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Evaluation of Fine Particles Removal from Invert Emulsion Drilling Fluid by Novel

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Evaluation of Fine Particles Removal from Invert Emulsion Drilling Fluid by Novel
Technologies

by

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Abstract

Accumulation of fine particles in invert emulsion drilling fluids is known to adversely affect drilling performance and pose severe risks such as “stuck pipe”. Solid control systems fail to separate these particles mainly because of gelation and stable oil wet particles. As a result, the performance characteristics of the drilling fluid degrade over time. When a drilling fluid no longer meets operation requirements, or it is no longer cost-effective to treat the fluid, the fluid is replaced and a mud changeover is performed and the old drilling fluid becomes a waste. This research looks into the technologies capable of removing fine particles and recycling invert emulsion fluid to extend operation life or facilitate disposal.

Two novel technologies (i.e. microwave and ultrasound) are investigated to enhance phase separation and fine particles removal in invert emulsion drilling fluids. These two methods selectively target emulsion droplets and fine particles by heat generation (microwave) and orthokinetic, acoustic wake effect and mutual radiation pressure interaction mechanisms (ultrasound). In this thesis, invert emulsion drilling fluid was first contaminated with rev dust particles and aged for 24 h to simulate used drilling fluid. The contaminated samples underwent two treatments (i.e. microwave and ultrasound) for 5 minutes and centrifuged for 20 min at 3000 RCF, left at a standstill and visually observed for phase separation. The electrical stability and density of supernatant oil were measured along with microscopic analysis to provide an understanding of the mechanisms of phase separation after microwave and ultrasound radiation.

Microwave was proven to be very effective for dewatering invert emulsion and phase separation. More than 50% of the initial base oil in the invert emulsion was recovered by the microwave treatment after centrifugation. Ultrasound was not as effective as microwave in terms of phase separation; however, very large aggregates of rev dust particles were formed after 5 min of sonication. Both methods greatly improved the phase separation and centrifugation efficiency.

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LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURE

a	Particle radius
h	Height of the separated layer
H	Entrainment function
n	Total number of observations
r_0	Tube radius
r_l	Cap radius of the truncated cone
R_{Oil}	Volume ratio of the separated oil phase
$R_{Sediment}$	Volume ratio of the separated sediment
SS_E	Sum of squares of differences of observations within a treatment from the treatment mean
$SS_{Treatments}$	Sum of squares of differences between treatment means
SS_T	Total corrected sum of squares
U_p	Particle velocity
U_0	Fluid velocity
V_0	Volume of the truncated cone
y_{ij}	Response (i.e. phase separation)
\bar{y}_i	Average of i th row
$\bar{y}_{..}$	Average of all responses
γ	Interfacial tension
θ	Three phase contact angle
ρ_p	Particle density
τ_d	Relaxation time
ω	Angular frequency

PREFACE

Drilling fluid is used in the rotary drilling process to (1) clean the rock fragments beneath the bit and transport cuttings to the surface, (2) exert sufficient hydrostatic pressure to balance against subsurface formations to prevent formation fluids from flowing into the well, (3) keep the newly drilled borehole open until steel casing can be cemented in the hole, (4) cool and lubricate the rotating drillstring and bit [1]. It is known that rheological properties of drilling fluids have an enormous impact on the drilling efficiency. Drilling fluid properties including fluid loss, lubricity and viscosity have a great influence on the drilling Rate Of Penetration (ROP) and overall drilling costs; for instance, penetration depth is decreased by increasing mud weight and plastic viscosity. Drilling fluid additives, therefore, are added to the base fluid (i.e. water or oil) to enhance the performance of the system. Close and constant monitoring of drilling fluid properties is indispensable to maintain its influential properties during drilling. Physical and chemical properties of the drilling fluid are closely monitored by the drilling fluid specialist on sites to ensure desirable qualities in drilling. When a drilling fluid is no longer cost effective and meets sufficient requirements of the operation, the fluid is replaced and a mud changeover is performed, and the old drilling fluid becomes a waste. Since drilling fluid costs comprise a major part of overall drilling operation's expenses—in some areas, drilling fluid costs often exceeds \$1 million on a single deep well [1]— recycling and waste management techniques are of paramount importance to reduce both the total costs and environmental impact of drilling operations.

With the growth of upstream operations in the oil industry, more sophisticated and advanced technologies are required to address the need of drilling waste management. According to the American Petroleum Institute (API), more than 18 billion barrels of waste fluids from oil and gas production are generated annually in the United States. As a result, successful application of drilling waste management techniques would considerably reduce drilling costs; for instance, a newly developed Holistic Fluid Management (HFM) program by Mabile et al (2011) reduced USD 69 million in total while drilling more than 4,200,000 ft (1,280,000 m) in 705 wells in a 24-month study period [2]. In drilling waste management, similar to waste water treatment, there is a three-step hierarchy to minimize the adverse environmental effects:

1. Employ technologies to minimize produced waste,
2. Reuse and recycle,
3. If neither of these tiers is practical, disposal is the last resort.

In the past, drilling wastes were regarded as undesirable effluent to be disposed immediately; all waste management techniques fell into the third tier, disposal. Land spreading, road spreading and ocean discharge were three of the discharging techniques widely practiced in the past to dispose drilling wastes. Nowadays these techniques have to comply with environmental regulations and restrictions. Today, any drilling waste or cuttings to be discharged must first undergo a sheen test for the amount of hydrocarbon contamination. The Environmental Protection Agency, EPA, has completely prohibited the discharge of drilling fluids or cuttings into surface water or any type of drilling fluid within 3 miles of shore in offshore regions [3]. As a result, the overriding need is to minimize produced waste or recycle as much waste as possible.

The design of biodegradable drilling fluids is the first step to reduce drilling waste disposal. Drilling fluids biodegradability is enhanced by selecting stable non-toxic surfactants under harsh conditions, replacing high toxic components (e.g. aromatics) and converting oil wet to water wet particles in non-aqueous drilling fluids to ease phase separation. Other approaches to minimize drilling fluids environmental impact include using alternative weighting agents, new drilling fluid systems to target drilling fluid products and achieve better performance, etc. Design of synthetic based fluids was a major advance in offshore drilling that possess all the favorable drilling properties and are less toxic.

With the advent of solid control equipment and technological advances in recycling of drilling fluids, not only has the environmental impact of waste disposal been minimized, but also drilling operation costs have been significantly reduced. If the drilling fluid and cuttings cannot be managed through minimization, the waste is transported off-site to be recycled. Today, drilling wastes are disposed at their onshore well-sites or discharged to the oceans at offshore platforms; however, some drilling wastes may be sent to offsite facilities for further treatments before disposal [4]. Thermal treatment, injection, bioremediation and the use of drilling waste as a

construction agent are the current technologies commonly used to recycle and discharge the waste.

Any practical technique for waste treatment should be well-planned in advance dependent upon a priori physical and chemical properties of the waste. In drilling operations, the waste comprises of a wide range of components, namely drilling fluids, water, asphaltene and heavy oil components, cuttings, etc. Drilling fluids are generally composed of a liquid phase (i.e. oil and water) containing suspended, finely divided solids of various types; commonly used liquids are water, diesel crude oil, mineral oil or a mixture of these, and the solids include high-density solids such as hematite, barite, and clays such as bentonite, attapulgite, sepiolite and organophilic clay, and polymers such as guar and xanthan gums, cellulose derivatives, and polyacrylamides.

Oil based drilling fluids have great performance in drilling shale formations and significantly increase the Rate Of Penetration and lubricity of the drilling bit. Diesel, synthetic and mineral base oil are the most common base oils used for drilling in extreme environments. Due to the environmental footprint of diesel oil (i.e. high toxic aromatic content), synthetic and mineral oil with lower toxicity are widely used to reduce the environmental impact of drilling wastes. The oil should also be relatively free of toxic polyaromatic hydrocarbons because they corrode the drilling tools and soften the blowout preventers. All of the commercial base oil contains from 5 % up to 50 % of water either contaminated from the formation or added initially to increase the viscosity or activate the clay particles in the drilling fluid. To overcome the problem of contamination of water, an emulsifier is added to the fluid to form some stable water-in-oil emulsions. "*Invert emulsions drilling fluids*" is the term for water-in-oil emulsions which mostly contain oil as the continuous phase and emulsified water.

As drilling fluid is reused for the drilling of multiple wells, it accumulates low gravity solids (solids with specific gravity of less than 2.8 g/L) and fine particles, which adversely affects the drilling efficiency by viscosity build-up, enhancing torque and drag, increasing the risk of pipe sticking, etc. Solid control facilities fail to fully separate low gravity solids. Shale shakers can remove drill solids down to 177 microns by 80-mesh screens. Furthermore, common distillers and disanders operating in higher pressures are capable of removing up to 95 % solid particles

larger than 15 microns. Centrifuges are often used in weighted mud systems to maintain the mud properties without diluting. Operating range of G-force for a typical centrifuge is between 900 up to 3000 G-force with retention time in the order of seconds. Centrifuges can remove fine solids down to two microns. Even though current solid control equipment can remove fine particle down to two microns, also known as ultrafine particles, its efficiency greatly varies accordingly as the rheological properties of the influent change. There are a number of unwanted factors that impact the rheological properties of drilling fluid in real-time drilling: water contamination, shale formation drilling, and fine particles build-up. Poor separation of fine solids from invert emulsions is attributed to the specific drilling fluids properties gained from the interaction of fine solids with invert emulsions such as gelation and solids' build-up into the oil-water interface. The gelation of fine solids in emulsion leads to solids retention while exerting mechanical forces (e.g. centrifugation). Moreover, solid particles diffused into the oil/water interface form rigid structures (films) that can sterically inhibit the coalescence of emulsions droplets and hence this film stabilizes the emulsions. Furthermore, solid particles in invert emulsions are oil wet that complicates the flocculation. Conventional methods (e.g. chemical treatment) are limited by high viscosity and poor diffusivity of fine-solid-contaminated invert and lead to a secondary source of pollution.

Regarding the shortcomings of the current technologies, further research is necessary to devise novel approaches to address the problem of solids retention. The **scope** of this project is to evaluate potential methods to enhance fine particle separation efficiency from drilling fluids through emulsions breaking, by means of physical treatment. We postulate that two physical treatments (i.e. microwave, ultrasounds) could enhance the fine particles separation. The first phase of this study is an evaluation of the bases for solids retention of invert emulsion drilling fluids. A series of experiments are designed to investigate the impact of several factors (e.g. pH, temperature, clay content) on the particles suspension in invert emulsion drilling fluids. The second phase is to remove the contaminated invert emulsion drilling fluids with the aid of microwave and ultrasound methods and their impact is assessed based on the phase separation.

This thesis is divided into four chapters. Chapter 1 provides a literature overview of the current technologies in waste water treatment and their applications, followed by a review of chemical

treatment methods used for waste water treatment and drilling fluids recycling. Novel technologies and a comprehensive review of their applications are introduced in the last section of **Chapter 1**. **Chapter 2 and 3** present the methodology used in the experiments, and results and discussion respectively. At last, conclusions are given in **Chapter 4**.

CHAPTER 1

LITERATURE REVIEW

1.1 Waste Water Treatment Technologies

Today a large number of waste water technologies are applied to other industries; for instance, water-based flotation process has been widely applied to the separation of bitumen from oil sands in Alberta [5]. Nowadays commercial oil sand recovery is comprised of a hot water treatment process that incorporates flotation as a significant unit operation. Flotation is a process of separation widely used in the wastewater treatment and mineral processing industries. More recently, electrophoresis has been successfully tested for fine particles separation from invert emulsion drilling fluids [6]. As a result, reviewing waste water treatment methods could give an insight into finding a practical remedy for drilling waste management. Drilling waste is heavily laden with solids, heavy oil components, such as asphaltene, to be removed before disposal. In this chapter, a number of the current waste water technologies are discussed and briefly described in terms of hydrocarbon and solid removal. A variety of waste water treatments exists for most wastes, but the methods vary in costs and efficacy. In other words, because produced water characteristics vary from each unit to another, a unique technique cannot be recommended for achieving all environmental standards, recycling and reuse requirements.

1.1.1 Removal of Suspended Hydrocarbons

1.1.1.1 Gravity Separation The constituents are separated from one another because of the Specific Gravity differences. The settling rate of particles is dictated by Stoke's Law. In a settling tank, water is typically passed through large tanks to allow the phase separation. Parallel plates in these tanks absorb the oil droplets and allow them to coalesce faster into larger droplets. Plate separators are relatively large and are not effective for very small oil droplets. They can reduce oil concentrations to 2-25 mg/l, with an average of 15 mg/l and can remove oil droplets down to about 20-30 micrometers in diameter. Plate separators may have some operational problems in some conditions such as plugging of plates, inability to handle emulsion, platform motion, oil slugs and surge loads. Even though

gravity separation is highly efficient in terms of simplicity and economic advantages, further advanced methods are required to separate stable emulsions and smaller particles.

