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Characterisation and applications of bentonite

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Abstract

A research was undertaken to find the suitability of Turkish calcium bentonite from the mines of the Company. Four samples of bentonite mines in the Ünye region are researched, the M1, M2, M3 and M4 mine. The suitability of drilling fluid, foundry sand, soil improvement and bleaching earth applications is found through research on the characteristics of bentonite and by testing the specifications of the chosen applications. In this research the following bentonite characteristics are determined: cation exchange capacity, chemical composition, free swelling capacity, liquid limit, methylene blue adsorption, moisture content, pH, plastic viscosity, specific surface, swelling index and yield point. Characteristics are tested according the associated methods of the specifications. For drilling fluid, the API 13A and OCMA Standard is used. The IS 12446:2007 by the Bureau of Indian Standard is used for foundry sand. For the applications of soil improvement and bleaching earth international standards cannot be found. For this reason a specification of the European Commission on soil improvement is used. Recommended ranges found in literature are used in testing the suitability of bentonite for bleaching earth.

The results of this research show a suitable outcome for the use of drilling fluid. The M1 and M4 sample are API qualified and the M3 sample is conform the OCMA Standard. For foundry sand the bentonite samples are not suitable, all samples are not performing good enough on water absorption and cation exchange. Due to found traces of lead contamination in the M1, M3 and M4 bentonite samples, but these samples are still suitable in soil improvement according to the specifications of the European Commission. However, in the M2 sample there is no trace found of any heavy metal contamination and is, except the low nutrient content, suitable for soil improvement. All samples are very close to the recommended ranges found in literature for bleaching earth, therefore all samples are suitable for the application.

Keywords: bentonite, characterisation, drilling fluid, foundry sand, soil improvement, bleaching earth.

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Chapter 1

Introduction

In this first chapter of this thesis the subject will be introduced in Section 1.1 and the research area in Section 1.2. Next, the main research question of this thesis will be stated in Section 1.3. This chapter is concluded with the outline of this thesis in Section 1.4.

1.1 Relavance

Bentonite is a strongly absorbing clay, this property is very often used in several applications of large industrial processes. It is mined in numberous countries worldwide, such as the United States of America, China, Greece and Turkey. Turkey is a major player in the European production of bentonite with 12.1% of the total European production (Brown, Idoine, Hobbs, and Mills, 2014). Among other companies the Company is mining bentonite in the North of Turkey from four mines. The mined bentonite is used for the production of cat litter, an industry where the swelling property as result of fluid absorption is very important. The production of the bentonite mines is high enough for a production of 70.000 tons cat litter in 2013. After evaluation, the potential of the Turkish bentonite mines might be higher than thought of, production can be increased and applications of bentonite, other than cat litter, are looked for. Besides the Company there are other mining companies excavating bentonite in the same region, but the bentonite from these companies is used in other products than cat litter. It is therefore also very interesting to research the suitability of the bentonite mined by the Company. for other applications.

This study will research the possible applications of the bentonite mined by the Company. The advantage of producing for a different industry is the probable volume or profitability increase of the bentonite. Cat litter can be seen as a cheap product, where in other applications the bentonite is more valueble. Standards are higher, so more processing steps need to be done to make the bentonite suitable for the end product. Before starting with investing in the processing, the bentonite should meet with basic standards to confirm the suitability.

1.2 Origin of the samples

The research area of thesis is in the region of Ünye, a district of the Ordu Province in the Black Sea region of Turkey. Figure 1.1 shows various bentonite deposits in this hilly region where, besides the overflowing hazelnut production, numberous bentonite mines are in production. The mines of M1, M2, M3 and M4 are property of the Company, where other bentonite mines are owned by BB Mining, Ünye Mining and Clariant.

1.3 Objectives and Methods

The objective of this thesis can be summarized as follows:

> *"In which industrial processes, other than cat litter, can the bentonite mined by the Company be used for?"*

The following steps are taken to support the objective of this thesis:

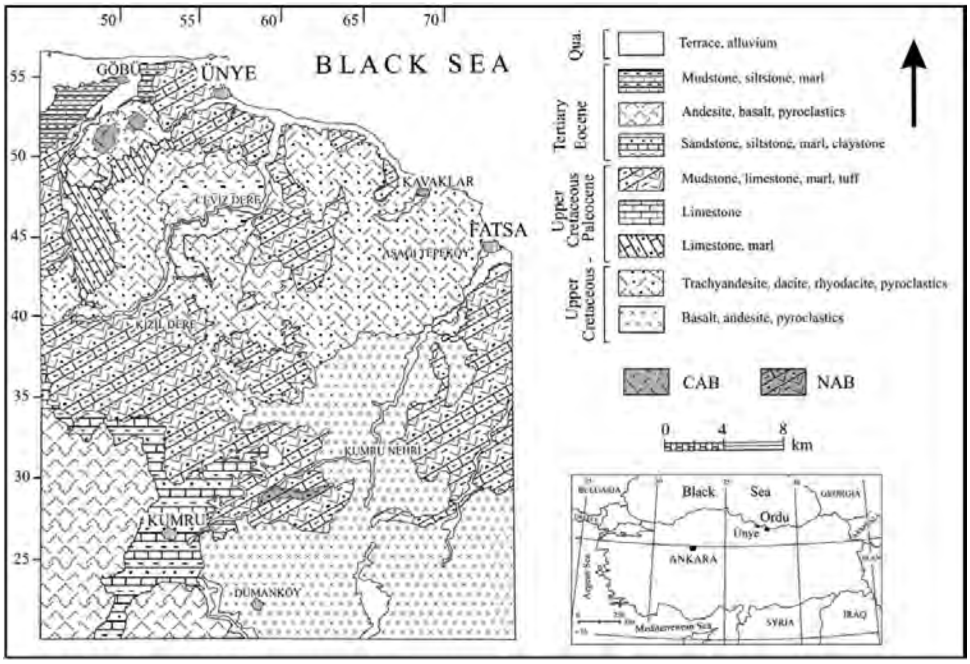


Figure 1.1: Simplified regional geological and location map of the study area (Keskin et al., 1998).

1. Study the characteristics of bentonite in relation to the applications and demands in industrial processes, to get understanding in use of bentonite in the industry.
2. Investigating the demands of the applications of bentonite, to asses the parameters of the bentonite mined by the Company.
3. Obtain information about the characteristics of bentonite mined by the Company, to be able to compare the results with the specifications of drilling fluid, foundry sand, soil improvement and bleaching earth.
4. Conclude the suitability of the bentonite mined by the Company. for the selected applications. Applications will be suitable, not suitable or suitable after making the requiered processings steps.

The following two methods will be used to reach the objective:

1. Literature research, to get insight in the characteristics of bentonite, applications and demands in different industrial processes.
2. Experimental research, to obtain the characteristics of the bentonite used by the Company, to compare with the demands of other industrial applications.

1.4 Thesis structure

This thesis has the following structure:

Chapter 2 gives background information on bentonite as a clay mineral and on the important characteristics of bentonite.
Chapter 3 introduces the variety of applications for bentonite. In this chapter also four applications are chosen and researched for specifications.
Chapter 4 presents the methods and results of the laboratory experiments with focus on testing the bentonite on the specifications of the chosen applications.
Chapter 5 presents the conclusions of the research as well as recommendations for future research.

Chapter 2

Characterisation of bentonite

Determining the characteristics of the bentonite is very important, because they give information about the suitability of the bentonite for a certain application. This chapter will discuss bentonite as a clay mineral and its characteristics.

General information on bentonite is given in Section 2.1 and the characteristics of bentonite in Section 2.2. The characteristics of bentonite are divided in different physico-chemical properties. Firstly, the rheological and plastic properties are treated in Section 2.2.1, followed by the sorptive properties in Section 2.2.2. Next, the chemical properties are discussed in Section 2.2.3 and this chapter is concluded by the properties of the surface area in Section 2.2.4.

2.1 Bentonite as a clay mineral

Bentonite is a very interesting clay mineral because of the absorbing properties, which makes it suitable for multiple applications in industrial processes. The term bentonite was defined by Ross and Shannon (1926) as a clay altered from glassy igneous material, usually a tuff or volcanic ash. Grim and Guven (1978) redefined the term bentonite to be any clay predominantly composed of a smectite mineral, regardless of its origin. Definitions of bentonite vary a lot in the performed literature study, also the mechanism of formation is not always clear. Bentonite deposits may be formed by any of the following three mechanisms:

1. Hydrothermal alteration of volcanic glass.
2. Digenetic alteration of volcanic glass in an aqueous environment.
3. Formation of smectite-rich sediments in salt lakes environment.

Mainly, bentonite is formed by the hydrothermal alteration of volcanic glass and pyroclastic rocks (Clem and Doehler, 1959). This is as well the case with the bentonite in the Ünye region. The bentonites are mainly hydrothermal in origin and are derived from in-situ alteration of volcanoclastic material, possibly in a sub-aerial environment (Karakaya, Karakaya, and Bakir, 2011).

In the groups of clay minerals bentonite belongs to the smectite group. Montmorillonite is the most abundant mineral of the smectite clay minerals, bentonite consists therefore primarily of montmorillonite. Besides the presence of montmorillonite, it contains small portions of other mineral matter, usually quartz, feldspar, volcanic glass, organic matter, gypsum or pyrite (Clem and Doehler, 1959). The structure of the smectite mineral group is a layer composed of two silica tetrahedral sheets with a central octahedral sheet. Smectite crystals are negatively charged due to the substitution of the trivalent aluminium ions by bivalent ions like Mg^{2+} and Fe^{2+} and substitution of tetrahedral Si^{4+} by Al^{3+}. The mentioned minerals are placed in a complex structure, which is giving the typical characteristics of bentinite like the water absorption. Water is taken up between the structural layers, which gives them the ability to exchange cations (Grim, 1962). In Figure 2.1 the structure of a smectite mineral is shown. Detailed information of structural and mineralogical characteristics of clay minerals are given in Appendix A.

Bentonite can be divided in different groups based on the most dominant exchangeable ion. Calcium bentonites, which has Ca^{2+} as the dominant exchangeable cation and sodium bentonites with Na^{+}. The influence of the most dominant exchangeable ion can be seen in the physical and chemical properties of the types of bentonite. Calcium bentonites are characterized by low water absorption and swelling capabilities, the inability to stay suspended in water and the absorbent usages. Sodium bentonite is

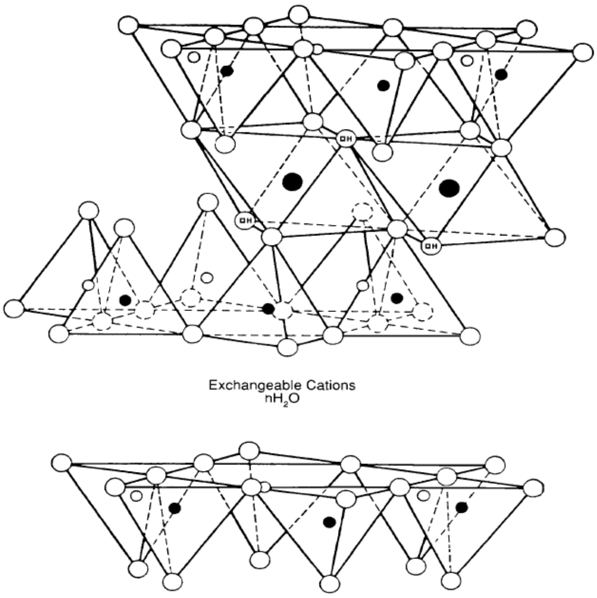


Figure 2.1: Diagrammatic sketch of the structure of smectite according to Hofmann, Endell, Wilm, Marshall, and Hendricks (Grim, 1962).

characterized by the ability to absorb large amounts of water and form viscous, thixotropic suspensions (Karakaya et al., 2011).

In the region of Ünye multiple bentonite mines can be found and also research is done on the Turkish bentonite. Research on the potential applications of the sodium and calcium bentonites is done in the Ordu region by Karakaya et al. (2011), the exact same region where the samples of the M1, M2, M3 and M4 mine are originated. The calcium bentonites are found south of the Göbö area and the sodium bentonites are located east of the Kumru area. Önal, Sarikaya, Alemdaroğlu, and Bozdoğan (2002) did research on the Reşadiye reserve, a sodium bentonites in the Tokat region. In the Arguvan region (MalatyaTürkiye) research is done on calcium bentonites (Kirali and Laçin, 2006). Sodium and calcium bentonite are spread over the Ünye region, the type of bentonite is best indicated by the research of Karakaya et al. (2011). The research area of the bentonite used in this research is closed located to the research area of this thesis. The indication is that the type of bentonite of this research is a calcium bentonite.

2.2 Characteristics

The characteristics of bentonite determine the type of bentonite, the quality of the resource and the suitability of the bentonite for the applications. Each application is demanding different values for the characteristics, some characteristics are more important for a certain application than others. Characteristics are sorted by their physico-chemical properties. A difference is made between characteristics, like rheological/plasticity properties and properties of the surface area.

The characteristics of rheological and plasticity properties are the Atterberg Limits, moisture content, plastic viscosity and yield point. The sorptive properties are influenced by the swelling action of the bentonite. X-ray fluorescence, cation exchange capacity, methylene blue adsorption and pH are regarded as chemical properties of bentonite and the specific surface area is a surface area property.

2.2.1 Rheological and plasticity properties

Atterberg Limits: Atterberg (1911) introduced the liquid limit (w_L) and the plastic limit (w_P) to determine the relation between clay mineral composition to the properties of clay materials as determined in soil mechanics studies and to consider the fundamental way in which the clay mineral composition influences the properties. The Atterberg Limits can be determined for constant soils, depending on the moisture content of the soil, the Atterberg Limits are distinguished into four states: solid, semi-solid, plastic and liquid. In each state, the consistency and behaviour of a soil is different. Changing soil

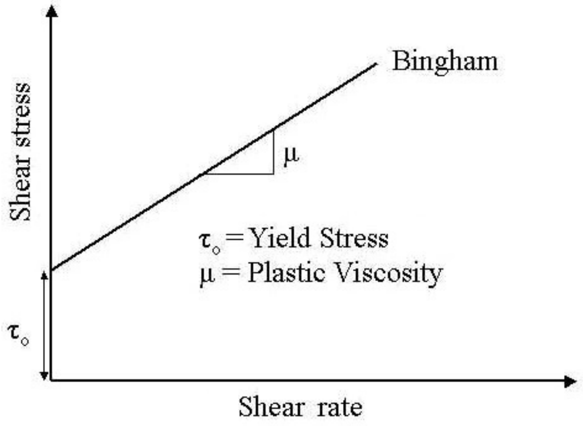


Figure 2.2: Diagrammatic sketch of a Bingham plastic.

behaviour will therefore also result in different engineering properties. The liquid and plastic limits are often used because the limits can be correlated with other soil properties. The liquid limit is the transition of the plastic behaviour of soil to liquid behaviour. Rheological properties, or the flow of soil in liquid state, are within the region of liquid behaviour. The rheological behaviour of some sensitive clays has shown that there are positive relationships between plastic viscosity, yield stress, remoulded shear strength, and liquidity index (Locat and Demers, 1988). The liquidity index gives the relation between the liquid limit, plastic limit and gravimetric water content of the soil. The following equation is given for the liquidity index:

$$LI = \frac{w_n - w_p}{w_L - w_p} \tag{2.1}$$

Gravimetric water content is a characteristic which is often used in geotechnical research. Besides gravimetric water content there is also volumetric water content, but is not used in this research. When referred to moisture content, the gravimetric water content is meant. The moisture content is the quantity of water contained in soil and is expressed by mass:

$$w_n = \frac{m_w}{m_t} \tag{2.2}$$

Where:

- m_w, mass of water [g].
- m_t, bulk mass [g].

