pH 10 and pH 4. The opposite is the case with kaolinite SPS and Acid Washed.

The zeta potential of kaolinite Q38 and Snobrite 80 is almost pH independent indicating the broken bonds at the edges to have no impact at all. The small change in zeta potential can be due to the change in ionic strength when adding acid.

The zeta potential of kaolinite SPS and Acid Washed is highly pH dependent compared to the other kaolinites indicating the impact of the pH depended edges to be greater than for the rest of the kaolinites.

After the measurements from pH 10 to pH 4, the pH is increased again. There is no significant change in zeta potential from pH 4 to pH 10 compared to the zeta potential from pH10 to pH 4, besides from Acid Washed Kaolinite, see Figure 12.



Figure 12: The zeta potential of Acid Washed Kaolinite as function of pH. The pH of the sample is decreased from pH 10 to pH 4 and subsequently increased from pH 4 to pH 10.

As it is seen in Figure 12 a small difference in zeta potential is observed. The maximum difference in zeta potential is approx 7 mV. As the pH is decreased some irreversible

adsorption on the surface may occur and the zeta potential will be numeric lower as the pH is increased again.



The zeta potential of bentonites are also measured, see Figure 13.



Figure 13: zeta potential as function of pH for bentonites; Active Gel 50, Active Gel 53 and Benotnite 150. It was not possible to determine the zeta potential for ROM Volclay.

It was not possible to obtain any valid data for ROM Voclay, i.e. a fit error under 5 %. Similarly measurements for Active Gel 53 gave only valid data from pH 10 to pH 7. The specific reason for this is unknown but it can be due to the large particles of bentonites. If the particles are too large and too slow to respond to the alternation voltage, "Zeta Potential Analysis", page 10.267.

Compared to the zeta potential found in the literature [Mpofu *et al.* 2005] and the propagated isomorphous substitution, the zeta potential was expected to be more negative.

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5.3.2 Electrophoresis Analyses on Bentonite

The zeta potential as function of pH measured with electrophoresis is shown in Figure 14.



pH [-]

Figure 14: the zeta potential as function of pH measured on an acoustosizer (\blacksquare) and by electrophoresis (\blacksquare).

The maximum standard deviation is 7.5 % and hence it is not possible to tell the difference between the data measured with electrophoresis.

When measuring the potential by electrophoresis only small particles are measured, thus it is assumed that large and small particles have the same potential.

The zeta potential measured with electrophoresis has a higher numeric zeta potential than the zeta potential measured with electro-acoustics. The solid concentration is significantly lower when measuring with electrophoresis. This will give an increase in double layer and give a higher numeric zeta potential.

5.4 SHEAR RHEOLOGY ANALYSES

The shear yield stress was measured with the vane technique developed by Nguyen and Boger [1985]. It was not possible to measure the shear yield stress of kaolinite P532A as not enough clay sample was available. The results is depicted in two figures as some are pH independent and some pH dependent shear yield stress, see Figure 15 and Figure 16, respectively.



Figure 15: The shear yield stress as function of pH independent kaolinite; K15GM, Q38, ROM Skardon River and Snobrite 55



Figure 16: The shear yield stress as function of pH dependent kaolinite; Acid Washed, Snobrite 80 (2 repetitions) and SPS

Kaolinite Snobrite 80 is repetited once, they are consistence and hence the reproducibility of the sample is good.

The shear yield stress of kaolinite K15GM, Q38, ROM Skardon River and Snobrite 55 is independent of the pH as the shear yield stress is approx the same from pH 10 to pH 4. This is due to the insignificantly change in zeta potential. The shear yield stress of kaolinite Acid Washed, Snobrite 80 and SPS is pH dependent as the zeta potential changes as a function of pH.

A maximum between pH 4-7 was expected as the "house of cards" formation is favoured [Johnson *et al.* 1999]. However a maximum in shear yield stress and a subsequently decrease is not observed from pH 10 to pH 4 and hence the data cannot be normalised. The missing maximum can be due to too fast pH changes. If the equilibrium between the bulk and the clay particles has not been established, the shear yield stress differs more from the "true" value.

RESULTS

It was not possible to estimate the shear yield stress for the bentonites as the pH was drifting and the shear yield stress measurements were untrustworthy.

