BEHAVIOUR OF BENTONITE SUSPENSIONS IN NON-AQUEOUS MEDIA

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ABSTRACT

BEHAVIOUR OF BENTONITE SUSPENSIONS IN NON-AQUEOUS MEDIA

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Bentonite is a smectite type clay mineral and swells in water. In this thesis, the effect of acetone, methyl-ethyl ketone, n-hexane on the properties of bentonite was determined by thermal analysis and water absorption tests. The tests indicated no significant change with treating bentonite with organic liquids.

Because of the swelling property, only small amount of bentonite can be suspended in water. This may limit certain applications of bentonite. In this thesis, feasibility of suspending large quantities of bentonite in a non-aqueous media was studied. The concentrations for a pumpable high solid bentonite slurry were determined. As aqueous slurry showed pumpable properties up to 30-35 pounds/barrel, this concentration was as high as 125-150 pounds/barrel for acetone, 175-200 pounds/barrel for methyl-ethyl ketone and 325-350 pounds/barrel for n-hexane.

Bentonite deposite has a complicated composition, containing free silica minerals, such as quartz, cristobalite, and opal; silicate minerals, such as feldspar, mica, and zeolite; carbonates or sulfates of alkaline earth metals, such as calcite, dolomite, and gypsum; and, in addition, iron compounds and humus. As mined it is primarily broken and dried and then pulverized by means of an attrition grinding machine. In this study dispersion of raw bentonite by high shear blending and shaking forces in the presence of acetone, methyl-ethyl ketone and n-hexane and eliminating the non-clay impurities by screening were studied.

Many attempts have been made to provide a bentonite composition retaining the full swelling properties of the bentonite by the addition of non-aqueous liquids for obtaining a flexible waterproofing sheet. In this research the possible method for deposition of bentonite in a sponge by saturating the sponge with bentonite using organic liquids was investigated.

Keywords: Bentonite, clay, non-aqueous, suspension, montmorillonite, swelling

ÖZ

BENTONİT SÜSPANSİYONLARININ SU DIŞI SIVILARDA DAVRANIŞI

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Bentonit suda şişme özelliğine sahip, semektit türü bir kil mineralidir. Bu tezde aseton, metil-etil keton ve n-hekzanin bentonite üzerindeki etkileri termal analiz ve su emme deneyleriyle belirlenmiştir. Deney sonuçlari, bentonitin özelliklerinin organik sıvılarla değişmediğini göstermiştir.

Şişme özelliğinden dolayı, sulu süspansiyonlarda çok az miktarlarda bentonit kullanılmaktadır. Bu da, bentonitin kullanım alanlarını sınırlamaktadır. Bu tezde bol miktarda bentonite içeren süspansiyonların su dışı ortamlarda eldesi incelenmiştir. Pompalanabilir bentonit süspansiyonlarının konsantrasyonları belirlenmiştir. Bu konsantrasyon sulu süspansiyonda 30-35 pound/varil'ken, aseton süspansiyonu için 125-150 pound/varil, metil-etil keton için 150-175 pound/varil n-hekzan süspansiyonu için 325-350 pound/varil olarak bulunmuştur.

Bentonite maden yatağı serbest kuvartz, kristobalit, opal gibi silisli mineralleri, feldispat, mika, zeolit gibi silikatlı mineralleri, kalsit dolomite, jips gibi alkali toprak metallerini karbonat ve sülfatlarından ve ek olarak demir bileşimleri ve humusu kapsayan karmaşık bir yapıya sahiptir. Cevher çıkardıldıktan sonar ilk once kırılır ve kurutulur ve daha sonra öğütme aletleriyle öğütülür. Bu çalışmada ham bentonitin yüksek makaslamayla karıştırılması ve salllama kuvvetleriyle ayrıştırılması ve eleme suretiyle kil dışı safsızlıkların giderilmesi çalışılmıştır.

Bentonite su dışı sıvıların eklenmesiyle, bentonitin şişme özelleklerini koruyarak, esnek su geçirmez tabaka elde etmek için bir çok çalışma yapılmıştır. Bu çalışmada bentonitin organik sıvı yardımıyla sünger içine depolanmasıyla böyle bir yapı eldesi incelenmiştir.

Anahtar Kelimeler: Bentonit, kil, süspansiyon, montmorillonit, şişme

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CHAPTER 1

INTRODUCTION

Bentonite is an important commercial mineral mainly composed of smectite group of clay minerals. It has wide application areas such as drilling mud, or drilling gel, the metal casting industry, foundry molding sand, cat litter, feed pelletizing industry, sealing freshwater ponds, irrigation ditches, reservoirs, sewage and industrial water lagoons, grouting permeable ground in detergents, fungicides, sprays, cleansers, polishes, ceramic, paper, cosmetics and medicines, and applications where its unique bonding, suspending or gellant properties are required.

Bentonite is highly colloidal and readily swells in water to form viscous, thixotropic gels which render these clays useful as viscosity builders in the foregoing and in many additional industries and applications. As with most minerals, however, these powders are difficult and expensive to handle. They also are subject to considerable "dusting", i.e. evolution of dust during handling, so that they can, in some cases, cause environmental problems, and even health risks. To minimize these problems, many minerals are sold by the manufacturer as high solids aqueous slurries. Such high solids slurries can be easily stored, shipped, transferred, e.g. pumped and metered, with significantly less capital expenditures and many fewer problems than are associated with powdered minerals, as mentioned above. In most applications, nevertheless, it is not economical to ship smectite clay slurries because of the large quantity of water present in shippable slurries. It has not heretofore been practical to produce and ship high solids slurries by the usual methods since smectites are indeed good viscosifiers. In general, only about 8% -10% solids slurries of good quality swelling smectite can be produced in water. Indeed, at solids contents greater than about 8%, the viscosities of the slurries can become so high that they cannot readily be pumped by conventional equipment and gelling upon standing becomes a problem. At higher solids it becomes virtually impossible to form a uniform paste without special equipment. Thus, there is a need for slurries containing substantially greater than 8% by weight of smectite clay, which have viscosities low enough to allow pumping. In addition, the more such clay which can be incorporated into the slurry the more economical it is to ship the clay since the total weight of the slurry will include less fluid weight [1].

Bentonite deposit has a complicated composition mainly formed of smectites and containing free silica minerals, such as quartz, alpha-cristobalite, and opal; silicate minerals, such as feldspar, mica, and zeolite; carbonates or sulfates of alkaline earth metals, such as calcite, dolomite, and gypsum; and, in addition, iron compounds and humus. Since bentonite ore mined from bentonite deposit usually has a water content of 15 to 35%, it is primarily broken and dried in the sun or hot air to obtain bentonite ore having a water content of 5 to 10%. The dried bentonite ore is pulverized by means of an attrition grinding machine, such as a centrifugal roller mill, or an impact mill, such as a hammer mill. As stated above, bentonite for these uses basically has a composition based on the natural bentonite deposit, containing much non-clay substances. Purified bentonite powder, which is obtained by dispersing bentonite in water, removing unfavorable non-clay substances by spontaneous sedimentation or centrifugal separation, subjecting a suspension of the bentonite to shearing, attrition and impact forces in a homogenizer of the type and drying the resulting purified bentonite sol by evaporation, is used as a rheological adjuster for aqueous coatings, aqueous emulsions, or the like aqueous colloidal dispersion products. [2].

Many attempts have been made to provide a bentonite composition having sufficient cohesiveness and structural integrity to provide a modeling clay-like or putty-like consistency. Such bentonite compositions can be in a paste or putty-like form for handleability so that a desired quantity can be applied in a selected location for water seepage control. [3]. Such waterproofing material finds wide applicability in construction industry, the waterproofing surfaces such as soil, plaza decks, subterranean foundation surfaces and the like in the formation of waterproofed construction areas; soil structure, such as lagoons; and hazardous or toxic waste containment areas the penetration of water and hazardous or toxic materials into the earth, and to provide lagoons, ponds and other water containment areas [4].

Organic solvent-bentonite mixtures can be important for three standpoints: production of a pumpable high concentration bentonite slurry, beneficiation (purification) of bentonite of lesser quality, deposition of bentonite in a porous structure.

This research undertaken during the course of this thesis aimed at determining the conditions under which the aforementioned objectives could be achieved using three organic solvents; acetone, methyl-ethyl-ketone and n-hexane. Thermal analysis studied for investigating thermal properties of the bentonite samples treated with acetone, methyl-ethyl ketone, n-hexane and to determine the differences of the thermal properties of the samples. The water adsorption characteristics of bentonite samples treated with organic liquids and untreated bentonite sample were determined to investigate the effect of organic liquids on the water absorption of bentonite. Three non-aqueous organic liquids were tested as high-bentonite slurry for low viscosity and effective usage for applications and compared with aqueous slurry. In the beneficiation of clay a new method can be proposed by treating the raw bentonite clay in a organic liquid slurry without grinding, just exposing the high-solid organic-bentonite slurry to shaking or high shear blending and purifying the bentonite ore by eliminating the non-clay impurities. The organic liquid might be recovered in a closed circuit process. The deposition of bentonite in industrial sponge can be easily done with the aid of a high solid content organic liquid bentonite slurry. The final product can find many industrial applications as waterproofing bentonite sheets for industrial applications.

CHAPTER 2

LITERATURE SURVEY

2.1 Chemistry and Mineralogy of Clays

2.1.1 The Structures of Clays

Mineralogists use the term "clay minerals" for a group of hydrous layered magnesium- or alumino-silicates (phyllosilicates). In many of these minerals various metallic cations, such as lithium, magnesium, and aluminum, act as proxy wholly or in part for the magnesium, aluminum, or silicon, respectively, with alkali metal and alkaline earth metal cations present as exchangeable cations. Iron (di- or trivalent) is also a common substituent of aluminum and magnesium. Each magnesium- or alumino-phyllosilicate is essentially composed of two types of sheets, octahedral and tetrahedral, designated O and T, respectively. Each sheet is composed of planes of atoms, arranged one above the other, a plane of hydroxyls and/or oxygens above a plane of aluminums and/or magnesiums or silicons, the latter above another plane of hydroxyls and/or oxygens, and so on. Variations among clay minerals and the differences in their physical and chemical properties arise from the various combinations of octahedral and tetrahedral sheets and the electrostatic effects that chemical substitutions have on the units [5].

A continuous linkage of SiO_4 tetrahedra as illustrated in Figure 1 through sharing of three O atoms with three adjacent tetrahedra produces a sheet with a planar network. In such a sheet the tetrahedral silica groups are arranged in the form of a hexagonal network, which is repeated indefinitely to form a phyllosilicate with the composition $[Si_4O_{10}]^{4-}$. A side view of the tetrahedral sheet shows that it is composed of three parallel atomic planes, which are composed of oxygens, silicons, and oxygens, respectively. The tetrahedra are arranged so that all of their apices point in the same direction with their bases in the same plane. The oxygens form an open hexagonal network in this plane, often referred to as the hexagonal or perforated oxygen plane (or O-plane). In reality the silica tetrahedra are slightly distorted, and consequently, the cavities bordered by six oxygens are ditrigonal rather than hexagonal. This perforated oxygen plane is an important contributor to the surface properties of the clay minerals. Each oxygen atom is covalently bound to two silicons, thus becoming the active component of an Si-O-Si (siloxane) group [5].

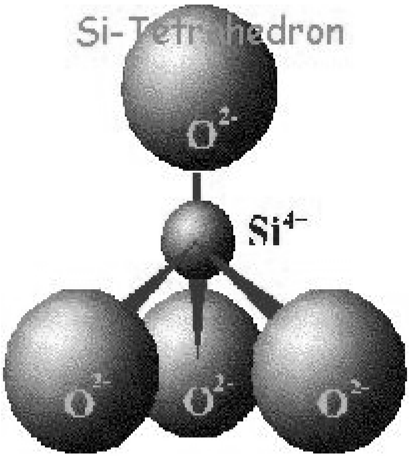


Figure. 1 A structural scheme of Si-Tetrahedron [6].

An Octahedral sheet is obtained through condensation of single $Mg(OH)_6^{-4}$ or $Al(0H)_6^{-3}$ as can be seen in Figure 2. Each O atom is shared by three octahedra, but two octahedra can share only two neighboring O atoms. In this sheet the octahedral groups are arranged to form a hexagonal network, which is repeated indefinitely to form an $[Mg_60_{12}]^{12-}$ or $[Al_4O_{12}]^{12-}$ layer. The minerals brucite, $Mg(OH)_2$, and gibbsite, $AI(OH)_3$, have such sheet structures. A side view of the octahedral sheet shows that it is closely packed, being composed of a dense hexagonal plane of Mg of Al atoms sandwiched between two dense hexagonal "hydroxyl planes." All the octahedra are filled with Mg atoms in brucite or its clay derivatives, but only two thirds of the octahedra are filled with Al atoms in gibbsite and its derivatives [5].

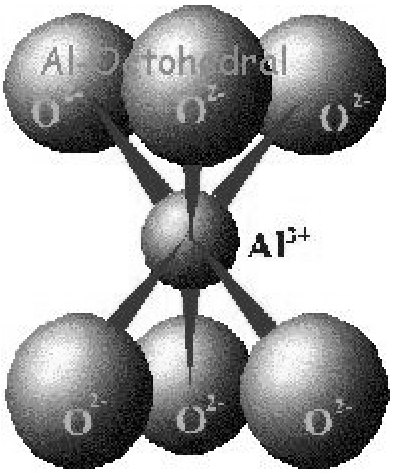


Figure. 2 A structural scheme of Al-Octohedral [6].

2.1.2 The Structures of Smectites

Bentonite is defined as a clay composed dominantly of a smectite clay mineral and whose properties are a consequence of this mineral component regardless of its mode of origin. Some bentonites are hydrothermal alteration products of igneous rocks, rather than altered ash. Commercial production of bentonite began in the United States in the 1920s. The unique physical properties of this clay and its widespread use were powerful incentives for much clay mineral research. Bentonites were not recognized and developed in Europe until the 1930s, some years after the development of the Wyoming deposits. The widespread commercial use of bentonite has caused a world-wide search for this clay, and today, it is extensively mined in many countries, including the United Kingdom, Germany, Italy, Greece, India, Japan, and Russia [7].

Minerals of the smectite consist of TOT layers. They differ from talc and pyrophyllite in that a small fraction of the tetrahedral Si atoms is isomorphically substituted by Al and/or a fraction of the octahedral atoms (Al or Mg) is substituted by atoms of lower oxidation number. The resulting charge deficiency is balanced by hydrated cations, mainly K, Na, Ca, and Mg, of which more than 80% is located between the parallel clay layers as shown in Figure 3. These ions are hydrated due to the fact that, in nature, smectites are formed in aqueous environments. Because they are hydrated, these cations are only loosely held by the negatively charged clay layers. In very dilute aqueous suspensions, Li- and Na-smectites dissociate into large negatively charged silicate layers and small cationic species and exhibit many properties of a polyelectrolyte. Smectites saturated with other cations dissociate in aqueous suspensions into exchangeable cations and tactoids, which are composed of several parallel TOT layers, held together by electrostatic forces by some of the exchangeable cations that remain in the interlayer space [5]. Tactoids are spindle shaped regions in a sol in which the particle concentration is higher than the bulk of the sol. Occasionally, they separate as a bottom sediment. They are spontaneously formed in some sols of plate- or rod like particles. In tactoids, the particles are oriented parallel to each other at distances of the order of 100 A. Tactoid formation is a special case of coacervation, that is, the separation of a sol in two liquid phases of different concentration [8]. Because they dissociate, the original cations are exchangeable by other inorganic and organic cations. The negative charge per unit cell from isomorphic substitution ranges between 0.5 and 1.3 electronic charges. In smectite tactoids electrostatic forces keep the layers together. Parallel TOT layers are packed one above the other and the exchangeable hydrated cations are located between the layers [5].

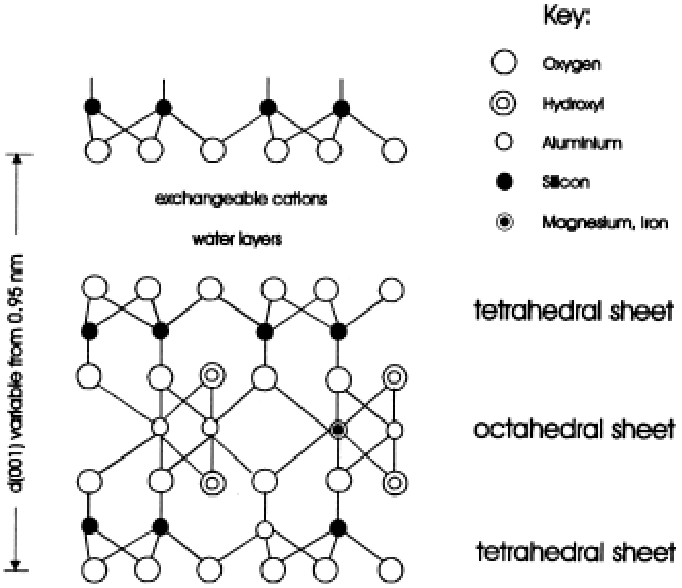


Figure. 3. The layer structure of montmorillonite according to Hofmann, Endell, Wilm, Marshall, Maegdefrau and Hendricks [9].

Water and polar organic molecules are attracted by the exchangeable cations and may intercalate between the layers, causing the structure to expand in the direction perpendicular to the layers. The interlayer space between the TOT layers, obtained as a result of the expansion of the clay, has special chemical properties. The swelling of this space depends on several factors, such as the exchangeable cation, the humidity of the environment and the vapor pressure, and the temperature. The basal spacing may vary from 1000 pm (for dry smectites) to more than 2000 pm. In dilute aqueous suspensions of Li- and Na-smectites, separations between layers larger than 4,000 pm have been identified [5].

2.2 Electrochemical Properties of Clays

2.2.1 Electrical Double Layer

Clay particles in suspension owe their stability to mutual repulsion when their intersecting diffuse electrical double layers interact on approach. In clay-water systems, a double layer is made up of the negative surface charge and the balancing cation charge as seen in Figure 4. In the case of clay particles, the negative charge is a consequence of imperfections within the interior of the crystal lattice. Clay colloids possess a constant charge, because its surface charge arises from isomorphous substitution [10].

The counter-ions are electrostatically attracted by the oppositely charged surface as illustrated in Figure 4a. These ions have a tendency to diffuse away from the surface to the bulk solution where the concentration is lower. Therefore, the concentration of the counter-ions near the particle surface is high, and it decreases with increasing distance from the surface. The diffuse layer does not only consist of an excess of ions of opposite sign; there is a deficiency of ions of the same sign near the surface, since the ions are electrostatically repelled by the surface. This diffuse character of the counter-ion atmosphere was recognized by Gouy [11] [12] and Chapman [13], who presented a theoretical treatment of the counter-ion distribution. Their theory predicts an approximate exponential decay of the electrical potential Ψ of the solution with distance x from the plane surface. This is represented by the following equation:

$$\Psi = (\Psi_0 \exp(-\kappa\ \chi) \qquad (2\text{-}1)$$

where ψ_0 is the surface potential and κ^{-1} the extension or thickness of the double layer. The above expression is valid for a certain distance from the charged surface, where the potential is relatively low and decreases exponentially as can be seen in Figure 4b [10].

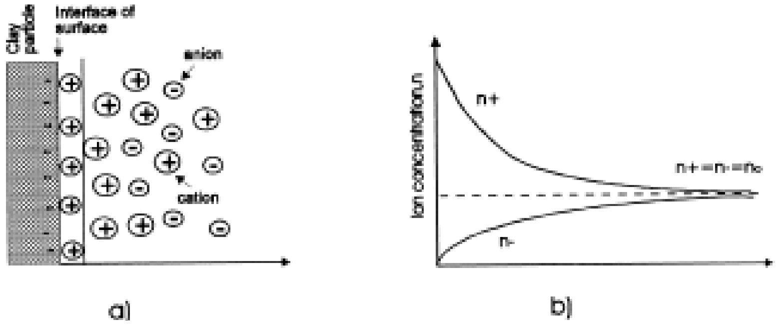


Figure. 4. (a) The structure of a diffuse electrical double layer at the surface of a clay particle or silicate layer; and (b) distribution of the concentration of cations (n+) and anions (n-) with distance from the surface for a symmetrical electrolyte with a bulk concentration of n_o [10].

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_0 \, R \, T}{F^2 \sum_i^n c_i \, z_i^2}} \qquad (2\text{-}2)$$

where: F is the Faraday constant, c_i the electrolyte concentration, z_i the valence of the ion, ε_0 the dielectric constant of the medium, R the gas constant (1 atm/mol K) and T the absolute temperature (K) [10].

The Gouy-Chapman theory leads to unrealistically large ion concentrations at high potentials, since it assumes that the counterions are point charges. To correct this, Stern [14] postulated the existence of an adsorbed layer of finite sized counterions adjacent to the surface. The potential in the Stern layer falls off linearly from its surface value (ψ_0) to the Stern potential (ψ_δ) after which it decays exponentially. The thickness of the Stern layer has been estimated for different clay systems [15]. The outer Helmholtz plane lies outside the Stern layer and marks the boundary between the fixed and mobile part of the diffuse double layer, and is called the plane of shear [16]. At this plane the potential is called the zeta potential (ζ) and in practice it is assumed that it is equal to the Stern potential (ψ_δ) [10].

The edge of the clay particle is assumed to possess an electrical double layer of a different nature to that of the flat surface described above. This double layer is due to the adsorption of potential determining ions on the broken bonds of the tetrahedral silica sheets and octahedral alumina sheets. There is a strong possibility that in a neutral clay suspension a positive double layer is created on the edge surfaces owing to the exposed alumina sheet, whereby it may become more positive with decreasing pH and its sign may be reversed with increasing pH. Various studies indicate that the edges of clay particles are positively charged at pH 7-8 and some data suggest that the edges are neutralized at pH 6. The existence of positive sites on the edges have been demonstrated by the addition of a negative gold sols to the clay-type kaolinite, where the resulting electronmicrograph showed the gold particles adsorbing only at the crystal edges [10].

A theoretical analysis of the interaction between colloidal particles has been developed by Derjaguin and Landau [17] and Verwey and Overbeek [18]. The fundamental feature of what is known as the DLVO Theory is that this interaction is determined by a combination of the interparticle double layer repulsion energy (V_R) and the Van der Waals attractive energy (V_A). Colloidal stability may be explained by means of the superposition of both energies [10].

2.2.1.1 Interparticle Double Layer Repulsion.

As two particles approach each other in suspension due to Brownian motion, their diffuse double layers begin to interfere. Consequently, there is a change in the distribution of ions surrounding both particles leading to an increase of the free energy of the system. The amount of work required to carry out those changes and to bring the particles from infinite separation to a given distance is the repulsive energy or repulsive potential [10].

The repulsive potential decreases exponentially with increasing particle separation and the range of repulsion is considerably reduced with electrolyte concentration. The DLVO theory assumes that the dispersed particles are not hydrated and hence do not have an additional repulsive force when two particles approach one another in aqueous solution. It appears likely that for Na-montmorillonite, the total interaction between the charged platelet surfaces should involve both short range repulsion forces, due to partially bound hydrated cations and a longer range repulsion due to hydrated counterions in the double layer [10].

2.2.1.2 Van der Waals Attractive Forces.

There are three types of intermolecular attraction that are recognised: dipole-dipole interaction; induced dipole-dipole interaction and attractive forces between non-polar molecules (London dispersion forces). The London dispersion forces, which are due to the polarization of one molecule by fluctuations in the charge distribution in the second molecule, account for nearly all of the Van der Waals attraction in colloidal systems [10].

2.2.1.3. Total Interaction Energy.

The net or total interaction energy V_t is the sum, of the repulsive potential V_R and attractive potential V_a [10].

$$V_t = V_r + V_a \tag{2-3}$$

A representation of V_r, V_a and V_t as a function of the interplate separation for low electrolyte concentrations (10^{-2} M).and high surface potentials (>50 mV) is shown in Figure 5. Of significant importance is the occurrence of a maximum energy (V_m) at intermediate distances, which is considered as an energy barrier that the particles must overcome if they are to 'fall' into the deep primary minimum at close distances and thus come together. The height of V_m therefore determines the relative stability of the system, and a value of 15-25 kT is normally required for long-term stability. The term ΔV_b represents the barrier to redispersion. At large interparticle separations, a secondary minimum may occur since V_r falls off more rapidly with increasing distances than V_a. Particle coagulation taking place here is fairly reversible, since the minimum is quite shallow [10].