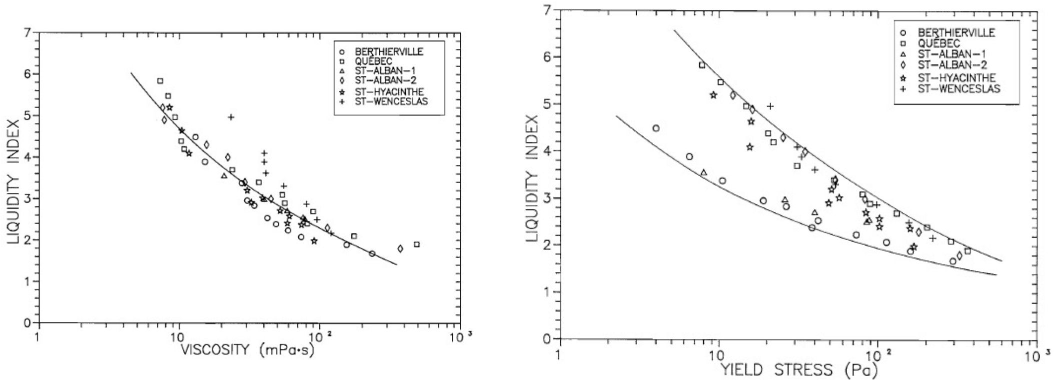
Plastic Viscosity: The plastic viscosity of clay is the slope of the shear stress and shear rate line above the yield point. The plastic viscosity represents the viscosity of the clay mineral when extrapolated to infinite shear rate on the basis of the mathematics of the Bingham model. In Figure 2.2 a graphical representation is given of a Bingham plastic. The slope of the line above the yield point is the plastic viscosity.

Yield point: The yield point in fluid mechanics is the point of applied stress where the yield is large enough a fluid starts to flow. The fluids with yield stress are called Bingham plastics. The definition of a Bingham plastic according to Bird, Stewart, and Lightfoot (2007) is:

$$\begin{array}{ll} \tau_{yx} = -\mu_0 \frac{dv_x}{dy} + \tau_0 & \tau_{yx} \geq \tau_0 \\ \frac{dv_x}{dy} = 0 & -\tau_0 \leq \tau_{yx} \leq \tau_0 \\ \tau_{yx} = -\mu_0 \frac{dv_x}{dy} - \tau_0 & \tau_{yx} \leq \tau_0 \end{array} \tag{2.3}$$

Where:

- τ_{yx}, shear stress [Pa].
- $\frac{dv_x}{dy}$, shear rate [s^{-1}].
- μ_0, plastic viscosity [$Pa \cdot s$].
- τ_0, yield stress or yield point [Pa].



(a) Relationship between liquidity index and viscosity.

(b) Relationship between liquidity index and yield stress.

Figure 2.3: Relations by the research of Locat and Demers (1988).

Locat and Demers (1988) did research on the relationships of viscosity, yield stress, remolded strength and liquidity index for sensitive clays. In Figure 2.3 an exponential relationship between liquidity index, viscosity and yield stress is presented. For determining the rheological behaviour of soil multiple tests are required to find the optimal conditions. Finding the optimal rheological behaviour is essential for using bentonite in applications with the use of these rheological properties.

2.2.2 Sorptive properties

Swelling: The greatest use of bentonite is the swelling action. Bentonite swells bacause water is taken up between the structural layers, which give them the ability to exchange cations (Grim, 1962). Especially sodium bentonite absorbs large amounts of water, where calcium bentonite has low water absorption. Swelling of the soil will lead to volume increase and expansive soils like bentonite could cause considerable distress when subjected to moisture (Yukselen and Kaya, 2008). Researches attempted to predict the swell potential of soils for this reason using soil index properties such as plasticity index, clay content, and activity (Holtz, 1959; Seed, Woodward, and Lundgren, 1959). In the research of Seed et al. (1959) an empirical relation is found between the activity, the clay content and the swelling potential:

$$\text{Swelling Potential} = S = 3.6 \cdot 10^{-5} \cdot Ac^{2.44} \cdot CC^{3.44} \tag{2.4}$$

Where:

- Ac, activity.
- A_m, clay content.

However, determining the activity and clay content is very time consuming, so for other techniques are looked for (Yukselen and Kaya, 2008). Free swelling capacity and swelling index are good characteristics to measure the swelling of bentonite. The free swelling capacity of a clay mineral is determined by the amount of absorbed liquid material in a test tube and the swelling index is the ratio of water to the minimum mass of bentonite at which the suspension just fails to flow.

2.2.3 Chemical properties

X-Ray Fluorisence: X-ray fluorescence spectrometry is a well-established analytical technique and one of the most versatile methods for elemental oxide composition of minerals. In this method, primary high-energy X-rays are used to excite characteristic secondary radiation from the analysed soil sample. The basis of this technique lies in the relationship between the wavelength (or energy) of X-ray photons emitted by the sample element and the atomic number. By removal of an inner electron by an energetic photon, an electron from an outer shell drops into its place. However there are a limited number of ways in which this can happen. The main transitions are given names: an L → K transition is traditionally called Kα, an M → K transition is called Kβ, see Figure 2.4. Each of these transitions yields a fluorescent photon with a characteristic energy equal to the difference in energy of the initial and final orbital (Bloemsma, 2010). Because of the known relationship between emission wavelength and atomic number,

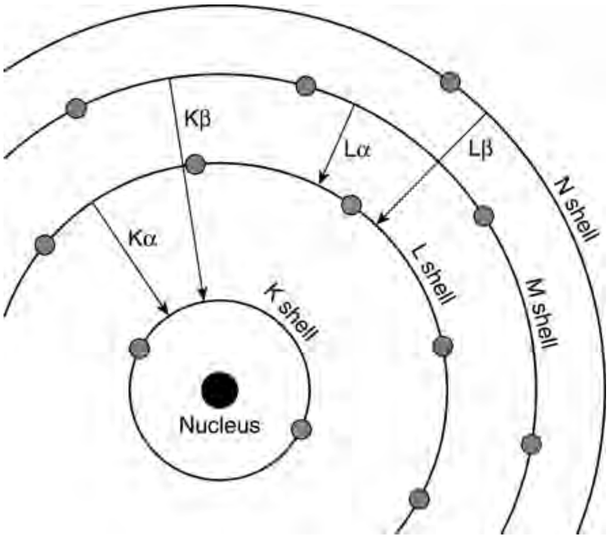


Figure 2.4: Possible transitions of a fluorescent photon with a characteristic energy equal to the difference in energy of the initial and final orbital.

isolation of individual characteristic lines allows the unique identification of an element to be made, and elemental concentration can be estimated from characteristic line intensities (Mahto and Sharma, 2008). Typically these characteristic line intensities are presented in a spectra with distinct energy peaks for the associated elements.

One of the major problems of the interpretation of these spectra is the result of the frequency overlap between the characteristic lines of adjacent elements (Swerts and Van Espen, 1993). As a consequence, the method requires the use of sophisticated spectrum evaluation methods to obtain interference-free and background-corrected net peak areas, by solving least squares problems (Bloemsma, 2010).

The result of a XRF analysis is percentage sorted list with the containing element oxides in the sample. By the characterisation of bentonite, besides other oxides, the percentage of sodiumoxide and calciumoxide is important. The ratio of the two minerals determines the type of bentonite. With the XRF analysis also contaminations can be found, like heavy metals.

pH: The value for the pH gives an indication about the acidity or basicity of the soil. The influence of pH on the soil is seen in the values for other characteristics. In the research of Benna, Kbir-Ariguib, Magnin, and Bergaya (1999) the effect of pH on rheological properties of purified sodium bentonite suspensions is studied. The effect of the pH is large, characteristics like yield point decreased when the pH is increased. Characteristics of crude bentonite can be altered by changing the pH, this is the reason in processing bentonite activation steps are included. Activation is done by either adding acid or soda, depending on the desired pH value. The pH is increased by adding sodium carbonate to the bentonite. The decreasing yield point of Benna et al. (1999) is an example of soda activation. Acid treatment is expected to lower the pH value and improve the specific surface area and the bleaching effectiveness (Didi et al., 2009). The activation steps are based on the ability of bentonite to exchange cations, the so called cation exchange capacity.

Cation Exchange Capacity & Methylene Blue Adsorption: Cations are positively charged ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), sodium (Na^{+}) hydrogen (H^{+}), aluminium (Al^{3+}), iron (Fe^{2+}), manganese(Mn^{2+}), zinc (Zn^{2+}) and copper (Cu^{2+}). The capacity of the soil to hold on to these cations is called the cation exchange capacity (CEC) (CUCE, 2007). These cations are general for all soils and not especially for clay minerals. More specific for smectite clay minerals, the high charge on the smectite layer is satisfied by cations such as Na^{+}, Ca^{2+}, Mg^{2+}, Fe^{2+} and Li^{+}. Cation exchange capacity is reported in terms of milliequivalents (mEq) per 100 g of clay. Smectites have a high cation exchange capacity which is generally of the order of 60-100 mEq/100 g of clay (Murray, 1999). The property of the ion exchange is of great fundamental and practical importance in the research of clay minerals. In application of clay mineralogy it is important because the nature of the exchangeable ion may influence substantially the physical properties of the material (Grim, 1968). Grim (1968) summarized two causes of cation-exchange capacity of the clay minerals:

1. Broken bond around the edges of the silica-alumina units would give rise to unsatisfied charges which could be balanced by absorbed cations. The number of broken bonds, hence the exchange capacity, would increase as the particle size decreased. In the smectite minerals broken bonds are responsible for a relatively small portion (20%) of the cation-exchange capacity.
2. Substitutions within the lattice of trivalent aluminium for quadrivalent silicon in the tetrahedral sheet and for trivalent aluminium in the octahedral sheet result in unbalanced charges in the structural units of the clay minerals. In the smectite minerals 80% of the total cation-exchange capacity is within the lattice cause.

The cation exchange capacity is tested with the methylene blue spot test. The amount of methylene blue adsorbed by the bentonite sample determines the capacity to exchange ions. The characteristic methylene blue adsorption is determined with the same methylene blue spot test and also gives the capacity of the soil to hold cations. The difference between the cation exchange capacity and the methylene blue adsorption is the unit in adsorption. Where the cation exchange capacity is given in mEq/100 g of clay, the methylene blue adsorption is given in mg methylene blue/g clay.

2.2.4 Surface Area

Specific Surface Area: The combined effects of particle size and slenderness in a measurement, complementary to grain-size distribution, is the specific surface area. The specific surface area is increased as the particle size becomes small. The specific surface area is also increased if the sample has pores. The specific surface area is important for the industrial processes and chemical reactions, like in use of bleaching earth.

The specific surface area of particles can be determined by the amount of absorbed methylene blue in the methylene blue spot test. The surface area covered by one methylene blue molecule is typically assumed to be 130 Å^2. It is important to highlight that the technique is done in water suspensions, thus expansive minerals can expose all available surface area (Santamarina, Klein, Wang, and Prencke, 2002). Hang and Brindley (1970) found a correlation between the cation exchange capacity and the specific surface area. The following equation is given for the specific surface area:

$$SSA = M_f \cdot A_m \cdot 6.02 \cdot 10^{-2} \tag{2.5}$$

Where:

- M_f, amount of mEq of methylene blue are adsorbed per 100 g clay when the surface is covered. Better known as the cation exchange capacity.
- A_m, area covered by one MB molecule.

The relation between the cation exchange capacity and the specific surface area assumes that there is also a relation between the cation exchange capacity and the fineness of the soil sample. There is still discussions about this hypothesis. The results of Yukselen and Kaya (2008) show that there is no significant difference in the amount of adsorbed methylene blue of the soil samples. On the other hand, Hills and Pettifer (1985) reported that the particle size affects the adsorbed methylene blue.

Chapter 3

Applications of bentonite and relevant material characteristics

Clay-based industries are of fundamental importance to all countries, where bentonite is one of the markets in this clay-based industry. In order to gain more insight in the applications of bentonite and their demands, a literature study is performed on applications and associated specifications.

In Section 3.1, the applications of bentonite are introduced and divided into their pysico-chemical properties. Next, in Section 3.2, an essential step is taken to select four applications followed by general information and specifications of these applications in Sections 3.3, 3.4, 3.5 and 3.6. In 3.7 the chapter will be concluded with an evaluation of the applications, special interest is on the characteristics of the applications.

3.1 Applications of bentonite

Bentonite is a very diverse resource, used in all kinds of different industries, from the cat litter industry to the oil and gas exploration and from the food industry to ceramics. Bentonite is used in cat litter, drilling mud, ceramics, paper, pharmaceuticals, paint, oils, rubber, perfumes and plastics. It is also used as a binding agent in foundry sand and iron ore palletization.

Certain industrial applications become clear from an understanding of the composition and structure of bentonite and the properties. The most important properties are rheology, adsorption capacity, hydration and swelling, binding properties and impermeability. The suspension of bentonite and water is used most of all as industrial application, because physical properties of the mixture changes as the water to clay ratio changes (Clem and Doehler, 1959). The addition of water also gives the greatest use of bentonite, the swelling action. Bentonite can also be used as dried powder or granule.

Bentonite, used in industrial applications, all have to meet certain specifications. The specifications of each industrial application are different, for a certain application the bonding property is more important than rheological properties or adsorption. To find the suitability of a bentonite for an application, the characteristics have to meet the specification.

A lot of research is done to applications of bentonite in several industrial activities (Mahto and Sharma, 2008; Murray, 1999; Clem and Doehler, 1959; Hassan and Abdel-Khalek, 1998; Boylu, 2011; Önal et al., 2002). In Figure 3.1 a summary is given of major applications for crude bentonite sorted in different activated stages (type of bentonite). Each application is using different properties of bentonite. Adsorptive properties, surface area, rheological properties, impermeability, bonding properties and plasticity are the most important properties, the so called physico-chemical properties. The relationships between the major applications and these physico-chemical properties are given in Table 3.1.