5.5 CORRELATION BETWEEN SHEAR YIELD STRESS, ZETA POTENTIAL AND PARTICLE SIZE

To find a correlation between shear yield stress, zeta potential and particle size the correlation proposed by Scales *et al.* [1998] is used. The shear yield stress times the surface area weighted particle size as function of zeta potential squared is plotted in Figure 17 and in Figure 18.



Figure 17 Shear yield stress times surface area weighted particle size as function of zeta potential squared of kaolinites; K15GM, Q38, ROM Skardon River and Snobrite 55



Figure 18: Shear yield stress times surface area weighted particle size as function of zeta potential squared of kaolinites; Acid Washed, Snobrite 80 and SPS

Kaolinite K15GM, Q38, ROM Skardon River and Snobrite 55 have a steady shear yield stress times the surface area weighted particle size and hence they are pH independent. This is due to the insignificant change in zeta potential between pH 4-10. Kaolinite Acid Washed, Snobrite 80 and SPS have an increase in shear yield stress times the surface area weighted particle size as function of zeta potential squared. This is the trends from pH dependent surface charge.

According to the assumption made from equation 6 a linier correlation between shear yield stress times particle size as function of zeta potential squared was expected. This is to some extent the case for kaolinites with a pH dependent surface charge in Figure 18. The kaolinites with pH independent surface charge do not change and a correlation cannot be found.

6 DISCUSSION

Is this section the results are compared.

6.1 SAMPLE PREPARATION

According to the x-ray diffraction the kaolinites have impurities in form of other minerals. If the sample used for x-ray diffraction is not homogenous, it can give some deviations in the results. As the concentrations of the minerals only are used as an indication of the amount of impurities, it is not taken into account.

6.2 PARTICLE SIZE ANALYSIS

The results from the light scattering measurements have some errors introduced as the Mie theory is based on spherical particles and the refractive index and adsorption is not subjective evaluated. Due to the former, the particle size is overestimated. The particle size of kaolinites and bentonites are measured with light scattering.

It is difficult to compare SEM, gas adsorption and light scattering analyses, partly because SEM and BET surface area analyse dry particles when light scattering analyse suspended particles and partly because the difference in type of particle size. The SEM is a 2D analyses where the faces of the particles are depictured. As the particles are not spherical it is difficult to choose a diameter which represents the particle size, for instance the maximum length or the minimum length. The volume weighted particle size can be estimated from a SEM image, but the deviation will be significantly large if a single particle is left out of the calculation and if the small area in the image is not representable for the rest of the particle. Gas adsorption is a surface area analyses and the surface area weighted particle size can be calculated. The clay particles are to some extent porous and the surface area of the pores must be subtracted. This is not done in this thesis as the porosity is unknown and thus the surface area weighted particle size is

under estimated. The light scattering gives a surface area weighted particle size and hence it can be compared with the particle sizes estimated from the BET surface area. When comparing the surface area weighted particle size estimated from gas adsorption and light scattering no trends between them are found. This can be due to formation of tactoids in the suspension.

As the particle size measured by light scattering gives the best estimation of the clay particles suspended, this particle size is used when looking at correlation between shear yield stress, zeta potential and particle size.

6.3 SURFACE CHARGE ANALYSIS

The zeta potential is an approximation as this theory behind electro-acoustics and electrophoresis assumes spherical particles and not platelets. However, many journals are still using these methods to estimate the zeta potential of clay.

Acid Washed Kaolinite is the only kaolinite which differs is zeta potential after the decrease in pH and a subsequently increase. These can be due to surface alternations as precipitation of metal hydrolysis product in alkaline environments. As Acid Washed Kaolinite is the only one washed to remove some of or all the surface impurities, it is assumed that the rest of the kaolinites have irreversible impurities on the surface of the particles. Acid Washed Kaolinite have the highest numeric zeta potential which indicates exposed towards the bulk and does not have big amounts of impurities on the surface as the rest of the kaolinites might have.

Some of the kaolinites have a pH dependent surface charge and some kaolinites have a pH independent zeta potential. According to Felhi *et al.* [2008] kaolinites may be poorly crystalline due to the presence of impurities, and poor crystalline kaolinite is constituted by small particles with broken edges. If this is the case, pH dependent kaolinite are poorly crystalline. It is not possible to see a correlation between the impurities measured with x-ray diffraction and the pH dependent kaolinites. However it must be noted that the so called impurities (minerals beside the clay) may also improve

DISCUSSION

crystalline of clay. To verify this subject it is necessary to measure the degree of crystalline.