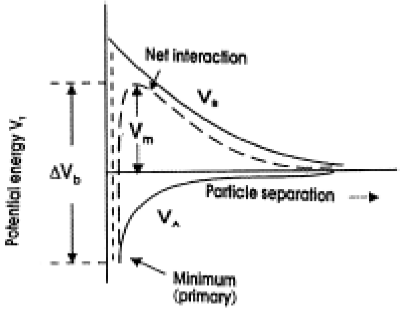


Figure. 5 Total interaction energy V_t for parallel flat plates as a function of particle plate separation [10].

The Na ions of the montmorillonite particles form diffuse ionic layers surrounding them and create an electrostatic repulsion between the particles. The addition of electrolytes in the system or an increase in temperature will reduce Vm and so the clay particles will come into contact with one another and agglomerate. The aggregation of particles is known as coagulation or flocculation. The extent to which the particles become flocculated depends upon the degree of compression of the double layer, which is dominated by the concentration and valence of the ions of opposite sign to the particle charge. Low electrolyte concentration produces slow coagulation, which is retarded by a long-range repulsion. At high electrolyte concentration attraction predominates at any particle distance except at very close approach. In this case, particle agglomeration occurs at a maximum rate and the process is called rapid coagulation [10]. A more detailed description of the different modes of particles association is discussed in section 2.2.2.

2.2.2 Particle Association in Clay Suspensions

If the concentration of clay is high enough, flocculation will cause the formation of a continuous gel structure instead of individual flocs. The gel structures build up slowly with time, as the particles orient themselves towards positions of minimum free energy under the influence of Brownian motion. The concentration of clay present in the system and the salt content are decisive factors in the length of time required for a gel to attain maximum strength. For Na-montmorillonite, this concentration is usually above 3% (w/w) [10].

When a suspension of plate-like clay particles flocculates, three different modes of particle association may occur: face-to-face (FF), edge-to-face (EF) and edge- to-edge (EE). The electrical interaction energy for the three types of association is governed by three different combinations of the two double layers. Also, the rate of diffusion of the particles as they approach each other in these three ways is not the same, and they may not occur simultaneously or to the same extent when the clay suspension is flocculated. The various modes of particle association are illustrated in Figure 6. FF association leads to thicker and larger flakes, and EF and EE association lead to three-dimensional voluminous ‘house-of-cards’ structures [10].

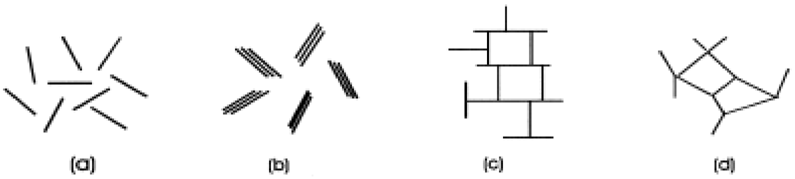


Figure.6. Modes of particle association in clay suspensions: a) dispersed; b) face-to-face (FF); c) edge-to-face (EF); and d) edge-to-edge (EE) [19].

Aggregation is best described by FF association, and refers to the collapse of the diffuse double layers and the formation of aggregates of parallel platelets spaced 20 A° or less apart. It decreases the gel strength because it reduces the number of units available to build gel structures and the surface available for particle interaction. The reverse for aggregation is known as dispersion [10].

Flocculation of clay suspensions has been referred to as a consequence of EF and EE association, responsible for the continuous gel-like structure in the montmorillonite clay suspensions. However, other theories describing the modes of interaction between montmorillonite particles have been proposed. Including the above mentioned, they are:

- Mutual repulsion of the particles as a result of the interactions between their double layers.

- Edge-to-edge association to form cross-linked ribbons, due to the high repulsive potential between basal surfaces as shown in Figure 7a.

- Parallel association of plates, held together by crystalline water between them.

Norrish [20] opposed Van Olphen's theory of the house of cards structure, suggesting that the gel structure in montmorillonite suspensions was a consequence of the repulsive force caused between the interacting double layers. Callaghan and Ottewill [21] actually demonstrated that the gel properties of these dispersions are the consequence of long-range interactions between the faces of the particles. This theory is substantiated by the fact that the area of the edge is small; therefore the electrostatic attraction between the edge and face is small compared to the repulsion between the two faces when two particles approach each other. These authors supported more the existence of a band-like structure or the 'Bander-model' which was first proposed by Weiss and Frank as shown in Figure 7b [10].

Figure 7. Alternative models describing the association of clay particles a) edge-to-edge (EE) ribbons; and b) 'Bandermodel' [22].

2.3 Adsorption Characteristics of Clays

The interlayer space of an expanding TOT clay mineral lies between two parallel silicate layers, bordered by two O planes, the oxygens belonging to siloxane groups. The wettability and resulting structure of the interlayer water are the outcome of (1) thermal motion of water molecules in the environment of the mineral, (2) electrostatic attraction forces between water molecules and the exchangeable cationic species, and (3) attraction and dispersion forces between TOT layers [5].

Swelling is the process by which the clay mineral expands beyond its original limit, which is 0.950 nm, as a result of adsorption of water into the interlayer space. The uptake of water molecules is dependent on the humidity and water vapor pressure in the environment of the mineral. Since it causes a gradual expansion of the clay crystal along the c axis as shown in Figure 8, it can be followed by x-ray diffraction. This expansion can be monitored by the use of an adsorption isotherm. In most published works swelling has been determined in air or in atmospheres with various controlled humidities, but it has also been determined for aqueous suspensions or under conditions where the vapor was obtained from boiling water [5].

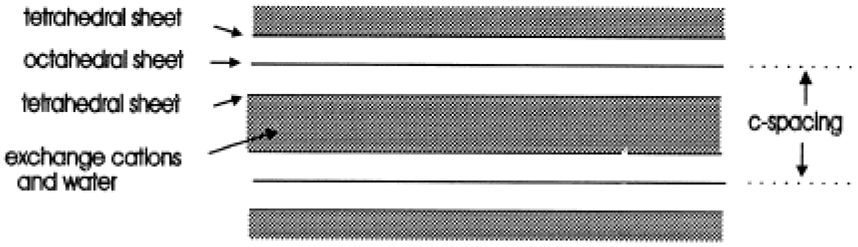


Figure. 9. Representation of a three-layer expanding clay lattice. [10].

A dry montmorillonite powder swells spontaneously when contacted with water. The dry clay usually imbibes water and becomes a gel, and it can be stirred up with more water to yield a suspension or sol. The swelling of a clay is particularly spectacular in the case of montmorillonites. The montmorillonite clay first takes up one to four monolayers of water between the layers. This interlayer or intracrystalline swelling causes, at most, a doubling of the volume of the dry clay. However, the swelling process continues, and an amount of water is imbibed which is many times the volume of the original clay. The additional swelling is a result of the double layer repulsion between the surfaces of the individual particles, which pushes them apart. Formalistically speaking, the swelling may be called osmotic swelling since the water tends to equalize the high concentration of ions between two particles, which are so close together that their double layers overlap, and the low concentration of ions far away from the particle surfaces in the bulk solution. Under suitable confining conditions, a fluid pressure is created which is called the osmotic or the swelling pressure of the clay. This pressure is a direct measure of the balance of the forces between the particle faces [10].

Sometimes, the question is debated whether spontaneous swelling of the clay finally leads to complete disintegration of the gel to a sol, or whether the swelling is limited and stops as soon as a certain gel volume is established. The reason that there is doubt about this question is because it is difficult to perform an unambiguous experiment in which all external forces are excluded, such as hydrodynamic convection forces which tend to disperse the particles, or gravity forces which usually operate against the further dispersion of the gel [10].

In principle, sol formation will be spontaneous only if at any particle distance at any configuration of the particles in space, repulsion predominates. In that case, the sol formation properly may be called spontaneous. However, it seems that most clays-even certain sodium montmorillonites are not spontaneously dispersed. Usually, at certain particle separations and at certain particle configurations, attractive forces cancel the repulsion, for example, van der Waals forces and the important edge-to-face cross-linking forces. Entropy effects are probably relatively small in these systems [10].

More recently, X-ray diffraction studies on Na-montmorillonite suspensions were carried out to determine the alignment of the clay particles upon swelling. For high Na-montmorillonite concentrations a straight column model was used to describe the swelling behaviour observed in Norrish's work as can be seen in Figure 9a, but it failed to describe the swelling at higher water content .A zig-zag column model was found to agree with the swelling observed at both low and high water content, where the layers swell not only longitudinally but also laterally, assuming that the layer size is 1 μm as shown in Figure 9b [10].

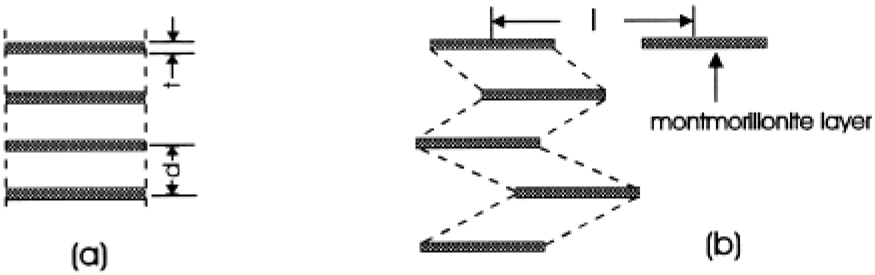


Figure. 9. Schematic diagram of straight column model a) and zigzag column model b), for the arrangement of layers in montmorillonite aqueous suspensions [23].

Since uncharged polar organic molecules are adsorbed essentially by replacement of the interlayer water, the behaviour of such molecules is likewise strongly influenced by the exchangeable cation. Evidence is accumulating to show that, at least at lower water contents, cation-dipole interactions are of paramount importance in their effect on the adsorption of polar organic species by clay minerals. [5].

2.3.1 The Mechanism of Adsorption of Organic Compounds Inside the Interlayer Space of Swelling Clay Minerals

Many organic compounds with a dipole character are adsorbed on the layer surfaces and probably also on the edge surfaces of a clay, in analogy with the behavior of water. The adsorption energy of many of these compounds is probably of a magnitude comparable with that of water. They can displace adsorbed water from clays, but frequently the organic compounds can be removed from the clay by washing with water [8].

As in the case of the adsorption of water on clays, we do not know exactly to what extent the polar groups of the organic molecules associate with the counter-ions of the clay, and to what extent they are hydrogen bonded with the oxygen surfaces. However, infrared absorption indicates that the latter is less important [8].

Organic clay complexes with polar molecules can be prepared either by contacting the dry clay with polar organic liquids or vapors, or by mixing the polar liquid and a clay-water suspension [8].

When montmorillonite clays are treated with polar organic compounds, such as alcohols, glycols, or amines, the organic molecules penetrate between the layers and displace the interlayer water as illustrated in Figure 10. The basal spacing of the complex depends on the size of the organic molecules and on their orientation and packing geometry [8].

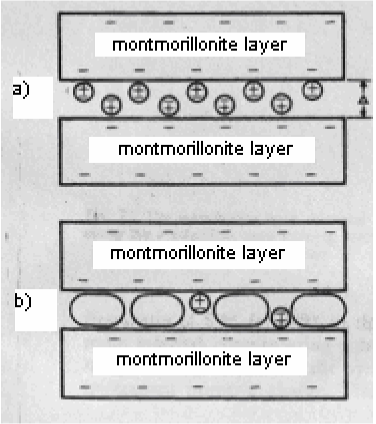


Figure. 10. Relationship between layer charge characteristics of montmorillonite a) polar molecules in montmorillonite b) mainly non-polar groups with some polar groups in montmorillonite [24].

Alternatively, when certain organic compounds are added to an unknown mixture of clays, a basal spacing typical for the complex of that compound will indicate the presence of montmorillonite in the mixture. Ethylene glycol which gives a basal spacing of about 17 A with most montmorillonites, is commonly used for this identification purpose [8].

When the clay surface becomes covered with polar molecules containing a substantial proportion of hydrocarbon groups, the surface becomes oleophilic, and in this condition, clay-oil dispersions can be prepared with the treated clay. However, since the exchange cations are still present in the complexes, they are usually rather sensitive to water. For example, a pyridine complex of bentonite in the presence of water initially hydrates stepwise, as shown by X-ray diffraction at low water concentrations, and disperses completely when a large amount of water is added. Pyridinium ion (or other organic cation) exchange complexes are not affected by water. Exceptions are low molecular weight alkane ammonium complexes of n-butylammonium) which show a spectacular interlayer swelling with water [8].

The addition of a polar organic compound to a clay-water suspension often causes flocculation of the clay. It has been pointed out before that this effect is predicted by the Gouy theory. Sometimes, a peptizing effect is observed, which might be explained by changes occurring in the Stern layer. The effect of polar organic compounds on the stability of clay suspensions is therefore rather unpredictable [8].

The Gouy theory shows that the "thickness" of the double layer decreases when the dielectric constant of the medium is reduced. Such a reduction may be achieved by the addition of water-miscible solvents, such as alcohols or acetone, to the sol. Because of the compression of the double layer, the range of particle repulsion is reduced and the size of the energy barrier becomes smaller when the dielectric constant of the medium decreases. Therefore, the theory explains the well-known fact that most polar solvents enhance the flocculating power of an electrolyte markedly. If a sol in water is till stable at a certain level of contamination by an electrolyte, the addition of an organic solvent may induce flocculation [8].

Exceptions to these rules do occur, and they must be explained by considering secondary effects of the organic solvent on the double-layer structure, as discussed hydration theory of stability [8].

The hydration theory of stability has been popular in colloid chemistry for a long time. In this theory, the repulsion between particles is attributed to the orientation of water dipoles in the electric field around the charged particle. In such a "solvation shell," the degree of orientation of the dipoles would gradually decrease with increasing distance from the charged surface. When these diffuse hydration shells begin to interfere when the particles approach each other, the mutual repulsion of the oppositely oriented water dipoles around the colliding particles would account for particle repulsion [8].

For hydrophilic colloids, the hydration repulsion was considered an additional stability factor over and above the double-layer repulsion. The high resistance of the hydrophilic colloids to added salt was attributed to the presence of the extra stability factor. Also, in certain hydrophobic sols, hydration repulsion was thought to contribute to the stability [8].

The argument against the hydration theory of stability is that the orientation effect of the charged particles on the water dipoles can be expected to be significant only up to a few water-molecule diameters away from the surface. The energies involved are not sufficiently large to affect the balance of the double-layer and van der Waals interaction energies at the large distances from the surface where the fate of the colliding particles is decided. Actually, many facts of colloid chemistry appeared to be incompatible with the hydration theory of stability, which is now obsolete. Nevertheless, hydration repulsion should not be entirely disregarded. As mentioned previously, it is important in the short-range interaction of particles. A thin layer of water a few molecules thick is usually more or less strongly adsorbed at the particles surface; hence in bringing the particles close together, the required work of desorption of the water is manifested as a short-range repulsion [8].

The presence of a thick hydration shell around sol particles has also been assumed to be the cause of gelation in hydrophilic sols and in certain hydrophobic sols, such as alumina, silica, or clay sols. The rigidity of these gels was thought to be the result of a rigidifying effect of the charged particles on the water phase. However, the interparticle distances in gels are often very large and beyond any sensible range of hydration forces emanating from the surfaces. The alternative explanation of gelation on the basis of skeleton formation by particle linking is perfectly sensible and appears to supply a good basis for an understanding of the mechanism of the creation as well as the destruction of gels by the addition of small amounts of chemicals to the liquid phase [8].

It should be mentioned that moderately long-range effects of charged surfaces on certain properties of the water phase, such as the density or the activation energy of viscous flow, are still claimed to exist [8].

The properties of the water in the first few monolayers which are adsorbed at the surface may differ significantly from those of bulk water. It is generally accepted that the dielectric constant of the adsorbed water layers is much lower than that of free water. In the Stern model of the double layer, the lowering of the dielectric constant in this region must be taken into account in computing the capacity of the molecular condenser and the Stern potential [8].

When alcohols or other organic polar solvents are added to the sol, these compounds may be adsorbed on the surface in competition with water. Therefore, they my affect the capacity of the Stern layer and hence the Stern potential. In addition, the point of zero charge may be shifted, and possibly even the van der Waals forces may be affected. Therefore, the change of the composition of the medium may have several effects on the constitution of the double layer and the particle-interaction energy. An analysis of such effects in particular cases has explained why an alcohol does not always have the flocculating effect predicted by the Gouy theory as a consequence of the lowering of the dielectric constant of the bulk liquid [8].

Most of the published data deals with montmorillonite and, to a smaller extent, also with hectorite and other smectites. In the first half of the twentieth century the principal techniques for the study of organo-smectite interactions were chemical analysis, x-ray diffraction, and differential thermal analysis. In 1934 Hoffmann showed that the basal spacing of montmorillonite varied following treatment alcohol, acetone and ether. Jordan measured by x-ray diffraction the basal spacings of treated with n-alkylammonium montmorillonite (Wyoming bentonite) treated with n-alkylammonium cations. He showed that the increase in basal spacing with the length of alkyl chain is a stepwise process. Alkylammonium montmorillonites with 3-10 carbon atoms have a basal spacing of 1.36 nm, whereas those with 12-18 carbon atoms have a basal spacing of 1.76 nm. The stepwise separation of the TOT layers in increments of 0.4 nm, which is about the van der Waals thickness of a methyl group, indicates that the chains lie flat along the O-plane with the planes of the zigzag carbon chains parallel to the plane of the mineral. According to Jordan, when the organic cation occupies no more than half of the available area per exchange position, the organic cations on the top surface of one layer fit into the gaps between those on the bottom surface of the layer above it. The resulting separation of the two TOT layers is the thickness of the hydrocarbon chain, which is 0.4 nm. When the chains occupy more than 50% of the surface area per exchange position, adjacent laminae are unable to approach more closely than 0.8 nm, which is the thickness of two carbon chains [5].

During the last four decades, with the development of spectroscopic techniques, such as IR, NMR, ESR, and Mossbauer, the study of organo-clay interactions was undertaken mainly with the purpose of clarifying the fine structures of the organoclay complexes. The types of bonding occurring between the clay functional groups and the adsorbed organic species were also studied. The principal interactions between the clay and the adsorbed polar organic species are of the acid-base type. The clay external surface and its interlayer space are populated by Bronsted and Lewis acidic and basic sites. Anhydrous metallic exchangeable cations serve as Lewis acid sites, whereas hydrated cations are Bronsted acid sites. Depending on the basic strength of the adsorbed organic species and the polarizing power of cation, the adsorbed compounds may accept protons from water molecules, and thereby gain a positive charge, or they may just form H-bonds with the polar water molecules. Adsorbed water molecules, which are H-bonded to the O-planes by proton donation, may become H-bonded with the organic compounds by proton acceptance. Other basic sites are the oxygen atoms of the O-planes of silicate layers, which may donate electron pairs to acidic sites in the organic species [5].

Organic cationic species are found in the interlayer space smectites as a result of a first-stage cation exchange reaction or due to a second-stage protonation of adsorbed organic bases. The negative smectite layers attract organic cations by electrostatic forces. Cations are adsorbed by the cation exchange mechanism, in which the inorganic cations initially present in the mineral are replaced by the organic cations. Many of the organic salts are water soluble, and, if possible, cation exchange reactions are performed in aqueous solutions. Negatively charged oxygen planes border the interlayer space, and, consequently, negatively charged species should be repelled from the space. Anions are adsorbed from aqueous solutions by smectites only if they can form positively charged coordination species [5].

The adsorption of organic polar molecules can be treated in the light of Bronsted and Lewis theories on acids and bases. This adsorption is accompanied by proton transfer from interlayer water to the organic molecule or vice versa, or by the formation of a coordination bond between the metallic exchangeable cation and the organic species. Exchangeable metallic cations and the hydration state of the clay play major roles in the adsorption of polar organic molecules. The polarizing power of the cation on water molecules in the hydration sphere determines the strength of Bronsted surface acidity of the clay. Adsorbed hydrated cations are better proton donors than hydrated cations in an aqueous solution since the dielectric constant of water in the interlayer space is less than in bulk solution. The bare exchangeable metallic cation determines the nature and the strength of the Lewis surface acidity of the clay. A complex can also be formed between a previously adsorbed organic species and a newly adsorbed species [5].

In the adsorption of polar organic liquids from aqueous solutions, adsorption is usually increased by raising the solute (organic) concentration as or, in the extreme case, by elimination of water from the system. Thus ethylene glycol, glycerol, and pentanediol-1:5, none of which shows preferential uptake over water, form stable, well-ordered interlayer complexes with montmorillonite by evaporating the aqueous clay suspension containing these substances. Such a treatment, which removes the more volatile component (water) leaving the clay and the organic compound behind, may be likened to immersion of the clay in the corresponding organic liquid. If, on the other hand, the organic compound has a low boiling point relative to water, solute and solvent will evaporate together, leaving the pure clay behind. For example, acetylacetone, which gives high adsorption from aqueous solution, fails to form a complex with calcium-montmorillonite when the suspension is allowed to dry in a desiccator [24].

Larger molecules with more than five units-both aliphatic and aromatic may be adsorbed to an appreciable extent by montmorillonite in the presence of excess water. That is, they can displace the water molecules associated with the exchangeable cations. The increase in affinity with molecular size or chain length can be generally applied to the adsorption of organic compounds by clays and is attributed to the increased contribution of van der Waals interactions become important because these forces are essentially additive and tend to orient the molecule so that maximum number of contact point is established. And in addition to chain length the chemical character of the organic molecule influences the adsorption behaviour. If the molecule is sufficiently large to be adsorbed from dilute aqueous solution the adsorption process is determined by its ‘character’; that is, the presence or absence of certain structural groupings [24].

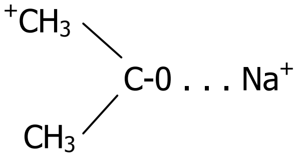
Polar organics occupy similar sites to water at the silicate surface to satisfy the coordination requirement of the interlayer cation. On the other hand, ion-dipole effects are not expected to play an important part in the interactions of clays with non-polar compounds, which are thought to be adsorbed by relatively weak, non-specific London-van der Waals (dispersion) forces alone [24].

In dehydrated systems where the silicate layers of a clay crystal are fully collapsed, intercalation of non-polar organic liquids and gases is either absent or proceeds only with difficulty. This is attributed to the fact that the compounds, being weakly adsorbed, are incapable of forcing the silicate layers apart. Adsorption then takes place predominantly on external crystal surfaces. In partly dehydrated or air-dry systems where the layers are already slightly separated, intercalation may be limited by the inability of non-polar molecules to replace the interlayer water or to establish links to the exchangeable cation through water bridges [24].

2.3.1.1 Complexes with Ketones

Complex formation with polar organic compounds is profoundly affected by the nature of the exchangeable cation and by the water content (hydration status) of the clay. The influence of adsorbed water on acetone uptake by montmorillonite was demonstrated as early as 1943 by Glaeser [25]. She reported, for example, that sodium- and calcium-montmorillonite previously dried by evacuation at 523°K gave one-layer complexes (d(001) - 1-32 nm) when treated with acetone vapour ($P/P°$ = 0.1 to 1-0) alone. On the other hand, exposure of the clay to saturated acetone vapour and water vapour (50 per cent relative humidity) simultaneously, gave rise to two layer complexes (d(001) = 1-75 nm). Interstratifications of three- and four layer acetone-water structures seemed to have occurred when the montmorillonite samples were exposed to the saturated vapour of both acetone and water simultaneously. Apparently, hydration of the clay facilitated acetone uptake, presumably by expanding the mineral interlayers. The data also indicated that water and acetone might interchange giving rise to mixed acetone-water (in reality, acetone-water-cation coordination) complexes. A similar situation had earlier been reported by Mackenziesa [26] for ethylene glycol and by Dowdy and Mortland [27] for ethanol and ethylene glycol. In an attempt to prepare acetone complexes using MacEwan's [28] method, Glaeser found that dehydrated calcium-montmorillonite invariably yielded a two-layer complex whereas the corresponding sodium clay gave either a single- or a double-layer complex. This difference between calcium- and sodium-montmorillonite in their behaviour towards polar organic liquids accords with later findings of German and Harding [29] and Bissada et al. [30] for ethanol- and acetone-montmorillonite systems and is ascribable to the greater solvation energy of the calcium ion compared with that of the sodium ion [24].