Swirling or vortex accelerates the gravity separation by causing a relative pressure difference between the surface and bottom of the separator. The difference exerts a downward force on denser particles and settles them in the center of the separator. Moreover, the greater radial velocity in hydrocyclones accelerates the normal gravitational force. Hydrocyclones can be used to further separate oil and water. Depending on the conditions, hydrocyclones can reduce oil concentrations down to 10 ppm, but 30 ppm is a more common average. The operational problems encountered in this method are erosion, corrosion and sand build up. Inlet pressure for hydrocyclones should be sufficient enough to drive the flow and induce a spinning in the hydrocyclone [7]. Decanting centrifuging is another related technique to enhance gravity separation. Centrifuges differ from hydrocyclones in that the spinning is mechanically driven in a centrifuge. Vanden Broek and Vander Zande compared oil removal efficiencies of different de-oiling systems. Their rankings with respect to performance of three physical separators were: centrifuges, hydrocyclones, and plate separators. In addition to the low removal efficiency of these systems, dissolved and hazardous components could not be removed [8]. A number of studies are ongoing to enhance the separation efficacy of hydrocyclones. Recent developments in this method include incorporation of gas flotation to separate phases such as Epcor Compact Flotation Unit (CFU). Miller et al. (1981) first suggested the use of air-sparged hydrocyclone simply by introducing gas through membrane porous membrane while wastewater is pumped through the hydrocyclone [9]. Liu et al. successfully used a new type of double-cone air-sparged hydrocyclone for produced water from polymer flooding with a viscosity range of 2.5 - 4 cP [10]. Miller (1981) first suggested the use of ASH for separation of particles from fluid suspension [11]. Gas is introduced through the porous membrane while wastewater is pumped through the hydrocyclone. A schematic diagram of typical hydrocyclone is shown in Figure 1.1.

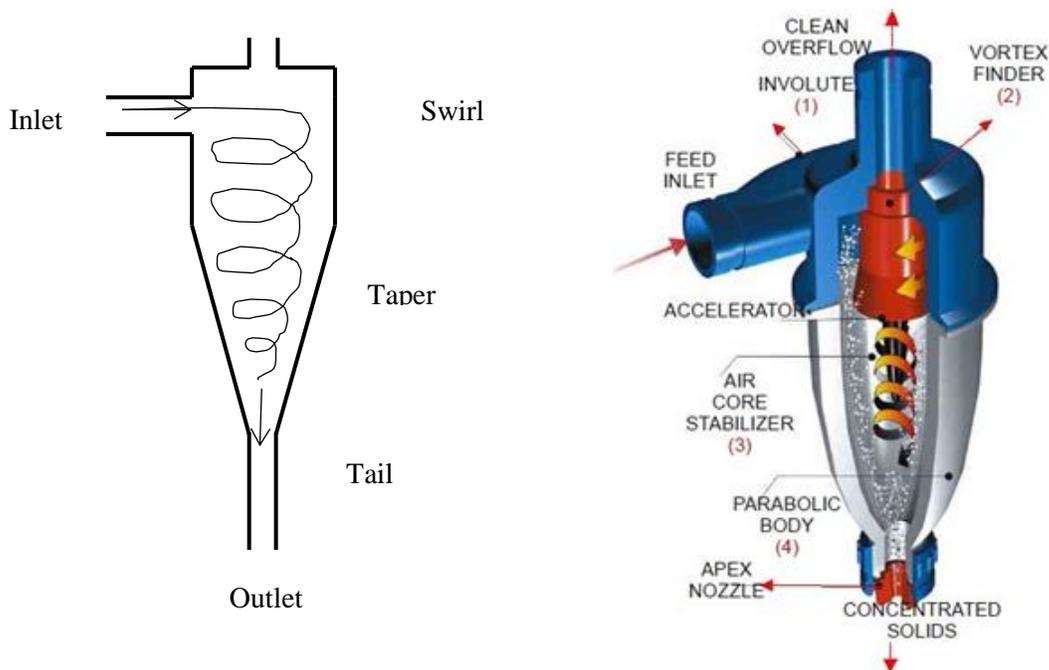


Figure 1.1 A schematic diagram of a typical hydrocyclone and distiller. Waste is fed through inlet and separated to a light overflow and heavy underflow [7].

1.1.1.2 Heat Treaters heat the influent to lower fluid viscosity and interfacial tension allowing the oil and water to separate faster. More energy intensive techniques include evaporation/ distillation used to purify and remove dissolved hydrocarbons in the influent. The technique poses several considerable difficulties, namely a large energy input is required (more than 95% of the operating cost of distillation is energy), concurrent condensation of chemical contaminants with low boiling points with water, hazards of hydrocarbons' vapors at high temperature, alteration of chemical structures rendering them useless in some application such as drilling muds, forming a heavy residual tar on the solids which cannot be distilled, and pyrolysis and coke formation at higher temperatures [7]. Becker proposed wastewater distillation using two Proprietary New Designed Systems (PNDS) that recovers over 95% of the energy required to distill water as follows:

1. New Mechanical Vapor Recompression (MVR) system to recycle produced water into distilled water
2. Waste steam as the feed to produce distilled water

Becker also studied the effectiveness of water purification technologies for dealing with various types of contaminants and concluded that distillation is the preferred method because of its ability to deal with various types of contaminants [12].

1.1.1.3 Gas Flotation if gas bubbles are propelled through an emulsion of oil-in-water, the oil droplets will attach to the bubbles and be carried to the top of the mixture where they can be easily skimmed out. Rubio et al. could reduce oil concentrations to 15-100 mg/l for a waste water influent with a typical average of 40 mg/l [13]. Gas flotation is often aided by the addition of chemical coagulants such as carbon dioxide. The difficulties in this method are inability to handle emulsions, level control problem¹, platform motion, oil slugs, poor froth formation, interference with treatment chemicals, poor mechanical durability, scale/sludge buildup, creation of foam, and being operator maintenance intensive [7]. In addition, micro-bubbles do not float dense and big particles, especially at high solids content (4–5%, w/w). Lemlich (2012) divided all flotation processes into two adsorptive flotation and adhesive flotation based on the substrate solubility [14].

A number of techniques for both conventional and emerging flotation were described by Rubio et al [13]. Also a number of techniques were proposed for removal of ions, e.g. precipitate flotation, gas aphyrons flotation, etc., which do not necessarily result in the foam formation. Since the flotation depends on multiple interconnected factors, many considerations should be taken into account when selecting a flotation device, its capacity, and the techniques to be employed such as equalization² of the influent waste, gas input rate and volume of gas entrained per unit volume of liquid, bubble size distribution and degree of dispersion³, surface properties of the suspended compounds, hydraulic design of the flotation chamber, concentration and type of dissolved and suspended materials, chemicals added, and temperature and pH of the influent need to be taken into consideration.

¹ Controlling flotation bank pulp levels to maintain consistent pulling rates in the face of changing feed slurry flow rates, varying mineral types, and inconsistent addition reagent additions can be daunting [154].

² Equalization is essential since industrial waste fluctuates in quantity and quality and most treatments are sensitive to flow rate, PH and temperature.

³ The number and size of the bubbles are a function of both physical and chemical content of waste water. Katz reported that as surface tension decreases, smaller bubbles in large numbers are formed [60].

1.1.1.4 Filtration Another technique to remove oil droplets from water is to pass the water through water-wet filters or membranes to trap oil by capillary pressure. More advanced filtration processes include cross flow membranes such as microfiltration and ultrafiltration. Some current literature studied the efficiency of the use of ultrafiltration and surfactants in removing oil droplets. Microfiltration processes may be ineffective for hydrocarbon removal because the filters and membranes foul easily by oil and have short useful lifetimes. Chen et al. pretreated the produced water chemically to prevent the membrane fouling. They also studied the effects of experimental parameters, e.g. pore diameter, feed concentration, etc. on the pressure rise [15]. In a study by Li et al., they studied a tubular ultrafiltration model equipped with polyvinylidene fluoride membranes modified by inorganic nano-sized aluminum particles to treat oilfield produced water and concluded that nano-sized alumina particles can improve antifouling performance of membranes [16].

In water treatment plants using membranes, microorganisms attach to the membrane surface, grow and form a biofilm layer which causes flux decline. Non-biological substances are also involved in biofilm development by serving as nutritional substrate [17]. As a result, control of fouling is of utmost importance in membrane technique. Some techniques have been suggested to alleviate fouling such as pretreatment of feed which can reduce the particulate density onto the membranes [18]. Lee et al. studied a treatment process by ultrafiltration preceded by a hydrocyclone to reduce the oil concentration to less than 50 ppm. They reduced the total oil and grease concentration to less than 2 mg/L with the operating cost of 9.7 cents/bbl for a full scale membrane. Pretreatment and washing were done frequently to prevent membrane fouling [19].

1.1.1.5 Chemical Coagulants The technique is commonplace to overcome the electrostatic repulsion on droplets or solids and allow them to coagulate into larger agglomerates. Coagulation and flocculation can be used to remove suspended and colloidal particles, but are not effective for removing dissolved constituents [20]. Common chemicals used include lime, alum, and polyelectrolytes. A number of chemical treatment methods have

been suggested in different literature: chemical oxidation⁴, electrochemical process, photocatalytic process, fenton process, treatment with ozone, and use of demulsifier. Li et al. compared treatment of produced water by photocatalysis, electro-oxidation, and photoelectrocatalysis. Results showed that at equivalent doses, photoelectrocatalysis exhibited the greatest capability to reduce genotoxicity, whereas photocatalysis was the least effective and did not cause appreciable change in mutagenicity, but results of both biological and chemical analysis indicated that photoelectrocatalysis was the most effective technology for degradation of oilfield wastewater [21]. Electrocoagulation or electrochemical processes are other techniques to separate oil from water by applying electric voltage. Because oil-water emulsions are negatively charged, they migrate toward the positive electrode. Metal hydroxide such as iron and aluminum hydroxides can be used along electric field to aid in neutralization and flocculation of the droplets. Chemical methods are only effective if properly applied, but it suffers from several pitfalls, namely susceptibility to changes in influent quality and larger volumes of waste, customization at every site to determine the type and the quantity of chemicals required, close controlling and skilled operating to achieve optimal operation, large volume of sludge production, significant footprint, high operating costs, depending on the application, corrosion due to acidification, mechanical problem due to clogging of chemical feeding lines [22]. Moreover, non-target dissolved solids can consume the chemicals, hence affect the target dissolved solids' costs, some side products are undesirable, and many of the products of chemical reactions become dissolved solids [12]. A comprehensive review of chemical treatments and mechanisms is given in Chapter 2.

1.1.1.6 Biological Processes The principal aim of bioremediation technologies is to select and cultivate tolerant degraders to survive in the highly contaminated media such as drilling fluids. Unfortunately, the tolerance of most microorganisms is very low, and therefore, not well suited to high aromatics environment. Furthermore, the mechanism is too slow and is not appropriate for real time drilling operations. Large quantities of oil can limit mass transfer of oxygen and nutrients to bacterial colonies that degrade the hydrocarbons. Also a large amount of space is needed for a separator unit.

⁴ Chemical oxidation is the usual method for decomposing refractory chemicals in wastewater in which a strong oxidant, catalysts, and irradiation are used (except ozone treatment).

Water wastes contain dissolved hydrocarbon in addition to suspended hydrocarbon and solid particles. A variety of techniques are available in the industry to remove dissolved hydrocarbons. Because the research is not concerned with removing dissolved hydrocarbons, we skip over the techniques. The techniques commonly used in waste water industry are adsorption, volatilization, air stripping [23], precipitation, ultraviolet irradiation and biological process.

1.1.2 Removal of Suspended Solids

Removing suspended solids from wastes has a practical application in treating drilling fluid suspended solids such as drill cuttings, clay particles' contamination, etc. prior to disposal or recycling. A variety of techniques exists to separate solids from any contaminating water or hydrocarbon (e.g. gravity separation, filtration, heating, and coagulation). These techniques are sub-grouped into water and hydrocarbon removal dependent upon their primary treatment objective.

1.1.2.1 Removal of Water

The most common dewatering technologies to treat drilling cuttings and reserves pits are shale shakers, settling ponds, or hydrocyclones widely used to separate free liquid and larger solids from drilling fluids. To further reduce the water content of the sludge, more advances (and expensive) technologies can be employed including high-pressure filter presses, centrifuges, and vacuum filtering [7]. The dewatering of most fields can be improved by preconditioning before mechanical separation with nonionic or low charge anionic polymers with high molecular weights. Wojtanowicz et al. have comprehensively studied the chemical dewatering of drilling fluids [24] [25] [26] [27]. The effectiveness of mechanical methods is largely dependent on the solid type and size, initial contamination level as well as physical parameters of the solid waste. The smaller the solid size, the more pronounced the effect on the fluid properties and more difficult to remove or control its effect. The largest formation particles are rock cuttings, the size typically larger than 0.1 to 0.2 mm, removed by shale-shaker screens at the surface. Smaller particles, typically larger than about 5 μm , will pass through the screens, and must be removed by centrifuge or other means [28]. A schematic diagram of typical mud removal

system with mud cleaner and centrifuge is shown in Figure 1.2. Wojtanowicz et al. studied the effectiveness of several mechanical separations methods for reserves and production pits. Waste volume reduction for belt press and centrifuge is almost the same for reserve pits, however belt press outperforms centrifuge in terms of volume reduction for production pits.