Often the properties are not good enough for a certain application, therefore activation steps are performed to increase the adsorption and the bleaching properties. Activation of bentonite is often done by addition of acid or soda ash. Even good quality bentonite, in natural form, may not meet the required standards for drilling muds as drilling-fluid additives.

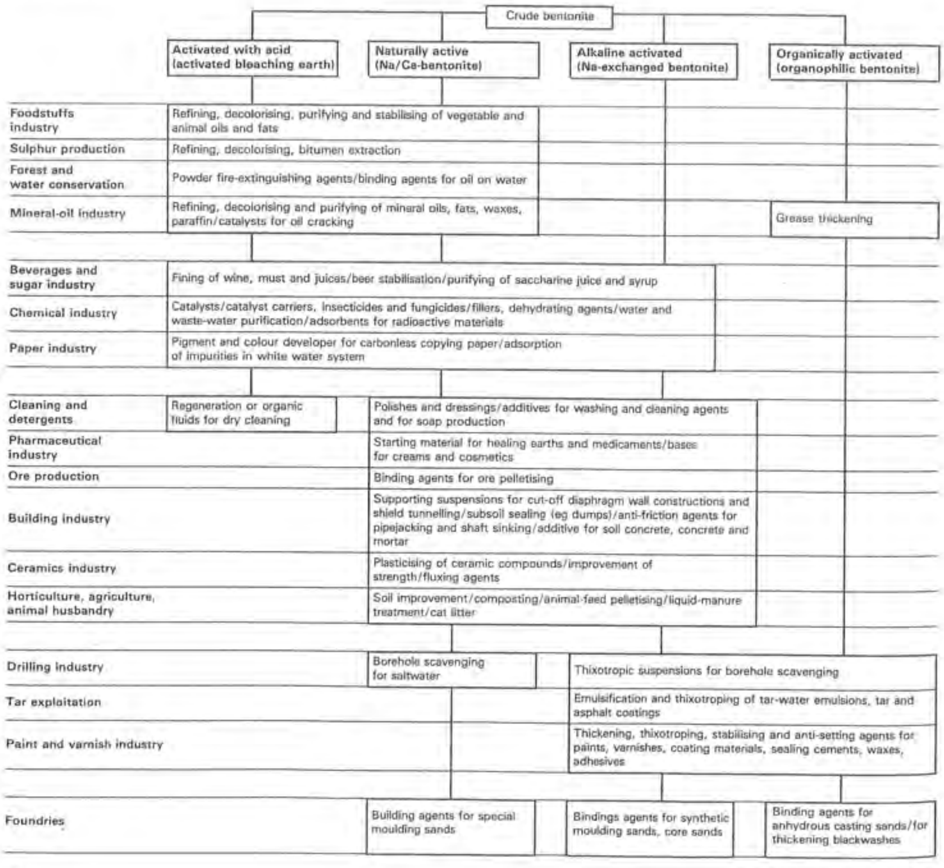


Figure 3.1: Major areas of applications for bentonite (Süd Chemie).

Table 3.1: Commercial applications of bentonite in relation to physico-chemical properties (Highley, 1972).

Sorptive properties (may be increased by acid treatment)	
In suspension	Refining and bleaching of glyceride oils Clarification and purification of sugar solutions, syrups and wines Water purification, sewage and effluent treatment
In dry state (or paste)	Pharmaceutical and therapeutic preparations Absorbent (pet and animal litter, oil spillage on factory floor)
Surface area (may be increased by acid activation)	
	Catalytic action, carrier for catalysts Carrier for insecticides and fungicides Mineral filler and extender
Rheological properties	
Viscosity and suspending powers	Drilling fluids Paints (oil and water-based) Fertilizer sprays Bitumen emulsions Formulation of ceramic glazes
Thixotropy	Wall support for boreholes Civil engineering (diaphragm wall construction) Non-drip paints
Impermeability, coating properties	
	Civil engineering (Grouting, impermeable membrane) Drilling in permeable strata
Bonding properties	
	Bonding foundry moulding sands Pelletising iron ore concentrates Pelletising animal feedstuffs
Plasticity	
	Formation of mortars, putties, adhesives and ceramic bodies

3.2 Justification of downscoping

This thesis focuses on the applications of bentonite originated from North-east Turkey. The list of bentonite applications is extensive, as shown in Figure 3.1. For the practical purpose a selection is made from the list of applications. This selection is based on the time schedule for this thesis. The workload of testing the bentonite on all applications would be to high. The selection of the applications of foundry sand, drilling fluid, soil improvement and bleaching earth are made for several reasons. According to the literature these are large markets whithin the bentonite industry. Also the wishes of the Company are tried to full fill, their wishes are based on experience in the bentonite industry and knowledge of the companies in the near of the Ünye region and their applications for bentonite.

Large markets of industrial applications for bentonite are foundry sand and drilling fluid (Inglethorpe, Morgan, Highly, and Bloodworth, 1993). For this reason these two applications which are going to be tested. The markets for foundry sand and drilling fluid are the biggest and consumes the most bentonite, where specifications demand a high bentonite.

Other markets with potential are the soil improvers and the bleaching earth. This is known in the Company and these last two applications are therefore chosen. The markets of soil improvement and bleaching earth is having close connections with the environment and the food industry. Strict specifications are needed to provide safety for the environment, animals and humans. But these markets are not always having specifications of some sort. Commissions of the related industries are setting up specifications especially concerning upper limits for contaminants.

In the next sections the four different applications are discussed, general information about the applications is given and the associated specification is presented.

3.3 Drilling Fluid

3.3.1 General

In the petroleum industry drilling fluid is often used while drilling oil and gas. The drilling fluid is having multiple functions during drilling, like cool and lubricate drill bit, remove cuttings from well, maintain well-bore stability and seal permeable formations. Good drilling fluid is based a high viscosity and improved thixotropic properties. With the correct plastic viscosity and yield point, the drilling fluid is able to flow but also to hold and transport cuttings. In drilling fluids, important property is that of great filter-cake impermeability, or, a low water loss when the fluid is filtered. Bentonite, with a predominance of sodium ions in its exchange complex, is widely used as an additive to drilling fluids (Mahto and Sharma, 2008). As described in Section 3.1, dispersion of bentonite in water is easily done. Sodium bentonites are having the unique swelling property which makes them necessary ingrediënts in most water-based drilling fluids (Murray, 1999).

3.3.2 Specifications

There are regulations for using bentonite in drilling fluid, listed by the American Petroleum Institute (API) and the Oil Companies Materials Association (OCMA). Where the API specifications is based on the Wyoming bentonite, the OCMA specifications is used for lower quality clays, including sodium-exchanged bentonites. The used specifications relate to the viscosities of suspensions of fixed solid content, requiring the measurement of the plastic viscosity, yield point and the filtrate loss of the suspension (Inglethorpe et al., 1993). Specifications are given in Table 3.2. The drilling-grade of non-treated bentonite has to meet the requirements of the API, conform to the physical specifications of Table 3.3.

Table 3.2: Bentonite physical specifications (API, 2010).

Requirement	Unit	API Standard	OCMA Standard
Suspension property:			
Viscometer dial reading at 600 r min^{-1}	[-]	Min 30	Min 30
Yield point/plastic viscosity ratio	[-]	Max 3	Max 6
Filtrate volume	[mL]	Max 15	Max 16
Residue of diameter greater than 75 μm	[mass %]	Max 4.0	Max 2.5

Table 3.3: Non-treated bentonite physical specifications (API, 2010).

Requirement suspension property	Unit	Standard
Yield point/plastic viscosity ratio	[-]	Max 1.5
Dispersed plastic viscosity	[mPa · s]	Min 10
Dispersed filtrate volume	[mL]	Max 12.5

3.4 Foundry Sand

3.4.1 General

The use of bentonite in foundry sand is one of the largest applications. Bentonite is used as a bonding agent in silica sand for the production of foundry sand moulds for ferrous (iron and steel) and non-ferrous (copper, aluminium, brass) metal castings. Aside from bentonite and silica sand foundry sand, also contains pulverized coal and water. Since bentonite is used as a binder in foundry sand, changes on bentonite properties will affect the moulding properties of the silica sandbentonite mixture (foundry sand) to form the mould with desired properties. Such ability will provide the means to handle it before and after operation and also during the casting process (Boylu, 2011). The important foundry properties of bentonite are green compression strength, dry compression strength, hot strength, flow ability, permeability and durability (Murray, 1999). Swelling is also an important characteristic in foundry sand, swelling can be either desired or unexpected expansion will cause great distress in the constructed mould (Yukselen and Kaya, 2008). Both sodium and calcium bentonite are used as foundry bonding clays, blends of the sodium and calcium bentonites are commonly used to gain the optimum properties for the moulding sand which is needed for a particular metals. Inglethorpe et al. (1993) summarized the properties of the different types of bentonite in foundry sand as follows:

- Sand mixtures produced from natural natrium bentonites have medium to low green strengths but high dry strengths and wet tensile strengths. Important are the thermal properties, sodium bentonites usually show good high-temperature durability and the bonding properties are not destroyed by moderate heat.
- Sand mixtures made from calcium bentonites have medium green strengths and low dry strengths.
- Sand mixtures made from sodium-exchanged calcium bentonite have high green strengths and low dry strengths.
- Natural sodium bentonite blended with calcium bentonite or activated bentonite gives specific properties to the sand mixture. Such blends are used where high clay levels are necessary to produce strong sands at low moisture contents.

3.4.2 Specifications

The Bureau of Indian Standards has published the IS 12446:2007 Standard for foundry grade bentonite (IS, 2007). This standard covers the requirements for bentonite used as a binder for preparing the foundry sand in foundries. This standard is a revision of the earlier IS 6186:1971 standard. Specifications of bentonite in the use of foundry sand are given in Table 3.4. The values of the characteristics are covered for three types of bentonite. One calcium grade bentonite and two sodium grade bentonite. The sodium bentonites are diveded based on their methylene blue adsorption.

3.5 Soil Improvement

3.5.1 General

In the agriculture soil is managed to maintain and restore the soil fertility, make a certain agricultural process (more) economical or help increasing the yield of the product. Bentonite can be used in the soil management as a soil improver or fertiliser. The fertility of the soil increases when bentonite is added to the soil. The bentonite will increase the fertility of the soil if the organic content is high enough. Bentonite is also capable in holding nutrients effectively, the bentonite then timely releases nutrients to the soil. Before using bentonite as a soil improver it has to be tested on contamination of heavy metals. Heavy metals are the metals with harmful effects on the environment, like cadmium, mercury,

Table 3.4: Requirements bentonite for foundry sand (IS, 2007).

SI No.	Characteristics	Na 450	Na 370	Ca 220
1	Fineness			
	Dry, maximum percent retention by mass on IS sieve sizes			
	125 μm	3	3	3
	63 μm	7	7	7
	Pan	90	90	90
	Wet, maximum percent retention by mass on IS sieve sizes			
	45 μm	5	5	5
2	Moisture content [%]	6-12	6-18	5-12
3	pH at 2% suspension [-]	9.0-10.5	9.0-10.5	8.0-9.0
4	Liquid limit [%]	800-900	600-800	100-200
5	Gel formation index [mL]	60, Min	50, Min	30, Min
6	Free swelling capacity [mL]	36, Min	28, Min	10, Min
7	Gelling time [min]	1, Max	2, Max	5, Max
8	Swelling index [mL]	33, Min	25, Min	10, Min
9	Cation exchange capacity			
	a) mg of MB/g of bentonite	450, Min	370, Min	220, Min
	b) meq of MB/100 g of bentonite	120, Min	98, Min	59, Min
10	Cone fusion temperature [°C]	1300	1300	1175-1225
11	Bonding properties			
	Bentonite 7% moisture percent, high silica sand AGS-250 to 355 μm			
	CCS [gcm^{-2}]	1000, Min	1000, Min	800, Min
	CCS [gcm^{-2}]	500, Min	500, Min	400, Min
	DCS [gcm^{-2}]	5000, Min	5000, Min	5000, Min
	Shatter index [%]	75-80	75-80	55-60
12	Chemical composition 12.1, replaceable Ca^{2+} as CaO by mass in percent			
	a) Na_2O, K_2O [-]	2.5-3	2.5-3	0.75-3
	b) Na_2O/CaO [-]		1.0-1.7	0.1-0.4
13	LOI [%]	10, Max	10, Max	10, Max
14	Na^+/Ca^{2+} [-]	2.5-4.5	2.5-4.5	0.001-0.4

lead, arsenic and nickel. Using bentonite in soil improvement or fertiliser not much research is done, this makes it hard to give a scientific background on soil improvement.

3.5.2 Specifications

Recently there were no specifications for soil improvement or fertilisers. The available products for this applications did not always performed well enough to improve the soil. The European Commission made in cooperation with the Technical Working Groups of 2012 specifications for this application in the agriculture. The specification mainly tests the product on the presence of heavy metals and nutrient content. Because bentonite is used in the soil improvement, bentonite also has to meet the specifications before it can be used. In Table 3.5 the upper limits are given for heavy metal for straight use in mixtures of B, Co, Cu, Fe, Mn, Mo or Zn fertilisers in dry matter and micro-nutrients. The European Commission is making a distinction between soil improver for dry matter and micro-nutrient. It is striking that the regulations for dry matter are more strict compared to micro-nutrients. An explanation for the broader ranges of micro-nutrients is that micro-nutrients are nutrients which are only required in small quantities. No excessive intake of micro-nutrients will lead to higher upper limits.

Table 3.5: Specifications for soil improvent.

Heavy metals	Max content [mg/kg dry matter]	Max content [mg/kg micro-nutrient]
As	60	1000
Cd		200
Cd (for products containing 5% P_2O_5)	3	
Cd (for products containing 5% P_2O_5)	EU limit 60, Opt-in 40 or 20	
Cr VI	2	
Pb	150	600
Hg	2	100
Ni	120	2000

The nutrients in the bentonite are present in the organic part. In order to act as a fertiliser, the bentonite has to have a certain nutrient content. The minimum nutrient on commercialised products is also regulated by European Commission. The minimum values containing in bentonite is given in Table 3.6.

Table 3.6: Minimum nutrient content on commercialised products.

Nutrient	Minimum content [%]
Total N components	1
P_2O_5	0.3
Water-soluble K_2O	0.5

3.6 Bleaching Earth

3.6.1 General

Vegetable oils contain color body impurities like carotenes and chlorophyll that requires removal for optimum oil quality. Crop harvesting conditions can result in wide variations of impurity levels. Bleaching is a method to remove these impurities, based on the physical adsorption, chemical adsorption, ion exchange, and chemical decomposition of colouring organic pigments and other impurities on the bleaching earth. Good quality bleaching earth will effectively remove color bodies and other impurities like soaps, phospholipids, phosphatides, fatty acids, gums, trace metals, oxidation products and metals and enhances the stability of the refined oil (Kirali and Laçin, 2006; Foletto, Colazzo, Volzone, and Porto, 2011). Especially sodium bentonites have good protein absorption properties as well as good clarifying effects (Allo and Murray, 2004). The bleaching effectiveness is strongly dependent on the crude bentonite composition and the kind of oil to be bleached. The bleaching capacity of bentonites is greatly increased by activation treatment. While some of these clays are naturally bleaching, some have to be treated with mineral acids (Foletto et al., 2011). Sometimes activation may not be needed, as concluded by Kirali and Laçin (2006). He found that a higher bleaching capacity is reached with non-activated Turkish bentonite than acid activated bentonite. The origin of this Turkish bentonite is not far of the research area of this thesis in Arguvan.