Parfitt and Mortland [31] showed that after degassing and prior to treatment with acetone, the basal spacing of the sodium clay stood at 0,97 nm, indicating the presence of only traces of residual water. On exposing this material to acetone vapour followed by degassing, the basal spacing was 1,26 nm, corresponding to the formation of a one-layer complex in which the organic molecules assumed an orientation. These observations suggest that the intercalated acetone is physically adsorbed (1,7I4 cm^{-1}) and also directly linked to the sodium ion by electrostatic interactions probably through the formation of the following resonance structure.



When the acetone-clay complex was exposed to air (40 per cent relative humidity) the 1,714 cm^{-1} band weakened and the water deformation band shifted from 1,632 to 1,650 cm^{-1}. As more water was adsorbed the 1,690 cm^{-1} band shifted to 1,700 cm^{-1}, indicating a weakening of the electrostatic interactions between acetone and sodium. Parfitt and Mortland [31] postulated that the water molecules formed a hydration shell around the sodium ion so that the carbonyl group was now linked through this water to sodium rather than directly to the cation [24].

2.3.1.2 Complexes with Aliphatic and Aromatic Hydrocarbons

X-ray diffraction measurements by Barshad [32] have indicated that liquid benzene and n-hexane enter the interlayer space of some montmorillonite and vermiculite samples when these have previously been dehydrated at 293°K. However, the same specimens, dried at 523°K, failed to intercalate these hydrocarbon liquids. By boiling air-dry samples of montmorillonite (saturated with Ca^{+2} or NH_4^+ ions) with the organic liquid, MacEwan [28] observed no interlayer penetration by n-hexane and n-heptane but benzene, naphthalene, and tetrahydronaphthalene were intercalated [24].

The report by Eltantawy and Arnold [33], presented evidence for the interlayer sorption of n-hexane and n-dodecane by calcium-Wyoming montmorillonite is, if somewhat unexpected, illuminating in that it provides a clue as to the likely factor limiting the intercalation by montmorillonite of non-polar gases and liquids. These workers were able to form a single-layer complex with n-hexane having a sharp basal spacing of 1-41 nm on exposing the air-dry clay to the hydrocarbon vapour for about 3 hours at room temperature. The complex so formed contained 110 mg of n-hexane per g of oven-dry (383°K) clay. Increasing the exposure period beyond 3 hours yielded a mixed single- and double-layer complex which could also be obtained by immersing the air-dry mineral in liquid n-hexane (d(001) spacings 1,403 and 1,796 nm). Infra-red examination of the n-hexane complex showed that a considerable amount of water was retained in the interlayer space. This suggests that ion-organic interactions were not significant and, C-H . . . O-Si hydrogen bonding was also unlikely to be important. Yet, as indicated by the results of differential thermal microanalysis the complex, was markedly stable [24].

It would seem that water influences the rate of intercalation. Thus, immediate X-ray examination of the material previously heated at 493°K for 24 hours and then immersed in water-free liquid n-hexane failed to show any evidence of interlayer complex formation. Intercalation did occur, however, when this sample was left immersed for 2 weeks. Similar results were obtained for n-dodecane. These observations strongly suggest that n-alkanes can penetrate the interlayer space of montmorillonite but at a very slow rate. This would largely account for the failure on the part of some workers to observe interlayer sorption of non-polar organic molecules when insufficient time was allowed for significant intercalation [24].

Following De Boer and Zwikker [34], Eltantawy and Arnold [33] explained their data in terms of dipole-induced dipole interactions, that is, the electrostatic field at the clay surface induces the formation of dipoles in the hydrocarbon molecules. This postulate is by no means unlikely since, as the analysis of Fripiat [35] has shown, the electric field arising from the exchangeable cations can be quite substantial ($\sim 10^8$-10^9 volt cm-^{1}), capable of inducing a dipole of appreciable magnitude in the adsorbed species. Why the intercalation rate is apparently so slow is an open question because, in theory, van der Waals adsorption occurs instantaneously. An important factor likely to slow down intercalation is the rate at which the n-alkanes diffuse into the montmorillonite interlayers. In addition, the intercalated molecules must be distributed and ordered in a certain way and this would cause a further delay in complex formation [24].

On the other hand, the nature of the interlayer cation present, so crucial in the adsorption of polar organic compounds, is apparently of no great influence in the intercalation of n-alkanes. Slight variations in basal spacing between samples containing different interlayer cations were described by Eltantawy and Arnold [33] to differences in the packing and orientation of the molecules in the interlayer space. Basal spacings were 1.1418 nm for Ca^{+2}, 1.473nm for Mg^{+2} 1.237nm for Na^{+} 1.228 nm K^{+} interlayer cation montmorillinites treated with n-Hexane [24].

2.4 Rheological Behaviour of Clays

The flow behaviour of any system is described in terms of the relationship between the shear stress τ and the shear rate γ. The shear rate is defined as the change of shear strain per unit time, and the shear stress as the tangential force applied per unit area. The ratio of shear stress τ to shear rate γ is called apparent viscosity

$$\eta = \frac{\tau}{\gamma} \qquad (2\text{-}4)$$

hence η is a measure of the resistance to flow of the fluid [10].

The plot of the shear stress vs. the shear rate is called a consistency curve. Four different types of flow may be distinguished: Newtonian, pseudoplastic, Bingham plastic, and dilatant, as illustrated in Figure 11. When the shear stress is directly proportional to the shear rate, the fluid is Newtonian and exhibits a constant apparent viscosity. In the other types of flow behaviour, the apparent viscosity varies with the shear rate and these are called non-Newtonian fluids [10].

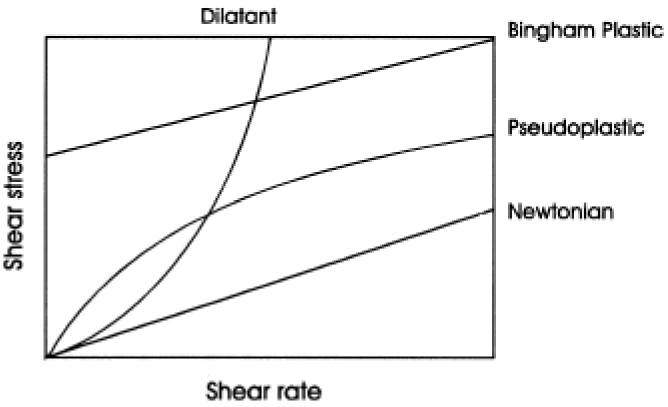


Figure. 11. Consistency curves for four different types of flow [10].

Aqueous clay suspensions that possess a relatively high particle concentration have been described traditionally in accordance to the Bingham theory of plastic flow. The Bingham model postulates that a finite stress must be applied to initiate flow and at greater stresses the flow will be Newtonian as shown in Figure 11. The resistance of the suspension to flow can therefore be considered as consisting of two parts: a Newtonian part in which the shear stress is proportional to the shear rate and a non-Newtonian part in which the shear stress is constant irrespective of the shear rate. The equation for the Bingham model is:

$$\tau = \tau_B + \eta_{pl}\, \gamma \tag{2-5}$$

where η_{pl} is the plastic viscosity, defined as the slope of the curve, and τ_B is the Bingham yield stress normally taken as the intercept of the flow curve at zero shear rate [10].

Very dilute clay suspensions or drilling fluids that contain polymers behave as pseudoplastic fluids, which may be described by the power-law equation [10].

$$\tau \quad = \quad K\,(\gamma)^n \qquad (2\text{-}6)$$

where K is a measure of the consistency of the fluid; and n the flow-behaviour index, which is a measure of the decrease of apparent viscosity with shear rate. Other models have been considered in describing the rheological behaviour of clay suspensions, such as the Casson equation:

$$\tau^{1/2} \quad = \quad k_0 + k_1\,\gamma^{1/2} \qquad (2\text{-}7)$$

and the Herschel-Bulkley equation

$$\tau \quad = \quad \tau_y + K(\gamma)^n \qquad (2\text{-}8)$$

Both equations have been used to describe the consistency curves of drilling fluids, with the Herschel-Bulkley equation being the most suitable. In both cases, the suspension has an initial yield stress at low shear rates, and afterwards presents pseudoplastic or 'shear-thinning' type behaviour at higher shear rates. If n is smaller than 1, the apparent viscosity decreases with shear rate [10].

The parameters of the above equations may be divided between two groups. The first group, the Bingham yield stress, consistency coefficient and Casson yield stress are affected by changes in the low shear properties. In the second group, the plastic viscosity, flow-behaviour index and the Casson viscosity, reflect the high shear rate behaviour of the fluid [10].

Clay suspensions frequently show a time dependent flow behaviour, known as thixotropy. After mixing the suspension, the yield stress and plastic viscosity decrease but will recover with time if left standing. In Figure 12, Curve 1 represents the original flow behaviour and after mixing the suspension displays a flow behaviour represented by Curve 2. After a period of rest, the initial Curve 1 will be obtained. Concentrated clay suspensions are very sensitive to shear and their rheological properties will vary during the determination of the rheogram (shear stress vs. shear rate). If the shear rate is ramped-up and then immediately ramped-down, the stresses recorded for each rate of shear will be lower and a 'hysteresis loop' is obtained (Curve 3). This occurs because the fragments of the network which are broken under shear, need time to be linked again to a three-dimensional network. In addition, when the clay system is subjected to a constant rate of shear, the viscosity decreases with time as the gel structure is broken down, until an equilibrium viscosity is reached. In view of their shear and time dependency, the clay suspensions require the same preparation, handling and measurement conditions if comparisons are to be made between the rheological properties of different samples [10].

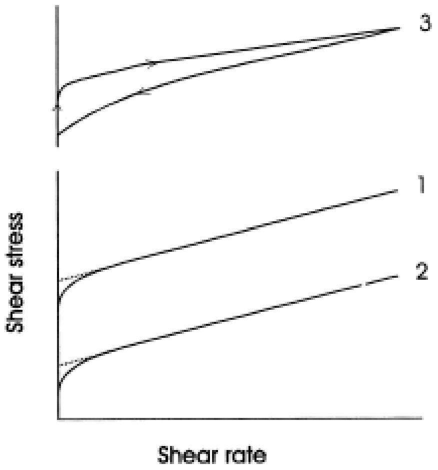


Figure. 12. Typical flow curves for concentrated thixotropic clay suspensions. 1. initial flow curve; 2. flow curve after mixing; and 3. Thixotropic loop [10].

Various factors affect the flow behaviour of clay suspensions. Naturally, the clay concentration will bring about an increase of all rheological properties. Due to the negative particle charge and double-layer structure, the yield stress and viscosity change with variations of the pH of the suspension and electrolyte concentration. Also, differences in the rheological properties are observed depending on the type of electrolyte in solution and on the nature of the exchangeable ions. A rise of the temperature increases the interparticle attractive forces, which in turn, leads to enhanced particle-particle interactions affecting the yield stress and suspension viscosity. The suspension viscosity also depends to a great extent on the viscosity of the medium, which is also a function of temperature. Pressure effects may also alter the flow properties on clay suspensions, due to the exponential increase of liquid viscosity with pressure and the differential compression of clays and liquids [10].

2.5 Bentonite Slurries

Bentonite is a generic term of a number of aluminum silicate clay minerals which in native form appear as flakes or sheets, not unlike mica. Structurally, bentonites consist essentially of flat plates of aluminum-oxygen-silicon molecules laminated together like the pages of a book. In contact with water, bentonite swells as it "unleafs". It is believed that a strong electrostatic force between the layers of the mineral draws in the polar liquid water and the sheet-like structure swells up to eight times its original size as water forces itself between the "pages" [36].

However, their very property of swelling in water upon which useful applications of bentonites are based, leads to serious problems in the handling, delivery and transportation of bentonite clays. Pumpable aqueous slurries of bentonites do not commonly exhibit a solids content of more than about 7%, above which settling or caking occurs which impairs or destroys the pumpability of the slurry. Not only is the maximum solids content of a pumpable aqueous bentonite slurry only about 7%, but stock aqueous slurries of bentonite must be kept agitated to prevent settling and caking which is very difficult to reverse [36].

Another illustration of the limitations inherent in the use of aqueous bentonite slurries is afforded by the use of such slurries in field applications, such as tunnel stabilization. Bentonite must be pumped at the site at solids contents of only 1-5%. This has the desired effect of placing the bentonite into selected locations, but "uses up" a significant portion of the total water absorbency of the bentonite clay [36].

It has been a generally recognized need to provide a suspension medium for bentonite slurries which itself is of high fluidity (therefore permitting enhanced bentonite solids content) but which does not interfere with the desired end-use subsequent swelling of bentonite by water. As noted above, as a carrier any aqueous medium causes swelling and uses up some of the absorbency [36].

A number of approaches are known which seek to resolve this problem through the addition of any of a wide variety of additives or processing stages. While some of these approaches have resulted in the preparation of higher solids slurries up to about 15% bentonite solids--they generally increase costs considerably and usually harm subsequent use of the bentonite as a thickener. Additionally, the control of the swelling process is often not reproducible from batch to batch and problems of settling and caking are still present [36].

Attempts have been made to use non-aqueous fluids as carriers of the mineral, but these often brought their own problems such as flammability, toxicity, or interference with the commercial process in which bentonite serves as the thickener, e.g. paper-making. Some likely candidates as carriers proved useless because of almost instantaneous interaction with the bentonite to cause gelling or solidification of the mixture [36].

According to U.S. patent 6,399,544 pumpable and flowable bentonite clay slurries having a bentonite solids content of about 50% or greater have been prepared through the use of a non-aqueous fluidizing agent, characterized by being a highly-saturated hydrocarbon oil with low affinity for reactivity with bentonite or other hydrophilic swelling agents such as starches, guars and xanthans [36].

U.S Patent No. 5,391,228 is a method for preparing a time-stable, low viscosity, pumpable high solids aqueous bentonite slurry which has good application properties upon dilution and use. An aqueous solution of at least first and second salt components is prepared in which there is dispersed at least 8% by weight of the resultant slurry of a powdered bentonite. The first salt component is selected to give if used alone an acceptably low viscosity to the slurry at said high solids and at least good application properties upon the dilution and use. The second salt component is selected to act in combination with the first salt component to substantially further decrease the acceptably low viscosity at a specified high solids content or to enable increase of the solids content while maintaining the acceptably low viscosity, while not substantially impairing the application properties [1].

Van Fisk, U.S. Pat. No. 4,359,339 proposes the addition of a water soluble aluminum salt, such as aluminum sulfate, to permit the making of pumpable aqueous slurries of bentonite of up to 26% by weight of clay, primarily for use in making foundry sand compositions used in the making of molds. While apparently suitable for the purpose disclosed, aluminum salts have not been found to be satisfactory for making clay slurries of higher solids content, which are frequently desired for many purposes, especially when shipping is involved. Van Fisk also points out that certain other ions, such as calcium ion have been known to depress the gelling properties of bentonites in aqueous slurries, but that the properties are not readily reversible upon later dilution, thus limiting the value of such use. While aluminum ion appears to be less subject to this objection, to a considerable extent it suffers from the same problem. All multivalent cations tend to strongly bind the clay platelets together, which prevents dispersion and inhibits performance in applications where good dispersion is needed (viscosifiers, fabric softeners, retention aids) [1].

In application Us Ser. No. 631,919, filed Dec. 21, 1990, it is disclosed that a smectite clay, such as a bentonite clay, may be provided as an elevated solids aqueous slurry e.g. up to 50% solids, by slurrying the smectite clay in an aqueous medium wherein the aqueous medium has an effective concentration of a salt having a monovalent cation. When such a salt is present in the clay slurry, the clay does not swell appreciably, is essentially inactive, and the slurry can be shipped, pumped and stored without creating a gelling problem. When this slurry is diluted with fresh water at the point of application to make it of the desired solids content for use, e.g. even to less than 1% solids, the smectite clay exhibits all of the desired properties, such as fabric softening, retention, etc. in most applications [1]

In a procedure according to the Ser. No. 631,919 application, a time-stable, low viscosity, high solids aqueous bentonite slurry is prepared by the steps of first preparing an aqueous solution of a monovalent salt; and thereupon dispersing in the solution at least 8% by weight of a powdered bentonite, by adding the powder to the solution with concurrent low shear mixing. The bentonite is preferably a sodium bentonite, which is added to the solution as from 8 to 50% by weight. The monovalent salt may comprise from about 1 to 35% by weight of the solution, and preferably comprises from 3 to 15%. The monovalent salt is preferably sodium chloride. The salt and clay can also be added to the aqueous phase at the same time. This gives a significant improvement over adding salt to a dispersed clay slurry but is not as effective as dissolving the salt first, and then adding the clay [1]

In the application Ser. No. 631,919 it is also shown that potassium salts can be very effective in producing high solids bentonite slurries of desirably low viscosity. However, such salts are shown in our earlier disclosure to have an unacceptable negative effect on application properties of the said slurries. For example, in the Ser. No. 631,919 application, high solids slurries based upon different monovalent cations were diluted to 5% solids with salt-free water, sheared and viscosity measured. These slurries were then tested for their ability to improve water release from paper pulp slurries used in paper making. This technology is described in U.S. Pat. No. 4,305,781. In this test the shorter the "drainage" time (measured in seconds), the better. The optimum slurry would give low viscosity, low liquid separation and good flowability at high solids. Upon dilution for use in commercial applications, however, the optimum slurry would give high viscosity at 5% solids for rheological application and low drainage rate numbers for paper making applications. The data found in experiments of this type showed that potassium ion had a relatively detrimental effect when measured by such "application properties", thus apparently limiting its usefulness for such purposes [1]

U.S. Patent. No. 5,407,480 is an application of aqueous slurry of smectite clay of elevated solids content, comprising an aqueous solution or emulsion of from about 0.5 to about 13% by weight of said slurry of a salt of a low molecular weight amine salt, in which is dispersed from about 10 to 47% by weight of the slurry, of a smectite clay. The amine salt is effective to prevent the smectite from swelling appreciably, whereby the slurry can be shipped and stored without creating a gelling problem. The inhibiting or suppressing effect of the amine salt on the swelling of the clay and on gelling of the slurry is reversible upon subsequent dilution with water, thereby facilitating use of the smectite in typical applications, e.g. as a retention aid in paper making, or as a viscosifier [37]

In U.S. Pat. No. 5,223,098, bentonite swelling clay is provided to a paper making mill as a fluid concentrate containing more than 15% bentonite. Swelling of the bentonite is. suppressed by an inorganic electrolyte in the concentrate. The bentonite swells upon dilution either before addition of the cellulosic suspension or after addition. While both U.S. Pat. No. 5,223,098 discloses high solids smectite slurries which meet the needs above discussed, it is nonetheless sharply focused on use of certain inorganic electrolytes, which can introduce undesired ionic species into the smectite slurry. Furthermore, the efficacy of these salts for use as reversible swelling suppressants at higher smectite solids can be undesirably limited [37]

The fluidizing agent used in preparing high-solids bentonite slurries is effective for the purpose by reason of its physicochemical inertness relative to the hydrophilic and reactive surface of the bentonite clays. For that reason, the fluidizing agent is also suitable for a number of materials other than bentonite commonly used as swelling agents in aqueous media such as xanthan gums, polyacrylamides and guar gums [36].

2.6 Purification of Bentonite

Bentonite deposit has a complicated composition mainly formed of smectites and containing free silica minerals, such as quartz, cristobalite, and opal; silicate minerals, such as feldspar, mica, and zeolite; carbonates or sulfates of alkaline earth metals, such as calcite, dolomite, and gypsum; and, in addition, iron compounds and humus. Since bentonite ore mined from bentonite deposit usually has a water content of 15 to 35%, it is primarily broken and dried in the sun or hot air to obtain bentonite ore having a water content of 5 to 10%. The dried bentonite ore is pulverized by means of an attrition grinding machine, such as a centrifugal roller mill, or an impact mill, such as a hammer mill. In the clay industry, crude clays are commonly washed to remove grit that may be present [2].

In addition, raw clay is frequently allowed to stand to permit coarse particles to settle out (see U.S. Pat. Nos. 2,885,360 and 2,531,427). Additional treatments for clay including fractionation by settling or centrifugation are disclosed, for example, in U.S. Pat. Nos. 3,253,791, 4,018,673 and 4,451,440. 3,408,305 U.S. Pat. 5,292,908 suggests a suitable way for substantially water-free purified bentonite which is obtained by removing non-clay substances from a crude bentonite suspension using spontaneous sedimentation or centrifugal separation to recover a purified bentonite solution, evaporating the resulting purified bentonite solution, and finally drying at a temperature of from 150 to 200 ^{0}C. U.S patent 5,529,622 shows a process for treatment of bentonite for use as a paper coating pigment. Bentonite clay is first dispersed in water in a conventional procedure to produce a slurry. Preferably the solid content of this slurry will range from about 5 to about 50 percent and more preferably from about 10 to about 30 percent. As previously stated, preferably, separate calcium and sodium smectite clay slurries are produced. The smectite clay slurries are next treated to remove foreign substances such as sand, feldspar, quartz, calcite and other hard impurities (sometimes referred to as "grit"). This precleaning or degritting of the clay slurries can be carried out by a number of procedures conventional in the industry including grinding, sorting, cyclone separators and other such conventional degritting processes (U.S. Pat. Nos. 2,885,360 and 2,531,427). Preferably, the slurry is degritted by use of centrifugation, such as by use of hydrocyclone. Further, centrifugation, using higher g-force, may be useful to remove additional quartz, feldspar and other grit impurities from the bentonite clay and thus control the particle size of the clay. Such additional degritting will enhance the quality of the smectite clay end product [38].

A suitable way in U.S patent 4,483,934 is suggested, raw bentonite is beneficiated by treating a substantially iron oxide-free bentonite, as an aqueous suspension, with an alkali; washing the alkali treated bentonite at least once with water; and then subjecting a suspension of the alkali-treated and washed bentonite to shearing, attrition and impact forces in a homogenizer of the type wherein the suspension is forced in the form of a film through a thin, hard-surfaced gap under pressure [39].

U.S. Patent 6,730,719 describes a research on the smectite mineral when crushed, ground, slurried in water and screened to remove grit and other impurities. The component mineral can then be subjected as a dilute (1 to 6% solids) aqueous slurry to high shearing in a suitable mill. Most preferred for use in this shearing step is a homogenizing mill of the type wherein high speed fluid shear of the slurry is effected by passing the slurry at high velocities through a narrow gap, across which a high pressure differential is maintained. This type of action can e.g. be effected in the well-known Manton-Gaulin "MG") mill which device is sometimes referred to as the "Gaulin homogenizer" [40].

As can be seen from the prior researches the non-clay impurities are usually eliminated by grinding, high shearing, attrition, impact forces, centrifugation, settling or screening the non-clay impurities in aqueous suspension. In this research, the possible methods for beneficiation the raw bentonite ore, exposing bentonite to shearing or shaking forces in non-aqueous media where elimination of non-clay impurities is achieved at the same time the dispersion of bentonite is obtained. A high-solid bentonite suspension which does not effect the desired properties of bentonite can be proposed using a non-aqueous organic liquid for treatment of low quality bentonite.

2.7 Waterproofing Bentonite Material

It has been a great research area and developing industrial field to provide a waterproofing material containing swelling bentonite mineral. Such waterproofing material finds wide applicability in construction industry, the waterproofing surfaces such as soil, plaza decks, subterranean foundation surfaces and the like in the formation of waterproofed construction areas; soil structure, such as lagoons; and hazardous or toxic waste containment areas the penetration of water and hazardous or toxic materials into the earth, and to provide lagoons, ponds and other water containment areas [4].