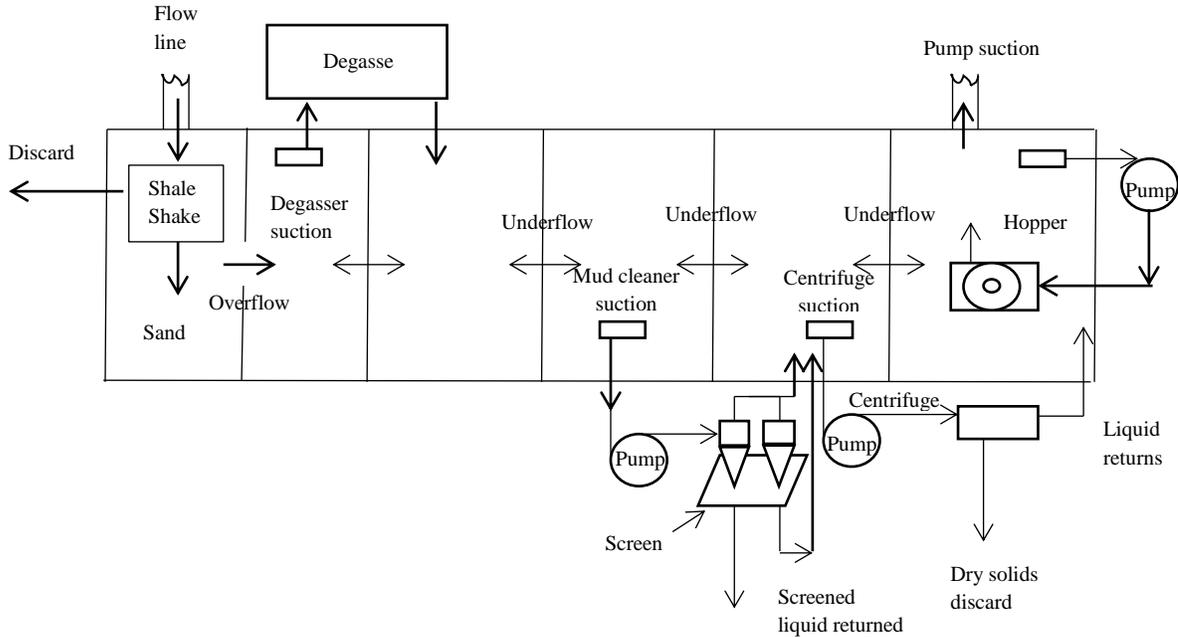


Figure 1.2 A schematic diagram of typical mud removal system with mud cleaner and centrifuge [30]

1.1.2.2 Removal of Hydrocarbon

A number of techniques are available to remove hydrocarbon from solids, namely washing, adsorption, filtration, heating, solvent extraction, incineration, and biological degradation. In washing, solids or slurry are to be washed with upward-flowing high-velocity water or fed into low toxicity base oil tank to reduce the original hydrocarbon or replace the original hydrocarbon with a lower toxicity hydrocarbon. A solvent with a low boiling point can be used to wash the oil from solids and to be separated and reused by a distillation method. In adsorption process, organic compounds of produced water are adsorbed onto the porous membrane of activated carbon, organoclay, copolymers, etc. Activated carbon can remove soluble BTEX⁵, but organoclay⁶ can remove insoluble free

⁵ Benzene, toluene, ethylbenzene, and xylenes

hydrocarbons that contribute to Total Petroleum Hydrocarbons (TPH). The difficulties encountered in this method are the high cost of adsorption in relation to the amount of dissolved solids removed, not all dissolved solids will adhere to inexpensive media, and the media has to be treated as a hazardous waste.

Removing dissolved solids is absolutely vital for waste water treatments because most waste water contains dissolved solids such as salt, heavy metals and hardness ions. Hardness ions readily precipitate and cause fouling of equipment. Some of the available techniques to treat these waters are ion exchange [29] [30], precipitation [31], reverse osmosis and evaporation/distillation [7] [12].

1.1.3 Summary

A number of state-of-the-art technologies and their applications were briefly discussed in the preceding sections. Gravity separation is the most economical method in terms of cost and efficiency; however, further complementary techniques are required to meet the standards of the stringent regulations. Some of the described techniques such as filtration may not be well suited to drilling wastes because drilling fluid contains a large amount of solid particles which may foul the filters. A number of factors need to be taken into the account when designing a unit process for all treatment industries:

1. How clean the final outlet from our plant must be;
2. The quantities and the nature of the influent we need to treat;
3. The physical and chemical properties of the pollutants we need to remove or render neutral in the influent;
4. The physical, chemical and thermodynamic properties of the solid wastes generated from treating the influent; and
5. The cost of treating the influent, including the cost of treating, processing and finding a field for solid wastes.

⁶ Organoclay is produced by combining sodium clay with a cationic quaternary amine salt.

In addition to the aforementioned technologies, there are a variety of novel methods to treat waste water and sludge, namely energy intensive technologies such as Ozone, and solidification. These techniques have not been incorporated in this thesis due to less pertinence and feasibility.

1.2 Drilling Fluids, Coagulation and Flocculation

1.2.1 Drilling Fluids

There are three principal types of drilling fluids classified according to their base: water base muds, oil base muds (i.e. invert emulsion mud) and gas. Air or gas is used in low pressure hydrocarbon formations to circulate cuttings out of the wellbore. This type of drilling fluid offers several advantages such as little formation damage, prevention of lost circulation and higher penetration depth. However, the use of gas or compressed air requires special surface equipment to ensure safe management of the cuttings and formation fluid.

Water based muds are the most commonly used drilling fluids. In many drilling wells, available natural water in the area is used in the water based drilling fluids, and therefore, incurs lower costs on drilling operations. Some clays hydrate readily in water and greatly increase the fluid's capacity to carry the rock cuttings to the surface. The clay particles also form a mud cake on the wall that reduces the amount of water loss to the permeable zones. Even though adding clay particles to water based mud can have beneficial effects, the presence of hydrated clay has undesirable effects such as a reduction in penetration depth and an increase in frictional pressure loss.

Oil based or invert emulsion drilling fluids remedy certain deficiencies of water based mud. Oil based mud is an alternate term for invert emulsion mud, where water is emulsified in oil. Invert emulsion drilling fluids offer a more inhibitive behavior in terms of clays hydration than its water based counterpart. In addition, invert emulsion muds have superior lubricating characteristics and exhibit good rheological properties at temperatures as high as 500°F. On the other hand, Invert emulsion muds are generally more expensive and require stringent pollution control protocols. However, the higher initial mud and disposal costs are offset against the operational advantages of drilling in troublesome formations (e.g. drilling in shale formations) because oil does not react with shale beds.

There is a large application of invert emulsion drilling fluids in the formations adversely affected by water base muds. A typical invert emulsion drilling fluid is comprised of between about 50:50

to 95:5 by volume oil phase to water phase, a primary emulsifier, weighting agent such as clay. Invert emulsion drilling fluids are commonly formulated with diesel, mineral oil or low toxicity olefins and paraffins. The emulsion should remain stable after water contamination. Bentonite mostly composed of smectite clays is commonly used as the primary emulsifier.

Smectite (e.g. sodium bentonite) is one of the clay mineral groups widely used in drilling fluid. In their crystal lattice, two tetrahedral sheets are adjacent. As a result, the bonding is weak because of opposite oxygen atoms and also high repulsion caused by isomorphous replacement (see 1.2.2 for isomorphous replacement). The easy cleavage between the two sheets allows water to enter between the layers and expand the lattice. This phenomenon is termed crystalline hydration (or sometimes called surface hydration). Water molecule is bonded on the surface by hydrogen bonding to the hexagonal network of oxygen atoms. The succeeding layers of water are similarly held to the preceding layer. The absorption of water molecules on crystal surface greatly increases c-spacing, the distance between a plane in one layer and the corresponding layer in the next layer (see Figure 1.3).



Figure 1.3 Diagrammatic representation of 3-layer expanding clay lattice [34]. The absorption of water molecules on crystal surface greatly increases c-spacing, the distance between a plane in one layer and the corresponding layer in the next layer.

Another mechanism responsible for surface hydration is osmotic swelling. Water is drawn between layers because the concentration of cations between layers is greater than that of bulk solution. Water absorption develops a new layer around platelets called diffuse double layer. A colloidal particle such as clay mostly consists of a compacted layer (or fixed layer), a diffused layer, outside the fixed layer, which both contain positive and relatively larger number of negative charged ions. These two layers represent the region surrounding the particle where there

is an electrostatic potential as shown in Figure 1.4. The concentration of the counter ions decreases from the particle surface to that of bulk solution at the outer boundary of the diffused layer. The shear plane or shear surface surrounding the particle is the bound water or water envelope that moves with the particle.

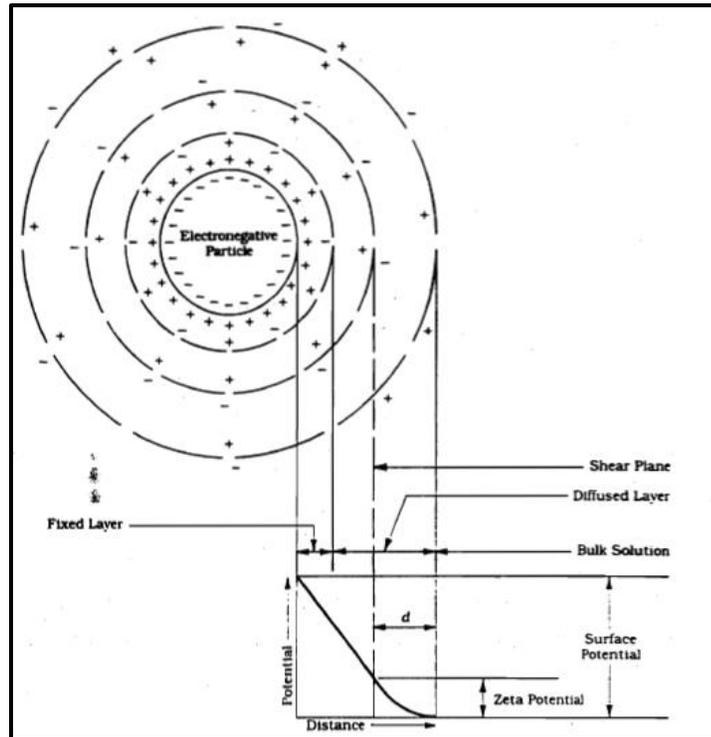


Figure 1.4 A negative colloidal particles with its electrostatic field [34]. A diffused layer, outside the fixed layer, contains both positive and relatively larger number of negative charged ions. These two layers represent the region surrounding the particle where there is an electrostatic potential.

The presence of a bound water layer and its thickness affect colloidal stability since the layer⁷ prevents the particles from coming into contact. In addition, colloidal particles acquire a surface charge which influences the molecular rearrangement of water. The surface charge is most commonly acquired through (1) isomorphous replacement, (2) structural imperfections, (3) preferential adsorption, and (4) ionization. The surface charge, which enhances stability, must be overcome if these particles are to be aggregated (flocculated) into larger particles to settle by

⁷ The electrostatic potential at the shear surface is termed zeta potential and is an indirect measure of the electrical charge of the colloidal particle. The greater is the repulsion force, the larger is the zeta potential of colloidal particles, and more stable is the suspension.

gravity force. The following is a summary of the surface charge acquisition mechanism and is summarized from [31]:

1. **Isomorphous Replacement** When ions from solution replace ions in the lattice structure, surface charge is developed through isomorphous replacement (e.g. the replacement of Si^{4+} with Al^{3+}) leading to a deficiency of positive charge on the crystal lattice; for instance, if in an array of solid SiO_2 , tetrahedral, a Si atom is replaced by an Al atom (Al having one electron less than Si), a negatively charged framework is established. Clay is an example of such atomic substitutions. Surface charges of this type are independent of the pH of the liquid.
2. **Structural Imperfections** In clay and similar particles, because of broken bonds on the crystal edge and imperfections in the formation of the crystal, surface charge is developed. Hydrolysis (water reaction) of broken Si-O and Al-OH bonds causes the surface charge on the clay lattice; for instance, O^- ions bond with H^+ to form amphoteric surface hydroxyls (can react with both H^+ and OH^-). The net charge could be either positive or negative depending on the silicate structure, pH, and salinity of the solution.
3. **Preferential Adsorption** When oil droplets, gas bubbles, or other chemically inert substances are dispersed in water; they will acquire a negative charge through the preferential adsorption of anions (particularly hydroxyl ions) by London-van der Waals forces or hydrogen bonding. In addition, organic dipoles and large organic ions are preferentially absorbed onto the solid surface primarily because their hydrocarbon parts have little affinity for water. Simple inorganic ions such as Na^+ , Ca^{2+} , and Cl^- may remain in solution, even if they are attracted to the solid surface, because they are readily hydrated in aqueous solutions. Fewer hydrated ions, such as Cs^+ , CuOH^+ , and more anions tend to seek positions at the solid surface to a larger extent than easily hydrated ions.
4. **Ionization.** Many solid surfaces contain functional groups which are readily ionizable, such as $-\text{OH}$, $-\text{COOH}$, and OPO_3H_2 . Moreover, solid particles or colloidal materials may absorb hydroxyl ions and become negatively charged. pH of the solution plays a significant role in the degree of functional groups' ionization. At low pH values, a positively charged surface, and at higher pH, a negatively charged surface prevails. At some intermediate pH (the isoelectric point), the charge will be zero. Surface charges can

also emanate from processes in which solutes become coordinately bound to solid surfaces.

The acquired surface charge of colloidal particles leads to a variety of particles modes' association shown in Figure 1.5 between clay platelets: for instance, these platelets form face-to-face structures made up of either aluminum or magnesium atoms in coordination with oxygen atoms. The structures are composed of geometrical sheets stacked together face-to-face sharing common oxygen atoms. Figure 1.6 shows the structure (known as *Hoffmann structure*) of these sheets forming a network of tetrahedral and octahedral sheets. Cross-linking between parallel plates, through positive to negative surface linkages (also called house-of-cards structure) is another association mode of clay platelets. Benna et al. (1999) concluded that this mode of association between particles leads to thicker and larger particles [51].