6.4 SHEAR RHEOLOGY ANALYSES

The vane technique is used as it is a simple method to indicate the interactions between particles. However one must take into account that it is not the true shear yield stress. The stress is assumed to be uniformed around the vane and it is highest near the edges of the vane. The shear yield stress is used as an indication of the interactions between colloids in a suspension and hence it is acceptable that it is only an estimate.

Some kaolinites have a pH dependent zeta potential and hence a pH dependent shear yield stress. As the numeric zeta potential decreases the shear yield stress increases due to the decrease in repulsive forces. Some of the kaolinites only have a minor numeric decrease in zeta potential. This results in kaolinites with pH independent shear yield stress as the particle surface does not change.

The model of Scales *et al.* [1998] is used to find a linear correlation between shear yield stress, surface area weighted particle size and zeta potential. The progress of the shear yield stress times the particle size was expected to increase as zeta potential squared decreases. This is not the case for all the kaolinites. Three kaolinites with pH dependent surface charge follow this progress. Two of these show a linear correlation between shear yield stress times the particle size as function of zeta potential squared, see Figure 18. The four kaolinites with pH independent surface charge do not have a linear correlation. Two of these kaolinites have a low surface charge, i.e. low zeta potential squared into account the shear yield stress was expected to be similar.

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7 CONCLUSION

The particle size was estimated with light scattering, zeta potential with electroacoustic and shear yield stress with the vane technique by Nguyen and Boger [1985]. It was not possible to measure the shear yield stress of bentonite with the sample preparation used in this thesis, hence it is not possible to correlated shear yield stress, particle size and zeta potential.

Some kaolinites have a pH dependent zeta potential and hence a pH dependent shear yield stress. As the numeric zeta potential decreases the shear yield stress increases due to the decrease in repulsive forces. Some of the kaolinites only have a minor numeric decrease in zeta potential. This results in a pH independent shear yield stress as the particle surface does not change.

The tendency of pH dependent and pH independent surface charge of kaolinite suspensions is expressed when plotting the shear yield stress time surface area weighted particle size as a function of zeta potential squared. The shear yield stress times the surface area weighted particle size in a kaolinite suspension with a pH dependent surface charge is increasing as the surface charge, i.e. zeta potential squared is decreasing. This is in agreement with the correlation, based on the mathematic model proposed by Scales *et al.*[1998]. The shear yield stress times particle size in a kaolinite suspension with a pH independent surface charge does not change as the surface charge decreases due to the minor change in zeta potential between pH 4-10.

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8 FURTHER INVESTIGATIONS

As it is stated in this thesis some of the kaolinites have a pH dependent surface charge and some a pH independent surface charge. This can be due to the impact of the lattice charged.

The next step in investigating the shear yield stress, zeta potential and particle size of kaolinite suspension is to wash the kaolinite before the analysis. Hence the impurities on the surface are washed off and the effect of the lattice charge can be studied.

According to Felhi *et al.* [2008] the impurities in the kaolinite can cause poor crystalline and the kaolinite will have an increased number of exposed edges. By determine the degree of crystalline in the kaolinites one may be able to predict the pH dependency/independency. AALBORG UNIVERSITY

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$10\,Appendix$

10.1 PARTICLE SIZE METHOD ANALYSES

When measuring particle size sample preparation is an important step. In this study a dispersed sample and a stable particle size distribution when measuring is desirable.

A sample was prepared with background electrolyte and pH 9 to get a dispersed sample. As the sample is loaded to a stirring dispersant unit full with tap water, the pH and conductivity change when the sample is loaded.

To avoid coagulation under the measurement ultra sounds in the dispersant unit is used.

A dispersant is added to get a well dispersed suspension and a stable sample when measuring.

10.1.1 RESULTS AND DISCUSSION

10.1.1.1 EFFECT OF CHANGE IN PH AND CONDUCTIVITY

The same sample preparation method when measuring electro-acoustics is used, however the ionic strength and pH differ from the sample to the tap water in the dispersion unit from 650-750 μ S/cm at pH 8.1-8.9 and 68 μ S/cm at pH 7, respectively. According to the DLVO theory a decrease in ionic strength will increase the repulsion between the particles and thus favour the dispersion. However a decrease in pH will lower surface charge of the clay platelets and thus favour aggregation.