In constructing various building structures, numerous water stoppers have been used, which are made of rubber, plastics, asphalt and the like. Such water stoppers of the prior art have shortcomings in that most of them have good adhesiveness but they are too soft and sometimes sticky, and that their properties vary with temperature variation, for instance, they become too hard in winter to use in the field. Besides, after being used for a long period of time, the water stopper of the prior art tends to reduce their resiliency or to become subject to creep phenomenon, so that the water stopper becomes less adaptable to fluctuation of structural gaps and fails to maintain full water stopping ability thereof [41].

Many attempts have been made to provide a bentonite composition having a handleable consistency such as in a paste-like or putty-like form while retaining the full swelling properties of the bentonite by the addition of non-aqueous liquids, such as set forth in U.S. Pat. No. 4,279,547 and the McGroarty U.S. Pat. No. 4,316,833. Generally, the addition of liquid organic additives to bentonite will inhibit the swelling capacity of the bentonite to various degrees depending on the characteristics of the organic additive, and most notably dependent upon the polarity of the organic additive. In accordance with the McGroarty U.S. Pat. No. 4,316,833, an attempt is made to provide a cohesive bentonite composition having a paste-like consistency without hydrating the bentonite by the addition of adhesive agents, such as hydrocarbon resins. In accordance with the McGroarty U.S. Pat. No. 4,316,833 "if the adhesive penetrates the bentonite, it will destroy the ability of the bentonite to swell and thus will destroy its waterproofing capabilities". In an attempt to prevent the adhesive agent penetration, the McGroarty bentonite is first saturated with a liquid fluidizer; such a mineral spirits, to prevent the adhesive agent from substantially, penetrating the bentonite particles after saturation with the liquid fluidizer [3].

United States Patent No. 4,810,573 relates to a layered water sealing article of manufacture including a layer of a flexible sheet material adhered to a layer of a composition comprising a non-hydrated water-swellable clay intimately contacted with a polypropene, polybutene, or mixtures thereof particularly useful as a water barrier. According to patent the water swellable clay composition can be adhered to the flexible sheet material in any manner, such as by extruding the composition in sheet form onto a layer of sheet material. The clay composition layer is sufficiently tacky to adhere to the sheet material on one major surface, and is sufficiently tacky for adherence to a wall, conduit, floor, roof, or other structure to be protected from water contact, on an exposed major surface in areas of potential water flow to prevent the seepage of water through the bentonite clay composition layer. In one embodiment, the clay composition layer includes a polypropene and/or a polybutene and an elastomer, such as butyl rubber, having sufficient resilience to stretch or expand with the expanding water-swellable clay composition upon hydration and to aid in maintaining the structural integrity and cohesiveness of the clay composition. In another embodiment, the clay composition layer comprises a water-swellable clay, an elastomer, and any plasticizer compatible with the elastomer [3].

U.S. Pat. Nos. 4,209,568 and 4,279,547 describe other attempts to provide a bentonite composition having a consistency for good handleability such as a stiff putty-like consistency without hydrating the bentonite and without saturation of the bentonite with bentonite-inhibiting organics by forming a gel and adding the bentonite to the gel to prevent bentonite saturation while maintaining its swellability [3].

The Ishido U.S. Pat. No. 4,366,284 discloses a bentonite composition having 10-40% rubber, 10-40% plasticizer and 10-20% silicic filler. The silicic filler in an amount of at least 10% by weight is disclosed to be critical for swellability.It has been found that the composition set forth in U.S. Pat. No. 4,279,547 and in the McGroarty U.S. Pat. No. 4,316,833, while generally satisfactory in terms of composition consistency and maintenance of swellability, inhibit the swelling of the bentonite to a limited extent. A number of patents disclose the use of a liquid impermeable liner of polymeric sheet material, bentonite clay, or layers of the two to prevent escape of liquid or liquid waste materials to the surrounding environment. Examples of such patents include U.S. Pat. Nos. 4,255,067 to Wright; 4,035,543 to Draper et al; and 4,344,722 to Blais. [3].

Other patents disclose the use of various plastic sheet or resin materials as water-proofing layers: U.S. Pat. Nos. 3,234,741 to Ionides; 3,326,001 to Stapelfeld; 3,383,863 to Berry ; 3,415,022 to Schaefer et al.; and

3,474,625 to Draper et al. The following patents disclose the use of asphalt or other bituminous material together with other materials, reinforcements or liners for lining earthen formations: U.S. Pat. Nos. 2,190,003 to VanHulst; 2,771,745 to Bramble; 3,160,512 to Cash et al.; and 3,380,254 to Rossi. The VanHulst patent No. 2,190,003 discloses the combination of bituminous substances and clay for admixture with soil [3].

A new kind of waterproofing material can be proposed by deposition of bentonite in an industrial sponge type material by using a high-solid non-aqueous bentonite slurry.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Bentonite used in the research was obtained from Tokat/Reşadiye, one of the largest sodium bentonite reserves in Turkey. Its potential reserves have been estimated at 200 million tons by the Mineral Research and Exploration Institute of Turkey. This bentonite produces muds of high plasticity when mixed with water. It is currently used in the preparation of drilling fluids and in iron ore pelletizing [42].

Table.1 Chemical Composition of the Tokat Resadiye Bentonite [42].

CEC (eqv kg−1)		0.65
Chemical Analyses		
SiO_2	%	62.6
TiO_2	%	0.29
Al_2O_3	%	16.65
Fe_2O_3	%	3.44
MgO	%	1.63
CaO	%	3.37
Na_2O	%	2.59
K_2O	%	0.98
LOI	%	8.45

In this research acetone, methyl-ethyl ketone and n-hexane were chosen as organic fluidizing agents according to their interactions with clay minerals, volatility, cost and toxicity. The organic liquids were obtained from Aklar Kimya and the specifications are given in Appendix A.

Acetone is a manufactured chemical that is also found naturally in the environment. It has a boiling point of 56 ^{0}C. It is a colorless liquid with a distinct smell and taste. It evaporates easily, is flammable, and dissolves in water. It is also called dimethyl ketone, 2-propanone, and beta-ketopropane. Acetone is used to make plastic, fibers, drugs, and other chemicals. It is also used to dissolve other substances. It occurs naturally in plants, trees, volcanic gases, forest fires, and as a product of the breakdown of body fat. It is present in vehicle exhaust, tobacco smoke, and landfill sites. Industrial processes contribute more acetone to the environment than natural processes [43].

Methyl ethyl ketone is a colourless liquid with a faint sweet odour. It has a boiling point of 79 ^{0}C. Methyl ethyl ketone is a flammable liquid. It is partially soluble in water, and soluble in most other organic solvents. It will float on water while it rapidly dissolves in it. Methyl ethyl ketone is used as a solvent for lacquers, adhesives; for cleaning materials to be electroplated; for degreasing; in rubber and rubber cement, printing inks, paints, wood stains, varnishes and paint removers and in cleaning solutions; as a catalyst; and as a carrier. The primary sources of methyl ethyl ketone emissions are the industries that either manufacture it or use it in production, such as the chemical industry, rubber manufacturers, the pharmaceutical industry, the semiconductor industry, heavy equipment manufacturing, manufacturers of millwork, veneer and plywood, and manufacturers of paints, inks, varnishes and lacquers.

These are emissions to the air unless there is a spill. Methyl ethyl ketone occurs naturally in volcanoes, forest fires and bushfires, products of biological degradation, and in some foods [44].

Hexane is an alkane hydrocarbon with the chemical formula $CH_3(CH_2)_4CH_3$. It has a boiling point of 69 ^{0}C. It is a chemical made from crude oil. Pure n-hexane is a colorless liquid with a slightly disagreeable odor. It is highly flammable, and its vapors can be explosive. Pure n-hexane is used in laboratories. Most of the n-hexane used in industry is mixed with similar chemicals called solvents. The major use for solvents containing n-hexane is to extract vegetable oils from crops such as soybeans. These solvents are also used as cleaning agents in the printing, textile, furniture, and shoemaking industries. Certain kinds of special glues used in the roofing and shoe and leather industries also contain n-hexane. Several consumer products contain n-hexane, such as gasoline, quick-drying glues used in various hobbies, and rubber cement. Hexane isomers are largely unreactive, and are frequently used as an inert solvent in organic reactions because they are very non-polar. The toxicity of hexane is relatively low, although it is a mild anesthetic. Inhalation of high concentrations produces first a state of mild euphoria, followed by somnolence with headaches and nausea [45].

3.2 Methods

3.2.1 Thermal Analysis

Thermogravimetric analysis (TGA) or thermogravimetry (TG) is a technique in which the mass of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. Derivative thermogravimetry (DTG) is a technique yielding the first derivative of the Thermogravimetric curve with respect to either time or temperature [5]. Both TGA and DTG are widely used in clay analysis.

Figure. 13 TGA equipment

Bentonite slurries were prepared by adding 10 grams of Resadiye Bentonite to 20 ml of organic liquid. After 5 minutes of stirring the slurries, the slurries and the blank sample was dried overnight at 105 ^{o}C. Then the samples was stored in sealed bags for future use. All experiments were performed by placing 20 mg sample and setting purge air flow and heating the samples at a constant rate of 10 ^{o}C/minute to the range of 900 ^{o}C.

3.2.2 Water Absorption Tests

A modified water absorption test was employed with reference to standard test method for water absorption of bentonite by the porous plate method designated by ASTM Committee E-1 given in Appendix B [46].The water absorption apparatus consists of a plastic water container, a sponge, Teflon ring and filter paper as shown in Figure 14.

1) The plastic box had dimensions of 31 cm in length, 22 cm in width and 11.5 cm in height.

2) The size of the sponge with a density of 15kg/m^{3*} used in the tests was 28 cm long, 21 cm wide and 9.5 cm high. 8 cm of the sponge was immersed in water

3) The Teflon ring had inside diameter of 2.50 cm outside diameter of 4.90 cm and height of 2.30 cm. The Teflon ring was used to control the spread of the bentonite sample which affects the water absorption of the bentonite sample.

4) .The filter papers were Machery-Nagel fiber filter (MN 640 d).

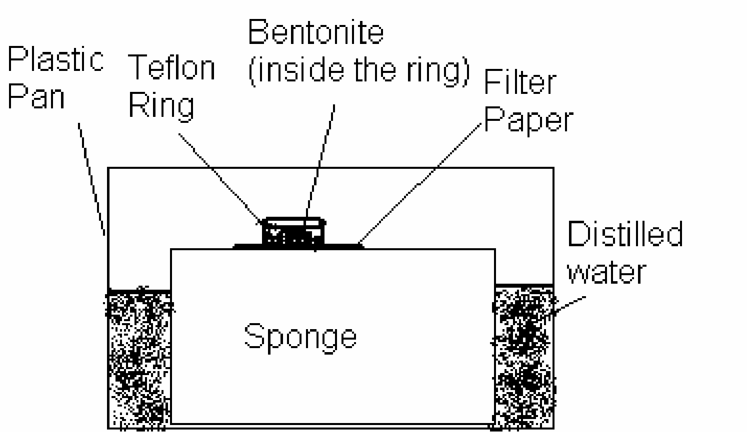


Figure. 14 Water absorption apparatus

(*Determined by İşbir Sünger Test Laboratory)

The test procedure was as followed:

a) The water absorption of blank filter paper was determined by weighing two filter papers allowed to wet on the sponge for given length of time. This was carried out once before the absorption tests.

b) Filter paper and the Teflon ring were weighed and placed on the wetted sponge.

c) 1 g bentonite sample was weighed, placed in the ring and uniformly spread.

d) The sample was allowed to absorb water for any given duration.

e) Teflon ring and filter paper was removed from the test container and weighed.

f) Water absorption capacity was determined according to the following equation:

$$Absorption\ \% \quad = \quad \frac{(Ww - Wd)}{Wd}\, x\, 100 \qquad (3\text{-}1)$$

$$W_w \quad = \quad W_t - (W_f + W_{tef}) \qquad (3\text{-}2)$$

Where

% Absorption = water absorption (% weight of water)

W_w = net weight of the hydrated bentonite

W_t = total weight of the hydrated bentonite, Teflon ring and the wetted filter paper

W_f = weight of the wetted filter paper

W_d = net dry weight of dry bentonite

W_{tef} = Weight of the Teflon ring

3.2.3 Rheological Behaviour Analysis

The quantitative field measurements of mud system were accomplished by utilizing a Fann VG meter, by measuring the shear stress at specific shear rates according to specifications of American Petroleum Institute (specification 13-c).The shear stress was read as the angular deflection of a precision torsion spring. The various shear rates are provided by 6 standard motor speeds (3, 6, 100, 200, 300, 600 rpm).The rheological behaviour analysis is described in the Appendix C.

3.2.4 Purification Tests

3.2.4.1 Purification of Bentonite by Using Non-Aqueous Media

The dispersion and purification of bulk bentonite was carried out by high shear blending in a Laboratory Waren Blender (mod32bl80). The dispersion of the bulk bentonite was determined by screening the dispersed bentonite and the water adsorption tests were carried out to determine the properties of undersize and oversize product.

Purification of bentonite samples by high shear blending procedure follows:

a- 50g Bulk Reşadiye bentonite was put into the experiment flask with 200 ml selected organic liquid.

b- Prepared slurry was subjected to high shear blending by Waring laboratory blender (glass jar) for 2 minutes and 4 minutes with cleaning the bounced bentonite from the jar inner surface with organic liquid every 30 seconds.

c- The mixed slurry was sieved with 100# and the undersize and oversize products were dried at 105 ^{o}C for 2 hours and the weights were recorded.

d- This procedure was repeated for all organic liquids; acetone, methyl-ethyl ketone and n-hexane.

e- The sieved samples and original bentonite sample were ground in the ring pulverizer and dried at 105 ^{o}C.

f- Water absorption tests were carried out for the untreated, undersize and oversize bentonite samples with duration of 24 hours.

Purification of bentonite by shaking was carried out by placing the prepared bentonite sample in a plastic bottle and 200ml of organic liquid was added to the flask containing 7 alumina balls with diameters of 1.50 cm. The flask was carefully set and allowed for 5 minutes shaking using a wet screen machine as can be seen in Figure 15. The dispersed bentonite samples were analyzed following the procedure for the procedure purification of bentonite samples by high shear blending.

Figure. 15 Wet screen shaking mechanism for purification of bentonite using non-aqueous media

3.2.4.2 Purification of Artificially Contaminated Bentonite by Using Non-Aqueous Media

As the received bentonite was rather clean, not much remained in the oversize material in the purification tests. Consequently, an artificially contaminated clay sample was subjected to purification. Resadiye bentonite used in this experiment was crushed into -1 mm then dried at 105 ^{o}C (overnight) to free the moisture. 40 grams (80%) of bentonite sample was mixed with 10 grams (20%) of quartz (+ 500 µm – 2000 µm) as gangue mineral. Sample was subjected to purification as before and was sieved with 100# and the undersize and oversize weights were recorded. This procedure was repeated for all organic liquids; acetone, methyl-ethyl ketone and n-hexane. The sieved samples and original bentonite sample was ground in the ring pulverizer and dried at 105 ^{o}C. Water absorption tests were carried out for the untreated, undersize and oversize bentonite samples with duration of 24 hours.

3.2.5 Bentonite Absorption of Sponge Tests

The bentonite uptake from a non-aqueous suspension by a porous medium was investigated by dipping a sponge cylinder into the non-aqueous bentonite suspension.

a- The sponge cylinders of approximately 4 cm diameter and 3.75 cm height were cut from a common purpose industrial sponge with density of 17 kg/m^{3*}and the weights were recorded.

b- The sponge cylinders were set into the beakers.

c- 25 grams of Reşadiye bentonite was added to 50 ml of organic liquid and the slurry was mixed for homogenizing with magnetic mixer for 5 minutes.

d- The homogenized slurry was poured to the beaker through the top of the sponge cylinders. The beaker was slightly shaken for diffusing the slurry inside the sponge.

e- The beaker was dried at 105 ^{o}C overnight. Then sponge was cleaned up from superficially attached bentonite and the weight of the adsorbed bentonite with the sponge mass was recorded. This procedure was repeated until the sponges were saturated with bentonite slurry with all 3 organic liquids.

(*İşbir Sünger Test Laboratory)

f- Percentage of the bentonite absorbed in the sponges to the void volume of the sponges were calculated according to the following equations.

% void volume bentonite absorbed inside the sponge was determined as:

$$\% \, Void \; Volume \; Bentonite \; Absorbed \quad = \quad \frac{\dfrac{W_{ben}}{d_{ben}}}{Void \; Volume_{sp}} \, x \, 100 \qquad (3\text{-}3)$$

Where

W_{ben} : Weight of the bentonite absorbed

d_{ben}: Density of the bentonite was measured with a pycnometer as 2.13 g/cm^3

And Void Volume of the sponge was determined by the equation

$$Void \; Volume \; of \; the \; sponge \quad = \quad \frac{W_{sp}}{d_{sp}} - \frac{W_{sp}}{d_p} \qquad (3\text{-}4)$$

Where

W_{sp}: Weight of the sponge cylinder used in the tests

d_{sp}: Density of the sponge used in the tests

d_p: Density of polyurethane used in the production of sponge (common industrial polyurethane density used in foam technology 1200kg/ m^3) [47].

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Effect of Organic Liquids on the Thermal Characteristics of Bentonite

The objective of this experiment was to investigate the thermal properties of the bentonite samples treated with different organic solvents and to determine the differences of the thermal properties of the bentonite treated with organic solvents and untreated bentonite sample. Thermal analysis of bentonite samples were carried by Thermogravimetric analysis-Derivative thermogravimetry (TGA-DTG) expressing the reactions occurred during heating such as dehydration, dehydroxilation

The bentonite samples analyzed in this experiment exhibited two main endothermic DTG peaks as shown in figures 17-20. The low temperature peak that occurred in the temperature range 54-61 ^{o}C and the weight loss event mainly corresponds to the evolution of remaining adsorbed liquid and interlayer water. The high temperature peak occurring in the range 690-694 ^{o}C corresponds to the dehydroxylation of clay minerals [5].

According to TGA/DTG of the samples no significant difference in the thermal behavior of acetone, methyl-ethyl ketone, and n-hexane treated samples and untreated blank sample was observed. This indicates that the organic compounds tested in this study do not change the structure of bentonite. The results of analysis are given in Figure 16-19.

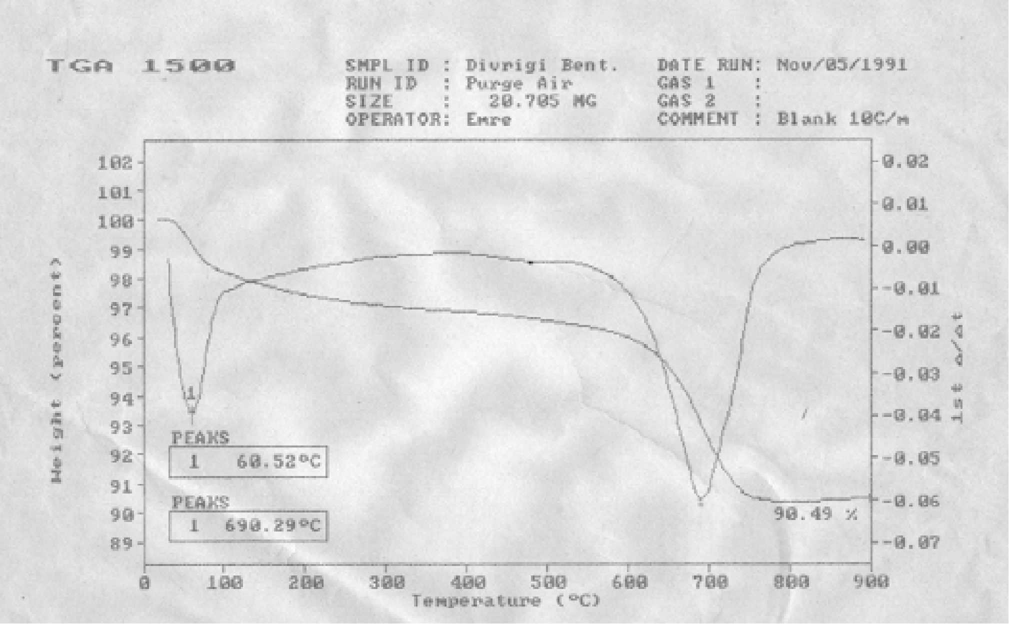


Figure. 16 TGA results for untreated bentonite

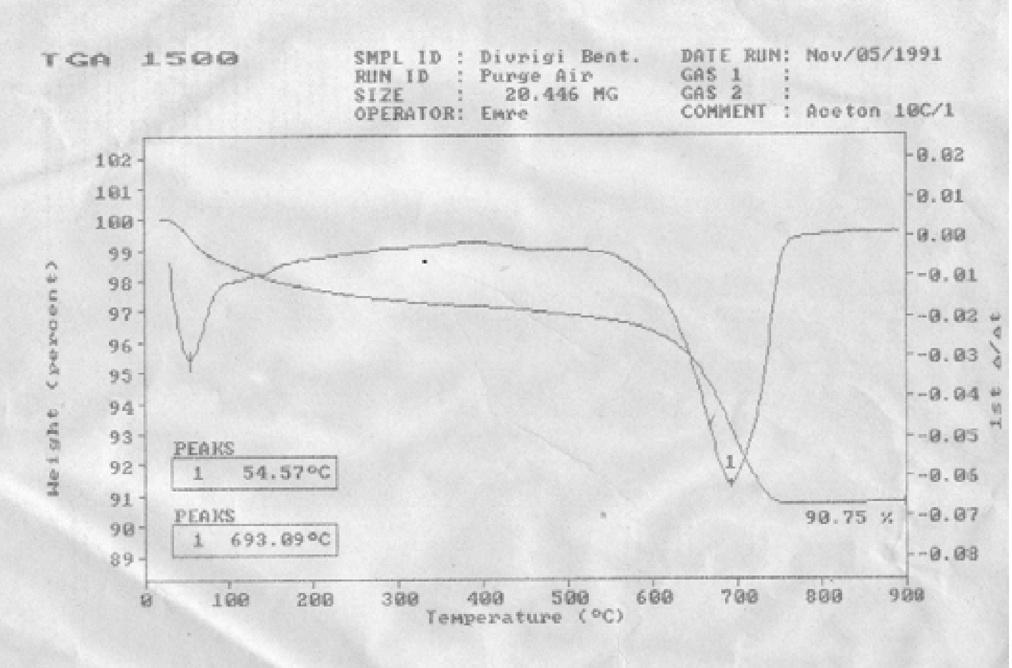


Figure. 17 TGA results for Acetone treated bentonite

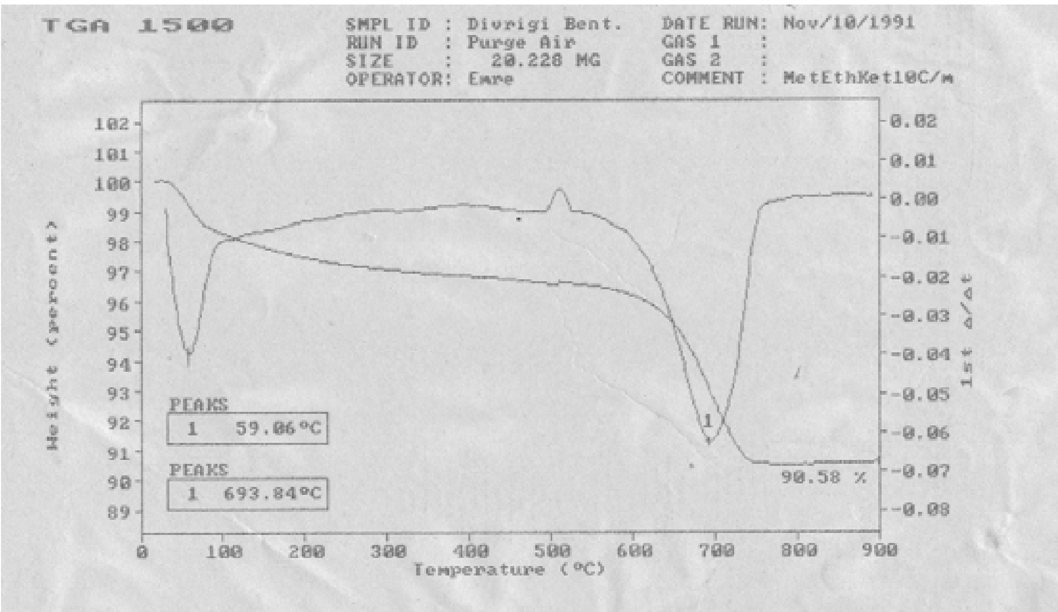


Figure. 18 TGA results for methyl-ethyl ketone treated bentonite

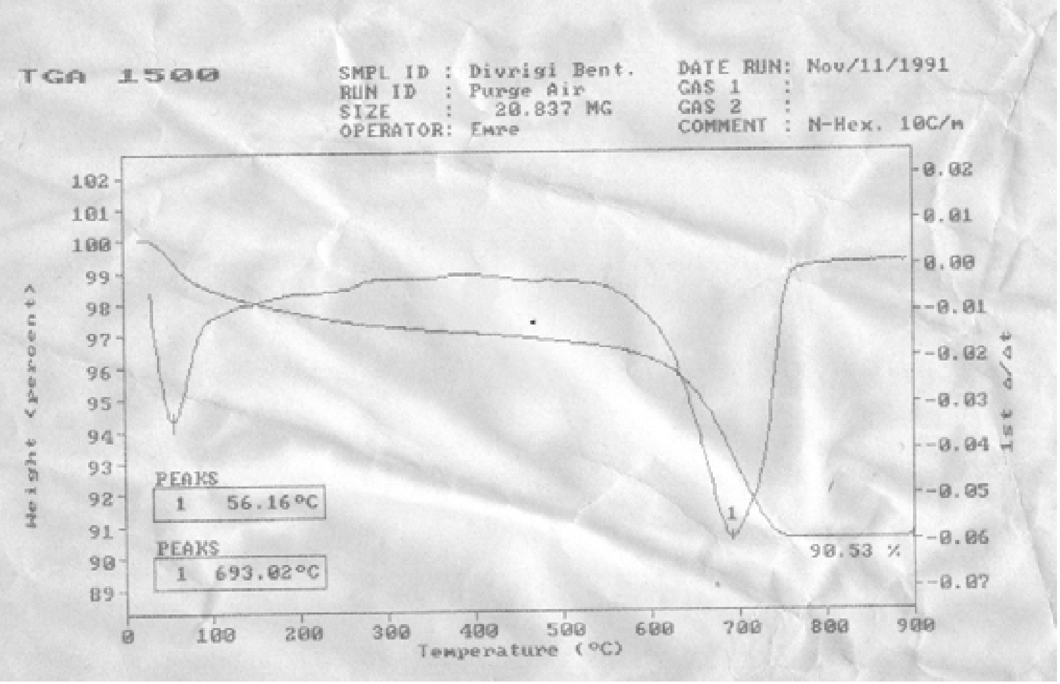


Figure. 19 TGA results for n-hexane treated bentonite

4.2 Effect of Organic Liquids on the Water Absorption Characteristics of Bentonite

The water adsorption tests were applied to organic liquid treated bentonite clay to determine the effects of organic liquids on the water absorption characteristics of clay and the differences between each liquid and untreated bentonite.