In a crowded system of platelets, orientation of the particles is restricted by spatial consideration. In addition, platelets are highly flexible films of diverse shapes and sizes. In such a suspension, local groups of platelets align according to their relative positions and magnitude of their surface and edge potentials. If the edges are positively charged, the platelets flex toward a negative charge base, and if they are negatively charged, the platelets parallel to the basal surface; for instance, because of relatively high repulsive potential between the basal surfaces, the preferred platelet orientation will be parallel with edge-to-edge association [52].

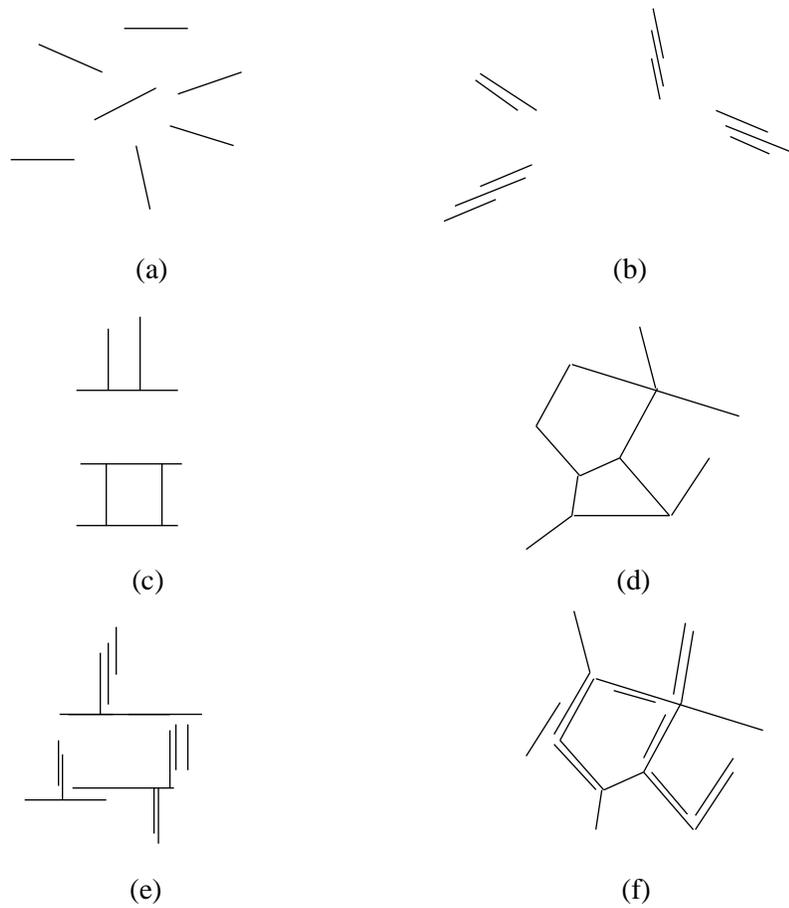


Figure 1.5 Modes of particle association in clay suspensions and terminology: (a) "Dispersed" and "deflocculated", (b) "Aggregated" but "deflocculated" (face-to-face association, or parallel or oriented aggregation), (c) Edge-to-edge flocculated but "dispersed", (e) Edge-to-face flocculated and "aggregated", (f) Edge-to-edge flocculated and "aggregated" [39]

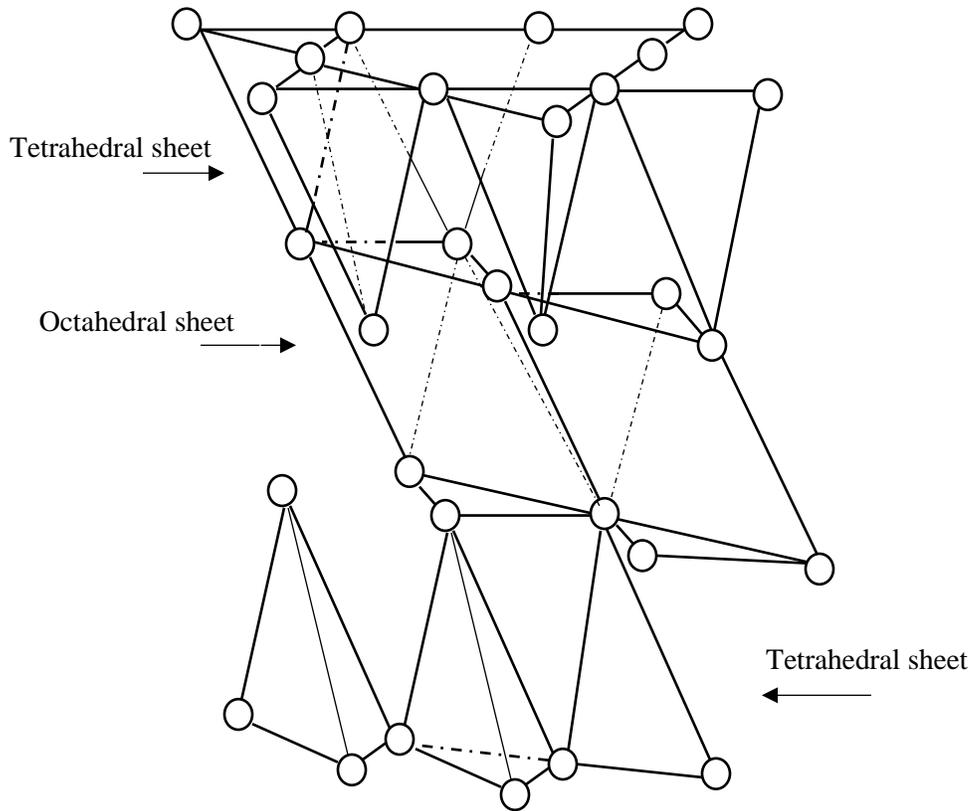


Figure 1.6 Bonding between octahedral sheet and two tetrahedral sheets through shared oxygen atoms [34]. Clay platelets form a network of tetrahedral and octahedral sheets (*Hoffmann structure*) or through positive to negative surface linkages and cross linking between parallel plates (*house of cards structure*).

Clay hydration thus far was discussed in an aqueous medium; however, in invert emulsion fluid where oil is the external phase, the hydration mechanism is not well-understood. Diesel base oil has been traditionally used as the external phase with water (brine) emulsified. Since 1990s, mineral oil replaced diesel because it is equally efficient as diesel drilling fluids, however, with lower environmental impact and aromatic components. The development process of clay compositions capable of forming gels in oil, similar to those formed by bentonite in water, was a major contribution to the technology of oil muds. E. A. Hauser discovered that hydrophilic clay could be converted to an organophilic condition by reaction with appropriate organic ammonium salts. J.W. Jordan et al [50] studied the reaction of bentonite with a series of aliphatic amine salts and found that the reaction products of amines having twelve or more carbon atoms in the straight chain will swell and form gels in nitrobenzene and other organic liquids. The organoclay complexes were formed by replacing the exchangeable cations of the bentonite with the cationic

groups of the amines and by further adsorption of the hydrocarbon chain on the clay lamina surface. The oil-dispersible clays would suspend solids in oil, without requiring additional soaps and surfactants.

In order to promote dispersion of water phase in oil (prevent the dispersed phase from coalescing and settling out of mixture), an emulsifier is used to form an interfacial film that increases the repulsion between the water molecules. Calcium and magnesium fatty acid soap frequently is used as an emulsifier for oil muds. Fatty acids are organic acids present in naturally occurring fats and oils that have a long hydrocarbon chain of the soap molecule that tends to be soluble in water. The soap molecules accumulate at the oil/ water interface with the water-soluble end residing in the water and oil-soluble end and forming a stable emulsion. The packing of soap molecules could have single or two hydrocarbon chains depending on what ion forms fatty acid soaps. In addition, oil wetting and dispersing solid additives appears to be essential in preventing settling since in oil based drilling fluid, it is much more difficult to build sufficient yield point and gel strength due to lower viscosity of mineral oils and insufficient electronic interaction of solids. Table 1.1 sums up the components of a typical oil based drilling fluid.

Table 1.1 Typical composition of oil based drilling fluid

Base oil	Diesel, synthetic or mineral oils
Water	Calcium chloride brine
Primary emulsifier	Calcium soap (lime and long-chain fatty acid)
Secondary emulsifier	Powerful oil wetting chemicals
Lime	It neutralizes the fatty acid, controls alkalinity and neutralizes acid gas
Fluid loss reduction	Organophilic lignites (amine treated lignites) Gilsonite or asphalt derivatives Polymers (polyacrylates, etc.)
Wetting agent	Oil wet the solids
Viscosifiers	Oleophilic clay, bentonite, hectorite or attapulgite or polymeric viscosifiers
Weighting agents	Calcite, barite and hematite, barium sulfate

1.2.2 Fine Particles Stabilization in Invert Emulsions

Drilling cuttings make up a large portion of the waste-stream generated in the drilling process. Clays such as claystone and shale intermixed with sandstones comprise the largest percentage of minerals in drilling. The cuttings, silt, and sand are removed from the drilling fluids through solid control facilities. Particle size in drilling fluids mostly falls into silt size comprised of particles with equivalent spherical radius of smaller than 100 millimeters. Colloids, the smallest visible particles under an optical microscope, significantly affect mud properties because of their high degree of activity. In an oil/water mixture, free oil is characterized with droplet sizes greater than 150 nm in size, dispersed oil as a size range of 20-150 nm and emulsified oil has droplets typically less than 20 nm. In drilling fluids, colloids consist mainly of clay minerals, and organic colloids such as starch, the carboxycelluloses, and polyacrylamide derivatives. Very small drilling cuttings, called fine particles, can build up in the drilling fluid, and consequently, increase viscosity and adversely affect the drilling fluid performance. The impact of drilling cuttings on the viscosity of the slurry, a mixture of a liquid with solid particles, varies depending on the size and concentration of the solid particles. In higher concentrations of fine particles, relative viscosity of the slurry exhibits a quadratic growth with fine particles concentration. Furthermore, fine particles present in the base oil are able to stabilize emulsion through several mechanisms, namely adsorption onto water/oil interface, and stable oil wet particles forming rigid that can sterically inhibit molecular coalescence, etc. Tambe and Sharma (1993) reported their results on the factors controlling the stability of colloid-stabilized emulsions. They showed that in addition to providing a steric hindrance to drop-drop coalescence, the adsorption of particles at the oil-water interface also affects the rheological properties of the interfacial region. At a sufficient high concentration of particles, the particle-packed interface will exhibit viscoelastic behavior. The viscoelastic interface affects emulsion stability both by retarding the rate of film drainage between coalescing emulsion droplets and by increasing the energy required to displace particles from the contact region between droplets [56].

The wettability of solid particles plays a significant role in the emulsion-stabilizing process. Solids act as an emulsifier only if they are wetted by both the oil and water phases. When solids are wetted by both the oil and water (intermediate wettability), they agglomerate at the interface and retard droplet/droplet coalescence. Three phase contact angle in water-oil interface is a

parameter that determines the wettability of a particulate. Figure 1.7 gives a schematic of the three phase contact angle and tensions between phases. Tadros and Vincent (1983) concluded that particles were likely to remain at an oil-water interface when the contact angle was 90° [53]. It is well-known that solids with a contact angle lower than 90° stabilize O/W emulsions while those with a contact angle greater than 90° favors W/O emulsions [54].

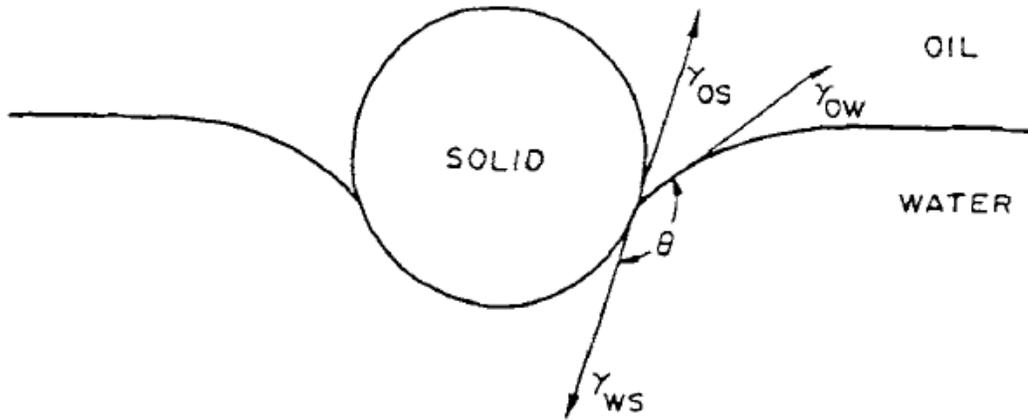


Figure 1.7 Definition of the three-phase contact angle. Three phase contact angle in water-oil interface plays a significant role in stabilizing the emulsions [53].

In addition to three phase contact angle, interfacial tension, γ_{ow} , at the oil-water interface plays a key role in stabilizing a particle. Assuming a small spherical particle with radius R (no gravity effect) resting at an oil-water interface, the energy, E , is required to remove the particle from the interface into the oil phase is given by:

$$E = \pi R^2 \gamma_{ow} (1 \pm \cos \theta)^2 \quad (1.1)$$

where γ refers to the appropriate interfacial tension and the subscripts s, o, and w represent the solid, oil, and water, respectively. The sign in the bracket is '-' for $\theta < 90^\circ$ and '+' for $\theta > 90^\circ$, which means that a particle is most strongly held at the interface for $\theta = 90^\circ$, and is more easily removed into water for $\theta < 90^\circ$ and more easily removed into oil for $\theta > 90^\circ$.