To determine the effect of the change in pH the volume weighted particle size distribution is measured at pH 7 and pH 8.8 on a kaolinite with a low numeric zeta potential, kaolinite P532A, as aggregation is most likely to occur, see Figure 19. The volume weighted particle size distribution at pH 7 and pH 8.8 (similar to the samples pH at 8.5) do not differ significantly compared to each other, see Figure 19. Thus impact of

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pH decrease is inconsiderable and a pH adjustment of the dispersion unit is not necessary. This is assumed valid for all kaolinite as the zeta potential does not change significantly in the range of pH 7-9 and the rest of the kaolinites have a numerically higher zeta potential.



Figure 19: the volume weighted particle size distribution of kaolinite P532A at pH 7 and pH 8.8 measured at the beginning (00:00) and after 2 min and 11 sec. (02:11). Note that the abscissa is logarithmic.

10.1.1.2 EFFECT OF ULTRA SOUNDS

The particle size distribution is measured three times and an average is calculated. The first and the third measurement which is measured after 2 min and 11 sec. is displayed in Figure 19. The mean volume weighted particle size changes from 9.7 to 8.9 and from 9.3 to 8.6 µm at pH 7 and 8.8, respectively, due to the decrease in ionic strength. Ultra sounds are used to promote the dispersion effect due to lower ionic strength so the sample is stabilized during measuring, see Figure 20. However ultra sounds enhanced aggregation. This can be due to enhance movement of the particle combined with a low secondary minimum.


Figure 20: the volume weighted particle size distribution of kaolinite P532A at pH 7 and pH 8 with ultra sounds when measuring. Note that the abscissa is logarithmic.

10.1.1.3 EFFECT OF DISPERSANT

To get a better dispersed and a more stable particle size measurement a dispersant, sodium polymetaphosphate is added to the samples, see Figure 21. When a dispersant is added the volume weighted particle size distribution is still changing from 7.8 to 8.0 μ m over 2 min and 11 sec it takes to make three measurements. Thus the dispersant does not stabilise the sample when measuring. But based on the change in mean volume weighted particle size, the stability is improved compared to the one without dispersant. Furthermore, the volume weighted particle size distribution with dispersant shows some fine particles not measured without dispersant. Thus using dispersant when measuring particle size gives the most stable sample when measuring.



Figure 21: the average volume weighted particle size distribution of kaolinite P532A in 0.01M KCl and kaolinite P532A with dispersant out of three measurements on the same loading. The measurement is repeated once and thus called A and B. Note that the abscissa is logarithmic.

As the sample is still changing over time when measuring, ten successive measurements were made, and the mean volume weighted particles size is plotted as function of time for kaolinite K15GM and Acid Washed as these have a numerically low and high zeta potential, respectively, see Figure 22. The mean volume weighted particle size is changing some in the beginning of the measurement; however it is not significant as for the bentonite in Figure 23. Thus the three first measurements are used for kaolinites and the three last is used for bentonites.



Figure 22: the mean volume weighted particle size plotted over time when measuring for kaolinite K15GM and Acid Washed. Note that the abscissa is logarithmic.



Figure 23: the mean volume weighted particle size plotted over time when measuring for all four bentonite. Note that the abscissa is logarithmic.

In the thesis the sample is made with disparsant and added to the dispersant unit without adjusting the pH before loading. No ultra sounds are used during measuring. The three first measurements are averaged for the kaolinites where as the three last, i.e. after 7 min to 10 min, are average for the bentonites.

10.2 ZETA POTENTIAL ANALYSIS

A charged particle suspended in an aqueous medium has an electrical double layer. It is technical impossible to measure the potential directly at the surface of a particle due to the strongly adsorbed counter ions at the surface. The zeta potential, the potential at the shear plane, is however possible to estimate through experiments [Hunter 1993]. Two methods is used to estimate the zeta potential; electrophoresis and by electro-acoustics, both methods determine the mobility of a charged particle when an electrical field is applied. The difference in the two methods is the type of electric field; in electrophoresis a direct voltage, is applied and in electro-acoustics an alternating voltage [Hunter 1993]. The basic theory related to electrophoresis and electro-acoustics are introduced in the following sections.