10 g Resadiye Bentonite was treated with 20 ml of each of the organic liquids and the slurry was fully dried at 105 ^{o}C (overnight). Then the samples were stored in sealed bags for future use. The water absorption properties of bentonite were investigated. The results are given in Table 2 and Figure 20.

Table 2 Water absorption of non-aqueous liquid treated bentonite samples

Time (hour)	% Weight of Water			
	Blank	N-Hexane	Acetone	M.-E.-Ketone
0	0	0	0	0
1	109.9	127.2	106.7	113.8
2	182.0	175.3	162.7	207.6
4	270.6	251.6	215.4	251.7
8	313.0	310.8	306.4	324.7
16	461.6	364.8	411.1	421.9
24	525.9	462.9	506.8	479.2
40	563.4	552.9	611.3	562.5
48	609.4	650.8	618.2	630.4
72	623.1	680.2	646.9	631.1

Figure 20 indicates no significant change in the water absorption characteristics of bentonite treated with acetone, methyl-ethyl ketone and n-hexane.

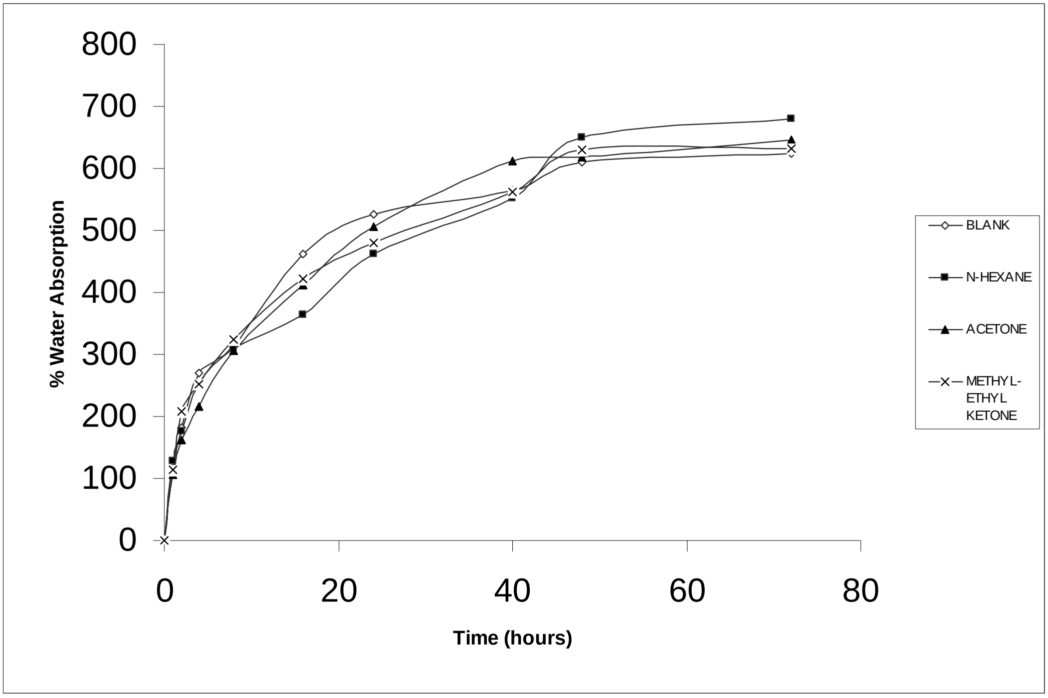


Figure. 21 Water absorption of non-aqueous liquid treated bentonite samples

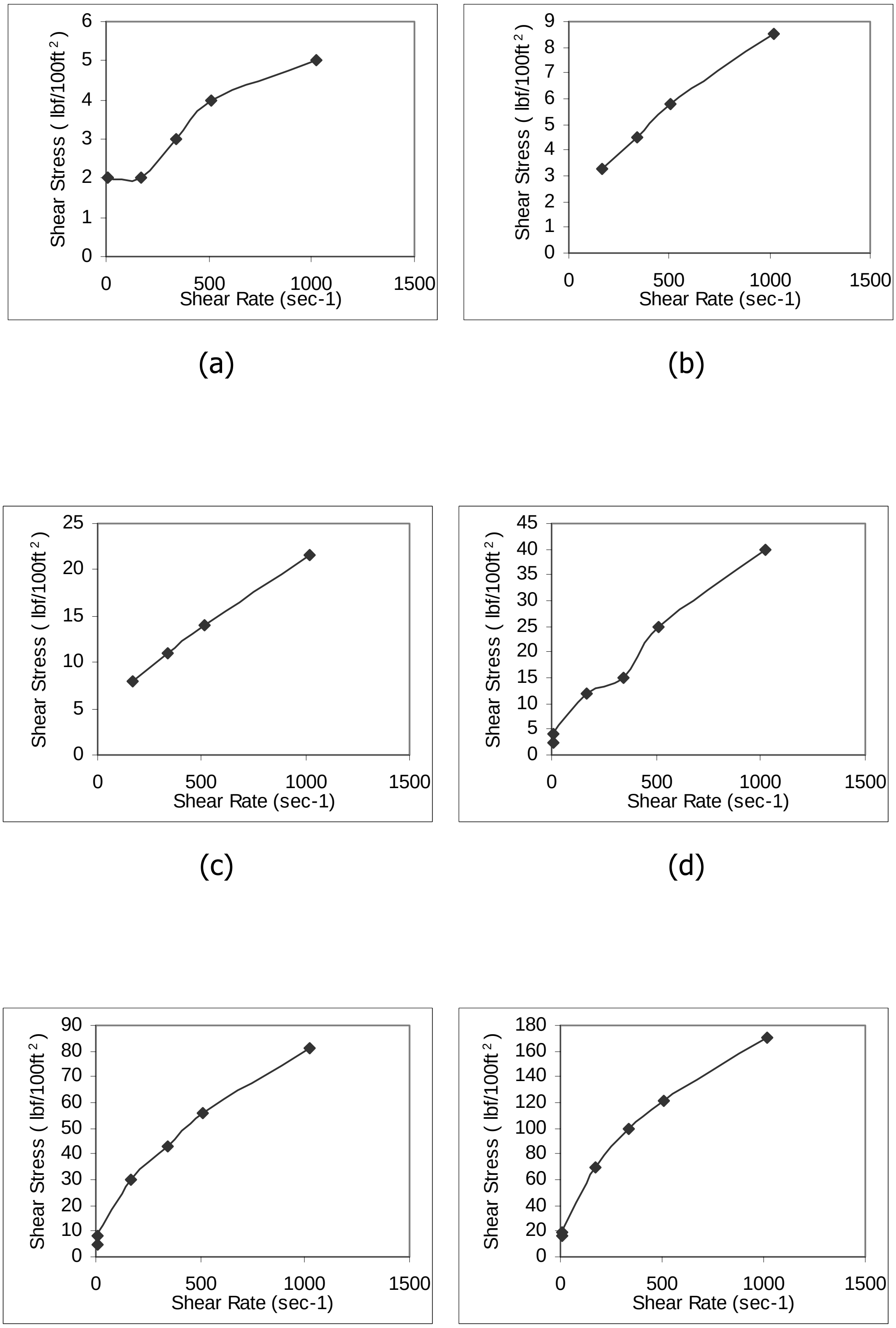
4.3 Rheological Behavior of Bentonite in Aqueous and Non-Aqueous Media

In this research, three non-aqueous organic liquids were tested as high-solid bentonite slurry for low viscosity and effective usage for applications and compared with aqueous slurry. All the measurements were carried out by Fann VG meter with different amounts of bentonite in 350 ml fluid (standard value).

For aqueous slurry the measurements were carried out with 10, 20, 30, 40 and 50 grams of bentonite in 350 ml. of water and shear stresses of different bentonite concentrations at different shear rates are given in table 3 and figure 21. The mud system showed fluidity for 10, 20, 30 and 40 grams of bentonite and the readings could not be obtained for 50 grams of bentonite.

Table.3 Shear Stresses (lbf/100 ft^2) of different bentonite concentrations for aqueous bentonite slurries at different shear rates

Shear Rate (sec -^{1}) / Bentonite Concentration	5.1 (3rpm)	10.2 (6rpm)	170 (100rpm)	340 (200rpm)	510 (300rpm)	1020 (600rpm)
10 g/ 350 ml	2	2	2	3	4	5
15 g/ 350 ml	2	2.5	3.3	4.5	5.8	8.5
30 g/ 350 ml	2.5	2.5	8	11	14	21.5
35 g/ 350 ml	2.5	4	12	15	25	40
40 g/ 350 ml	5	8	30	43	56	81
45 g/ 350 ml	16	19	70	100	121	170
50 g/ 350 ml	110	120				



(a) (b)

(c) (d)

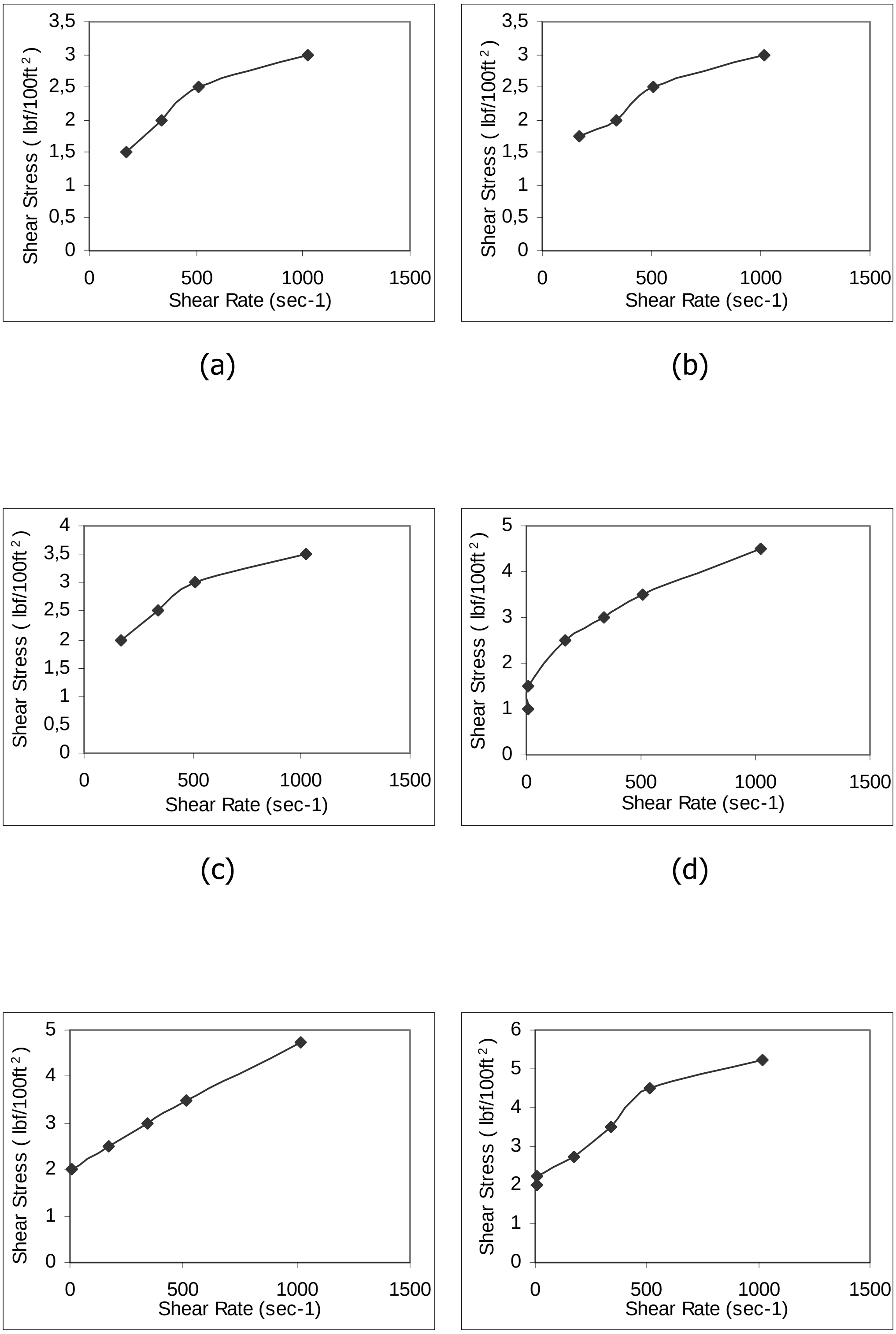
(e) (f)

Figure 21 Rheological behaviour of aqueous bentonite slurry at different concentration levels (a) 10 g/350 ml (b) 15 g/ 350 ml (c)30 g/ (d)35 g/350 ml (e)40 g/350 ml (f)45 g/350 ml

For the non-aqueous media the measurements were done with mixing the bentonite with acetone, methyl-ethyl ketone and n-hexane. Shear stresses at different shear rates are given in Table 4 and Figure 22 for acetone, Table 5 and Figure 23 for methyl-ethyl ketone and Table 6 and Figure 24 for n-hexane mixed slurries for different bentonite concentrations. The measurements were carried out with an initial concentration of bentonite and an extra amount of bentonite was added to the system for subsequent measurements. The flask containing slurry was weighed before each measurement and the amount of evaporated organic liquid was compensated. The interaction between bentonite, acetone and methyl-ethyl ketone caused the slurry to be fluid until 200 grams for acetone and 225 grams for methyl-ethyl ketone. With n-hexane, a different behaviour was observed. The bentonite particles settled down quickly after the mixer was stopped. and the system showed fluidity until 400 grams of bentonite.

Table .4 Shear Stresses (lbf/100 ft^2) of different bentonite concentrations for acetone bentonite slurries at different shear rates

Shear Rate (sec $^{-1}$) / Bentonite Concentration	5.1 (3rpm)	10.2 (6rpm)	170 (100rpm)	340 (200rpm)	510 (300rpm)	1020 (600rpm)
20 g/ 350 ml	1	1	1.5	2	2.5	3
30 g/ 350 ml	1	1	1.75	2	2.5	3
40 g/ 350 ml	1	1	2	2.5	3	3.5
50 g/ 350 ml	1	1.5	2.5	3	3.5	4.5
60 g/ 350 ml	2	2	2.5	3	3.5	4.75
70 g/ 350 ml	2	2.25	2.75	3.5	4.5	5.25
80 g/ 350 ml	2	2.5	3.5	4	5.25	6.5
150 g/ 350 ml			37	40	44	50
250 g/ 350 ml			137	145	151	171

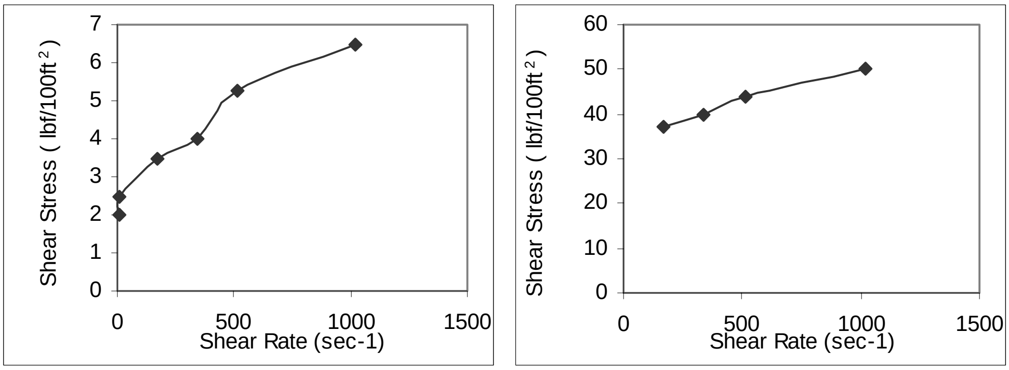


(a) (b)

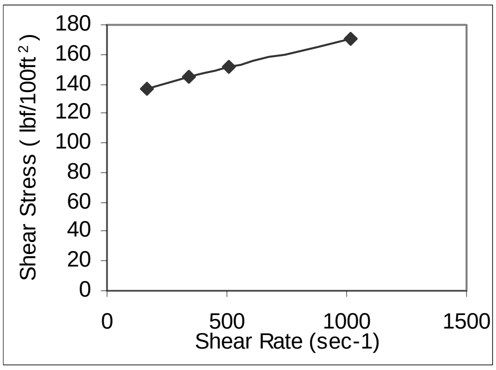
(c) (d)

(e) (f)

Figure 22. Rheological behaviour of acetone bentonite slurry at different concentration levels (a) 20 g/ 350 ml (b) 30 g/350 ml (c) 40 g/350 ml, (d) 50 g/350 ml (e) 60 g/350 ml (f) 70 g/350 ml (g) 80 g/350 ml, (h) 150 g/350 ml (i)250 g/350 ml



(g) (h)

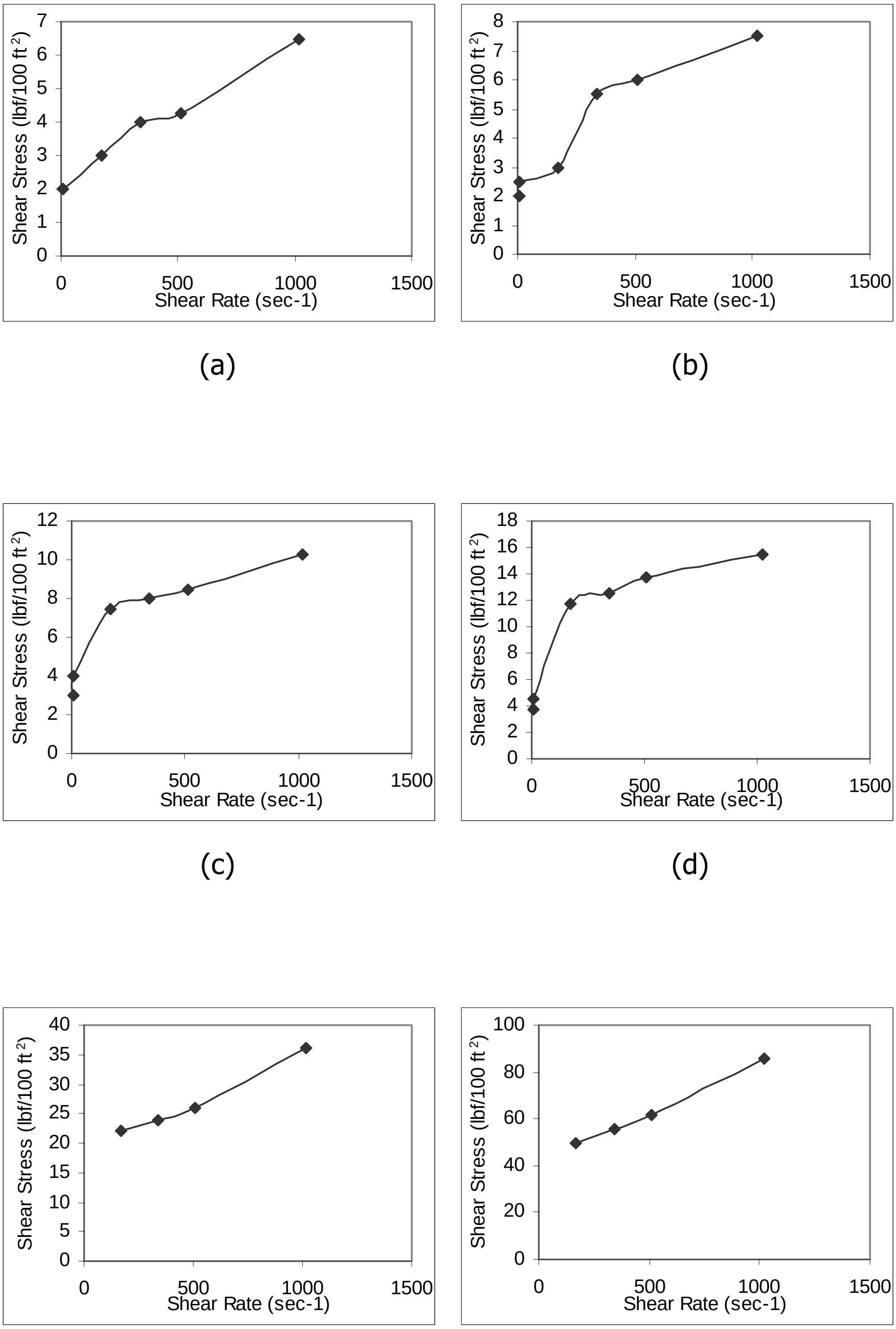


(i)

Figure 22. (continued)

Table 5 Shear Stresses (lbf/100 ft^2) of different bentonite concentrations for methyl-ethyl ketone bentonite slurries at different shear rates