1.2.3 Factors Affecting Fines Particle Stabilization

For droplet coalescence to occur, particles must be submerged into one of the bulk phases. Oil-wet particles will preferentially partition into the oil phase and will prevent the coalescence of water droplets by steric hindrance. Similarly, water-wet solids will stabilize water continuous or an O/W emulsion. Inorganic scales (e.g. CaCO_3 and CaSO_4), clays, and sand are examples of water-wet solids [57]. Yan et al. recommended making stabilized solids more hydrophilic in order to concurrently remove water and particles [58]. The hydration of clay particles significantly impacts the stability of fine particles. A number of researchers have studied clay particles hydration under different physical conditions.

1. **pH effects on clay behavior in emulsions.** Changes in pH of the aqueous phase can affect the zeta potential and wettability of clay particles, and thus dispersion of the clays in continuous aqueous phase and adsorption at the oil-water interface. As pH increases, zeta potential, net negative charge, critical coagulation concentration of clay and silica particles increase [59] [60] [61] [62]. As a result, stability of the emulsions (at least in oil-in-water emulsions stabilized by fine particles film) reduces when pH increases, and better demulsification can be achieved [60]. This is attributed to the fact that increasing zeta potential results in better affinity of the clay to water phase than to oil phase. Yan and Masliyah showed that clay particles adsorb from the aqueous phases with low pH (i.e. lower than 5) onto the oil droplet surface demonstrating that particles are hydrophobic. Thus, in the case of fine solids-stabilized emulsions in the absence of other surfactants, increasing pH will lead to emulsion destabilization. However, under alkaline conditions, clay particles desorb from oil droplets acquiring net negative charge and disperse in water to colloidal level via repulsions which prevent particles coagulation [61] [63]. Wang and Alvarado (2008) showed that emulsions are more stable around Zero Potential Charge (ZPC) of the clay particles or lower zeta potential.

Suarez (1984) found that hydraulic ⁸conductivity of two arid-solids (for both kaolinitic and montmorillonite) contacting mixtures of clays decreased from pH 6 to 9 indicating

⁸ It is believed that grain size, soil lithology and pH influence the hydraulic conductivity (i.e. filtration coefficient). Hydraulic conductivity describes the ability of a porous medium to transmit water through its interconnected voids.

better dispersion of particles. Chorom et al. (1995) postulated that at lower pH, Na^+ ions are replaced by H^+ , which increase the concentration of Na^+ in the solution and H^+ on the clay surface leading to a penetration of H^+ ions into the lattice. This penetration causes the clay particle to decompose and release di- or trivalent cations reducing net negative charge due to the inner sphere complexation of these ions with clay surfaces [64].

At high pH, OH^- ions interact with the edges of the clay particles making them neutral or negatively charged. Marinova et al. (1995) conjectured that the negative charge at the water-oil interface is caused by adsorption of hydroxyl groups to hydrogen atoms of water by hydrogen bonding and ruled out other hypotheses such as adsorption of other negative ions at the interface. Laboratory studies have shown that the rate of dissolution of silicate minerals increases with increasing pH above 8 [65]. In spite of increasing EC at high pHs, the clays dispersed because of the development of strong negative charge. Ngai et al. (2006) concluded that that microgel emulsions (without any surfactant) coarsen as the solution pH is decreased below pH 6.0. They concluded that at high pH, the microgel particles are deprotonated and hence behave like conventional polyelectrolytes. It was found that when pH increased from 4.0 to 8.0, size of microgel particles increased as well because carboxylic groups ($-\text{COOH}$) are deprotonated to the anionic $-\text{COO}^-$ enhancing the electrostatic double layer of microgel particles. Midmore (1997) used colloidal silica, flocculated with the homopolymer hydroxypropyl cellulose, as the stabilizing agent to produce a highly stable oil/water emulsion. As pH is decreased, HPC/ silica flocs are formed at lower pH resulting in its adsorption at the oil/water interface that must account for the considerable decrease in oil droplet size and increase in viscosity [66].

Goldberg and Glaubig (1987) showed that Critical Coagulation Concentrations (CCC) of both Na- and Ca-clay systems increased with increasing pH. They also found that the pH dependence for kaolinite was greater than that for montmorillonite, with the 50/50 mixture behaving more like montmorillonite [62].

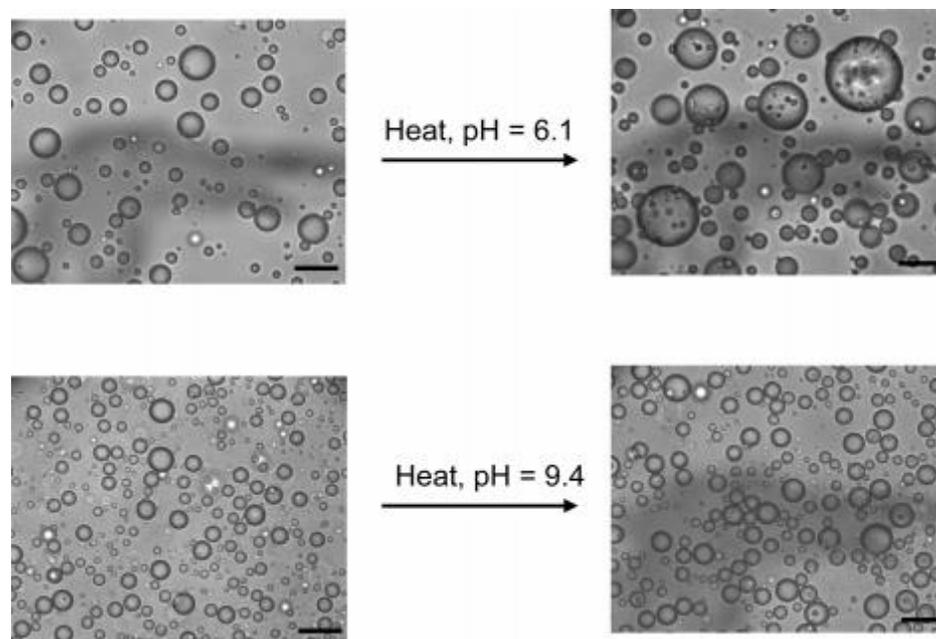


Figure 1.8 Optical micrograph illustrating the temperature-dependent stability of an octanol-water emulsion prepared with PNIPAM microgel particles at pH 6.1 and 9.4 [47].

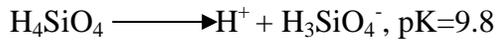
2. **Temperature effects on clay behavior in emulsions.** Rodriguez and Araujo (2006) studied the effects of temperature and pressure on the zeta potential of minerals (e.g. quartz, kaolinite). They found out that the zeta potential becomes more negative as the temperature increases. Also, at alkaline pH, elevation of the temperature caused significant changes in the final zeta potential values, partly due to the change in the pK of water and also due to the mineral solution equilibria [67]. Ngai et al. (2006) reported that increasing temperature caused particles to become more hydrophobic and collapsed the microgel particles [68].

The main cause for the quartz charge is the dissociation of the silanol groups at the surface. To understand the temperature dependence of the zeta potential of quartz it is necessary to analyze the mineral solution chemical equilibrium of the system at different temperatures. The temperature dependence of the solubility of crystalline quartz can be described by the following equations:



$$\log(\text{H}_4\text{SiO}_4) = 0.151 - 1162/T.$$

The reaction is independent of pH, and as can be seen, the H_4SiO_4 formation is favored at higher temperatures. The number of ionizable ions per silicon atom is higher for a silicic acid surface than for a fresh quartz surface. Thus, the silicic acid surface is expected to have a larger surface charge density and hence a larger magnitude of the zeta potential. H_3SiO_4^- is the only major ionic species in solution. In alkaline solutions the equilibrium for quartz dissolution is governed by:



$$-9.8 = -\log (\text{H}_4\text{SiO}_4) + \log (\text{H}^+) + \log (\text{H}_3\text{SiO}_4^-).$$

Thus, as the pH increases while K is constant, $\log (\text{H}_3\text{SiO}_4^-)$ must increase. Increases in both temperature and pH favor the formation of H_3SiO_4^- , leading to more negative zeta potential values.

Ross and Hendricks (1945) studied the relationships between vapor pressure of water and cleavage spacing of clay palates. It was found that increasing vapor pressure increased the grams of water per 100 grams of montmorillonite [69].

To summarize, several parameters play a significant role in an increase in the zeta potential of clay particles at elevated temperatures. Much of the literature on the subject seems to study the phenomenon under specific conditions such as hydration in aqueous medium, specific pH and group of clay. To conclude, it is believed that higher temperature leads to more clay hydration as a result of an increase in the particles zeta potential.

3. **Salinity and particles concentration effects in clay-emulsion interaction.** Wang and Alvarado (2008) concluded that lower salinity favors emulsion formation. They postulated that lower salinity results in an early onset of asphaltene. In their study, the zeta potential measurements results showed that clay concentration did not have a significant effect on zeta potential and size distributions. It was inferred from zeta potential measurements that particles in the brine with the lower salinity have larger negative zeta potential, which is a

result of lower ionic strength available to suppress the electrical double layer of the dispersed solids.

Sposito (1989) concluded that the presence of di- or trivalent cations in the electric double layer can decrease zeta potential by reducing net negative charge due to the inner sphere complexation of these ions with clay surfaces. Chorom et al. (1995) also showed that when the electrolyte concentration of NaCl is logarithmically increased, the zeta potential increases. The mechanism of this reaction is related to the thickness of the electrical double layer. When the electrolyte concentration of the suspension is increased, the double layer is compressed, resulting in a smaller zeta potential. Yukselen-Aksoy and Kalay (2011) also studied the effect of ionic strength on the zeta potential of kaolinite and quartz and concluded that when the concentration of KCl and CaCl₂ increases, the zeta potential of kaolinite becomes more positive. They also showed that an increase in solid contamination in the presence of distilled water slightly reduced the zeta potential of minerals (i.e. kaolinite and quartz), but the effect is comparatively much lower than electrolytes' effect.

Yan et al. (2006) reported that at low particle concentration, gravity sedimentation occurs because flocs cannot connect with each other and form a network structure. They also showed that adding salt to clay dispersions destabilize gel structures and form large flocs. Marinova et al. (1995) also measured the electrophoretic mobility, U_E , of droplets from four nonpolar oil types of different chemical nature. Their results also corroborated other studies on the effect of pH and electrolyte concentration. They found a very large magnitude in negative surface potential at high pH and observed decrease in the magnitude of U_E with increase of the NaCl concentration.

In summary, four physical parameters (i.e. pH, temperature, salinity and particles concentration) are studied in this research. The impacts of these factors on the clay hydration are discussed in Chapter 3. As reviewed in this section, higher alkalinity and temperature lead to higher clay hydration as a consequence of an increase in the zeta potential. Moreover, higher concentration

of electrolytes in the emulsion leads to a compression, or a decrease, in the zeta potential of clay particles.

There are a large number of parameters that impact the fine particles stability in addition to the aforementioned factors; for instance, elevated temperature and electrolytes in water-based drilling fluids inhibit the protective action of the added polymers and cause early gelation particularly during long round trip times. Asphaltene coating of solids and excessive mixing of the drilling fluids are two other parameters which supposedly have a significant impact on fine particles stability in the fluid. In petroleum, shale, coal and tar-sand systems, stable W/O emulsions exist because of the hydrophobic nature of the particles. In these systems, the hydrophobicity is due to the adsorption of natural surface-active components such as asphaltenes and maltenes, from the oil onto the mineral surfaces [70]. Polarity of the base oil in drilling fluids also plays a role in the absorption of the water-swollen microgel particles. Ngai et al found that the absorption of the water-swollen microgel particles to the oil water interface is substantially reduced when the polarity of the oil is decreased [68]. Roos et al. showed that rheological behavior of mineral oil system largely depends on the shear history of the system. This explains undesired viscosity and yield point when rheological properties when circulated in the well [71]. Further behavior of the fine particles depends on their critical concentrations: gelation and coagulation. At critical gelation concentration of the fine particles in aqueous phase (which is known to be below 3%), clay forms gel-like network which entraps other (even bigger) particles and droplets (stabilized by surfactants). Chemical demulsification and flocculation in this system is challenged by poor mass transfer through the gel. To break this system, clay concentration has to reach critical coagulation level, which significantly increases when pH increases.

1.2.4 Current Drilling Fluids Recycling Techniques

The accumulation of fine particles poses severe issues such as excessive viscosity, reducing rate of penetration, enhancing torque and drag, increasing the risk of pipe sticking, etc. in addition to the incurred dilution costs of drilling fluids. To achieve optimum drilling conditions, these fine particles should be treated out of the drilling fluid to redeem the principal qualities of the drilling

fluid (e.g. density, viscosity and relative oil and solids contents). Furthermore, stringent environmental regulations have prohibited waste disposal containing oil. Not so many disposal sites are available worldwide because of a lack in well-developed waste management infrastructure. Burial in landfill, injection to an underground formation, disposal to salt caverns are a number of available methods used for drilling waste disposal. In the last two decades, dewatering has been growing in popularity to recycle drilling fluids in site. Tailings treatment approaches can be applied to drilling fluids recycling because there are certain parallels between two treatments. In both, ultra-fine clay particles are to be removed from a hydrocarbon medium. As a result, an overview of dewatering mud waste pits and tailings treatment would give a real insight into the potential solutions for fine particle separation.