10.2.1 ELECTROPHORESIS

Under the influence of an applied DC electric field, charged colloid particles are attracted towards the electrode of opposite charge. The velocity at which they move is dependent on the magnitude of the surface charge density of the particle, the electric field and the ionic strength of the aqueous medium. The velocity of a particle in an electric field is referred to as its electrophoretic mobility, μ_e [Shaw 1992]. The zeta potential is related to the electrophoretic mobility and can hence be calculated when the electrophoretic mobility is experimentally determined. The correlation depends on the particle size to double layer thickness, called κa , where κ is the inverse double layer thickness and a the particle size [Shaw 1992].

The relationship for the calculation of the zeta potential, ζ , is described by Henry equation, see equation 9 [Shaw 1992].

$$\mu_e = \frac{\zeta \varepsilon}{1.5 \eta} f(\kappa a)$$
 Eq. 9

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where η is the viscosity of the medium and ε is the dielectric constant of the electrolyte medium. $f(\kappa a)$ varies between 1.0 for small κa and 1.5 for large κa .

It must be noted that the relationship between the zeta potential and the electrophoretic mobility has been derived for spherical and rigid particles [Shaw 1992]. Thus, in the use of this relationship some caution must be employed in the interpretation of the results.

10.2.2 ELECTRO-ACOUSTICS

The mobility of charged particles can also be determined by applying a high frequency alternating voltage to the colloid suspension, causing the particles to oscillate at a voltage that is depended on their size and surface charge. The oscillating movement of the particles generates a pressure that arises at the suspension boundaries producing pulses of sounds waves [Johnson *et al.* 1998]. This phenomenon is known as the electrokinetic sonic amplitude, ESA, effect. For an isotropic colloid suspension of volume fraction above 2 wt %, the ESA signal is related to the particle average dynamic mobility, μ_D , see equation 10 [Johnson *et al.* 1998].

$$ESA(\omega) = F(\omega)\phi \frac{\Delta \rho}{\rho} \mu_D$$
 Eq. 10

where the ω is the angular frequency of the applied field, F is an instrument constant, ρ is the density of the medium and $\Delta \rho$ is the density difference between the colloids and medium.

Due to the inertia of colloids there is a response time from the electric field is applied to the colloid responses, this is called the lag phase [Hunter 1993]. The bigger the inertia of the colloid, the more difficult it is for them to follow the electric signal. The ions in the double layer of the colloid are able to keep up with the signal to 15 MHz. As the lag phase is dependent on the inertia of the colloid, it is independent of the charge of the particle. By measuring the lag phase as function of frequency of the applied field it is possible to determine the mass average particle size [Hunter 1993]. When knowing

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the particle size it is possible to estimate the charge of the colloid by the magnitude of the ESA signal.

The acoustosizer is plotting the particle size distribution as either a lognormal or a logarithmic bimodal distribution. This is a presetting of the instrument. If the size distribution is preset at lognormal and the particles is logarithmic bimodal distributed, the zeta potential will be overestimated as the calculations does not take the effect of the large particles into account. For spherical particles with a small double layer, large κa and negligible surface conductance, the zeta potential can be estimated from the electro-kinetic mobility, see equation 11 [Johnson *et al.* 1998].

$$\mu_D = \frac{\varepsilon \zeta}{\eta} G(\alpha) \qquad \qquad \text{Eq. 11}$$

where η is the viscosity of the medium and ε is the dielectric constant of the electrolyte medium and $G(\alpha)$ is a complex inertial term dependent upon the particle size an density.

10.3 Shear Yield Stress Analyses

At the gel point a suspension forms a continuous network between the particles and at a concentration above the gel point a suspension have a yield stress. Yield stress is defined as the force required for breaking down a suspension's internal structure and initiating viscous flow [Hunter 1993]. The yield stress can be determined by applying a shear to the suspension and it is called the shear yield stress.

One way to measure the shear yield stress is by using the vane technique developed by Nguyen and Boger [1985]. A four bladed vane is slowly immersed into the suspension and rotated at a low shear rate. Calculation of the yield stress requires knowledge of the geometry of the vane and the stress distribution over the cylindrical yielding surface. It is assumed that the material yields along the cylindrical surface of the vane (the surface of cylinder with the diameter, D_v , and height, H_v) and the shear stress is uniformly distributed everywhere on the cylinder [Nguyen and Boger 1985]. Based on these assumptions the shear yield stress, τ_y , can be calculated from the maximum torque, $F_{\rm max}$, which is the force exerted on the vane shaft to get the vane into motion, see equation 12 [Nguyen and Boger 1985].

$$F_{\rm max} = \frac{\pi D_v^3}{2} \left(\frac{H_v}{D_v} + \frac{1}{3} \right) \tau_y$$
 Eq. 12

Where D_v and H_v are the diameter and height of the vane, respectively.