Shear Rate (sec $^{-1}$) Bentonite Concentration	5.1 (3rpm)	10.2 (6rpm)	170 (100rpm)	340 (200rpm)	510 (300rpm)	1020 (600rpm)
125 g/ 350 ml	2	2	3	4	4.25	6.5
150 g/ 350 ml	2	2.5	3	5.5	6	7.5
175 g/ 350 ml	3	4	7.5	8	8.5	10.25
200 g/ 350 ml	3.75	4.5	11.75	12.5	13.75	15.5
225 g/ 350 ml			22	24	26	36
250 g/ 350 ml			50	56	62	86



(a) (b)

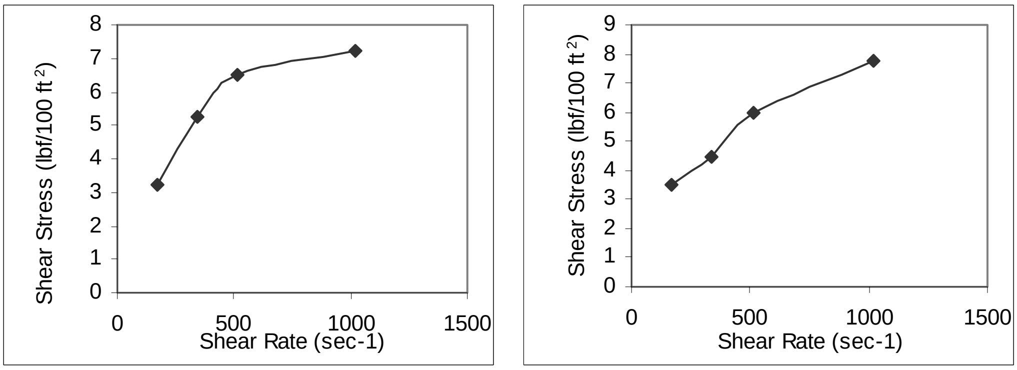
(c) (d)

(e) (f)

Figure 23. Rheological behaviour of Methyl-ethyl ketone bentonite slurry at different concentration levels (a) 125 g/350 ml (b) 150 g/350 ml (c) 175 g/350 ml (d) 200 g/350 ml (e) 225 g/350 ml (f) 250 g/350 ml

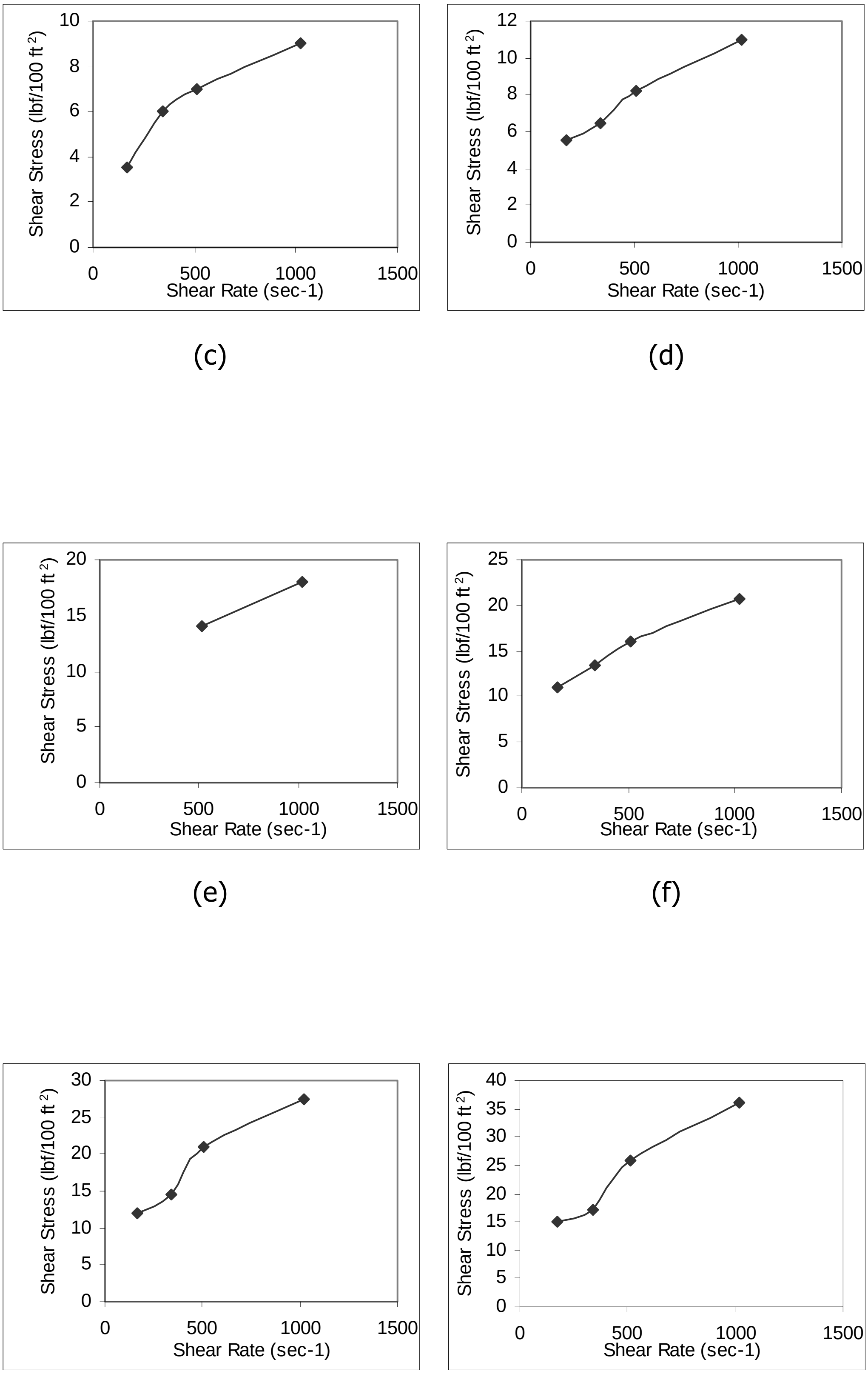
Table. 6 Shear Stresses (lbf/100 ft^2) of different bentonite concentrations for n-hexane bentonite slurries at different shear rates

Shear Rate (sec -^{1}) / Bentonite Concentration	170 (100rpm)	340 (200rpm)	510 (300rpm)	1020 (600rpm)
125 g/ 350 ml	3.25	5.25	6.5	7.25
150 g/ 350 ml	3.5	4.5	6	7.75
175 g/ 350 ml	3.5	6	7	9
200 g/ 350 ml	5.5	6.5	8.25	11
225 g/ 350 ml			14	18
275 g/ 350 ml	11	13.5	16	20.75
325 g/ 350 ml	12	14.5	21	27.5
350 g/ 350 ml	15	17	26	36
425 g/ 350 ml	27	42	70	92



(a) (b)

Figure 24. Rheological behaviour n-hexane bentonite slurry at different concentration levels (a) 125 g/350 (b) 150 g/350 ml(c) 175 g/350 ml (d) 200 g/350 ml (e) 225 g/350 ml (f) 275 g/350 ml (g) 325 g/350 (h) 350 g/350 ml.(i) 425 g/350 ml

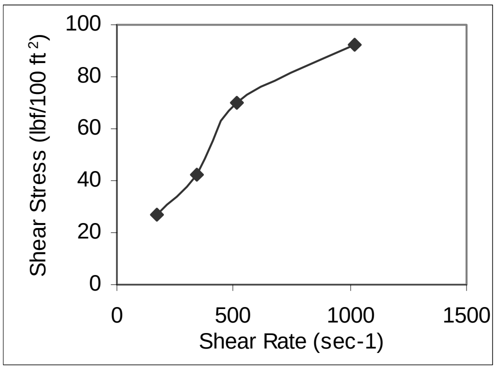


(c) (d)

(e) (f)

(g) (h)

Figure 24 (continued)



(i)

Figure 24 (continued)

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The yield points-plastic viscosities of different concentrations of aqueous and non-aqueous bentonite slurries were calculated and given in Figure 25-28.

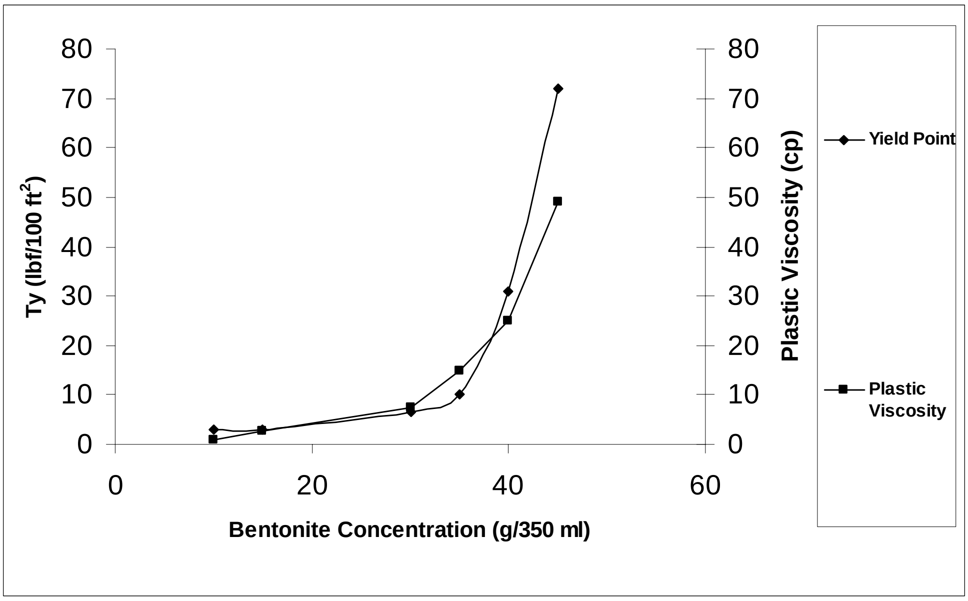


Figure 25 Yield Points-Plastic Viscosities of aqueous bentonite slurries at different bentonite concentrations

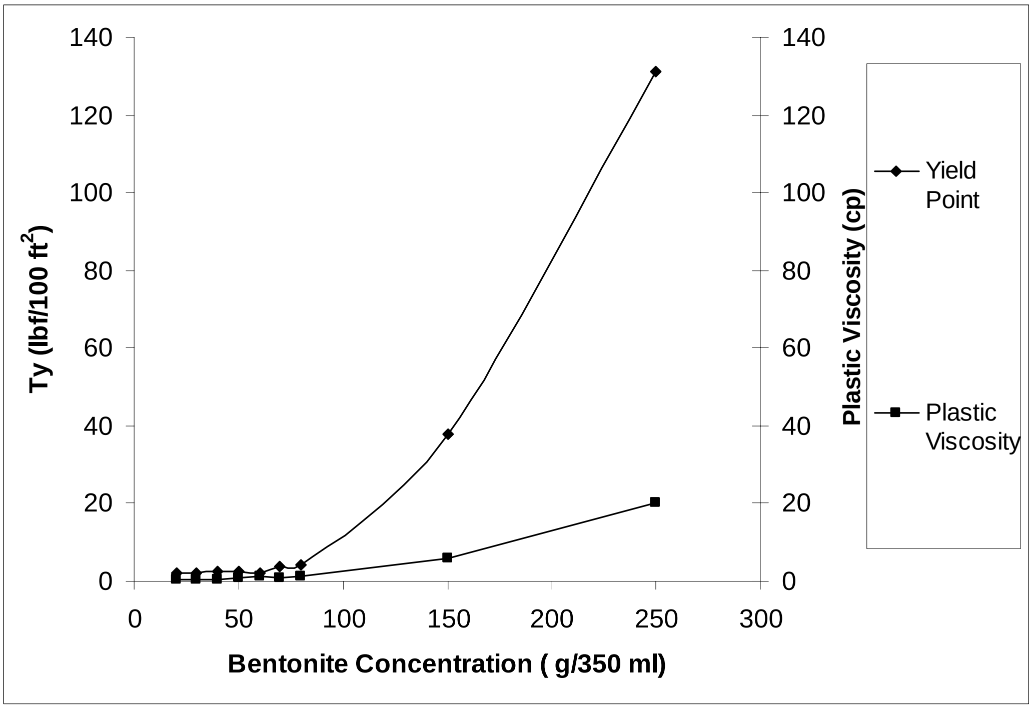


Fig. 26 Yield Points-Plastic Viscosities of acetone bentonite slurries at different bentonite concentrations

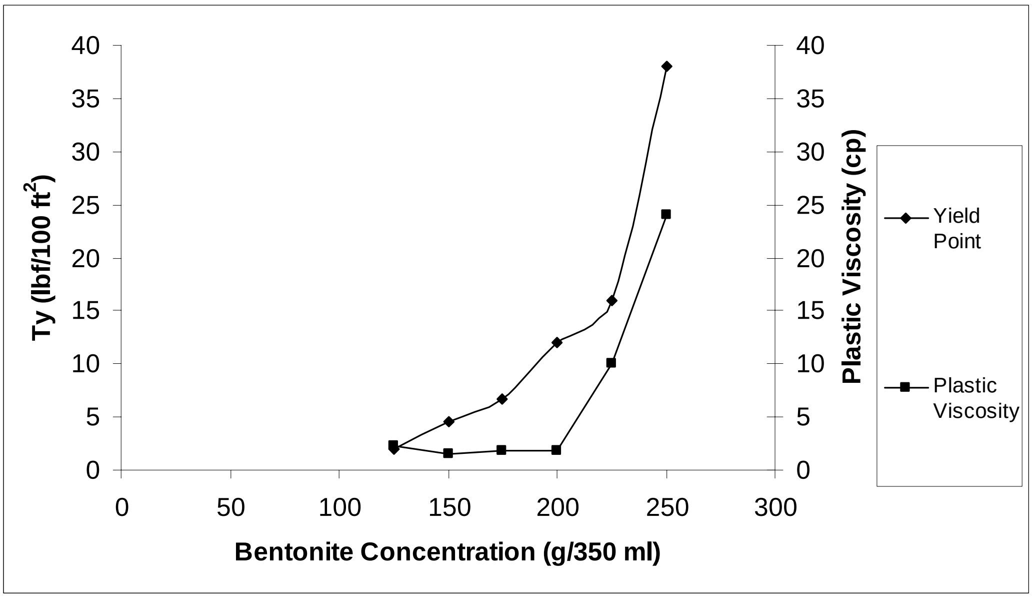


Figure 27 Yield Points-Plastic Viscosities of methyl ethyl ketone bentonite slurries at different bentonite concentrations

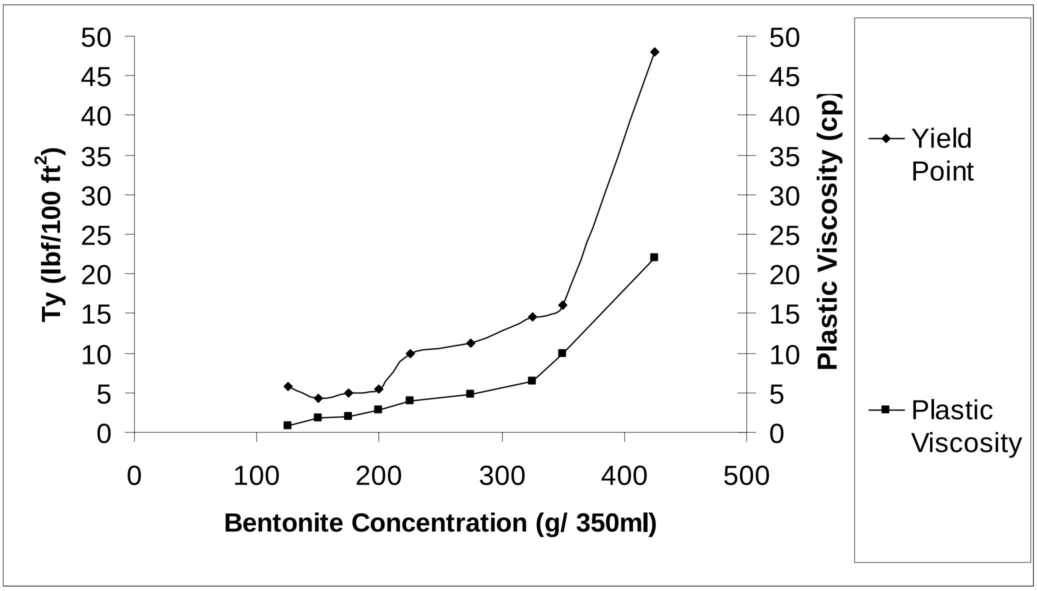


Figure 28 Yield Points-Plastic Viscosities of n-hexane bentonite slurries at different bentonite concentrations

The critical concentrations of bentonite to be used for pumpable high-solid slurries in aqueous and non-aqueous media were determined. The critical concentrations of bentonite from the yield points curve were determined where there are sudden increases on the yield point curves and the critical concentrations were determined from the plastics viscosities curves where there are sudden increases on the plastic viscosities curves. The concentrations in grams responses to pounds and 350 ml fluid to one barrel in the application field. The critical concentrations according to yield points and plastics of aqueous and non-aqueous bentonite slurries are given in Table 7.

Table. 7 Critical Yield Point-Plastic Point Concentrations for a pumpable Bentonite Slurry

Fluid Type	Critical Yield Point Concentration (pounds/barrel)	Critical Plastic Point Concentration (pounds/barrel)
Water	35	30
Acetone	120	150
Methyl-Ethyl Ketone	175	200
N-Hexane	350	325

4.4 Purification of Bentonite

4.4.1 Purification of Bentonite Using Non-Aqueous Organic Media

The purification tests were carried out by dispersion of the bentonite by shearing and shaking, eliminating the non-clay impurities by screening and characterizing the samples by water absorption. These researches are carried for investigating alternative methods in beneficiation of bentonite in the presence of organic liquids without grinding.

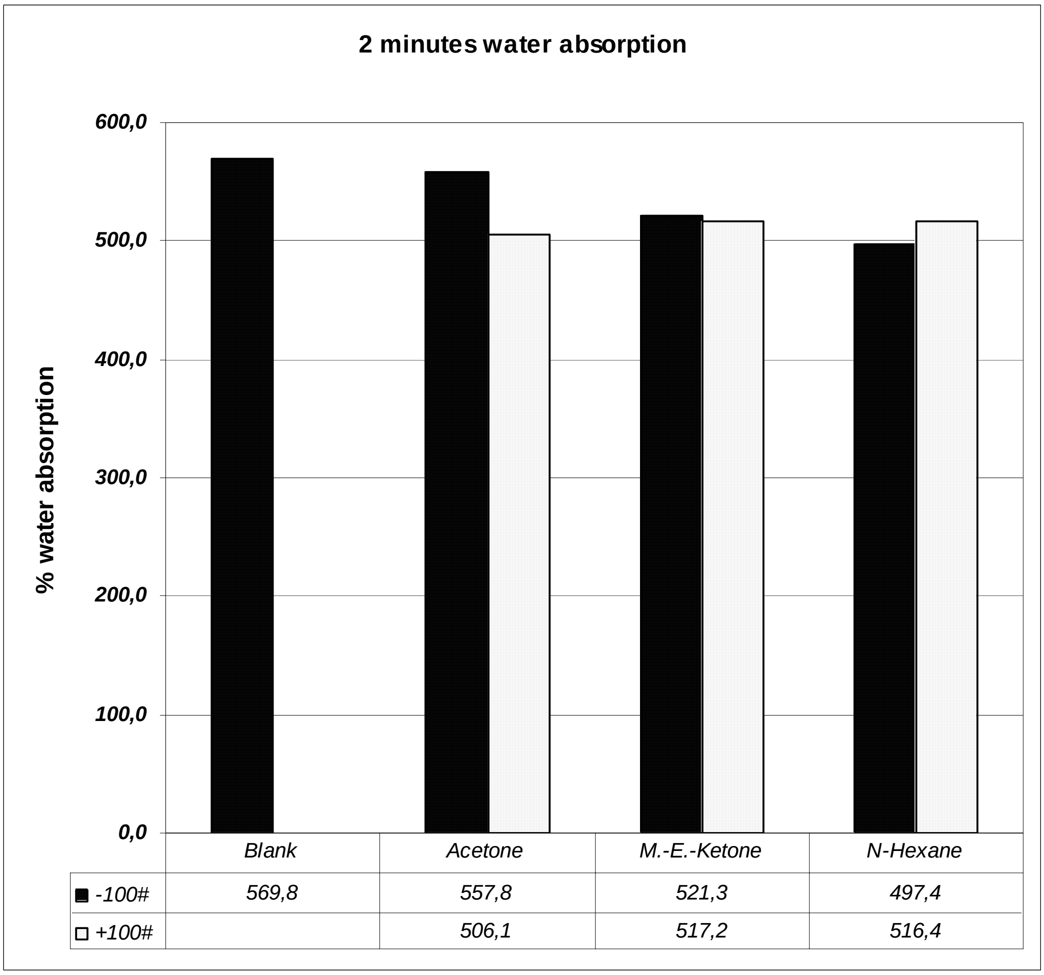
The results of the experiments conducted in order to test the method proposed in section 3.2.4 are explained in this section and a conclusion is obtained based on these results.

The test results for two minutes of blending raw bentonite in the presence of an organic liquid with Waring Blender are 84% for acetone, 83% for methyl-ethyl ketone, and 64% for n-hexane treated bentonite gained as a fraction of -100 meshes after screening. The dispersion and water absorption of bentonite samples are given in Table 8 and Figure 29. The water absorption of bentonite samples did not differ significantly due to the purity of the Resadiye Bentonite as can be seen in Figure 29.

Table 8. Dispersion and Water Absorption of Bentonite

Blending time: 2 minutes

Blending time (minute)	The Organic Liquid Used					
	Acetone		Methyl-Ethyl Ketone		N-hexane	
2 minutes	% weight	% Water Absorption	% weight	% Water Absorption	% weight	% Water Absorption
-100#	83.986	557.8	83.059	521.3	63.916	497.4
+100#	16.014	506.1	16.941	517.2	36.084	516.4



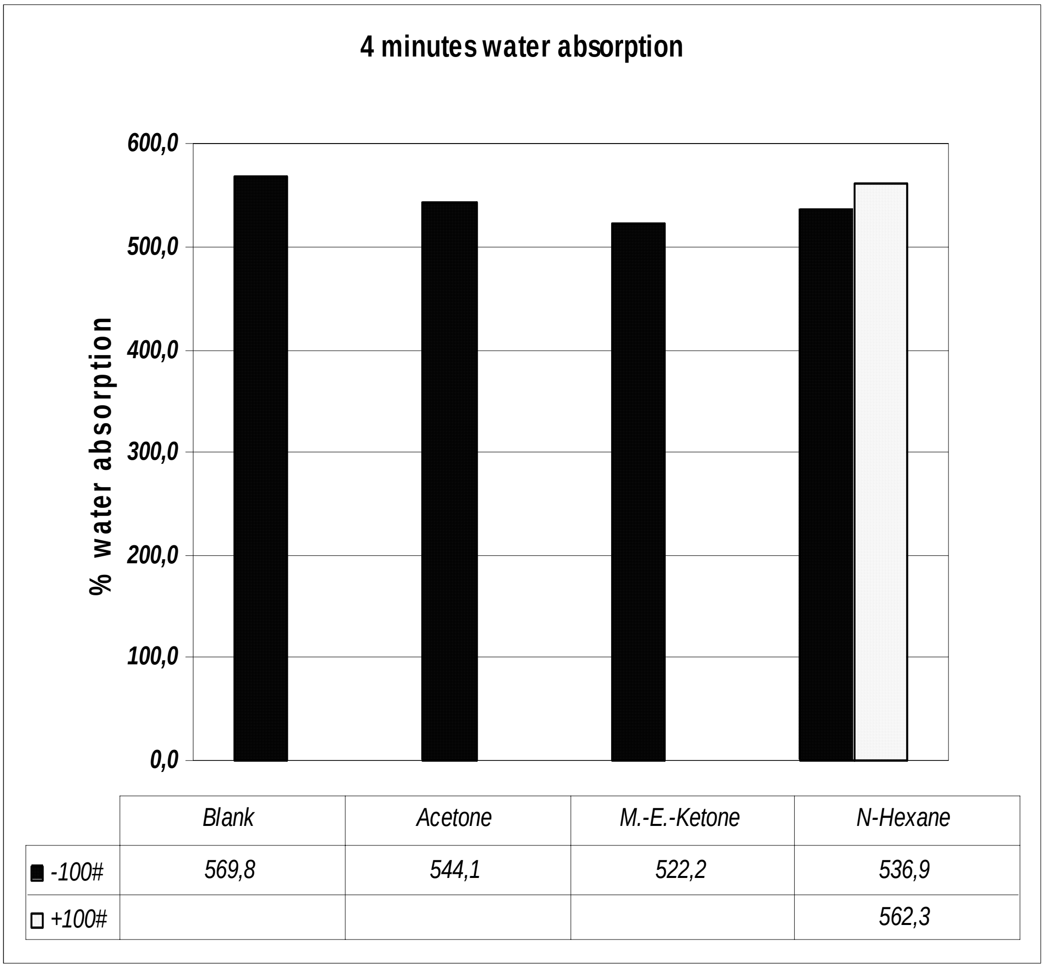
	Blank	Acetone	M.-E.-Ketone	N-Hexane
■ -100#	569,8	557,8	521,3	497,4
□ +100#		506,1	517,2	516,4

Figure 29 Water Absorption tests of -100# and +100 fractions of bentonite dispersed in organic solvents followed by screening. Blending time: 2 minutes

Next, tests were carried out for 4 minutes in order to improve the dispersion of raw bentonite. The tests proved that nearly all 50 grams of the bentonite could be gained as fraction of -100 meshes. Dispersion was effectively accomplished mostly in the presence of acetone and methyl-ethyl ketone. Water absorption tests did not indicate a significant change with the untreated bentonite sample and organic liquid treated samples. The results are given in Table 9 and Figure 30. The water absorption tests for oversized material of acetone and methyl-ethyl ketone treated samples could not be carried out since there were not sufficient amount of samples.