3.6.2 Specifications

The research done on the bleaching capacity of bentonite did not result in an international accepted specification. No statistical approach has been considered to study the correlation between the parameters for clay activation and the factors governing the oil bleaching process (Didi et al., 2009). Only the bleaching capacity has been reviewed (Kirali and Laçin, 2006; Foletto et al., 2011). The research of Didi et al. (2009) is giving recommended ranges for the characteristics and chemical composition for bentonite. Therefore, this research is used as the specification for bleaching earth. The recommanded ranges of Didi et al. (2009) are given in Table 3.7.

Table 3.7: Recommanded ranges of the characteristics (Didi et al., 2009).

Characteristics	Recommanded range
Moisture content [%]	12, Max
Cation Exchange Capacity [meq/100g]	45-50
Loss on ignition [wt.%]	11, Max
Acidity [meq/g dry clay]	0.8, Max
pH [-]	4
Specific surface area [m^2/g clay]	200
Chemical composition	
SiO_2 [%]	60-70
Al_2O_3 [%]	17-20
Fe_2O_3 [%]	1-3
Na_2O [%]	1-2
K_2O [%]	0-0.07
CaO [%]	-
MgO [%]	-

3.7 Evaluation on the applications of bentonite

For this thesis bentonite samples of the M1, M2, M3 and M4 mine, originated from the Ünye region, are tested for suitable applications. The applications which are going to be tested are drilling fluid, foundry sand, soil improvement and bleaching earth. There are specifications for the selected applications, where important characteristics are given. The bentonite is going to be tested on these characteristics, if the characteristics meet up with the given values for the characteristics in the application, then the bentonite is suitable for the application.

The following characteristics are important for the drilling fluid, foundry sand, soil improvement and bleaching earth applications. For drilling fluid yield point, plastic viscosity and filtrate volume are important. In foundry sand these are fineness, moisture content, pH, liquid limit, gel formation index, free swelling capacity, gelling time, swelling index, cation exchange capacity (or methylene blue adsorption), cone fusion temperature, bonding properties, loss on ignition and chemical composition. The chemical composition is very important for soil improvement, as well as the nutrient content of the bentonite. Characteristics which are used for bleaching earth are moisture content, cation exchange capacity, loss on ignition, acidity, pH, surface area and chemical composition. These physico-chemical properties can be obtained by a large range of laboratory tests. In Table 3.8 a graphical representation is given of the required laboratory tests for the bentonite applications. To conclude of the bentonite is suitable for the application all tests need to be executed.

Not all characteristics are possible to test, some are requiring advanced equipment, like for cone fusion temperature, bonding properties and filtrate volume. Other characteristics are not tested due to the limited time range of this thesis. The following characteristics are going to be tested: cation exchange capacity, chemical composition, free swelling capacity, liquid limit, methylene blue adsorption,

Table 3.8: Correlation between the chosen applications and associated characteristics.

	Drilling Fluid	Foundry Sand	Soil Improvement	Bleaching Earth	Cat Litter
Bonding properties		x			
Cation exchange capacity		x		x	x
Chemical composition		x	x	x	x
Cone fusion temperature		x			
Filtrate volume	x				
Fineness		x		x	x
Free swelling capacity		x			
Gel formation index		x			
Gelling Time		x			
Green compression strength		x			
Liquid limit		x			
Loss on ignition		x		x	
Moisture content	x	x		x	x
pH		x		x	x
Plastic viscosity	x				
Swelling index		x			x
Yield point	x				

moisture content, pH, plastic viscosity, specific surface, swelling index and yield point. The methods of the laboratory experiments are described in Appendix B. After the tests there can be concluded for which application the bentonite of the Company is suitable or not suitable.

Chapter 4

Interpretation of the results

The interpretations of the result will eventually lead to a conclusion of the research goal. In this chapter all necessary information to make a characterisation of the bentonite samples. In Section 4.1 the bentonite samples are described followed by the testing condition during the characterisation of the samples in 4.2. The results will be presented in Section 4.3. Next, in Section 4.4, the results are interpreted and eventually evaluated in Section 4.5.

4.1 Material

For this thesis samples have been taken from the mines of the Company. There are four samples taken, one from each mine. Each sample is composed of ten undisturbed small samples. The combination of the ten small samples gives one representative sample of the mine. The samples were taken by the local plant manager in the mines. The samples are kept at all time sealed in ziplock bags. It need to be mentioned that only one sample is used for the characterisation of bentonite originated from one mine. This sample is giving an indication for the whole mine, but multiple samples are needed to give a detailed characterisation of the bentonite from the mines.

4.2 Methods

In all tests, except the cone penetrometer test for the liquid limit, dry bentonite powder is used. The bentonite is dried in an oven for 24 hours at 105°C. After dehydration the moisture content is determined and the bentonite is further crushed by a hand mortar.

The methylene blue adsorption spot test is performed on the bentonite samples. A methylene blue solution of 3 g/L is used, which is having a normality of 0.0094 mEq/L. During constant stirring each time 0.5 mL of methylene blue solution is added until a permanent blue halo appeared around the soil aggregate spot onto the filter paper. At the end of this test the cation exchange capacity (CEC) and the methylene blue adsorption (MBA) is found with the added amount of methylene blue solution and dry sample weight.

For the free swelling capacity 2 grams of bentonite powder is suspended into demineralised water. Extra care is taken that every soil partcle is wetted by the demineralised water. The swell of the suspended bentonite is measured in a 500 mL glass graduated cylinder. After 24 hours the free swelling capacity is measured in terms of mL volume increase.

The liquid limit is determined by using the cone penetrometer method according the BSI (1990a). In IS (2007) the Casagrande method is used, the method using the cone penetrometer is preferred over using the Casagrande method, as the test is both easier to carry out and is capable of giving more reproducible results. The cone penetrometer divice is easier to maintain in correct adjustment and the test procedure is less dependent on the judgement of the operator. The results obtained with the cone penetrometer may differ slightly from those with the Casagrande apparatus, but in most cases up to a liquid limit of 100 these differences will not be significant and will be less than the normal variations likely to be obtained using the Casagrande apparatus.

The pH of the bentonite in suspension is determined by a glass electrode pH meter. Bentonite is first brought into suspension with distilled water of pH 5.63 at 20 °C. After heating the suspension to 27°C, the pH is measured.

A rheometer test is performed to obtain the plastic viscosity and the yield stress of the bentonite samples. For the rheometer test the Paar Physica UDS200 rheometer is used. Sensors are composed of two coaxial cylinders. The inner one, the mobile rotor (geometry device MC200 SN172615 GPIB-DEV1), which is linked to a gauge measuring the torque applied on the fluid. The outer cylinder is fixed and insures the temperature control by means of a liquid cooling/heating system. The test with rheometer is performed at 50°C ± 1°C. The gauge is controlled by the US200/32 V2.30 21001433-33024 software.

Due to corruption in the data, the rheometer dial reading at R_{300} with the M2 sample gave bad values, resulting in negative plastic viscosity. The value for the R_{300} read off is therefore left out of the dataset.

For the determination of the swelling index a range of weights of bentonite powder is brought into suspension with a constant amount of demineralised water. The suspension is kept in small test tubes of 10 mL. The minimum amount of bentonite were the suspension starts to flow out of the tube, the swelling index is defined.

A chemical analysis is performed on the bentonite samples. For XRF analysis the measurements were performed with a Panalytical Axios Max WD-XRF spectrometer and data evaluation was done with SuperQ5.0i/Omnian software.

4.3 Results

Results of the performed laboratory tests are given in Table 4.1 and results of the XRF analysis are given in Table 4.2. The calculations of the laboratory experiments are given in Appendix C.

Table 4.1: Summary of the laboratory results.

Test	M1	M2	M3	M4
Cation Exchange Capacity [mEq/100g]	54.1	49.1	48.9	40.4
Free Swelling Capacity [mL]	1.6	0.3	1.3	0.5
Liquid Limit [%]	126	87	80	81
Methylene Blue Adsorption [mg MB/g]	172.5	156.7	155.9	129.0
Moisture Content [%]	40.5	43.5	37.3	32.0
pH [-]	9.5	8.3	8.5	8.4
Plastic viscosity (μ_0) [mPa · s]	56.8	x	17.4	38.6
Specific Surface Area [m^2]	423	384	382	316
Swelling Index [-]	33.3	20.0	50.0	50.0
Yield point (τ_0) [Pa]	70.5	x	30.0	43.1

4.4 Interpretation of results in relation with the applications

As explained in Section 2.1 the most dominant exchangeable ion is important for the characteristics of the bentonite. Before other characteristics are evaluated, it is important to determine the type of the bentonite samples, this is done by the XRF analysis. In Table 4.2 the percentage of CaO and Na_2O is found, where the percentage of Ca^{2+} and Na^+ is calculated. The ratio of Na^+ and Ca^{2+} makes the bentonite a sodium bentonite or a calcium bentonite. IS (2007) is characterising bentonite with a ratio of Na^+ and Ca^{2+} within the range 0.001-0.4 as a calcium bentonite. The Na^+ and Ca^{2+} content of the bentonite samples obtained from the XRF analysis is given in 4.3, resulting in the determination of the bentonite samples. All four samples are calcium bentonites, but there is a large difference between the samples in sodium and calcium content. The sodium content of the M1 mine is 4 or 5 times higher compared to the other samples and on the other side the calcium content lower compared is with the M2, M3 and M4 sample.

Table 4.2: XRF Analysis of the bentonite samples.

	Weight percentage [%]			
Compound Name	M1	M2	M3	M4
SiO_2	77.251	76.492	73.212	74.195
Al_2O_3	13.022	12.641	16.389	15.270
MgO	2.784	1.977	4.069	3.431
Fe_2O_3	2.432	1.894	1.960	2.427
K_2O	1.998	1.382	0.473	0.563
CaO	1.629	5.031	3.394	3.569
Na_2O	0.501	0.130	0.131	0.074
TiO_2	0.154	0.169	0.144	0.182
MnO	0.065	0.155	0.052	0.031
ZrO_2	0.032	0.026	0.037	0.039
SrO	0.028	0.021	0.052	0.077
P_2O_5	0.025	0.021	0.024	0.034
Cl	0.025	0.017	0.012	0.013
SO_3	0.018	0.015	0.011	0.011
Nb_2O_5	0.010	0.007	0.011	0.014
Rb_2O	0.008	0.007	0.002	0.003
ZnO	0.008	0.004	0.007	0.006
Y_2O_3	0.004	0.005	0.005	0.010
ThO_2	0.004	0.006	0.007	0.009
PbO	0.003		0.004	0.004
CeO_2				0.036

Table 4.3: Na^+ and Ca^{2+} content of the bentonite samples.

Sample	Na^+ [%]	Ca^{2+} [%]	Na^+/Ca^{2+} [-]
M1	0.501	1.629	0.319
M2	0.130	3.596	0.027
M3	0.131	2.426	0.040
M4	0.074	3.569	0.021

It is important to mention is the presence of thorium in all four samples. This is no heavy metal (tested for the application of soil improvement), but a naturally occurring radioactive chemical element. Soil contains an average of about 6 parts of thorium per million of soil (6 ppm) (ATSDR, 1999). The M1 sample is containing 37 ppm thorium, the M2 sample 46 ppm, the M3 sample 65 ppm and the M4 sample 84 ppm. These values are far above average. The impact of the thorium presence in the bentonite samples is unknown. The relation with the specifications for bentonite applications is also not clear on this point.

4.4.1 Drilling Fluid

There are two international standards for the use of bentonite in drilling fluid, the API and the OCMA Standard. In Table 4.4 the rheometer test results are shown and the results are compared with the API and the OCMA Standard. The samples from the M1 and M2 mine are within the range of the given characteristics stated by the API. The M3 sample is exceeding the upper limit of the yield point/plastic viscosity ratio in the API Standard, but ratio is lower than the upper limit of the OCMA Standard. The other characteristics of the M3 sample are of API quality. Unfortunately, the reading of the 300 $r \cdot min^{-1}$ of the M2 sample was discarded, but the dial reading at 600 $r \cdot min^{-1}$ was above minimum reading in the API standard. The reading of the M2 sample went wrong due to evaporation of water in the rheometer. A steady dial reading was required to evaluate the API standard. This steady dial was not reached because water evaporated when keeping the outer cylinder on temperature. Evaporation leads to a decreasing moisture content which will immediately effect the plastic viscosity and yield point of the sample.

Table 4.4: Specification drilling fluid (API, 2010) and rheometer results.

Characteristic	API Standard	OCMA Standard	M1	M2	M3	M4
Viscometer dial reading at 600 $\mathrm{r \cdot min^{-1}}$ [-]	Min 30	Min 30	133.0	137.0	49.7	85.3
Yield point/plastic viscosity ratio [-]	Max 1.5	Max 6	1.24	x	1.72	1.12
Dispersed plastic viscosity [$\mathrm{mPa \cdot s}$]	Min 10	-	56.8	x	17.4	38.6

4.4.2 Foundry Sand

The specification for foundry sand (IS, 2007) has an extensive list of tests. For this application tests are performed, where the results are compared with the specification in Table 4.5. The results for cation exchange capacity and methylene blue adsorption are obtained with the same test, the result of this test are for all samples too low. Only the M1 sample is close to the minimum adsorption of methylene blue. The free swelling capacity is very low for all samples. The bentonite samples are classified as calcium bentonite, which are having poor water absorption. The M1 sample is performing best in water absorption, due to the higher percentage of sodium oxide. This is also the case with the test for the liquid limit. Only the M1 sample is within the range of 100-200%, the other samples are having a liquid limit which is too low for use in foundry sand. The moisture content in the samples is for this application too high, but it is common in the processing of each application to have a drying step. For controlling the pH there processing steps, but the pH is in the samples within the range, except the M1 sample which is too high. The swelling index of all samples is high enough.

Table 4.5: Specification foundry sand (IS, 2007) and laboratory results.