Drilling fluids dewatering consists of two steps: in the first step, barite is recovered through solid-control separator and recycled back to the well; in the second step, the diverted mud is diluted with water to improve chemical treatment which follows and then the diluted mud is treated by chemicals. In addition, returning the overflow to the mud dilutions reduces consumption and saves on chemicals dissolved in the mud-water phase. The presence of inert solids may distort the dewatering performance; for instance, high solids content in the dewatered salt/polymer may be misperceived as a high performance despite the low actual performance [24]. Polymers are widely used in dewatering to enhance flocculation of ultra-fine and colloidal drill cuttings. **Polymeric Flocculants** are long and high molecular weight organic chains with ionic or non-ionic groups. These polymeric flocculants are called polyelectrolytes because they have characteristics of both polymers and electrolytes.

The term polyelectrolyte is used to denote polymers which contain more than 15% of ionic groups, and those polymers with lower ionic group contents are called ionomers. The intensity of charge carried by polyelectrolytes depends on the degree of ionization of the functional groups, or on the degree of polymerization or substitutions. Polyelectrolytes are either natural or synthetic. Most common natural polyelectrolytes include polymers of biological origin and some derived from starch products such as cellulose derivatives and alginates. Synthetic polyelectrolytes can be grouped into *anionic* or *cationic* according to the type of charge on the polymer chain. In other words, polymers possessing negative charges are called *anionic* (e.g.

hydrolyzed polyacrylamide and polyacrylic acid) while those carrying positive charges are *cationic* (e.g. polydimethylammonium and diallyldimethylammonium). Certain compounds carry no net electrical charge and are called *nonionic* polyelectrolytes. Polyacrylamide (PAM) is the basis of many commercial flocculants. The amid groups of PAM can be hydrolyzed to give ionized carboxylic acid groups and anionic sites along the chain. Hydrolysis conditions mostly determine the distribution of carboxyl groups along the polymer chain.

Table 1.2 Examples of polyelectrolytes [104]

Type	Functional Group	Example
Cationic	Amine	Polyethyleneamine hydrochloride
	Quaternary	Polydiallyldimethylammonium
Nonionic	Polyalcohol	Polyvinylalcohol
	Amide	Polyacrylamide
Anionic	Carboxylic	Polymethacrylic acid
	Sulfonic	Polyvinylsulfonate

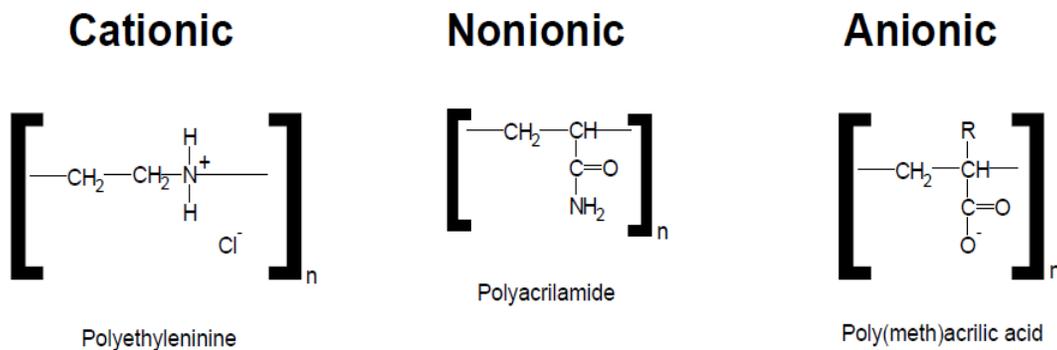


Figure 1.9 Functional groups of three examples of polyelectrolytes

Because of the great variety of monomers, molecular weight, charge density of polymers available, unsurprisingly a wide assortment of polyelectrolytes exists for the wastewater plant operator. A number of factors should be taken into consideration when selecting a specific polymer as a flocculent, namely size, density and ionic charge of the colloids; for

instance, high charge density of anionic polyelectrolytes may render the colloidal particles dispersed due to the repulsion between the polymer and like charged particles; however, some degree of charge is suitable, since repulsion between charged segments leads to expansion of the chains, which in turn should enhance the bridging effect. Therefore, there is an optimum charge density for the bridging flocculation of negatively charged particles and anionic polymers [36]. It is recommended to use a certain concentration of divalent ions as an electrolyte to reduce the repulsion and promote adsorption. The screening effect of these positive ions causes some affinity between the polymeric chains. The particles in solid-liquid phases can be destabilized through three main mechanisms: polymer **bridging**, charge **neutralization** (also known as **charge patch** model), and **polymer adsorption**. The responsible mechanisms for destabilization or aggregation may vary, depending upon **molecular weight** and the **charge density** of the flocculants and colloidal particles. Figure 1.10 shows a schematic demonstration of flocculation mechanisms.

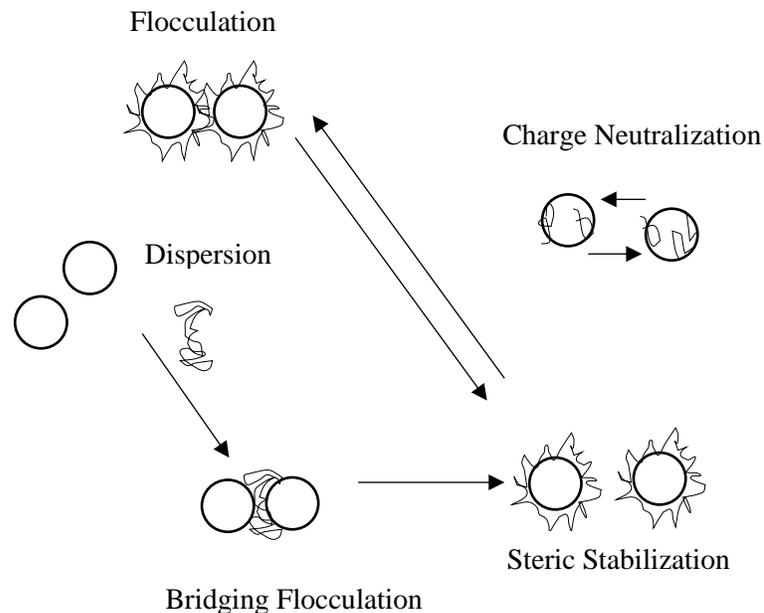


Figure 1.10 A schematic representation of the ways by which polymer can affect colloid stability [37]

High molecular weight, $(15 \div 20) \times 10^6$, low density charge, anionic or nonionic polyelectrolytes are known to have the best performance among various flocculants; this indicates that the bridging mechanism was important to oilfield waste slurry dewatering. However, Wang et al. (2010) concluded that starch-based cation copolymer is superior to anionic and non-ionic polyacrylamide for high density waste drilling mud [72]. Xu et al. (1999) reported that polyacrylamide (PAM) with 20% - 30% anionicity was the most effective for flocculation of the Syncrude tailings [73]. Sworska et al. (2000) chose Percol 727 to flocculate fine tailings from slurry of fine Syncrude tailings containing clays, sand and small amounts of bitumen [74]. Li et al. also (2005) studied the effect of Percol 727, derived from hydrolyzed polyacrylamide (HPAM), on both bitumen extraction and tailings treatment as applied to oil sands. They showed that HPAM (a high MW polymer with 17.5×10^6 and 22% anionicity) was effective to reduce the adhesion force and enhance liberation of fine particles by flotation up to a certain dosage (30 ppm) [75].

Wojtanowicz et al. found that anionic polyelectrolytes are preferred to cationic ones in drilling fluids dewatering because of their tendency to produce a clearer filtrate and less binding. The selection of a single flocculent can be based upon a “drop test,” which involves placing a drop of the flocculent on the surface of sludge and evaluating the degree of “wrinkling” at the contact surface.

Wang et al. (2010) used a high effective flocculent for high density waste drilling mud with starch, 2-Trimethylammonium ethyl methacrylate chloride (DMC) and acrylamide (AM) to separate three phases in the waste. They showed that increasing DMC to a certain level reduces the water content in filter cake (better phase separation) because DMC increases the cationic degree of copolymer. Since clays in waste drilling mud have a negative charge, increasing DMC further neutralize the negative charge. Wang et al. also indicated that the blend of copolymers with starch, DMC, etc. is significantly better than other flocculants in market such as non-ionic, cationic, and anionic polyacrylamide [72]. McCosh used an inverse polymer to flocculate fine particles in invert-emulsion drilling fluids. Through a series of optimization steps using the flocculation technology, drilling fluid was treated so fine solids were removed and the density of the fluid was reduced from 1.2 to $<0.9 \text{ g/cm}^3$ [79].

Jones et al. (2011) patented two approaches to treat waste drilling mud. One approach involves vaporizing all residual and water from solids, and burning off the vaporized oil. Another approach involves at least partially vaporizing the residual oil from the solids and recondensing oil [80]. Ivan et al. (2006) patented a method for recovering oil-based drilling mud by pumping the drilling fluid through a flow meter, adding a surfactant to the drilling fluid and blending the mixture with a flocculating polymer by passing them through a static mixer. A centrifuge is used afterwards to separate solid particles from the fluid [81]. Mueller (2005) patented a mobile apparatus and method for recycling an invert emulsion drilling fluid. The invert emulsion drilling fluid is initially mixed with an emulsion breaker, wherein the emulsion breaker is a mixture of an alkyl glucooside and an alkane sulfonate; which separates the oleaginous component of the invert emulsion drilling fluid from the aqueous component of the invert emulsion drilling fluid. He used a combination of alkyl polyglycosides, alkyl sulfonates and alkyl sulfates as the emulsion breaking system. Alkyl polyglycosides are commercially available substances that are produced by acid-catalyzed reaction of glycodies and fatty alcohol. The mixture was agitated after placing a measured quantity of process mud with measured portions of the emulsion clearance agent. The composition of the remaining Oil/Water (O/W) emulsion was measured by means of distillation (ROFI) [82].

1.2.5 Summary

Fine particles accumulation is the foremost challenge faced in drilling fluid recycling. There are certain conditions that cause fine particle stabilization in drilling fluid, namely shearing, elevated temperature, solid and salt contamination, etc. This would yield a gelled fluid that entraps in ultra-fine particles which cannot be removed with conventional solid removal technologies. A number of chemical techniques were discussed in this section, namely dewatering and flocculation using high density polyelectrolytes. Low density charge polyelectrolytes with high molecular weight were proven to be the most efficient polymers for drilling fluids.

Chemical treatment techniques demand detailed and thorough knowledge of coagulants, involved mechanisms, and more importantly, the influent characteristics. Since drilling fluids comprise a wide range of compositions, chemical optimization becomes more demanding. In this section, an overview of particles' stabilization was given to better understand the coagulation

process. Zeta potential is the best parameter to describe the stability of particles. The greater are the repulsion forces, the larger is the zeta potential of colloidal particles, and more stable is the suspension. Coagulants are used to decrease the zeta potential of particles. Aluminum Sulfate, Ferrous Sulfate and Lime are among the most common coagulants used in waste water treatment. Metal coagulants may not be efficient in oil based drilling fluids because water content in invert emulsions is not sufficient to allow hydrolysis of the coagulants. Polyelectrolytes may be an alternative proven to be efficacious in a wide range of applications such as waste water treatment and drilling fluids recycling. To date, high density anionic polymers with low electrical charge was reported to outperform their counterparts for drilling fluid dewatering.

1.3 Novel Technologies

As discussed in part 1.2, chemical and mechanical methods suffer from several pitfalls in removing fine particles from drilling fluids. To name a few, chemical treatments are susceptible to changes in influent quality such as viscosity and volume of waste, and therefore, require customization at every site. Mechanical treatment also (e.g. solid control facilities on rig sites) fail to fully separate fine particles and low gravity solids. Shale shakers can remove drill solids down to 177 microns by 80-mesh screens. Furthermore, common distillers and disanders operating in higher pressures are capable of removing up to 95 % solid particles larger than 15 microns. As a result, more complementary technologies are necessary to address the problem of ultra-fine particles separation.

We hypothesize that physical approaches with selective action towards emulsion components would facilitate emulsion breaking and solid-oil-water separation. The potential selective treatment may be achieved through selective heating by microwave irradiation, mechanical separation caused by ultrasonication, and electrical separation by electrophoresis. The methods presented in this chapter are at their very preliminary stages and their applications for emulsion breaking and solids separation are quite novel. These methods have been successfully experimented in other research areas such as food and mineral industries, water treatment and crude oil demulsification. To the best of our knowledge, only electrophoresis has recently been used for recycling drilling fluids [6]. None of these methods were tested in respect to treatment of extremely stable invert emulsions contaminated with fine solids. However, mechanisms of actions of these methods (as described in this section) make them potential candidates for effective treatment. All three methods need further research and experiments to fully understand the separation mechanisms in invert emulsions.

1.3.1 Microwave radiation:

Microwave is a non-ionizing electromagnetic radiation that causes dielectric heating by absorption of energy in dielectric materials, i.e., polar molecules which have an electrical dipole moment. Two complex quantities characterize the interactions between electromagnetic waves and matter: magnetic susceptibility and dielectric permittivity, ϵ . Magnetic component can

induce structure in magnetic moments while electric components can induce current of free charges. The dielectric permittivity of matter is described by:

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad (1.2)$$

The real part of the dielectric permittivity expresses the orienting effect and storage of electromagnetic energy, whereas the imaginary part of the polarization undergoes chaotic motion leading to thermal dissipation of the electromagnetic energy. The thermal dissipation of the particles with high dielectric loss emanates from the delay between electromagnetic stimulation and molecular response which ultimately leads to the heat generation. In other words, the alignment of the particles with high dielectric loss under electromagnetic fields (see Figure 1.11) is not sufficiently rapid to build-up a time-dependent polarization in equilibrium with the electric field at any moment. This delay between the generated heat directly depends on kinetic energy (molecular rotation) or dielectric properties of material.