Table 9 Dispersion and Water Absorption of Bentonite Blending time: 4 minutes

Blending time (minute)	The Organic Liquid Used					
	Acetone		Methyl-Ethyl Ketone		N-hexane	
4 minutes	% weight	% Water Absorption	% weight	% Water Absorption	% weight	% Water Absorption
-100#	97.759	544.1	95.239	522.2	70.644	536.9
+100#	2.241		4.761		29.356	562.3



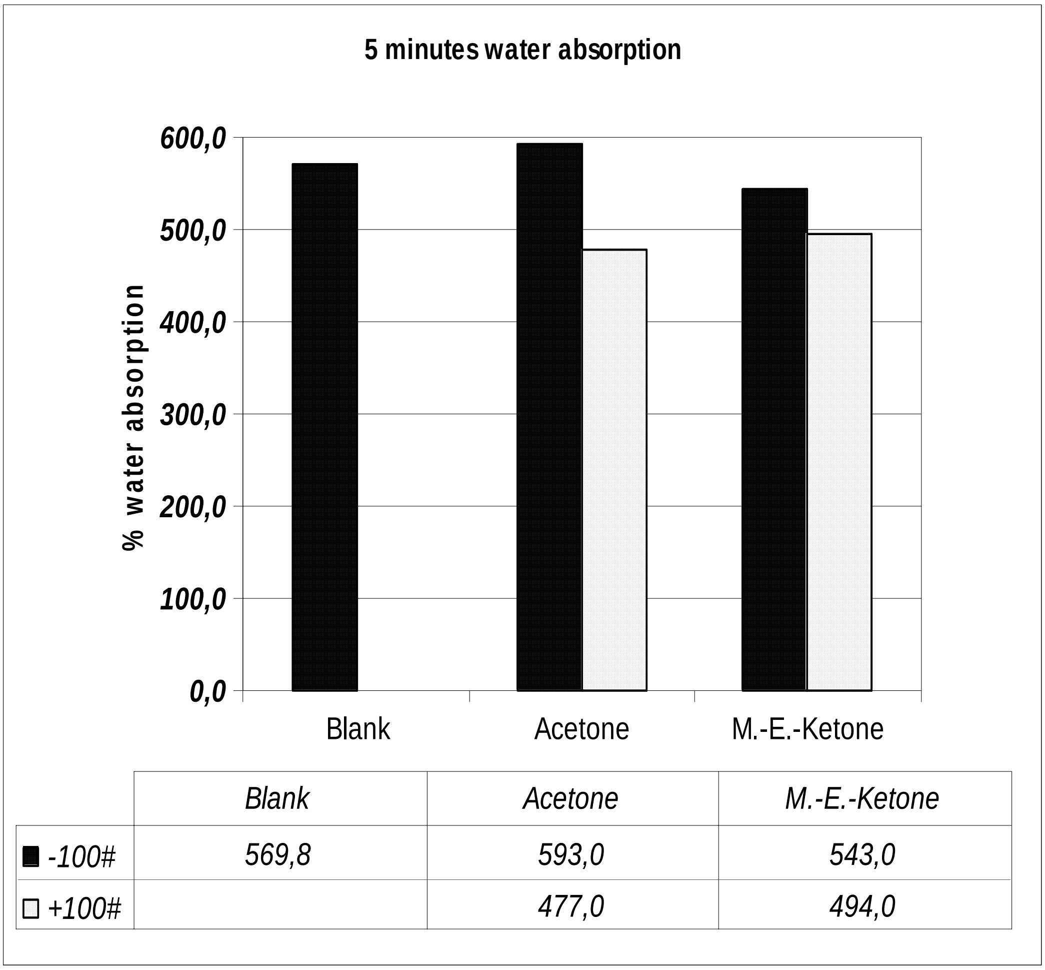
	Blank	Acetone	M.-E.-Ketone	N-Hexane
■ -100#	569,8	544,1	522,2	536,9
☐ +100#				562,3

Figure 30. Water Absorption tests of -100# and +100 fractions of bentonite dispersed in organic solvents followed by screening. Blending time: 4 minutes

Next, dispersion of bentonite samples were carried out exposing the bentonite samples to shaking forces for 5 minutes in the presence of organic liquids by using wet screen machine. The dispersion was effectively accomplished with the presence of acetone and methyl-ethyl ketone treated samples. The results are given in Table 10. However; the interaction of bulk bentonite with n-hexane was not sufficient for dispersion and showed no significant change. The water absorption tests indicate a clear improvement in the water absorption characteristics of acetone treated samples. The water absorption of bentonite samples for 5 minutes shaking experiments are given in Figure 31. The most satisfying results for purification of bentonite by blending and shaking were obtained for acetone treated samples.

Table 10 Dispersion and Water Absorption of Bentonite Shaking time: 5 minutes

Shaking time (minute)	The Organic Liquid Used			
	Acetone		Methyl-Ethyl Ketone	
5 minutes	% weight	% Water Absorption	% weight	% Water Absorption
-100#	94.529	593.0	86.984	543.0
+100#	5.471	477.0	13.016	494.0



	Blank	Acetone	M.-E.-Ketone
■ -100#	569,8	593,0	543,0
□ +100#		477,0	494,0

Figure 31. Water Absorption tests of -100# and +100 fractions of bentonite dispersed in organic solvents followed by screening. Shaking time: 5 minutes

4.4.2 Purification of Artificially Contaminated Bentonite by Using Non-Aqueous Media

The bentonite samples used in purification tests were highly pure. Therefore in order to investigate the purification of bentonite samples in the organic liquids, the bentonite was artificially contaminated by 20% quartz fraction by weight. The tests were realized by using a wet screen machine exposing the sample to 5 minutes of shaking. Most of the bentonite could be gained as -100 meshes by using acetone and methyl-ethyl ketone. The dispersion of bentonite by using n-hexane was smaller respectively. The results are given in Table 11.

Table 11. Dispersion and Water Absorption Tests for artificially contaminated Bentonite. Shaking time: 5 minutes

	Acetone		Methyl		Hexane	
5minutes	% weight	% Water Absorption	% weight	% Water Absorption	% weight	% Water Absorption
-100#	64.651	583.8	50.662	541.8	29.737	561.1
+100#	35.349	393.2	49.338	471.3	70.263	469.7

The water absorption characteristics of quartz contaminated bentonite samples were improved by dispersion in the shaking mechanism and eliminating the gangue in the presence of organic media. The acetone treated sample gave most satisfying results as it was also highly dispersed in the shaking mechanism as can be seen in Figure 32.

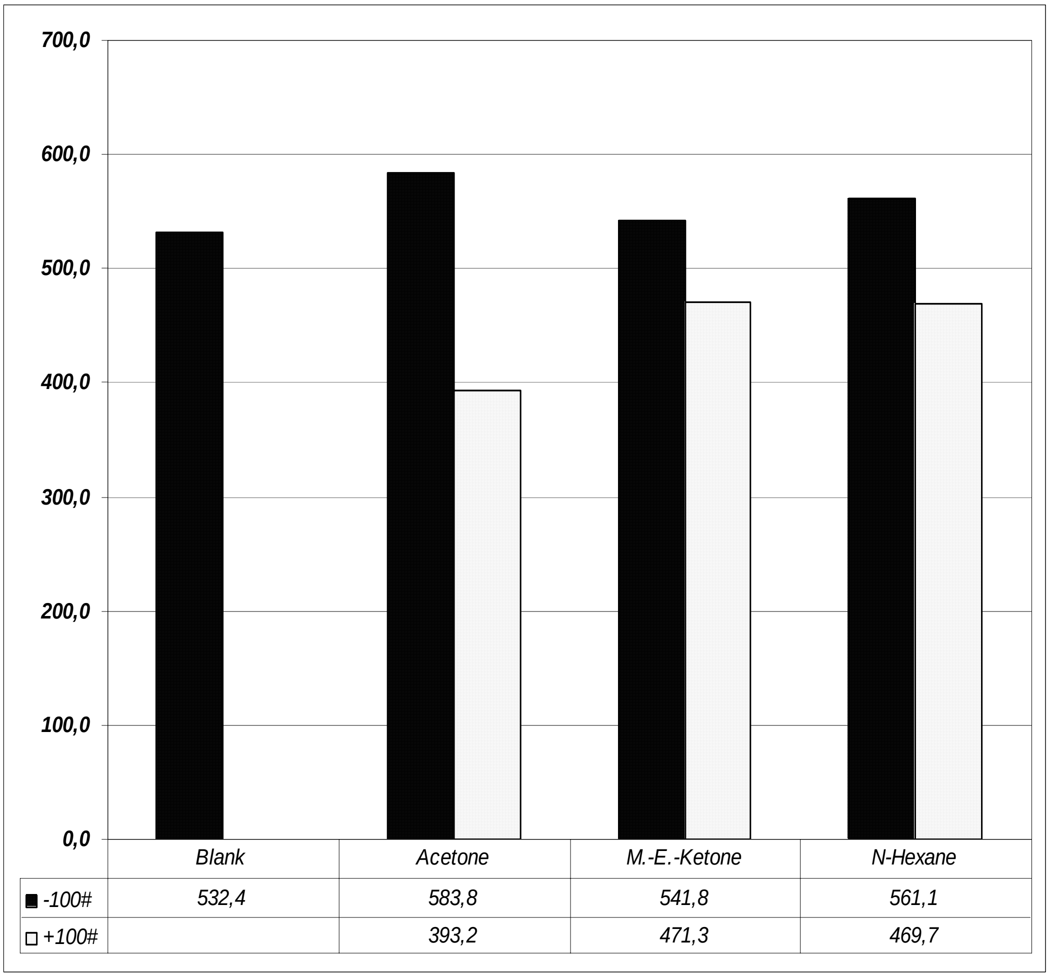


Figure 32. Water Absorption tests of -100# and +100 fractions of artificially contaminated bentonite dispersed in organic solvents followed by screening. Shaking time: 5 minutes

4.5 Bentonite Absorption Capacity for Sponge

Attempts were made for exploring a new kind of waterproofing bentonite sheet consisting of industrial sponge saturated with organic liquid treated swelling bentonite. During experiments the bentonite adsorption capacities of the sponges with different organic liquid bentonite slurries were determined.

The sponge cylinders used in the experiment were put in 100ml beakers and 25 grams bentonite in 50 ml organic liquid mixed organic liquid-bentonite slurries were slowly poured at the top of the sponge. The beakers were shaken for complete absorption of bentonite through the sponges. The sponges were dried and weighed, as explained in section 3.2.5. The test cycle was repeated until the sponges got saturated with bentonite. The weights of the sponges and the bentonite absorbed after each treatment is given in Table 12 and the weight of absorbed bentonite according to number of treatment is given in Figure 33.

Table 12. Bentonite absorption of Sponge

Number Of Treatment	Acetone-Bentonite with 0.994g sponge	m-e-ketone-bentonite With 0.993g sponge	n-hexane-bentonite with 0.982g sponge	Amount of Bentonite absorbed (acetone)	Amount of Bentonite absorbed (m-e ketone)	Amount of Bentonite absorbed (n-hexane)
1	20.946	21.376	16.113	19.952	20.383	15.131
2	31.569	45.616	30.403	30.575	44.623	29.421
3	42.023	46.669	40.187	41.029	45.676	39.205
4	45.052	46.334	46.315	44.058	45.341	45.333
5	45.339	*	*	44.345	*	*

* The sponge lost its ability to be used in experiment

According to procedure applied methyl-ethyl ketone-bentonite slurry was rapidly absorbed by the experiment sponge as can be clearly seen in the second recycled order of the experiment as shown in Figure 34. The test procedure was reapplied until the experiment sponges lost their property of absorbability and for all the non-aqueous slurry experiments ended up with similar absorbing capacities.

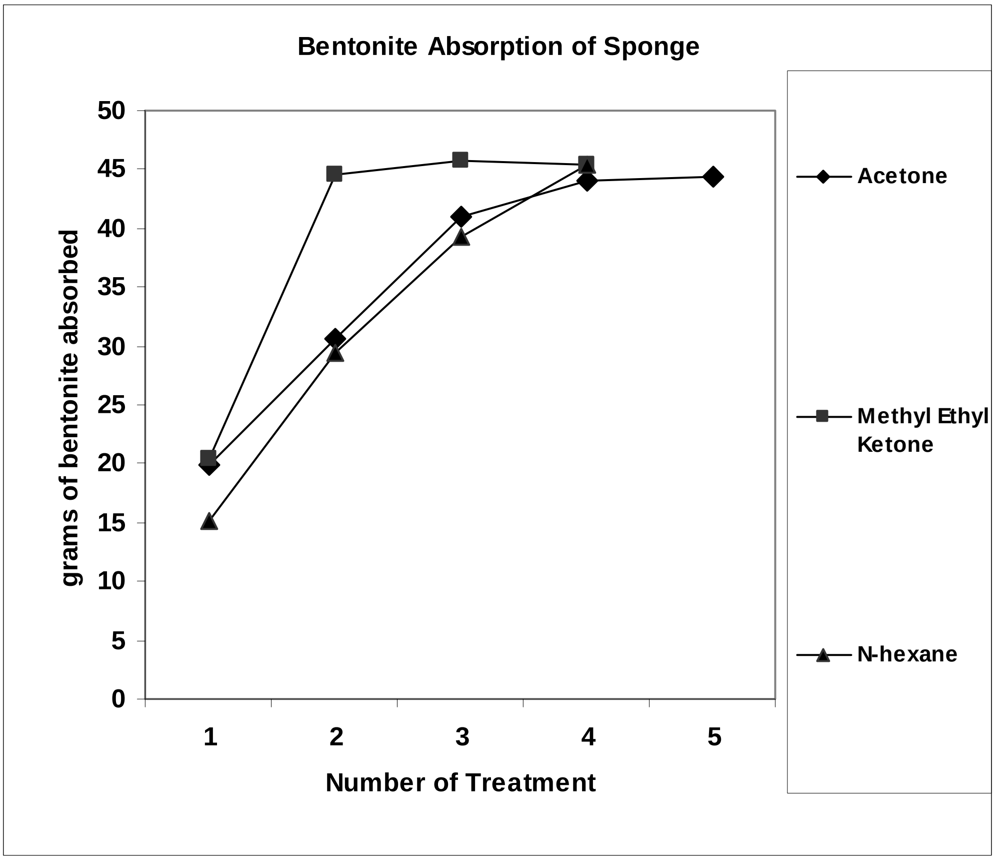


Figure 33. Bentonite absorption of sponge

The void volume of the sponges were determined as explained in section 3.2.5 by subtracting the polyurethane volume of the sponge from the actual volume of the sponge and are given in Table 13.

Table 13 Volume of the Sponges

Volume of the Sponges (cm^3)			Void Volume of the Sponges (cm^3)		
Acetone	M-E Ketone	N-Hexane	Acetone	M-E Ketone	N-Hexane
58.47	58.412	57.764	57.642	57.584	56.946

The volume of the bentonite absorbed and the percentage of void volume bentonite absorbed was determined and given in Table 14 and Figure 34.

Table 14.% Void Volume Bentonite Absorbed

Number of Treatment	Volume of the bentonite absorbed (cm^3)			% Void Volume Bentonite Absorbed		
	Acetone	M-E Ketone	N-Hexane	Acetone	M-E Ketone	N-Hexane
1	9.367	9.569	7.104	16.251	16.618	12.475
2	14.354	20.950	13.813	24.903	36.381	24.256
3	19.262	21.444	18.406	33.417	37.240	32.322
4	20.685	21.287	21.283	35.884	36.967	37.374
5	20.819			36.118		

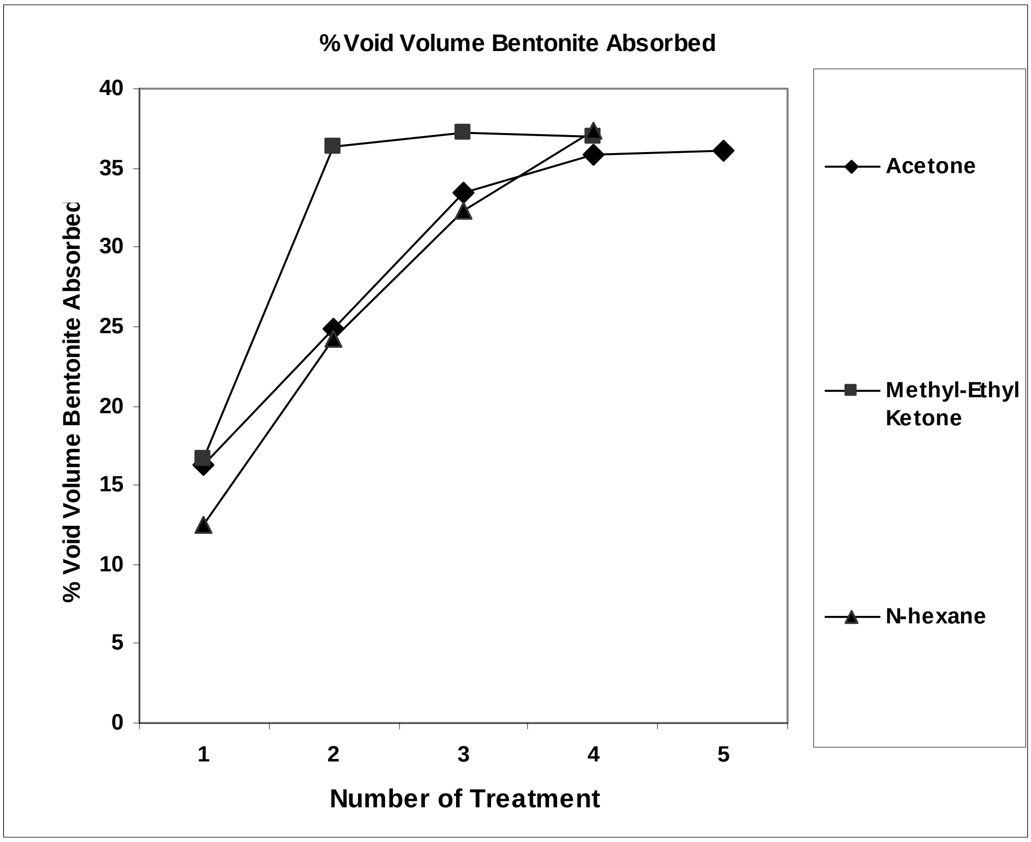


Figure 34. % Void Volume bentonite absorbed in the sponge Bentonite absorption of sponge

CHAPTER 5

CONCLUSIONS

1. Bentonite treated with acetone, methyl-ethyl ketone and n-hexane showed no structural changes as determined by TGA-DTG tests.

2. No significant changes were determined for the water absorption characteristics of acetone, methyl-ethyl ketone, n-hexane treated against untreated bentonite samples.

3. The rheological behaviour of bentonite slurries were investigated for high-solid pumpable slurry. As aqueous slurry showed pumpable properties up to 30-35 pounds/barrel, this concentration was as high as 125-150 pounds/barrel for acetone, 175-200 pounds/barrel for methyl-ethyl ketone and 325-350 pounds/barrel for n-hexane.

4. Dispersion of raw bentonite by exposing to high shear blending and shaking then eliminating the non-clay impurities were investigated. The bentonite was artificially contaminated with quartz (20 % by weight) and exposed to shaking. The water absorption tests were done for characterizing the samples. The presence of acetone gave the most appropriate results for purification of bentonite.

5. The possible method for deposition of bentonite in a sponge by saturating the sponge with bentonite using organic liquids was investigated. The tests resulted with similar bentonite quantities absorbed in sponges whereas the absorption of bentonite to the sponge with methyl-ethyl ketone treated bentonite slurry was significantly rapid.

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APPENDIX A

Table A1. Weights of Bentonite with wet filter for water absorption tests.

Weights of the Bentonites+Wet Filter Papers				
	Blank	N-Hexane	Acetone	M.-E.-Ketone
h(hours)	(grams)	(grams)	(grams)	(grams)
1	3.606	3.812	3.607	3.69
2	4.319	4.266	4.154	4.605
4	5.252	5.037	4.669	5.041
8	5.651	5.637	5.563	5.774
16	7.134	6.155	6.638	6.765
24	7.783	7.144	7.595	7.332
40	8.121	8.028	8.62	8.115
48	8.57	8.993	8.65	8.783
72	8.718	9.287	8.951	8.818

Table A2. Weights dry filter papers for water absorption tests.