Test	Requirement	M1	M2	M3	M4
Cation exchange capacity [mEq/100g]	59, Min	54.1	49.1	48.9	40.4
Free swelling capacity [mL]	10, Min	1.6	0.3	1.3	0.5
Liquid limit [%]	100-200	126	87	80	81
Methylene blue adsorption [mg MB/g]	220, Min	172.5	156.7	155.9	129.0
Moisture content [%]	5-12	40.5	43.5	37.3	32.0
Na^{+}/Ca^{2+} [-]	0.001-0.4	0.319	0.027	0.040	0.021
pH [-]	8-9	9.5	8.3	8.5	8.4
Swelling index [-]	10, Min	33.3	20.0	50.0	50.0

4.4.3 Soil Improvement

Bentonites used in soil improved as fertilizers are not allowed to exceed the maximum limit of heavy metals stated by the European Commission. In the samples of the M1, M2 and M4 mine traces of PbO is detected. Lead is a heavy metals which, is stated in Table 3.5. The upper limit of lead for dry matter is 150 mg/kg and 600 mg/kg for micro-nutrient. In Table 4.2 the percentage of PbO is given, 0.003 % in M1 and 0.004 % in M3 and M4. The percentage of Pb in M1 is 0.0028% and in M3 and M4 0.0037%. These values corresponds with 27.84 mg/kg Pb in the M1 sample and 37.12 mg/kg in the M3 and M4 sample, which is presented in Table 4.6. All three samples are not exceeding the upper limit for dry matter as well for micro-nutrient. In the sample of M2 there is no trace of PbO found. There are two explanations for the absence of PbO in the sample of M2: there is no presence of PbO in the M2 mine or the percentage PbO is too small to be detected by the spectrometer. In the samples is no other trace of heavy metal found, except lead.

Table 4.6: Specifications for soil improvent and XRF results on heavy metals.

Heavy Metal	Requirement [mg/kg dry matter]	Requirement [mg/kg micro-nutrient]	M1 [mg/kg]	M2 [mg/kg]	M3 [mg/kg]	M4 [mg/kg]
As	60, Max	1000, Max	-	-	-	-
Cd		200, Max	-	-	-	-
Cd (for products containing 5% P_2O_5)	3, Max	-	-	-	-	-
Cd (for products containing 5% P_2O_5)	EU limit 60, Opt-in 40 or 20, Max	-	-	-	-	-
Cr VI	2, Max	-	-	-	-	-
Pb	150, Max	600, Max	27.84	-	37.12	37.12
Hg	2, Max	100, Max	-	-	-	-
Ni	120, Max	2000, Max	-	-	-	-

The content of nitrogen (N) components, phosphate (P_2O_5) and potassium oxide (K_2O) are looked at for when testing the nutrient content of the soil. Table 4.7 shows that the percentage of P_2O_5 is ten times too low for to apply the bentonite samples for soil improvement. On the other hand, the percentage of K_2O in the samples of the M1, M2, M3 and M4 mine reaches the lower limit of the European Commission specification. Only the M3 sample doesn't contain enough K_2O in the sample. There is no trace found of nitrogen found in the bentonite samples, the cause for the absence is that nitrogen is detected with a different type of XRF analysis. Detection of nitrogen requires a XRF method with low energy X-rays in stead of high energy X-rays used in this XRF analysis (Kirtley, Mullins, van Elp, and Cramer, 1993).

Table 4.7: Specifications for soil improvement and XRF results on nutrient content.

Nutrients	Requirement [%]	M1 [%]	M2 [%]	M3 [%]	M4 [%]
Total N components	1, Min	-	-	-	-
P_2O_5	0.3, Min	0.025	0.021	0.024	0.034
Water-soluble K_2O	0.5, Min	1.998	1.382	0.473	0.563

4.4.4 Bleaching Earth

The bentonite samples are tested for the recommanded ranges of Didi et al. (2009), in Table 4.8 the results are compared with these ranges. Using bentonite as bleaching earth a moisture content of maximum 12% is required, where the results are ranging from 24% to 31%. The cation exchange capacity of the bentonite samples lies in most cases within the recommended ranges. M2 and M3 are within the ranges of 45-50 mEq/100g, where the sample of M1 is above the range with 54.1 mEq/100g and M4 underneath the range with 40.4 mEq/100g. For bleaching earth it is common to use acid activation to achieve a low pH. Also in this case the pH is in all samples too high, the recommend range is a pH of 4 and the samples are having a pH of 8-9. The specific surface area is calculated with Equation 2.5 from the research of Hang and Brindley (1970). The results for the specific surface area are positive, all samples have a high specific surface area and are above the 200 m^2/g clay given by Didi et al. (2009). The recommended ranges of the chemical composition are also given in Table 4.8. The percentage of SiO_2, Al_2O_3, Fe_2O_3, Na_2O and K_2O in all samples close to the ranges stated in Didi et al. (2009). In Allo and Murray (2004) sodium bentonite is more suitable for bleaching earth and the results in Table 4.3 shows that the bentonites are calcium bentonites. This is why the results of the XRF in Table 4.2 are too low for Na_2O.

Table 4.8: Recommanded ranges of the characteristics (Didi et al., 2009) for bleaching earth and the laboratory results.

Characteristics	Recommanded range	M1	M2	M3	M4
Moisture content [%]	12, Max	40.5	43.5	37.3	32.0
Cation Exchange Capacity [mEq/100g]	45-50	54.1	49.1	48.9	40.4
pH [-]	4	9.5	8.3	8.5	8.4
Specific surface area [m^2/g clay]	200	423	384	382	316
Chemical composition					
SiO_2 [%]	60-70	77.251	76.492	73.212	74.195
Al_2O_3 [%]	17-20	13.022	12.641	16.389	15.270
Fe_2O_3 [%]	1-3	2.432	1.894	1.960	2.427
Na_2O [%]	1-2	0.501	0.130	0.131	0.074
K_2O [%]	0-0.07	1.998	1.382	0.473	0.563
CaO [%]	-	1.629	5.031	3.394	3.569
MgO [%]	-	2.784	1.977	4.069	3.431

4.5 Evaluation on the results

The results of the tests on the characteristics has given an indication of the suitability of the bentonite for the chosen applications. The interpretations of the values for the characteristics are compared with the specifications. A summary of these interpretations is given in Table 4.9. The samples are not suitable for foundry sand, due to the many characteristics which need to be improved before the bentonite is suitable for foundry sand. For suitability on bleaching earth processing steps are required to provide the suitability. With the fairly simple processes of drying and activation, it can be said that the bentonite samples are suitable for bleaching earth.

Table 4.9: The suitability of the bentonite for the chosen applications.

Appilcation	M1	M2	M3	M4
Drilling Fluid	**Suitable**	Unknown	**Suitable**	**Suitable**
Foundry Sand	Not suitable	Not suitable	Not suitable	Not suitable
Soil Improvement	**Suitable**	**Suitable**	**Suitable**	**Suitable**
Bleaching Earth	*Suitable, if pH and moisture content is decreased*	*Suitable, if pH and moisture content is decreased*	*Suitable, if pH and moisture content is decreased*	*Suitable, if pH and moisture content is decreased*

Chapter 5

Conclusions and recommendations

5.1 Conclusions

This research focusses on the suitability of Turkish bentonite mined by the Company for industrial applications. The following conclusions can be drawn after literature study and laboratory experiments.

The Turkish bentonite of the Company is very suitable for using the crude bentonite for drilling fluid. The samples of the M1 and M4 mine are within the ranges of the API Standard and the M3 sample is suitable for using in drilling fluid according the OCMA Standard. The quality of the M2 sample is tested but no conclusions can be drawn from the obtained data.

Using the Turkish bentonite in foundry sand is determined as not suitable. Many characteristics are not according the IS Standard, like free swelling capacity, cation exchange capacity, methylene blue adsorption, moisture content and liquid limit. The quality of water absorption is not high enough due to the type of bentonite. The pH of the sample is in range of the specification, no activation steps are needed. Without activation of the bentonite the characteristics, which are not according to the IS Standard, cannot be improved. The sample from the M1 mine is showing the most potential for the use of foundry sand.

In the samples of M1, M3 and M4 there are traces of lead found, these values are not exceeding the upper limit stated by the European Commission of using bentonite as soil improver. In the sample of M2 there isn't a trace of lead found. In all samples there aren't other heavy metals than lead detected. This is in line with the specifications stated by the European Commission. Not all nutrients are present in the samples or are reaching the minimum content. All samples are very suitable for soil improvement. Except some nutrients the soil isn't contaminated with heavy metals.

All samples showing high moisture contents and pH values, but all other characteristics meet up with the recommended ranges of Didi et al. (2009). By adding the drying and acid activation process steps, all samples will be very suitable for the use of bleaching earth.

The goal of this research was to find the suitability of bentonite samples from the Turkish mines owned by the Company for various industrial applications which are using bentonite. The suitability is examined for four applications: drilling fluid, foundry sand, soil improvement and bleaching earth. After testing the samples against the specifications of the applications the samples are all very suitable for bleaching earth and drilling fluid. The sample of the M2 mine is also very suitable for soil improvement. The application of foundry sand is not suitable for the Turkish bentonite of the Company.

5.2 Recommendations

This research has given an indication on the suitability of the Turkish bentonite samples for industrial applications. Major recommendation, to be able to better interpret the results of the experimental work and to answer the suitability of the bentonite for industrial applications, are:

- Only one sample is used to represent the bentonite of one mine. This is statistically not representative enough to give a complete characterisation of the mine. More samples nee to be taken and tested on the described methods for the characteristics.
- Besides the study on the characteristics of different applications of bentonite, it is necessary to research the basic characteristics of the bentonite. Better understanding of the bentonite leads to better interpretation of the suitability for industrial applications.

- To examine the complete suitability of the bentonite samples for all characteristics have to be tested. In the time schedule of this research it was not possible to test all characteristics used in the applications. The residual characteristics are also important for the characterisation and are need therefore to be tested. Especially the filtrate volume for drilling fluid and green compression strength for foundry sand are interesting to determine.
- For determining the optimal drilling fluid use, a comparable research as Locat and Demers (1988) has to be done on the bentonite samples. This will lead to a better relationship between the liquidity index of the Turkish samples and the plastic viscosity and yield point. These relationships can also be found between other characteristics, like the pH value and the cation exchange capacity. For all relationships a curve can be found with an optimal value for the relation.
- Better research has to be done on the detection of heavy metals. In this research only traces of lead are found. The concentration of the other heavy metal is probably too low to be detected during the XRF analysis. With other analysis techniques it is possible to get a better understanding in the presence of heavy metal in the soil.
- The nutrient content is in all samples for soil improvement too low, an effective process has to worked out to increase the nutrient content to reach the minimum content stated by the European Commission.
- The presence of thorium in the bentonite samples has to be evaluated. Research should be done on the upper limit of thorium in soil, also is the influence of thorium on the industrial applications unclear.
- Processing steps have to be taken to reduce the moisture content and the pH value in using the bentonite for bleaching earth.

Bibliography

W.A. Allo and H.H. Murray. Mineralogy, chemistry and potential applications of a white bentonite in san juan province, argentina. *Applied Clay Science*, 25(3-4):237–243, 2004.

API. *API Specification 13A*. American Petroleum Institute, 2010.

ASTM. *ASTM Geotechnical Engineering Standards*. American Society for Testing and Materials International, 2003.

ATSDR. *Thorium, CAS 7440-29-1*. Agency for toxic substanves and disease registry, 1999.

A. Atterberg. Die plastiziteit der tone. *Internationale Mitteilungen fur Bodenkunde*, 1:10–43, 1911.

M. Benna, N. Kbir-Ariguib, A. Magnin, and F. Bergaya. Effect of ph on rheological properties of purified sodium bentonite suspensions. *Journal Colloid Interface Science*, 218(2):442–455, 1999.

R.B. Bird, W.E. Stewart, and E.N. Lightfoot. *Transport Phenomena*. John Wiley and Sons, 2th edition, 2007.

M. Bloemsma. Semi-automatic core characterisation based on geochemical logging data. Master's thesis, Delft University of Technology, 2010.

F. Boylu. Optimization of foundry sand characteristics of soda-activated calcium bentonite. *Applied Clay Science*, 52:104–108, 2011.

T.J. Brown, N.E. Idoine, S.F. Hobbs, and A.J. Mills. *European Mineral Statistics 2008-2012*. British Geological Survey, 2014.

BSI. *BS 1377-2: 1990 - Methods of tests for soils for Civil Engineering purposes - Part 2: Classification tests*. British Standardisation Institution, 1990a.

A.C. Clem and R.W. Doehler. Applied clay mineralogy today and tomorrow. *Tenth National Conference on Clays and Clay Minerals*, pages 272–283, 1959.

CUCE. *Cation Exchange Capacity (CEC), Agronomy Fact Sheet Series 22*. Cornell University Cooperative Extension, 2007.

M.A. Didi, B. Makhoukhi, A. Azzouz, and D. Villemin. Colza oil bleaching through optimized acid activation of bentonite, a comparative study. *Applied Clay Science*, 42(34):336–344, 2009.

E.L. Foletto, G.C. Colazzo, C. Volzone, and L.M. Porto. Sunflower oil bleaching by adsorption onto acid-activated bentonite. *Brazilian Journal of Chemical Engineering*, 28(1):169–174, 2011.

R.E. Grim. *Clay Mineralogy*. McGraw Hill, 2th edition, 1962.

R.E. Grim. *Applied Clay Mineralogy*. McGraw Hill, 1968.

R.E. Grim and H. Guven. *Applied Clay Mineralogy*. McGraw Hill, 1978.

P.T. Hang and G.W. Brindley. Methylene blue adsorption by clay minerals. dertermination of surface areas and cation exchange capacities (clay-organic studies xviii). *Clays and Clay Minerals*, 18:203–212, 1970.

M.S. Hassan and N.A. Abdel-Khalek. Beneficiation and applications of an egyptian bentonite. *Applied Clay Science*, 13:99–115, 1998.

D.E. Highley. *Fuller's Earth.* Mineral Resource Consultancy Commission Mineral Dossier, 3th edition, 1972.

J.F. Hills and G.S. Pettifer. The clay mineral content of various rock types compared with the methylene blue value. *Journal of Chemical Technology and Biotechnology*, 35A:168–180, 1985.

W.G. Holtz. Expansive clays-properties and problems. *Quarterly of the Colorado School of Mines*, 54 (4):89–125, 1959.

S.D.J. Inglethorpe, D.J. Morgan, D.E. Highly, and A.J. Bloodworth. *Industrial Mineral Laboratory Manual Bentonite.* British Geological Survey, 1993.

IS. *IS 12446: 2007 - Bentonite for use in foundries.* Bureau of Indian Standards, 2007.

M.C. Karakaya, N. Karakaya, and S. Bakir. Some properties and potential applications of the na- and ca-bentonites of ordu (n.e. turkey). *Applied Clay Science*, 54:159–165, 2011.

Í. Keskin, F.A. Yergök, H. Kara, M. Dönmez, and M. Arslan. Ünye-fatsa-kumru-korgan (ordu) dolaynn jeolojisi, mta raport 10182. *(unpublished)*, 1998.