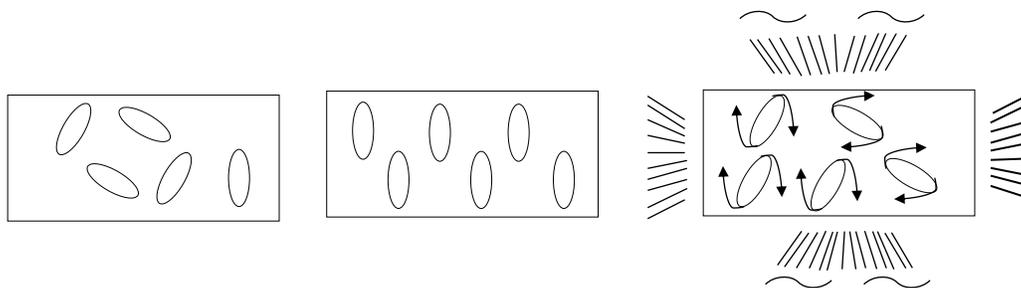


Figure 1.11 Effects of the surrounding electric field on the mutual orientation of dipoles (a) without any constraint, (b) submitted to a continuous electric field, and (c) submitted to an alternating electric field of high frequency.

Water has a high dielectric constant; oil is far less polar than water molecules, and is relatively transparent to microwave radiation due to the low dielectric loss. Solids, surfactants and other drilling fluid additives also have different dielectric losses and hence heat generation by microwave radiation. Solids present in the solution may absorb molecules depending on the chemical nature of the solid surface. Non-polar molecules can be heated by adsorption on solids with high dielectric loss (e.g. clay or alumina catalysts). The association of organic reagents with inorganic solids as alumina, silica, and clays strongly enhances the capacity to absorb microwaves. Loupy et al. have shown that the association of potassium acetate with alumina or silica strongly absorbs microwave raising temperature to 600 °C after heating for 1 min [70]. As

a result, the heat generation significantly varies for different components and results in temperature gradients and rearrangement of charges. Table 1.3 gives the dielectric constants and refractive indices for a few polar and dipole molecules. For apolar molecules, dielectric constant is equal to the square of the refractive index (Maxwell's theory) whereas for polar molecules the constant is different because of permanent dipoles [70].

Table 1.3 Relative static dielectric constant (ϵ_s), refractive index (measured at the frequency of sodium D lines, n_D^2) and dipole moment for a few molecules μ [60].

Molecules	ϵ_s	n_D^2	μ
Apolar			
n-Hexane, C ₆ H ₁₄	1.89	1.89	-
Carbon tetrachloride, CCl ₄	2.23	2.13	-
Benzene, C ₆ H ₆	2.28	2.25	-
Polar			
Methanol, CH ₃ OH	33.64	1.76	1.68
Ethanol, CH ₃ CH ₂ OH	25.07	1.85	1.7
Acetone, CH ₃ COCH ₃	21.20	1.84	2.95
Chlorobenzene, C ₆ H ₅ Cl	5.64	2.32	1.69
Water, H ₂ O	80.37	1.78	1.94

As indicated in Table 1.3, the significant difference between dielectric properties of water and organic matters appeals to the author to consider the application of the technology in water-in-oil demulsification. Loupey et al. (2006) cited a number of factors as the destabilization mechanisms:

1. Electrostatic polar effects lead to dipole-dipole-type interactions between the dipolar molecules and the charges of the electric field. The interaction results in energy stabilization which is electrostatic in nature. This phenomenon could be the origin of specific non-thermal effects and is comparable to dipole-dipole interactions induced by a polar solvent.
2. Selective heating reduces the continuous phase viscosity and interfacial tension, breaks the outer film of the droplets, thus, allowing for coalescence of droplets and gravity separation. The dielectric heating results from the tendency of the dipoles to follow inversion of the

alternating electric field and induce energy dissipation in the form of heat through molecular friction and dielectric loss.

3. Molecular rotation causes the electrical charge distribution rearranging and moving ions around the droplets. Rotating molecules collide with other molecules which distribute energy to the adjacent molecules and facilitate droplets and particles coagulation. For condensed phases, oscillations induced by the electrical field have quite a short-time and turn to vibration because of collisions. Electrical field, therefore, cannot induce organization in condensed phases such as liquid [70].
4. At last, a number of studies postulated that the microwave-induced molecular rotation may neutralize zeta potential of colloidal droplets; however, this phenomenon is still recondite and needs considerable study to understand fully because inter-molecular distances are small in liquids leading to molecular collisions rather than rotation. Having said that, Fu et al. (1998) and Fang et al. (1989) measured zeta potential of oil droplets in demulsification process and indicated that zeta potential is decreased under microwave radiation [71].

The author postulates that microwave is also capable of aiding in separating ultrafine particles such as smectile clay from water-in-oil emulsions. If the water in a smectile solution slowly evaporates, cation concentrations in water increase, and therefore, cations tend to diffuse away less from the clay surfaces. As a result, the Stern layer becomes compressed and clay lattices approach to eventually aggregate and settle out. These mechanisms result in the breaking of the emulsion, and droplets or solid particles coagulation without adding any chemical agent.

Tan et al. (2007) showed that simultaneous demulsification by the microwave and chemical treatment is more effective than only microwave treatment [72]. Thus, microwaves could be used to facilitate chemical demulsification and flocculation required for emulsion breaking and solids separation. Owens (1999) disclosed a microwave-assisted centrifuge to enhance separation of immiscible components. He conducted some field tests and assessed the test costs to be less than half of the price of chemical treatment [73]. The concept of microwave-assisted centrifuge is of great interest since mechanical forces facilitate the rupture of emulsions interfacial film after thinning of the film around the water droplet due to microwave heating and consequent

separation of emulsion components by gravity. Furthermore, mechanical agitation causes more uniform water droplets distribution within the sample, and therefore, more uniform heating [74].

A few field tests have been carried out, which all have indicated encouraging results in demulsification [75] [76]. Fang et al. (1989) conducted treatment of approximately 120 bbls of emulsion containing 50% oil, 22.5% bottom sediment and 27.5% water with microwave radiation in storage tank of 10 ft in diameter and 10 ft height. After 228 kWh of microwave energy was applied continuously at 20 kW, the temperature of the top portion of emulsion reached approximately 100°C and emulsion was separated to oil and water layers. A similar result was obtained in the field test in Louisiana for 188 bbls of crude oil/ water emulsion left in a tank. After 18.2 hours and 417 kWh of microwave radiation, the emulsion was separated to 146 bbls of dehydrated oil and 42 bbls of clear water.

1.3.1.1 Obstacles and Drawbacks

The process utilized in microwave heating is preferred to other conventional heating methods because microwave energy is delivered directly to materials. Hence there is a greater control of the heating or drying process, and equipment size is greatly reduced. However, the process suffers from certain deficiencies such as difficulty of temperature control, the use of expensive electrical energy and the problem of uneven heating [77].

1. One of the deep concerns for microwaves application is unwanted heating of drilling fluids additives under radiation. Most silicates, carbonates and sulfates, some oxides and some sulfides are transparent to microwave energy but other oxides are readily heated [77]. Chen et al. (1984) studied the dielectric properties of 40 minerals; however, dielectric losses of some drilling fluids additives are still unknown [77]. The knowledge of dielectric properties of the drilling additives would greatly contribute to design an optimum method.
2. Since microwave treatment is an energy-intensive method, energy efficiency plays a significant role in microwaves scale-up and commercialization. The amount of power used and the design of the magnetrons for the treatment should be scrutinized in order

to avert thermal runaway and overheating of high dielectric loss materials in the drilling fluid. Thermal runaway occurs because as temperature is raised, the relaxation time decreases and the loss tangent increases. As a result, converts more of the microwave energy to thermal energy. The relaxation time of most organic matters increases above 65 ps (in some cases it is larger than 1000 ps) and therefore it is not surprising that many organic solvents superheat in a microwave cavity. The preferred method of overcoming overheating (i.e. thermal runaway) is to use a continuous reaction mode combined with suitable reactor diameter [70].

The major obstacle to commercialization of the technology is coupling the power into influent emulsion. Tapered or canonical dielectric barriers are widely used in various shapes to apply microwave radiation, minimize microwave reflections, and dielectric barriers, and maximize power absorption into emulsions. To optimally apply microwave radiation, heat transfer to the surrounding medium must be kept to a minimum and heating rate ($\Delta T/\Delta t$) must be as high as possible.

To scale-up the technology from bench scale to a field treatment, the power density must be possibly high enough to rapidly convert water molecules to steam; this rules out multimode⁹ microwave cavities as viable scale-up option because of the inherently low peak power density and large power density distribution.

3. **Field homogeneity** and **penetration depth** of microwaves must be taken into consideration for commercialization of microwave treatment. Mechanical (or magnetic) stirrers can be used to tackle the problem of spatial non-uniformity. Other potential mechanisms have been suggested to improve the field homogeneity including microwave-assisted stripping and steam distillation by Robinson et al. The former was successfully used to enhance the efficiency of stripping to treat oil

⁹ There are two principal types of microwave cavities: The first of two types of applicators is a multimode cavity commonly used in most domestic microwave ovens. In a multimode cavity, microwaves are scattered using a mode stirrer and heating uniformity is ensured by placing the load on a turntable. In the second type, a monomode cavity, the microwaves are focused on the load - allowing for much faster heating rates [78]. Multi-mode cavities are more versatile than single-mode ones because of the number of modes.

contaminated cuttings [80]. Microwave assisted stripping with an inert gas flow such as nitrogen can enhance uniform heating of the sample [81].

The penetration depth of microwave depends largely material properties and wavelength used. The penetration depth is defined as the distance from the surface of a lossy dielectric material at which the incident power drops to 37% ($1/e$). Skin depth is, in fact, equal to twice the penetration depth [70]. The field or power penetration depth decreases as the frequency increases. Penetration depths at frequencies below 100 MHz are at the order of meters. Penetration depths within pure water at 2.45 GHz are at the order of centimeters (7 mm at 3 C and 2 cm at 40 C). Consequently, the penetration depth within a microwave reactor filled with lossy media is smaller. This is why 2.45 GHz is commonly used as a compromise frequency for domestic ovens because penetration depth drops at higher frequencies.

4. Microwaves are potentially hazardous. Since human body reacts to external heat not internally generally heat, the damage may not be noticed (Baden-Fuller, 1979). As a result, to commercialize the process, adverse side effect of microwave radiation must be taken into account. According to the United States Food and Drug Administration's Center for Devices and Radiological Health, a U.S. Federal Standard limits the amount of microwaves that can leak from an oven throughout its lifetime to 5 milliwatts of microwave radiation per square centimeter at approximately 5 cm (2 in) from the surface of the oven [Wikipedia]; however, energy balance considerations suggest 10 W.cm^{-2} as the safe upper limit probably because of the thermo-regulation of human body, which compensates for the absorbed heat [82]. The radiation produced by a microwave oven is non-ionizing. It, therefore, does not have the cancer risks associated with ionizing radiation such as X-rays and high-energy particles. Long-term rodent studies to assess cancer risk have so far failed to identify any carcinogenicity from 2.45 GHz microwave radiation even with chronic exposure levels, i.e., large fraction of one's life span, far larger than humans are likely to encounter from any leaking ovens.

1.3.2 Ultrasound

Ultrasound is an oscillating sound pressure wave with a frequency greater than the upper limit of the human hearing range (>20 KHz). Unlike electromagnetics, ultrasounds (i.e. acoustics) require a physical medium to propagate. The progression of a sound wave through a liquid medium causes the molecules to oscillate about their mean positions. During the compression cycle, the average distance between the molecules decreases, while during rarefaction the inter-molecular distance increases. The induced pressure waves lead to molecular agitation and shear stress, and vibrating motion along the propagation direction. In liquid phase, the particles displacement is in direction of wave propagation (i.e. longitudinal wave) because of smaller shear modulus.

There is a growing use of ultrasounds in electronic industry for jointing flip chip assemblies, and a diverse range of ongoing research in sonochemical processes including food processing, waste water treatment, water and food product sterilization, etc. [98] [99]. Depending on the frequency, this method may be used for either stabilizing emulsions by creating smaller droplets or breaking highly stable emulsions and solid separation [42] [100] [101] [102] [103] [104]. Sarabia et al. (2000) showed that ultrasonic treatment could be used to dewater fine particle from high concentration suspensions. Smythe et al. (2000) studied the use of acoustic and electric fields as filtration and dewatering aids. Encouraging results of ultrasounds in other similar research areas incite us to regard this method as a potential treatment for recycling drilling fluids. Hoffman et al. (1996) put down several separation mechanisms associated with solid-liquid separation under an acoustic field:

1. **Orthokinetic interaction:** The most basic interaction that particle gains momentum through the viscous forces of the oscillating fluid on the particle's surface. Particles relative motion differs from each other mainly due to the different radius, density and the applied frequency under acoustic field. The orthokinetic agglomeration hypothesis proposes that this relative motion causes collisions among the particulates and can, assuming attractive surface forces in the vicinity of the particles, lead to build-up of agglomerates. Orthokinetic effect reduces with increasing frequency, radius and density of the particle. Brand et al. verified König's

results and found an expression to describe relative entrainment of a particle in an incompressible fluid.

$$H = \frac{U_p}{U_0} = \frac{1}{1 - j\omega\tau_d} \quad (1.3)$$

where U_p and U_0 are the particle and the fluid velocity, respectively, ω is the angular frequency and the term τ_d is called the relaxation time given by

$$\tau_d = \frac{2}{9} \frac{\rho_p a^2}{\mu_0} \quad (1.4)$$

where a and ρ_p is the particle radius and particle density respectively; larger relaxation times refer to slower reactions of a particle. The entrainment function H constitutes the basis of the orthokinetic entrainment model. It is obvious from Equation (4) that larger and heavier particles as well as higher frequencies lead to reduced particle mobility. There is an optimum interval of the vibration frequency in which particles collide and agglomerate to form clusters. The model, however, fails to explain particles agglomeration in monodisperse aerosols because of the equivalent entrainment rates.