The container has to be sufficiently larger than the vane to avoid slip effect at the sides of the container [Nguyen and Boger 1985].

This method is used in this thesis as it is a simple way to estimate the shear yield stress. It must be taken into account that the measured shear yield stress is only an estimated value as the shear stress is not uniform around the vane. The shear stress is highest near the edge of the vane. The shear yield stress is used as an indication of the interactions between colloids in a suspension and hence it is acceptable that it is only an estimate.

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10.4 LIGHT SCATTERING ANALYSES

The particle size is measured with light scattering. A dispersed and almost stable sample is recirculated and lead pass a laser beam. The laser will be scattered in different directions depending on the size of the particle. The theory behind light scattering is reviewed in this appendix.

To calculate the size of the particles different models are used; the Frauenhofer Approximation and the Mie theory. The former is used on older light scattering instruments and can be used for particles larger than 40 times the laser wavelength, hence the particles must be larger than 25 μ m for a He-Ne gas laser with a wavelength of 630 nm [Rawle 2005]. The Frauenhofer approximation assumes that the particles are opaque and transmit no light. In modern light scattering instruments the Mie theory is used as it allows accurate results over a large size range from 0.02-2000 μ m [Rawle 2005]. The Mie theory assumes the particles to be spherical and homogeneous, the recirculated suspension to be diluted so the light is not back scattered, and that the optical properties of particles and medium are known. The Mie theory is used when measuring the particle size with light scattering in this thesis as it is the most accurate when measuring on clay particles. According to Malvern Instruments [2009] the refractive index for kaolinites and bentonites is 1.57 and 1.52, respectively, and the adsorption 0.1 for kaolinites. The adsorption for bentonites is assumed to be the same as for kaolinites.

As the laser is scattered by a particle, the Mie theory predicts the primary scattering from the surface of the particle with the intensity, predicted by the refractive index difference between the particle and water. The Mie theory also predicts how the particle's adsorption affects the secondary scattering signal caused by light refraction within the particle [Malvern Instruments Ldt. 2009]. The predicted intensity is compared to the measured intensity, and these are supposed to be similar if the refractive index and adsorption are correct [Eshel *et al.* 2004]. Malvern Instruments Ldt. [2009] recommended changing the refractive index and adsorption until the predicted

and the measured intensity are similar. The particle distribution will alter when the refractive index is changed. This fitting of the predicted and the measured intensity is a subjective evaluation and hence this can introduce an error in the data.

10.5 SCANNING ELECTRON MICROSCOPY IMAGES

The kaolinites and a bentonite Active Gel 50 are suspended with dispersant and air dried before taken the images. The images of the kaolinites are taken with the same dissolution and magnitude so they can be compared with each other. Furthermore, the images can be seen on the **CD ROM** with all the results.



Figure 24: Acid Washed Kaolinite.

The acid washed kaolinite has a gel-like behaviour where it is difficult to see individual particles, and hence evaluation of the particle size and the shape is not possible.



Figure 25: Kaolinite K15GM.



Figure 26: Kaolinite P532A.



Figure 27: Kaolinite Q38.



Figure 28: Kaolinite ROM Skardon River.



Figure 29: Kaolinite Snobrite 55.



Figure 30: Kaolinite Snorbite 80.



Figure 31: Kaolinite SPS.

The shape of the kaolinite particles is plate-like, except from Acid Washed kaolinite. It is impossible to determine the particle shape of Acid Washed Kaolinite as sample has a gel-like surface. It must be highlighted that the images is taken of a small part of the sample, but the images are still assumed to be representative for the whole sample as the images taken elsewhere look similar. All the samples have particles down to approx 500 nm and kaolinite Snobrite 80 and SPS have large flake-like particles.

When comparing the images with each other, the order of particle size is as following: K15GM = P532A < Q38 = Snobrite 55 < ROM Skardon River < Snobrite 80 < SPS. The order is based on a subjective analyses of the images.

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An image of bentonite Active Gel 50 is also taken, see Figure 32. This was difficult as the surface of the sample was not similar and hence it is not possible to reproduce the image and it is not representative for the sample. The image in Figure 32 shows a large particle over 100 μ m, which is not shaped as a platelet.



Figure 32: a SEM image of Active Gel 50.