E.G. Kirali and O. Laçin. Statistical modelling of acid activation on cotton oil bleaching by turkish bentonite. *Journal of Food Engineering*, 75:137–141, 2006.

S.M. Kirtley, O.C. Mullins, J. van Elp, and S.P. Cramer. Nitrogen chemical structure in petroleum asphaltene and coal by x-ray absorption spectroscopy. *Fuel*, 72(1):133–135, 1993.

J. Locat and D. Demers. Viscosity, yield stress, remolded strength, and liquidity index relationships for sensitive clays. *Canadian Geotecnical Journal*, 25:799–806, 1988.

V. Mahto and V.P. Sharma. Characterization of indian bentonite clay samples for water-based drilling fluids. *Petroleum Science and Technology*, 26:1859–1868, 2008.

H.H. Murray. Applied clay mineralogy today and tomorrow. *Clay Minerals*, 34:39–49, 1999.

M. O'Driscoll. Bentonite: overcapacity in need of markets. *Industrial Minerals*, 250:43–63, 1998.

M. Önal, Y. Sarikaya, T. Alemdaroğlu, and Bozdoğan. Specific surface: determination and relevance. *Canadian Geotecnical Journal*, pages 233–241, 2002.

C.S. Ross and E.V. Shannon. The minerals of bentonite and related clays and their physical properties. *Journal of the American Ceramic Society*, 9:77–96, 1926.

J.C. Santamarina, K.A. Klein, Y.H. Wang, and E. Prencke. Specific surface: determination and relevance. *Canadian Geotecnical Journal*, pages 233–241, 2002.

B. Seed, R.J. Woodward, and R. Lundgren. Prediction of swelling potential for compacted clays. *Journal of the Soil Mechanics and Foundations Division, Proceedings of the American Society of Civil Engineers*, 54(4):89–125, 1959.

J. Swerts and P. Van Espen. Partial least squares techniques in the energydispersive x-ray fluorescence determination of sulfur-graphite mixtures. *Analytical Chemistry*, 65:1181–1185, 1993.

M.J. Wilson. *Sheet Silicates: Clay Minerals.* The Geological Society, 2013.

Y Yukselen and A Kaya. Suitability of the methylene blue test for surface area, cation exchange capacity and swell potential determination of clayey soils. *Engineering Geology*, pages 38–45, 2008.

Appendix A

Clay Minerals

The term clay is hard to describe due to many varying definitions based on occurrence, plasticity or mineral content. To determine a clay, the sample does not have to meet all specifications. An international accepted definition is based on particle size where the particle size of the minerals need to be smaller than 2 μm. Clay minerals are exclusive to hydrous aluminium silicates which may also contain amounts of water and metal cations such as sodium, calcium, magnesium, lithium and iron. The typical sheeted atomic structure places the clay minerals in the phyllosilicate group of minerals (O'Driscoll, 1998). The structure of most clay minerals are built up by two units:

1. The first unit consists of two sheets with octahedral coordination of six oxygen (O^-) or hydroxyls (OH^-) atoms in which aluminium (Al^{3+}), magnesium (Mg^{2+}) and iron (Fe^{2+}) are embedded (Figure A.1).
2. The second unit consists of silica tetrahedron surrounded by four oxygen (O^-) or hydroxyls (OH^-) atoms. The structure of this unit when grouped is a hexagonal network (Figure A.2).

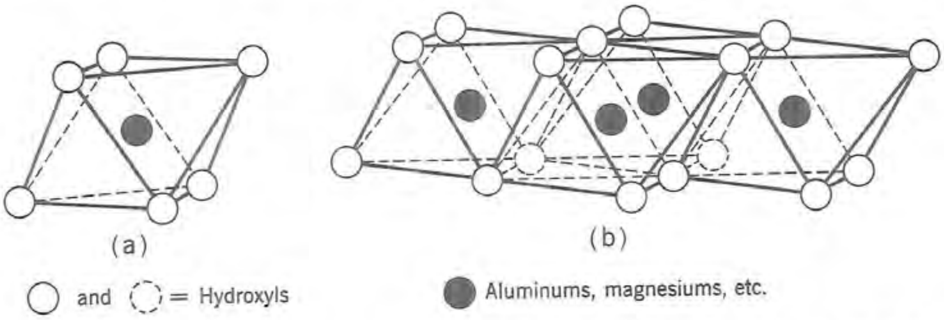


Figure A.1: Diagrammatic sketch showing (a) a single octahedral unit and (b) the sheet structure of the octahedral units (Grim, 1962).

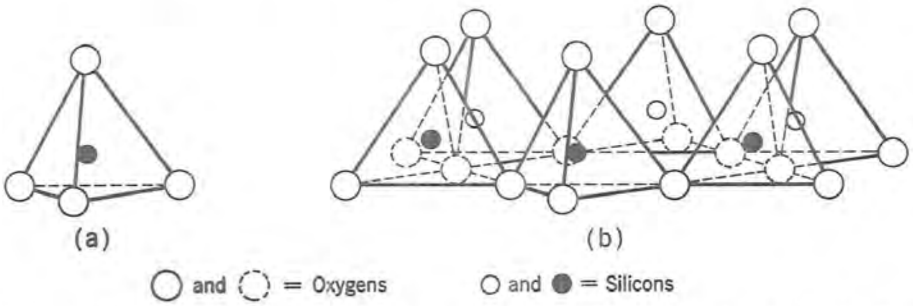


Figure A.2: Diagrammatic sketch showing (a) a single silica tetrahedron and (b) the sheet structure of the silica tetrahedrons arranged in a hexagonal network (Grim, 1962).

The clay minerals, whether in sedimentary deposits or not, are usually products of either weathering or hydrothermal alternation. Clays are defined as a result of different physico chemical conditions and the nature of parent materials, like feldspars, micas, volcanic glasses or ferromagnesian minerals (Wilson, 2013). Groups are based on the atomic structure of the clay minerals. The following five groups of clay minerals are considered (Wilson, 2013; Grim, 1962):

1. *Kaolinite Minerals.* This mineral group is a hydrous aluminium silicate, which structure is composed of a single silica tetrahedral and a single alumina octahedral sheet. The tips of the silica tetrahedrons and one of the layers of the octahedral sheets form a common layer. Halloysite is similar to the kaolinite minerals and is also a hydrous aluminium silicate, only in hydrated form. Resulting in water molecules between the single silica tetrahedral and a single alumina octahedral sheet.
2. *Illite Minerals.* The structure of this mineral group is a layer composed of two silica tetrahedral sheets with a central octahedral sheet, this structure similar to smectite minerals except that the silicon is replaced by aluminium. The principal interlayer cation is potassium, which shows similarity with micas.
3. *Smectite Minerals.* Minerals of this group are showing swelling behaviour when in contact with water. The structure of this mineral group is a layer composed of two silica tetrahedral sheets with a central octahedral sheet. Water is taken up between the structural layers, which give them cation exchange properties. Sometimes smectite minerals are called montmorillonite.
4. *Vermiculite Minerals.* The structure of this mineral group consists of trioctahedral micas or talks separated by layers of water molecules.
5. *Sepiolite/Palygorskite/Attapulgite Minerals.* The minerals in this group are hydrated magnesium aluminium silicates with chain-type atomic structure, rather than layered atomic structures, resulting in finely fibrous minerals.

A summary of the mineral group classification and mineral structure is shown in Table A.1.

Table A.1: A classification of the phyllosilicate clay minerals (Wilson, 2013).

Mineral Group	Example	Tetrahedral/ Octahedral combination	Octahedral structure	Layer charge (x)	Interlayer content
Kaolin	Kaolinite	1:1	Dioctahedral	0	None
	Halloysite	1:1	Dioctahedral	0	Water
Serpentine	Berthierine	1:1	Trioctahedral	0	None
Pyrophyllite	Phyrophyllite	2:1	Dioctahedral	0	None
Talc	Talc	2:1	Trioctahedral	0	None
Mica	Illite	2:1	Dioctahedral	1	Fixed K
	Biotite	2:1	Trioctahedral	1	Fixed K
Chlorite	Clinochlore	2:2	Trioctahedral	Variable	$Mg(OH)_2$
	Donbassite	2:2	Dioctahedral	Variable	$Al(OH)_2$
Smectite	Montmorillonite	2:1	Dioctahedral	0.2-0.6	Exchange cations
	Saponite	2:1	Trioctahedral	0.2-0.6	Exchange cations
Vermiculite	Vermiculite	2:1	Trioctahedral	¿0.6-¡1.0	Exchange cations
Vermiculite	Vermiculite	2:1	Dioctahedral	¿0.6-¡1.0	Exchange cations
Palygorskite/ Sepiolite	Palygorskite		Di/Trioctahedral	Variable	Water and exchage cations
	Sepiolite		Trioctahedral	Variable	Water and exchange cations

Appendix B

Methods of the laboratory experiments

In this appendix all the descriptions of the laboratory experiments are presented. The descriptions are originated from the standards of the applications, like API (2010) and IS (2007). Other descriptions are from international standards for testing geotechnical properties, BSI (1990a) and ASTM (2003).

B.1 Liquid Limit

- From a soil in the natural state containing little or no material retained on a 425 μm test sieve, take a representative sample weighing about 200 g. Cut it into small pieces using a knife or shredder and remove any coarse particles by hand or with tweezers.
- If coarse particles are present determine their mass and the mass of the sample used. NOTE. These weighings enable the approximate proportion of coarse material to be reported if required.
- Transfer the soil to a flat glass plate. Add distilled water and mix thoroughly with two palette knives until the mass becomes a thick homogeneous paste.
- Place the paste in an airtight container and allow to stand for about 24 hour for long enough to enable the water to permeate through the soil. NOTE. A maturing period of about 24 h is recommended for most soils but a shorter time may be acceptable for soils of low clay content. Very silty soils can be tested immediately after mixing.

- Take a sample of about 300 g from the soil paste and place it on the glass plate.
- Mix the paste for at least 10 min using the two palette knives. If necessary add more distilled water so that the first cone penetration reading is about 15 mm. NOTE. Some soils, e.g. clays of high plasticity and residual soils, may require upto 40 min of continuous mixing immediately before testing to obtain reliable results. If in doubt comparative tests should be carried out.
- Push a portion of the mixed soil into the cup with a palette knife taking care not to trap air. Strike off excess soil with the straight edge to give a smooth level surface.
- With the penetration cone locked in the raised position lower the supporting assembly so that the tip of the cone just touches the surface of the soil. When the cone is in the correct position a slight movement of the cup will just mark the soil surface. Lower the stem of the dial gauge to contact the cone shaft and record the reading of the dial gauge to the nearest 0.1 mm.
- Release the cone for a period of 5 1 s. If the apparatus is not fitted with an automatic release and locking device take care not to jerk the apparatus during this operation. After locking the cone in position lower the stem of the dial gauge to contact the cone shaft and record the reading of the dial gauge to the nearest 0.1 mm. Record the difference between the beginning and end of the drop as the cone penetration.
- Lift out the cone and clean it carefully to avoid scratching.
- Add a little more wet soil to the cup, taking care not to trap air, make the surface smooth and repeat the last steps.
- If the difference between the first and second penetration readings is less than 0.5 mm record the average of the two penetrations and proceed. If the second penetration is more than 0.5 m m and less than 1 mm different from the first, carry out a third test. If the overall range is then not more than 1 mm record the average of the three penetrations and proceed.

- Take a moisture content sample of about 10 g from the area penetrated by the cone and determine the moisture content as specified.
- Repeat all steps at least three more times using the same sample of soil to which further increments of distilled water have been added. Proceed from the drier to the wetter condition of the soil. The amount of water added shall be such that a range of penetration values of approximately 15 mm to 25 mm is covered by the four or more test runs and is evenly distributed. Each time soil is removed from the cup for the addition of water, wash and dry the cup.
- If at any time during the above procedure the soil has to be left for a while on the glass plate cover the soil with the evaporating dish or a damp cloth to prevent the soil drying out.

B.2 Plastic Viscosity & Yield Point

- Place a sample of the drilling fluid in a thermostatically controlled viscometer cup. Leave enough empty volume (approximately 50 ml to 100 ml) in the cup for displacement of fluid due to the viscometer bob and sleeve. Immerse the rotor sleeve exactly to the scribed line. Measurements in the field should be made with minimum delay from the time of drilling fluid sampling. Testing should be carried out at either 50 °C ± 1 °C or 65 °C ± 1 °C for reference comparisons to historical data. Testing at a lower temperature, such as 4 °C ± 1 °C, is recommended for low temperature effects. The place of sampling should be stated in the report.
- CAUTION The maximum recommended operating temperature is 90 °C. If it is necessary to test fluids above this temperature, a solid metal bob or a hollow metal bob with a completely dry interior should be used. Liquid trapped inside a hollow bob can vaporize when immersed in high-temperature fluid and cause the bob to explode.
- Heat (or cool) the sample to the selected temperature. Use intermittent or constant shear at 600 r/min to stir the sample while heating (or cooling) to obtain a uniform sample temperature. After the cup temperature reaches the selected temperature, immerse the thermometer into the sample and continue stirring until the sample reaches the selected temperature. Record the temperature of the sample.
- With the sleeve rotating at 600 r/min, wait for the viscometer dial reading to reach a steady value (the time required is dependent on the drilling fluid characteristics). Record the dial reading, R_{600}.
- Reduce the rotor speed to 300 r/min and wait for the dial reading to reach steady value. Record the dial reading R_{300}.

B.3 Methylene Blue Spot Test

- From the Methylene Blue solution 0.5 mL is added to the aggregate suspension by means of a 25 mL burette. Shaking during the addition is necessary, for which a magnetic stirrer may be used.
- Toperfarm the titration, add successive volumes of 0.5 mL of the Methylene Blue solution to the Erlenmeyer flask.
- After each addition, agitate the flask for 1 minutes and remove a drop of the dispersion with the glass rod and dab it carefully on a sheet of filter paper. Initially, a circle of dust is formed which is coloured dark blue and has a distinct edge, and is surrounded by a ring of clear water.
- When the edge of the dust circle appears fuzzy and/or is surrounding by a narrow light blue halo, agitate the flask for 1 more minutes and do another spot test. If the halo has disappeared, add more blue. If there is still a halo, agitate the flask for a further 2 minutes and do another spot test.
- Whatever the outcome of this test, add more blue, agitate for 2minutes do a spot test, then agitate for a further 2 minutes and do another spot test. This sequence, with a total of 4 minutes of agitation is repeated until there is a definite light blue halo. It is recommended to note down the sample number and the amount of methylene blue added below each spot on the filter paper.
- To determine the end-point, hold the filter paper up to daylight while it is still damp, and compare the dust circles made after 4 minutes of agitation. lt should be possible to see where the halo first appears and thus where the end-point is.
- The corresponding volume of Methylene Blue solution added is noted down.