Filter Paper (Grams) -Dry Weights				
h(hour)	Blank	N-Hexane	Acetone	M.-E.-Ketone
1	0.54	0.552	0.552	0.556
2	0.537	0.542	0.547	0.548
4	0.554	0.545	0.543	0.546
8	0.545	0.548	0.537	0.547
16	0.544	0.540	0.547	0.554
24	0.546	0.543	0.547	0.552
40	0.533	0.537	0.54	0.534
48	0.529	0.532	0.526	0.53
72	0.533	0.532	0.531	0.54

Table A3 Weights of Bentonite for 50 g/200 ml at 2 and 4 minutes purification of bentonite experiments

	Acetone	M.-E.-Ketone	Hexane
2 minutes	(grams)	(grams)	(grams)
-100#	39.02	38.39	28.27
+100#	7.44	7.83	15.96
4 minutes			
-100#	44.49	43.41	29.72
+100#	1.02	2.17	12.35

Table A4. Weights of Bentonite with wet filter papers for 2 and 4 purification of bentonite experiments

Weights of the Bentonites+Wet Filter Papers				
	Blank	Acetone	M.-E.-Ketone	N-Hexane
2 minutes	(grams)	(grams)	(grams)	(grams)
-100#	8.180	8.026	7.709	7.509
+100#	8.180	7.551	7.679	7.682
4 minutes				
-100#	8.180	7.889	7.715	7.89
+100#	8.180			8.071

Table A5.Weights dry filter papers for 2 and 4 minutes purification of bentonite experiments

Filter Paper (Grams) –Dry Weights				
	Blank	Acetone	M.-E.-Ketone	N-Hexane
2 minutes	(grams)	(grams)	(grams)	(grams)
-100#	0.531	0.519	0.536	0.55
+100#	0.531	0.534	0.54	0.544
4 minutes				
-100#	0.531	0.519	0.535	0.545
+100#	0.531			0.519

Table A6 Weights of Bentonite for 50 g/200 ml at 5 minutes shaking experiments

	Acetone	M.-E.-Ketone
5 minutes	(grams)	(grams)
-100#	41.99	37.69
+100#	2.43	5.64

Table A7. Weights of Bentonite with wet filter papers 5 minutes shaking experiments

Weights of the Bentonites+Wet Filter Papers			
	Blank	Acetone	M.-E.-Ketone
	(grams)	(grams)	(grams)
-100#	8.180	8.426	7.979
+100#	8.180	7.238	7.483

Table A8 Weights dry filter papers for 5 minute shaking experiments

Filter Paper (Grams) -Dry Weights			
	Blank	Acetone	M.-E.-Ketone
-100#	0.531	0.536	0.555
+100#	0.531	0.526	0.553

Table A9. Weights of Bentonite with wet filter papers for 5 minutes shaking experiments with gangue mineral

Weights of the Bentonites+Wet Filter Papers					
	Blank	N-Hexane	Acetone	M.-E.-Ketone	
	(grams)	(grams)	(grams)	(grams)	
-100#	7.859	8.115	8.32	7.908	
+100#	7.859	7.165	6.447	7.214	

Table A10. Weights of dry filter papers for 5 minutes shaking experiments with gangue mineral

Filter Paper (Grams) -Dry Weights					
	Blank	N-Hexane	Acetone	M.-E.-Ketone	
-100#	0.55	0.539	0.531	0.534	
+100#	0.55	0.526	0.543	0.538	

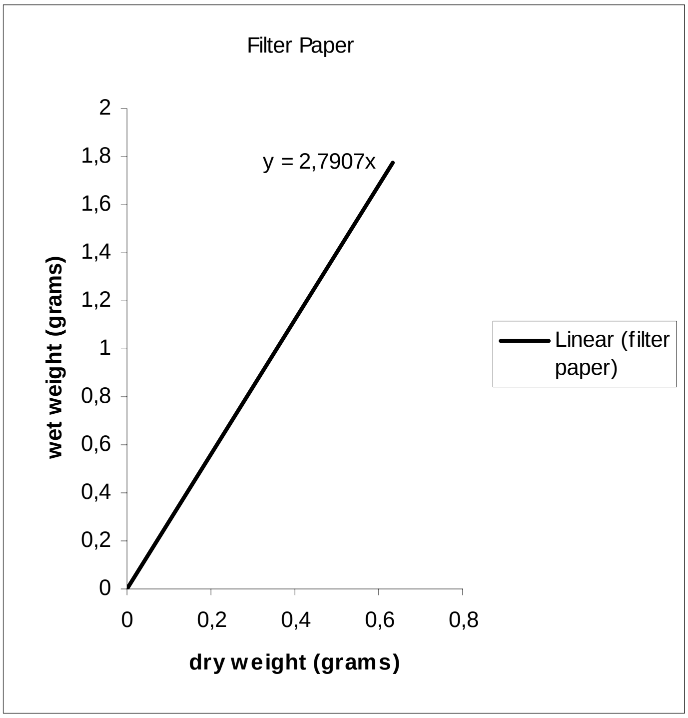


Figure A1 Water Absorption of filter paper

Table A11 Specifications for Acetone

Assay			99.5%
Colour Pt-Co			5 max
Density			0.7915 g/cm3
Water			0.18%
M			58.08g/mol
Flash point			-20 ^{0}C
Boiling Point			56 ^{0}C
Melting Point			-95 ^{0}C
Odor			Characteristic
$KMnO_4$ time (min)			>30
Acidity			0.0015%
Hydrocarbon Test			negative
Appearance			clear and free of susp
Solubility in Water			soluble
Ph			5-6

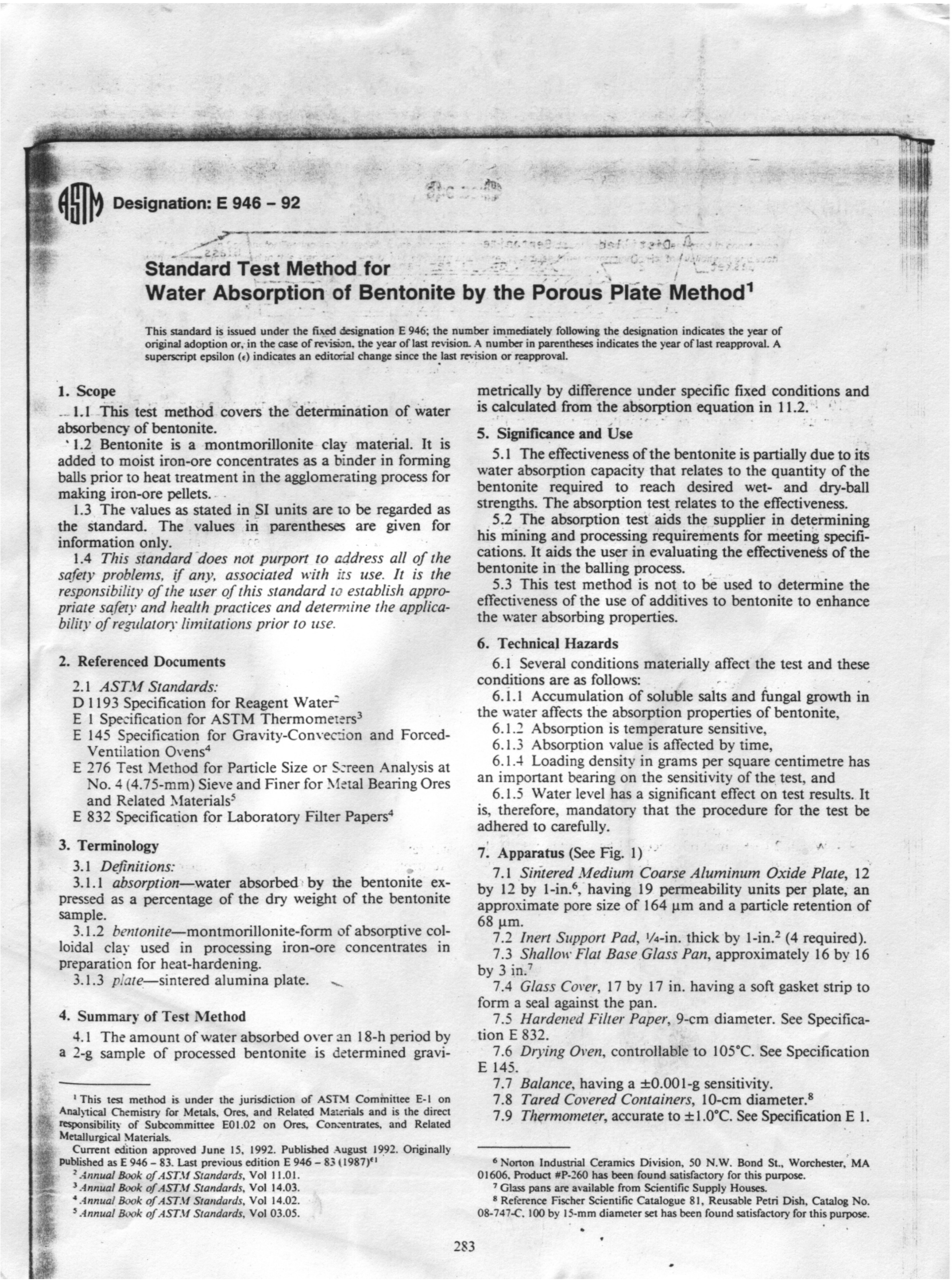
Table A12 Specifications for Methyl Ethyl Ketone

Density			0.805 g/cm3
Flash Point			-4 ^{0}C
Solubility in water			292 g/l
M			72.11 g/mol
Ph			5.5
Melting Point			-86 ^{0}C
Boiling Point			79 ^{0}C
Assay			99 ^{0}C

Table A13 Specifications for N-Hexane

Density			0.66 g/cm3
Solubility in Water			0.0095 g/l
M			86.18 g/mol
Melting Point			-94.3 ^{0}C
Boiling Point			69 ^{0}C
Assay			98% min
Water			0.01% max

APPENDIX B



Designation: E 946 – 92

Standard Test Method for Water Absorption of Bentonite by the Porous Plate Method[1]

This standard is issued under the fixed designation E 946; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of water absorbency of bentonite.

1.2 Bentonite is a montmorillonite clay material. It is added to moist iron-ore concentrates as a binder in forming balls prior to heat treatment in the agglomerating process for making iron-ore pellets.

1.3 The values as stated in SI units are to be regarded as the standard. The values in parentheses are given for information only.

1.4 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 1 Specification for ASTM Thermometers[3]

E 145 Specification for Gravity-Convection and Forced-Ventilation Ovens[4]

E 276 Test Method for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal Bearing Ores and Related Materials[5]

E 832 Specification for Laboratory Filter Papers[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *absorption*—water absorbed by the bentonite expressed as a percentage of the dry weight of the bentonite sample.

3.1.2 *bentonite*—montmorillonite-form of absorptive colloidal clay used in processing iron-ore concentrates in preparation for heat-hardening.

3.1.3 *plate*—sintered alumina plate.

4. Summary of Test Method

4.1 The amount of water absorbed over an 18-h period by a 2-g sample of processed bentonite is determined gravimetrically by difference under specific fixed conditions and is calculated from the absorption equation in 11.2.

5. Significance and Use

5.1 The effectiveness of the bentonite is partially due to its water absorption capacity that relates to the quantity of the bentonite required to reach desired wet- and dry-ball strengths. The absorption test relates to the effectiveness.

5.2 The absorption test aids the supplier in determining his mining and processing requirements for meeting specifications. It aids the user in evaluating the effectiveness of the bentonite in the balling process.

5.3 This test method is not to be used to determine the effectiveness of the use of additives to bentonite to enhance the water absorbing properties.

6. Technical Hazards

6.1 Several conditions materially affect the test and these conditions are as follows:

6.1.1 Accumulation of soluble salts and fungal growth in the water affects the absorption properties of bentonite,

6.1.2 Absorption is temperature sensitive,

6.1.3 Absorption value is affected by time,

6.1.4 Loading density in grams per square centimetre has an important bearing on the sensitivity of the test, and

6.1.5 Water level has a significant effect on test results. It is, therefore, mandatory that the procedure for the test be adhered to carefully.

7. Apparatus (See Fig. 1)

7.1 *Sintered Medium Coarse Aluminum Oxide Plate*, 12 by 12 by 1-in.[6], having 19 permeability units per plate, an approximate pore size of 164 μm and a particle retention of 68 μm.

7.2 *Inert Support Pad*, ¼-in. thick by 1-in.^{2} (4 required).

7.3 *Shallow Flat Base Glass Pan*, approximately 16 by 16 by 3 in.[7]

7.4 *Glass Cover*, 17 by 17 in. having a soft gasket strip to form a seal against the pan.

7.5 *Hardened Filter Paper*, 9-cm diameter. See Specification E 832.

7.6 *Drying Oven*, controllable to 105°C. See Specification E 145.

7.7 *Balance*, having a ±0.001-g sensitivity.

7.8 *Tared Covered Containers*, 10-cm diameter.[8]

7.9 *Thermometer*, accurate to ±1.0°C. See Specification E 1.

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[1] This test method is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.02 on Ores, Concentrates, and Related Metallurgical Materials.

Current edition approved June 15, 1992. Published August 1992. Originally published as E 946 – 83. Last previous edition E 946 – 83 (1987)$^{\epsilon 1}$

[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 14.03.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

[5] *Annual Book of ASTM Standards*, Vol 03.05.

[6] Norton Industrial Ceramics Division, 50 N.W. Bond St., Worchester, MA 01606, Product #P-260 has been found satisfactory for this purpose.

[7] Glass pans are available from Scientific Supply Houses.

[8] Reference Fischer Scientific Catalogue 81, Reusable Petri Dish, Catalog No. 08-747-C, 100 by 15-mm diameter set has been found satisfactory for this purpose.

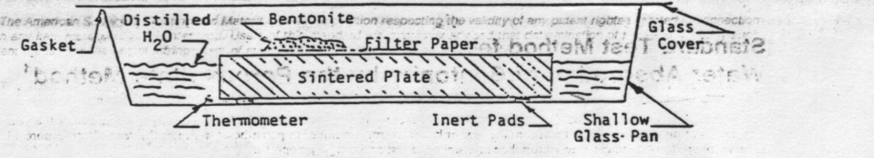

FIG. 1 Example of an Apparatus

7.10 *Washer-Type Template*, with a 5-cm diameter cut out for use in depositing the bentonite on the 9-cm filter paper.

8. Materials

8.1 *Bentonite Samples*, from the supplier or user inventory, ground to approximately 80 % of minus 200 mesh in accordance with Test Method E 276 and dried to a constant weight at 105°C (221 °F). The bentonite is described in 1.2.

8.2 *Distilled Water*—See Specification D 1193, Type II.

9. Procedure

9.1 Place a clean alumina plate that is supported by ¼-in. thick inert pads in the center of the pan and ensure the top of the plate is level. Before each test, add distilled water to within ¼ in. of the top of the plate, measuring to the water-plate contact, at least ⅜ in. away from the edge of the plate, then place the glass cover over the pan.

9.2 Allow the system sufficient time to reach ambient temperature.

9.3 Determine the average weight of a hydrated filter paper from the lot used in the absorbency test, by allowing four papers to absorb water on the alumina plate for 18 h and then weighing the papers.

9.4 Weigh 2 g (±1 mg) of processed bentonite, previously dried to constant weight at 105°C (220°F), onto the dry filter paper and spread it evenly within the 5-cm circle of the template on the 9-cm diameter paper. This can best be accomplished by using a vibrating spatula.[9] Remove the template and brush any remaining particles on top of the sample. Remove the template.

9.5 Place the paper and bentonite on the alumina plate. Up to four samples can be placed on the plate at one time.

9.6 Record the initial water temperature.

9.7 After 18 h, record the final water temperature. Carefully lift the filter paper and place it in a preweighed covered glass dish. Place a cover on the dish until ready to weigh.

9.8 Weigh the covered glass dish containing the hydrated paper and the hydrated bentonite.

TABLE 1 Derivation of Temperature Correction Factor, K[A]

Sample Number		77-219	77-218	77-230	78-292	76-40
18-h Average Water Temperature,		Water Absorption, Weight, %				
°F	(°C)					
63	(17.2)	664	907	756	745	579
73	(22.8)	650	938	768	753	606
		660	919	795	759	610
82	(27.8)	671	932	795	767	620
		676	942	781	787	624
Regression Analysis Slope, weight, %, °C		3.14	4.14	3.13	2.83	3.26

[A] Average temperature correction factor (slope) = 3.30 % weight/°C and 1.83 % weight/°F.

9.9 Following each test, the water should be changed and the plate and pan cleaned.

10. Calculation

10.1 Determine the net weight of the hydrated bentonite by subtracting the glass dish weight and the average weight of the hydrated paper from the total weight.

10.2 Calculate and report the absorbed moisture, as to the percent weight increase, over the dry bentonite weight as follows:

$$\text{Absorption, } \% = \frac{(Ww - Wd)}{Wd} \times 100 - (K(Ta - Tr))$$

where:

Absorption = water absorption (% weight) at 20°C/18 h,
Ww = net weight of hydrated bentonite, g,
Wd = net dry weight of dry bentonite, g,
Ta = average of initial and final water temperature, °C,
Tr = reference temperature = 20°C, and
K = temperature coefficient (weight, %/°C) = 3.30.

11. Precision and Bias

11.1 No statement is made about either the precision or the bias of Test Method E 946 since the result merely states whether there is conformance to the criteria for success specified in the procedure.

12. Keywords

12.1 bentonite; gravimetric; water absorption

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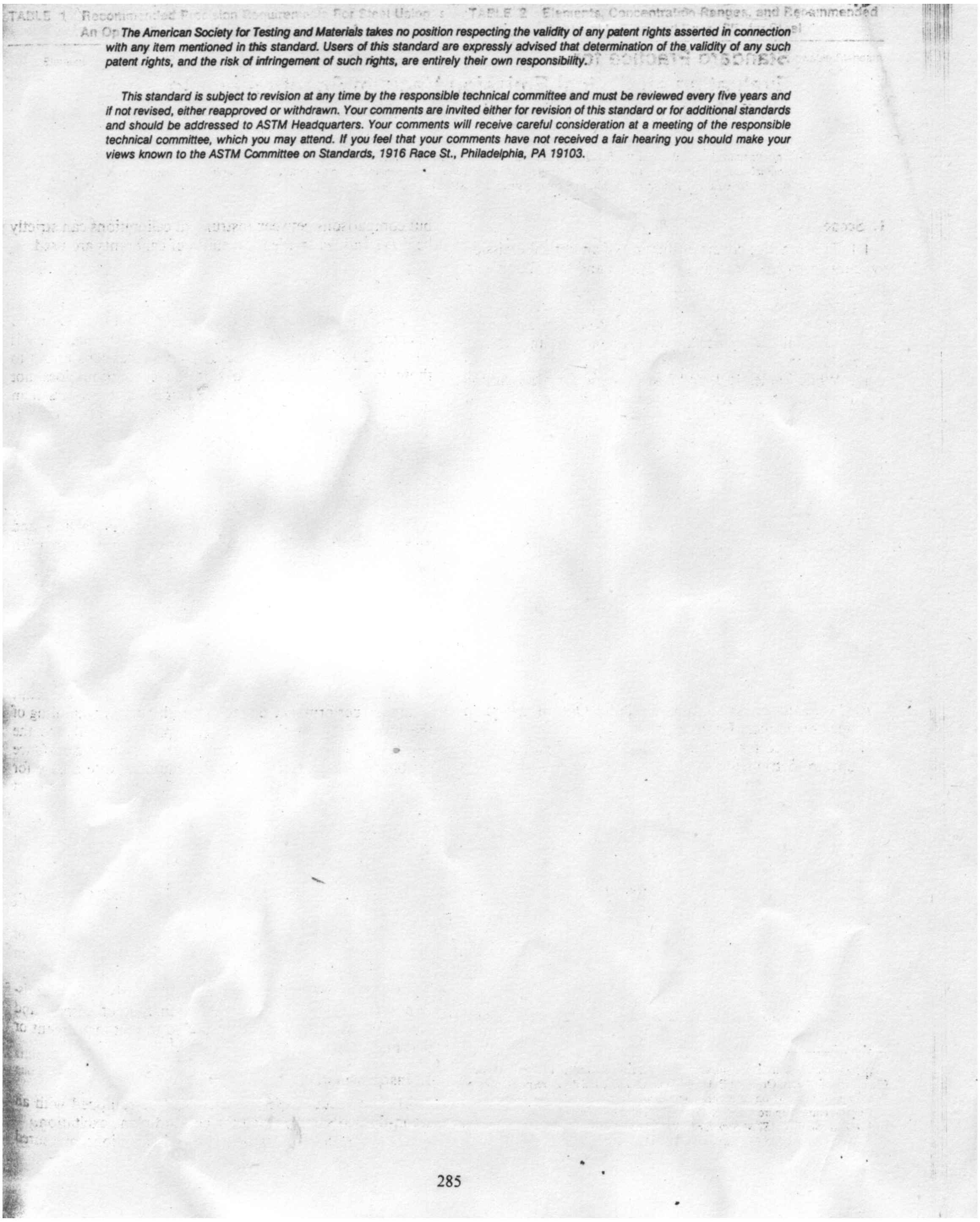
[9] Vibrating spatula manufactured by Mettler has been found satisfactory for this purpose.



APPENDIX C

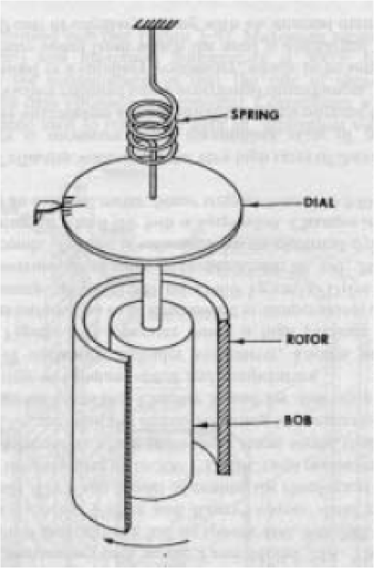
6.2 - Mud Viscosity:

There are two routinely conducted field measurements of viscosity:

- Qualitative measurement
- Quantitative measurement

The qualitative viscosity measurement or the funnel viscosity is a measurement used only to detect any variation in the viscous properties of the fluid. Marsh funnel is the instrument used for this purpose. The funnel viscosity is the time in seconds it takes for one quart of mud to flow out of the Marsh funnel. It is important to note that the funnel viscosity of a certain mud system is dependent on the flow properties of that mud, but not vice versa.

The quantitative field measurements of a mud system are accomplished by utilizing a Fann V-G meter. The numerical values of the mud properties obtained using a V-G meter are plastic viscosity, yield point and 10 second and 10 minute gel strengths.



The fluid viscosity at a given radius is related to the angular velocity, ω, by

$$v = r\,\omega$$

Thus, the change in velocity, v, with radius, r, is given as

$$\frac{dv}{dr} = r\frac{d\omega}{dr} + \omega$$

Assuming that the fluid layers were not slipping past one another but moving together as a solid plug, the change in velocity with radius would be

$$\frac{dv}{dr} = \omega$$

Thus, the shear rate due to slippage between fluid layers is

$$\gamma = r\frac{d\omega}{dr}$$

When the rotor is rotated, the torque, T, at the bob can be expressed for any radius between the bob radius and the rotor radius as

$$T = \tau\left(2\pi r h\right)r$$

The spring constant of the torsion spring is usually choosen as

$$T = 360.5\,\theta_N$$

where θ_N is the viscometer dial reading at rotational speed, N. Therefore, the shear stress can be defined as

$$\tau = \frac{360.5\,\theta_N}{2\pi\,h\,r^2}$$

In terms of viscometer dial readings, θ, and the rotational speed (rpm), the mud properties are calculated from the following expressions:
Newtonian Fluid : $\tau = \mu\,\gamma$

$$\mu = 300\frac{\theta_N}{N}$$

where μ is the Newtonian viscosity in cp, θ_N is the viscometer dial reading at rotational speed, N.

Bingham Plastic Fluid : $\tau = \tau_y + \mu_p\,\gamma$

$$\mu_p = 300\left(\frac{\theta_N}{N} - \frac{\tau_y}{N}\right)$$

For N=300 and 600 rpm:

$$\mu_p = \theta_{600} - \theta_{300}$$

$$\tau_y = 2\theta_{300} - \theta_{600}$$

where μ_p is the plastic viscosity in cp, τ_y is the yield point in lbf/100 ft^2

Power Law Fluid : $\tau = K\left(\gamma\right)^n$

$$n = 3.32\log\left(\frac{\theta_{2N} - \theta_o}{\theta_N - \theta_o}\right)$$

$$K = \frac{\theta_N - \theta_o}{\left(\gamma_N\right)^n}$$

where n is the Power Law index, K is the consistency index in lbf/100 ft^2(sec^{-1})^n and θ_o is the zero gel in lbf/100 ft^2. The shear rate, γ(sec^{-1}), can be expressed in terms of N as

$$\gamma = 1.7\,N$$

The control of the viscous properties of drilling muds within specified ranges is an essential prerequisite to the overall drilling cost control of a well. The importance of controlling mud viscosity is governed by the following factors:

- To maintain an optimum hole cleaning
- To prevent settling of weight material and drilled solids whether mud is in circulation or not
- To release generated cuttings at the surface for tray removal
- To control circulating frictional pressure losses in the circulating system
- To minimize swab and surge pressures during tripping and casing operations

The viscous properties of mud systems are governed by:

- The size, shape and amount of concentrations of total solids in the mud at a given temperature and pressure
- The flocculants or deflocculants added to the mud system
- The contaminants which are introduced into the mud during drilling