B.4 pH

- Take 2.0 g of the dried bentonite, add 100 ml of distilled water (pH = 7.0) and mix thoroughly. Determine the pH of suspension by means of a suitable pH meter using glass electrode. The test shall be carried out at 27 ± 2 °C.
- Always test distilled water against buffer solution before beginning any pH testing. Distilled water can absorb enough COZfrom the atmosphere to acidify. Ageing of clays will vary the pH value. The calorimetric method is not recommended since results cannot be measured precisely.

B.5 Free Swelling Capacity

- Accurately weigh 2 g of dried bentonite powder (moisture free) and divide the quantity into more than 20 approximately equal parts.
- Take each part by the tip of a spoon and sprinkle into a graduated cylinder containing 100 mL distilled water (pH = 7.0). Care is taken to see that every particle of bentonite is wetted and settled while sprinkled each time till all the 20 parts are over.
- Generally the time taken for completing the test is 1 to 2 h.
- The result will be recorded after one hour and after 24 h from completion of test by noting the volume of gel formed.
- The free swelling capacity is measured in terms of volume, in ml, of gel formed.

B.6 Swelling Index

- Add 0.2 g, 0.25 g, 0.3 g, 0.35 g, 0.4 g, 0.5 g, 0.6 g, 0.7 g, 0.8 g, 0.9 g and 1.00 g of dried sample of bentonite (moisture free) in different duly marked test tubes of 1.5 cm diameter.
- Add 10 mL of distilled water in each test tube. Shake the mixture well of each test tube to ensure full dispersion of bentonite.
- Keep the test tubes for 24 h for full swell.
- The suspended material with proper ratio will not flow out of the test tube when gently tilted to 45° and shall remain still for at least 1 min. The swelling index is the ratio of water (10 ml) to minimum mass of bentonite (g) at which the suspension just fails to flow.

Appendix C

Test Results

C.1 Liquid Limit

The liquid limit is determined by using the cone penetrometer method. The relationship between moisture content and cone penetration is obtained by the test results, with the percentage moisture content plotted against the cone pentration. The liquid limit is the read off the moisture content corresponding to a cone penetration of 20 mm. In Tables C.1, C.2, C.3 and C.4 the results of the cone penetrometer method is given and the relationship between moisture content and cone penetration is shown in Figures C.1, C.2, C.3 and C.4.

Table C.1: Liquid limit measurements M1.

Number	Weight Dish [g]	Wight total wet [g]	Weight clay wet [g]	Weight total dry [g]	Weight clay dry [g]	Moisture content [%]	Penetration [mm]
Z1	43.71	58.91	15.20	51.08	7.37	106.2415	14.30
Z2	46.87	60.48	13.61	53.50	6.63	105.2790	15.45
Z3	44.81	57.42	12.61	50.49	5.68	122.0070	18.10
Z4	43.64	59.63	15.99	50.40	6.76	136.5385	23.40

Table C.2: Liquid limit measurements M2.

Number	Weight Dish [g]	Wight total wet [g]	Weight clay wet [g]	Weight total dry [g]	Weight clay dry [g]	Moisture content [%]	Penetration [mm]
N1	49.55	65.14	15.59	58.43	8.88	75.5631	10.60
N2	46.11	56.77	10.66	51.74	5.63	89.3428	19.40
N3	49.31	67.69	18.38	58.90	9.59	91.6580	26.00

Table C.3: Liquid limit measurements M3.

Number	Weight Dish [g]	Wight total wet [g]	Weight clay wet [g]	Weight total dry [g]	Weight clay dry [g]	Moisture content [%]	Penetration [mm]
Me1	43.73	59.68	15.95	52.77	9.04	76.4381	16.60
Me2	45.06	63.25	18.19	55.08	10.02	81.5369	18.90
Me3	47.43	63.64	16.21	56.33	8.90	82.1348	25.50
Me4	46.48	67.50	21.02	57.75	11.27	86.5129	28.50

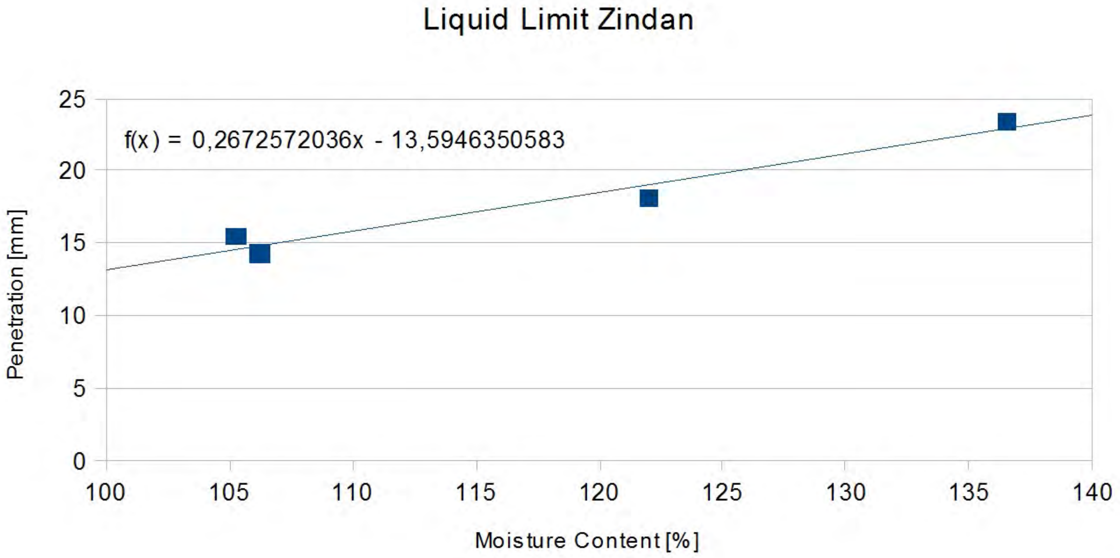


Figure C.1: Liquid limit of M1 sample.

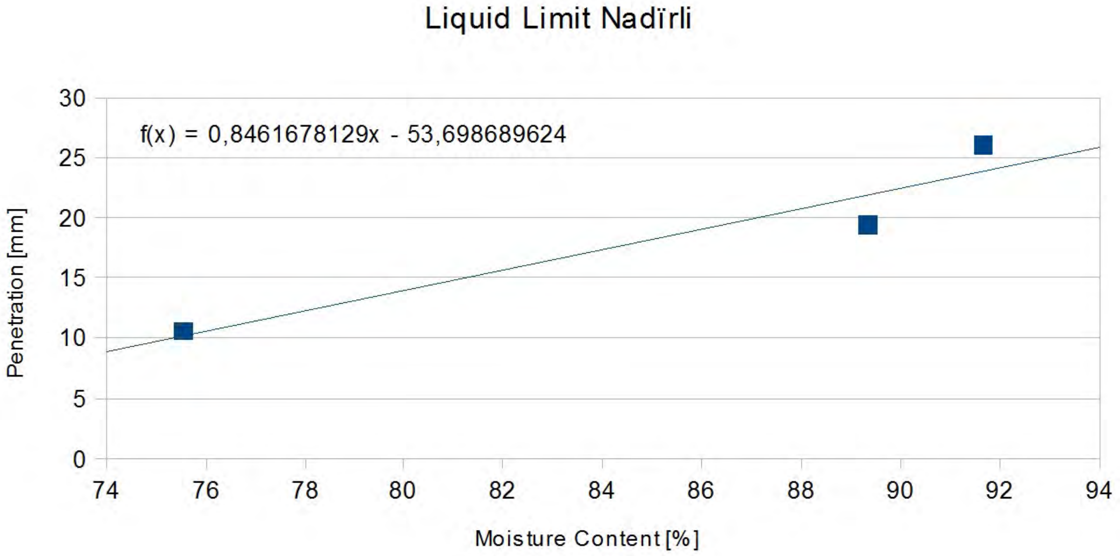


Figure C.2: Liquid limit of M2 sample.

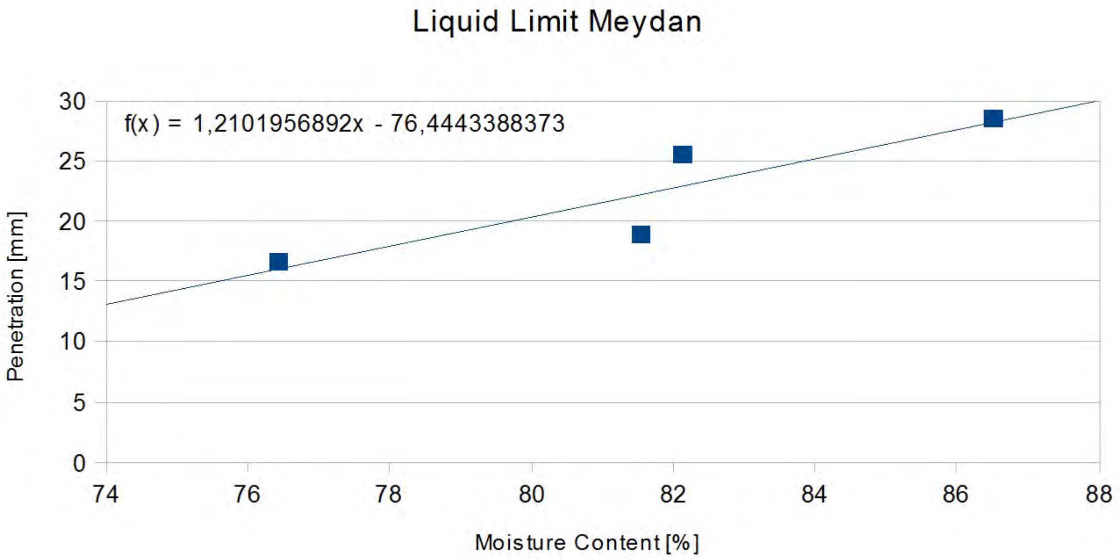


Figure C.3: Liquid limit of M3 sample.

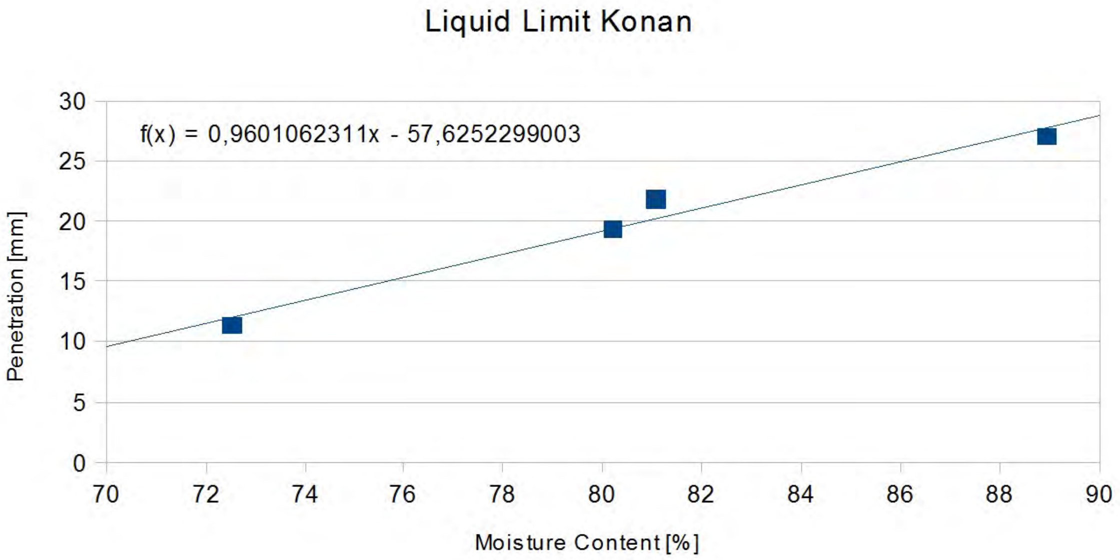


Figure C.4: Liquid limit of M4 sample.

Table C.4: Liquid limit measurements M4.

Number	Weight Dish [g]	Wight total wet [g]	Weight clay wet [g]	Weight total dry [g]	Weight clay dry [g]	Moisture content [%]	Penetration [mm]
K1	43,88	61,34	17,46	54,00	10,12	72,5296	11,30
K2	48,03	69,35	21,32	59,86	11,83	80,2198	19,30
K3	43,43	56,25	12,82	50,51	7,08	81,0734	21,80
K4	43,68	59,59	15,91	52,10	8,42	88,9549	27,00

Table C.5: Liquid limit of the bentonite samples.

Sample	Liquid Limit (w_L) [%]
M1	126
M2	87
M3	80
M4	81

C.2 Plastic viscosity & Yield Point

For the rheometer test the Paar Physica UDS200 rheometer, the geometry device MC200 SN172615 GPIB-DEV1 and the US200/32 V2.30 21001433-33024 software is used. The test with rheometer is performed at 50°C ± 1°C.

The plastic viscosity is determined by the following equation:

$$\mu_0 = R_{600} - R_{300} \tag{C.1}$$

The yield point is determined by the following equation:

$$\tau_0 = 0.48 \cdot (R_{300} - \mu_0) \tag{C.2}$$

Where:

- R_{600}, dial reading at 600 revolutions per minute [° deflection].
- R_{300}, dial reading at 300 revolutions per minute [° deflection].

The reading of rheometer is done in shear stress [Pa], for using the Equations C.1 and C.2 the reading has to be converted to degrees deflection. 1° deflection equals to a shear stress of approximately 0.511 Pa. In Table C.6 the results of the rheometer test is given.

Table C.6: Rheometer results of the bentonite samples.

Sample	Reading R_{600} [Pa]	Reading R_{600} [° deflection]	Reading R_{300} [Pa]	Reading R_{300} [° deflection]	μ_0	τ_0	τ_0/μ_0
M1	133.0	260.27	104	203.52	56.75	70.45	1.24
M2	137.0	268.10	x	x	x	x	x
M3	49.7	97.26	40,8	79.84	17.42	29.96	1.72
M4	85.3	166.93	65,6	128.38	38.55	43.12	1.12

C.3 Methylene Blue Adsorption

In the methylene blue adsorption spot test a Methylene Blue solution of 3 g/L is used with a normality of 0.0094 meq/L. From this test the methylene blue adsorption (MBA) and the cation exchange capacity (CEC) is found with the following equations:

$$MBA = \frac{\text{concentration MB solution} \cdot \text{MB solution added}}{\frac{\text{weight dry sample}}{100g}} \tag{C.3}$$

$$CEC = 100 \cdot \text{normality} \cdot \frac{\text{concentration MB solution}}{\text{MB solution added}} \tag{C.4}$$

In Table C.7 the results of the methylene blue adsorption spot test are given with the values of MBA and CEC, evaluated with Equations C.3 and C.4.

Table C.7: Swelling Index of the bentonite samples.

Sample	Weight dry sample [g]	Added MB solution [mL]	MBA	CEC
M1	2.00	115	17.3	54.1
M2	2.01	105	15.7	49.1
M3	2.02	105	15.6	48.9
M4	2.00	86	12.9	40.4

C.4 pH

The pH of the bentonite in suspension is determined by a glass elctrode pH meter. Bentonite was first brought into suspension with destilled water of pH 5.63 at 20 °C. After heating the suspension to 27 °C, the pH was measured. In Table C.8 the results of the pH measurements is shown.

Table C.8: pH of the bentonite samples

Sample	pH
M1	9.5
M2	8.3
M3	8.5
M4	8.4

C.5 Free swelling capacity

For the free swelling capacity 2 grams of bentonite powder is suspended for 24 hours into demineralised water. The swell of the suspended bentonite is measured in a 500 mL glass graduated cylinder. The laboratory set-up of the free swelling capacity test is shown in Figure C.5. In Table C.9 the results of the free swelling capacity test are given.

Table C.9: Free swelling capacity of the bentonite samples

Sample	Begin [cm]	End [cm]	Difference [cm]	Swell [mL]
M1	1,05	1,35	0,30	1,58
M2	1,00	1,05	0,05	0,26
M3	0,95	1,20	0,25	1,32
M4	0,95	1,05	0,10	0,53

C.6 Swelling Index

The swelling index is determined with the IS (2007). The swelling index is obtained by the minimum mass to let the bentonite flow out the test tubes. The laboratory set-up of the swelling index test is shown in Figure C.5. The following equation is given for the swelling index:

$$\text{Swelling Index} = \frac{10mL\text{water}}{\text{mass bentonite}} \tag{C.5}$$

In Table C.10 the results of the swelling index test are given.

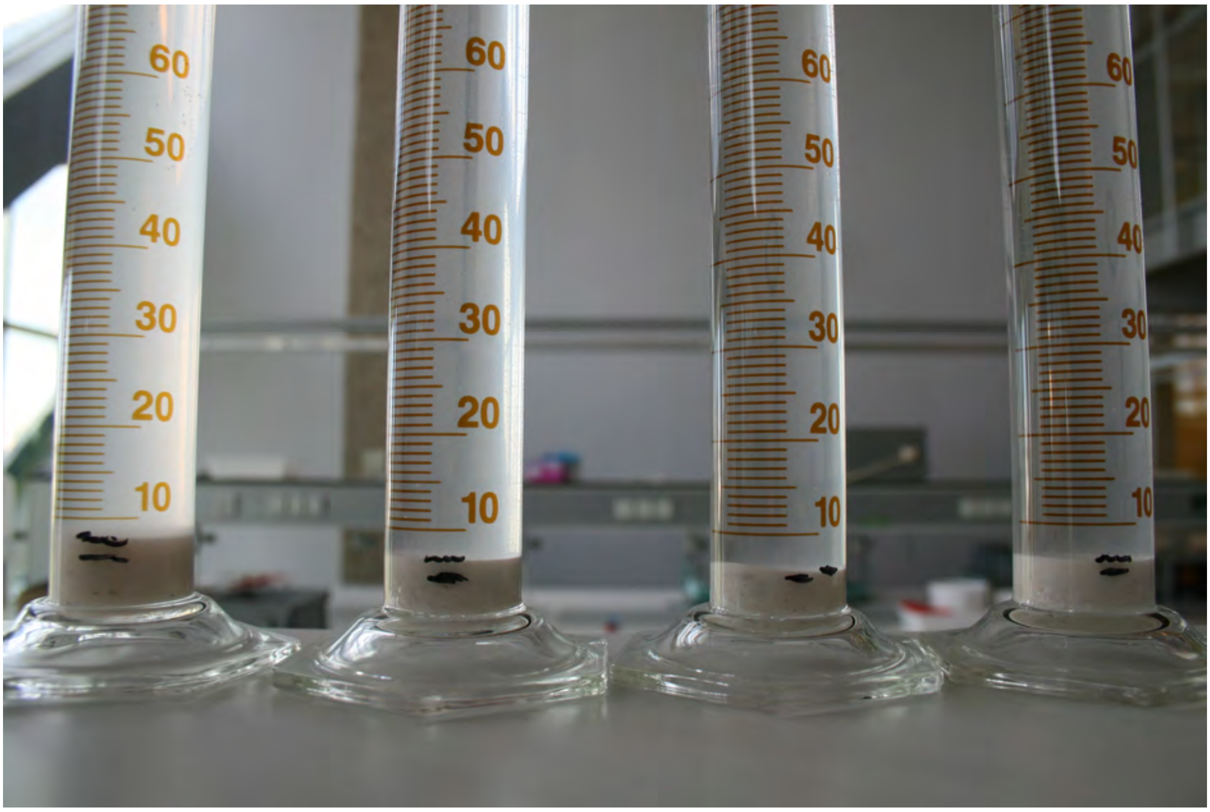


Figure C.5: Laboratory set-up free swelling capacity.

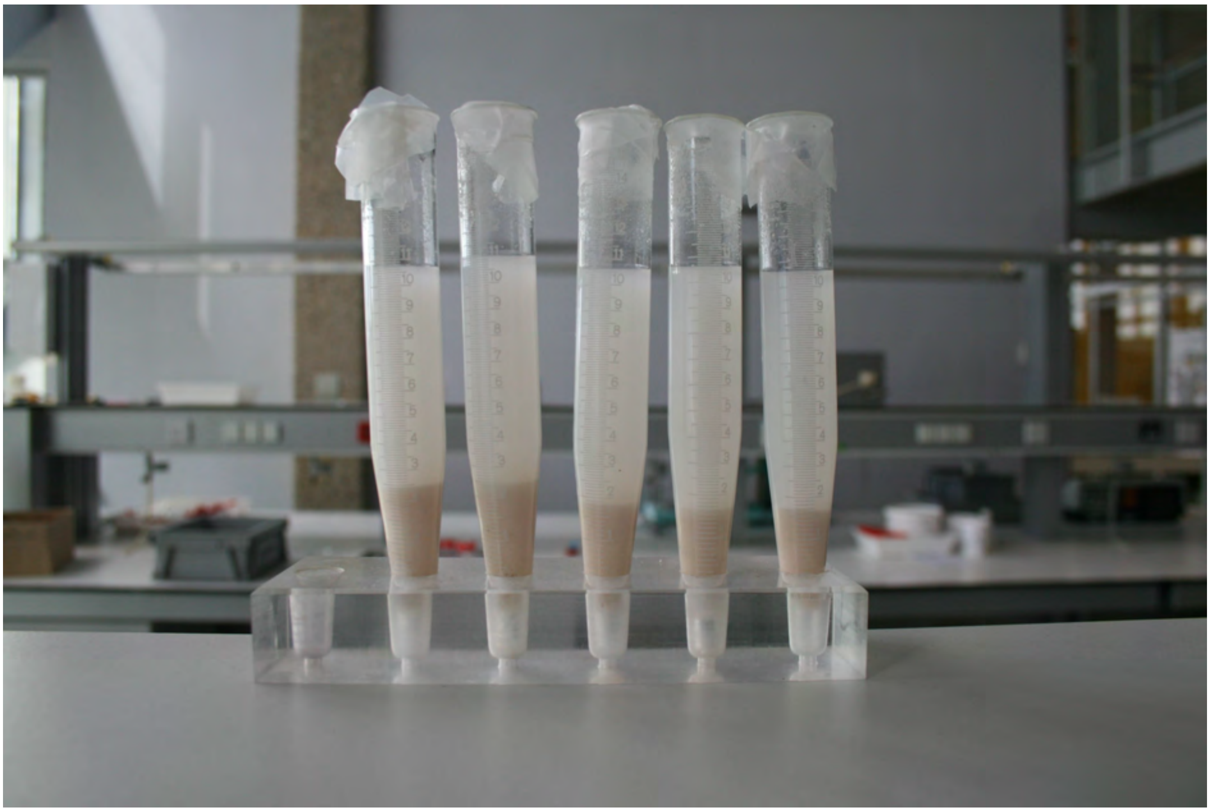


Figure C.6: Laboratory set-up swelling index.

Table C.10: Swelling Index of the bentonite samples.

Sample	Weight of bentonite	Flow or No Flow	Swelling Index
M1	0.2	No Flow	
	0.25	No Flow	
	0.25	No Flow	
	0.30	Flow	33.3
	0.35	Flow	
	0.40	Flow	
	0.50	Flow	
	0.60	Flow	
	0.70	Flow	
	0.80	Flow	
	0.90	Flow	
	1.00	Flow	
M2	0.2	No Flow	
	0.25	No Flow	
	0.25	No Flow	
	0.30	No Flow	
	0.35	No Flow	
	0.40	No Flow	
	0.50	Flow	20.0
	0.60	Flow	
	0.70	Flow	
	0.80	Flow	
	0.90	Flow	
	1.00	Flow	
M3	0.2	Flow	50.0
	0.25	Flow	
	0.25	Flow	
	0.30	Flow	
	0.35	Flow	
	0.40	Flow	
	0.50	Flow	
	0.60	Flow	
	0.70	Flow	
	0.80	Flow	
	0.90	Flow	
	1.00	Flow	
M4	0.2	Flow	50.0
	0.25	Flow	
	0.25	Flow	
	0.30	Flow	
	0.35	Flow	
	0.40	Flow	
	0.50	Flow	
	0.60	Flow	
	0.70	Flow	
	0.80	Flow	
	0.90	Flow	
	1.00	Flow	

C.7 XRF Results

For XRF analysis the measurements were performed with a Panalytical Axios Max WD-XRF spectrometer and data evaluation was done with SuperQ5.0i/Omnian software. R.W.A. Hendrix at the Department of Materials Science and Engineering of the Delft University of Technology is acknowledged for the X-ray analysis.

C.7.1 XRF Analysis M1

PANalytical
Quantification of sample Ooms, 1. M1, 04jun14, perstablet, in Helium
Sum before normalization: 74.1 %
Normalised to: 100.0 %
Sample type: Loose powder
Compton validation factor: 1.00
Oxygen validation factor: 0.00
Correction applied for medium: Yes
Correction applied for film: No
Used Compound list: Oxides
Results database: omnian 4kw 27he

Table C.11: XRF Analysis of M1.

	Compound name	Concentration weight [%]	Absolute error [%]
1	SiO_2	77.251	0.1
2	Al_2O_3	13.022	0.1
3	MgO	2.784	0.05
4	Fe_2O_3	2.432	0.05
5	K_2O	1.998	0.04
6	CaO	1.629	0.04
7	Na_2O	0.501	0.02
8	TiO_2	0.154	0.01
9	MnO	0.065	0.008
10	ZrO_2	0.032	0.005
11	SrO	0.028	0.005
12	P_2O_5	0.025	0.005
13	Cl	0.025	0.005
14	SO_3	0.018	0.004
15	Nb_2O_5	0.010	0.003
16	Rb_2O	0.008	0.003
17	ZnO	0.008	0.003
18	Y_2O_3	0.004	0.002
19	ThO_2	0.004	0.002
20	PbO	0.003	0.002

C.7.2 XRF Analysis M2

PANalytical
Quantification of sample Ooms, 2. M2, 04jun14, perstablet, in Helium
Sum before normalization: 72.9 %
Normalised to: 100.0 %
Sample type: Loose powder
Compton validation factor: 0.95
Oxygen validation factor: 0.00
Correction applied for medium: Yes
Correction applied for film: No
Used Compound list: Oxides
Results database: omnian 4kw 27he

Table C.12: XRF Analysis of M2.

	Compound name	Concentration weight [%]	Absolute error [%]
1	SiO_2	76.492	0.1
2	Al_2O_3	12.641	0.1
3	CaO	5.031	0.07
4	MgO	1.977	0.04
5	Fe_2O_3	1.894	0.04
6	K_2O	1.382	0.04
7	TiO_2	0.169	0.01
8	MnO	0.155	0.01
9	Na_2O	0.130	0.01
10	ZrO_2	0.026	0.005
11	SrO	0.021	0.004
12	P_2O_5	0.021	0.004
13	Cl	0.017	0.004
14	SO_3	0.015	0.004
15	Rb_2O	0.007	0.003
16	Nb_2O_5	0.007	0.003
17	ThO_2	0.006	0.002
18	Y_2O_3	0.005	0.002
19	ZnO	0.004	0.002

C.7.3 XRF Analysis M3

PANalytical
Quantification of sample Ooms, 3. M3, 04jun14, perstablet, in Helium
Sum before normalization: 76.3 %
Normalised to: 100.0 %
Sample type: Loose powder
Compton validation factor: 0.91
Oxygen validation factor: 0.00
Correction applied for medium: Yes
Correction applied for film: No
Used Compound list: Oxides
Results database: omnian 4kw 27he

Table C.13: XRF Analysis of M3.

	Compound name	Concentration weight [%]	Absolute error [%]
1	SiO_2	73.212	0.1
2	Al_2O_3	16.389	0.1
3	MgO	4.069	0.06
4	CaO	3.394	0.05
5	Fe_2O_3	1.960	0.04
6	K_2O	0.473	0.02
7	TiO_2	0.144	0.01
8	Na_2O	0.131	0.01
9	MnO	0.056	0.007
10	SrO	0.052	0.007
11	ZrO_2	0.037	0.006
12	P_2O_5	0.024	0.005
13	Cl	0.012	0.003
14	SO_3	0.011	0.003
15	Nb_2O_5	0.011	0.003
16	ZnO	0.007	0.003
17	ThO_2	0.007	0.002
18	Y_2O_3	0.005	0.002
19	PbO	0.004	0.002
20	Rb_2O	0.002	0.001

C.7.4 XRF Analysis M4

PANalytical
Quantification of sample Ooms, 4. M4, 04jun14, perstablet, in Helium
Sum before normalization: 68.3 %
Normalised to: 100.0 %
Sample type: Loose powder
Compton validation factor: 0.84
Oxygen validation factor: 0.00
Correction applied for medium: Yes
Correction applied for film: No
Used Compound list: Oxides
Results database: omnian 4kw 27he

Table C.14: XRF Analysis of M4.

	Compound name	Concentration weight [%]	Absolute error [%]
1	SiO_2	74.195	0.1
2	Al_2O_3	15.270	0.1
3	CaO	3.569	0.06
4	MgO	3.431	0.05
5	Fe_2O_3	2.427	0.05
6	K_2O	0.563	0.02
7	TiO_2	0.182	0.01
8	SrO	0.077	0.008
9	Na_2O	0.074	0.008
10	ZrO_2	0.039	0.006
11	CeO_2	0.036	0.006
12	P_2O_5	0.034	0.006
13	MnO	0.012	0.005
14	Nb_2O_5	0.014	0.004
15	Cl	0.013	0.003
16	SO_3	0.011	0.003
17	Y_2O_3	0.010	0.003
18	ThO_2	0.005	0.003
19	ZnO	0.006	0.002
20	PbO	0.004	0.002
21	Rb_2O	0.003	0.002