2. **Mutual radiation pressure interaction:** Assuming two particles in transverse orientation to a given flow field, a pressure reduction will occur between the particles due to the increased fluid velocity at this location. This effect accounts for the Bernoulli Effect which leads to attraction between the two particles. König extended the phenomenon for arbitrary orientation of the particles derived an expression for the force between two closely spaced spheres in acoustic field. The acoustic wave causes a transfer of momentum on the emerged object which exerts a force acting on the object, the so-called radiation pressure force. Mutual radiation pressure interaction corresponds to the action of the forces of the two adjacent scatters exert onto each other.

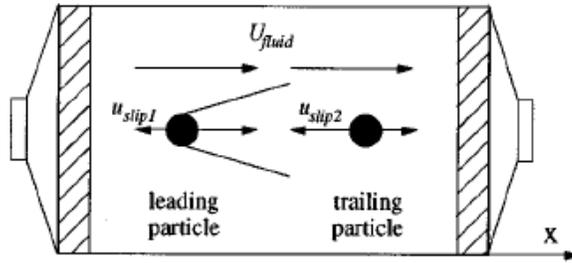


Figure 1.12 Convergence due to the acoustic wake effect versus repulsion due to mutual radiation pressure interaction for a pair of particles aligned on-axis

3. **The acoustic wake effect:** If we consider two closely spaced spheres moving along the acoustic velocity vector in on-axis orientation, the leading sphere will disturb the quiescent fluid and, independent of the Reynolds number, build up a wake in the area behind itself. If the second sphere is located close enough, it will travel within this disturbance. The wake leads to a pressure reduction in the area behind the leading particle so that the trailing particle experiences a drag reduction and moves with a higher speed than the “leader”.

Phase separation is another effect of ultrasounds on emulsions. Further improvement in demulsification was achieved under concurrent use of ultrasounds and electrophoresis [22]. Muralidhara et al. (1985) used ultrasounds and electrical field concurrently (for aqueous coal and ore slurries) and concluded that the method requires less energy for the combination of the electrical field and acoustic field to remove a unit of water from a suspension than the energy required if only an electrical field or an acoustical (sonic or ultrasonic) field were used separately or in sequence. The peak acceleration developed in the medium due to an ultrasonic wave at 20 kHz and amplitude of 0.024 mm is as high as 40000 G [102]. This is because particle displacement and velocity are negligible relative to the speed of the wave, thus the acoustic pressure can be significant compared to the ambient pressure.

1.3.2.1 High/ Low Frequency Sonication and the Phase Separation

At lower frequencies, when the wavelength of the sound is larger than the dimensions of the emulsion container, droplet coagulation occurs which play a major role in the separation process. Gautam et al. (2004) studied the coalescence of oil droplets from emulsions under a low-intensity ultrasonic field. The coalescence was attributed to the

negative acoustic contrast factor¹⁰ of oil droplets which drives them to the pressure antinodes of the standing wave.

Kyllönen et al. (2005) carried out a review of sonication effects on membrane filtration. The coagulation of aerosols is known to occur at lower frequencies [109]; however, in a liquid medium with colloidal dispersion of particles, coagulation takes place only at higher frequencies. At higher frequencies, when the wavelength of the sound is shorter than the dimensions of the emulsion container, a second phenomenon occurs concurrently. The radiation pressure moves the particles towards the pressure node or antinode places of the applied standing wave depending on the size and density of the particles. Under the influence of the high frequency ultrasonic standing waves, water droplets arrange themselves near the node or anti-node plane of the standing wave.

Law et al. (1998) studied high/low frequency ultrasounds on oil field emulsions separation. At lower frequencies, cavitation bubbles¹¹ are larger in size, and therefore, produce greater jet and collapsing energy because, for high frequencies sound wave, the time is not long enough during rarefaction cycle to create bubbles; for instance, at 20 kHz, the rarefaction cycle lasts 25 μs ($=1/2 f$), attaining its maximum negative pressure in 12.5 μs , whereas at 20 MHz, the rarefaction cycle lasts only 0.025 μs); as a result, it is concluded that as frequency increases, it becomes more difficult to achieve in the available time, and thus, greater sound intensities (i.e. greater amplitudes) are required to exceed the critical molecular distance and break down the liquid. That is why 20-50 kHz frequencies were generally chosen for cleaning purposes and have subsequently been found of value in sonochemistry.

1.3.2.2 Cavitation

Cavitation phenomenon occurs during sonication. In cavitation, microbubbles are created because of degassing and phase change to vapor. If a sufficiently large negative pressure P_c is applied to the liquid (here it will be the acoustic pressure on rarefaction, $P_c = P_h -$

¹⁰ Acoustic contrast factor is a parameter, depending on its sign, determines wh a particle in a given medium will be attracted to the pressure nodes or anti-nodes.

¹¹ Cavitation is the formation of vapor bubbles in the liquid when the static pressure of the liquid falls below its vapor pressure.

P_a), such that the average distance between molecules exceeds the threshold, critical molecular distance (R), to hold the liquid intact, the liquid will break down and voids or cavities will be created (i.e. cavitation bubbles will be formed). Once produced, two types of behavior are observed. In the first, bubbles created at low ultrasonic intensities ($1-3 \text{ W cm}^{-2}$) remain stable for many acoustic cycles. In the second, bubbles these cavities grow in size until the maximum of the negative pressure to be reached. In the succeeding compression cycle of the wave, however, they will be forced to contract, i.e. decrease in volume and some of them may even totally disappear (see Figure 1.13).

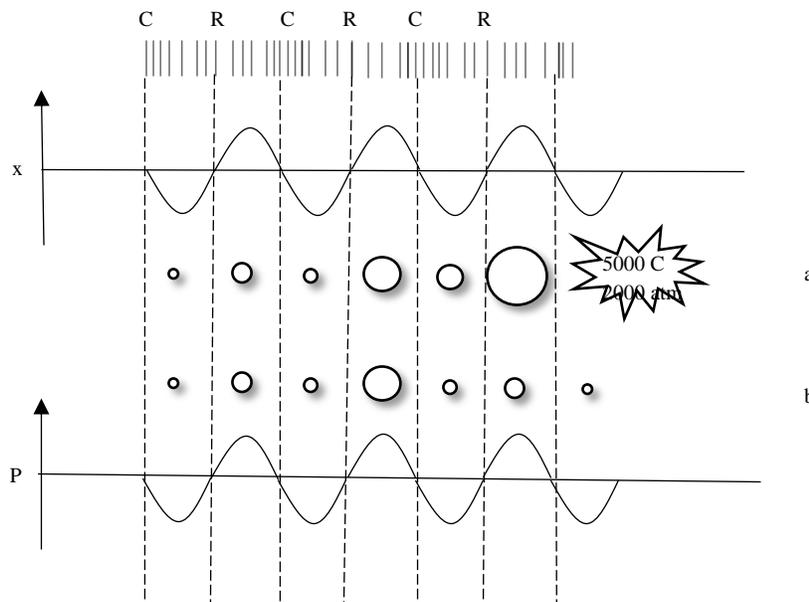


Figure 1.13 Creation of (a) stable and (b) transient cavitation [174]. The shock waves produced on total collapse in the stable cavitation of the bubbles has been estimated to be of the order of several of thousands of atmospheres and is thought to be the cause of the considerable erosion observed for components in the vicinity of the bubble [107]. Temperatures of more than 5000 K and pressures greater than 50 MPa are reported in cavitation collapse [99].

Cavitation is higher in the presence of solid particles because the microbubbles are formed on the surface of solid particles, reduce the surface energy and assist in separating the solids from liquid phase. In other words, the microbubbles are created on the surface of solids, impurities to nucleate. It is also believed that the heat generated by the absorbed ultrasonic energy into the medium will decrease the viscosity and further facilitate solids

removal [108]. In general, the threshold limit has been found to increase with a decrease in temperature. This may in part be due to an increase in either the surface tension or viscosity of the liquid as the temperature decreases, or it may be due to the decrease in the liquid vapor pressure (P_v).

1.3.2.3 Ultrasonic Device

Ultrasounds are generated and detected by transducers. In an ultrasonic device, transducers convert electrical to ultrasonic energy (transmitters) or vice versa (receivers). A variety of ultrasonic electrochemical apparatus exists to sonicate solutions. Among which, cleaning bath, probe and cup-horn are commonly used in diverse applications for laboratory use.

1. **The Cleaning Bath** The piezoelectric material is attached to the walls of the bath and transmits the ultrasound to water, and subsequently, the medium. Water transmits the ultrasound from the transducers to the reaction vessel. The water in the reaction tank is kept to a level just below the solution in the reaction vessel. Ultrasonic cleaning bath is a technique commonly used to remove dirt, grease, oil, and rust from materials.
2. **The Probe** The ultrasound is transferred via the probe (sonic horn or velocity transfer) tip to enter the media (direct sonicator). The power input is adjusted to control the vibrational amplitude and sonication intensity. The horn design is of utmost importance since it amplifies the vibration from the transducer. The vibrational amplitude of the piezoelectric crystal is normally small that cannot cause cavitation by direct coupling of the transducer to the medium. The shape of the horn will determine the gain and mechanical amplification of the vibration, and therefore, dictate the volume of sample that can be processed. A number of commercially available probe devices, referred to as cell disruptors before the advent of sonochemistry, mostly operates at 20 kHz and utilizes a wide range of different metal probes. There are three principal advantages of the probe method: much higher ultrasonic power since energy loss during the transfer of ultrasound through the bath media and reaction vessel walls are eliminated; the devices can

be tuned to give optimum performance in the reaction mixture for a range of powers; and the ultrasonic intensity and size of the sample to be irradiated can be matched fairly accurately for optimum effect. Although the use of probe provides several advantages over the use of baths, they also suffer from a similar disadvantage – they are only capable of operating at single fixed frequency. Also, with direct sonication, it is possible to generate radical species by the action of the probe tip on the solvent and erosion of the tip occurs with prolonged use.

3. **The Cup-horn** is an indirect sonicator, the energy is transmitted from the horn to the sample through water that operates as high intensity water baths. Cup horn sonicator is recommended for small samples because foaming and sample loss are eliminated. The horn is mounted within an acrylic cup filled with water. Cup horns offer the capability to sonicate multiple at one time.

1.3.2.4 Obstacles and Drawbacks

Unfortunately sonication suffers from some drawbacks such as low efficiency at higher influent viscosities. Prozorov et al (2004) showed the impact of viscosity on the slurries of metal particles. It is obvious that in sufficiently viscous media, the velocity of inter-particle collisions, and hence particles agglomeration, will probably be reduced [106].

There are a number of commercial applications of ultrasounds such as ultrasonic homogenizer, soldering baths, home humidifiers. Large scale application of ultrasounds suffers a series of setbacks:

1. Relatively larger outlay than other less expensive methods.
2. Volumetric effects requiring cavitation in upscaling such as energy consumption of cavitation, energy loss limits the total targeted volume.
3. General lack of knowledge in equipment designs, training.

A step towards upscaling of the method is guided not only by basic principles such as propagation, absorption, stress distribution, and other factors associated with ultrasonics, but also the nature of the materials and media, scale-up and implementation factors. It is very difficult to assess the effectiveness of the molecular interactions. Results obtained with different systems

appear to be dependent on process and geometry, frequency and power. Multiple frequencies in some cases outperform single frequency and give different efficiencies. At high level exposure, ultrasound has acute adverse effects on biological tissues through heating, acoustic cavitation and radiation force [111]. Having said that, there is not sufficient evidence of specific hazards and confirmed biological effects. Energy loss for the ultrasonic wave increases with increasing frequency. Internal organs also have different absorption coefficient when exposed to ultrasonic radiation. The absorption of ultrasound may cause heating. Current diagnostic ultrasonic equipment is very unlikely to cause severe damage to human body; however, the main concern is raised over unusual conditions or misuse of some non-medical devices, such as ultrasonic cleaning baths.

1.3.3 Summary

The separation mechanisms for two technologies were set out in this chapter and a comprehensive literature review was presented. It is believed that electromagnetics are capable to rupture the water film around the contaminants in the invert emulsion fluid and allow them to collide and aggregate and ultimately settle out by gravity. The ability of microwave to dewater sludge is very appealing in waste treatment applications. Microwave is preferred to the conventional heating process in a manner that it selectively heats the sludge instead of heating the bulk volume. The selective heating reduces the interfacial tension between particles and liquid phase and ease

Ultrasonic waves are capable of pulsing pressure and vibrating solids in the liquid medium. The pressure pulses lead to molecular agitation and shear stress, and separates solid particulates by orthokinetic, acoustic wake effect and mutual radiation pressure interaction mechanisms. Microbubbles are created under acoustic field when the exerted pressure exceeds the pressure threshold which holds the molecules together; the liquid will break down and cavities will be created. The phenomenon plays a prominent role in causing considerable agitation in the liquid and raising the possibility of particles' collisions. Lower frequencies are known to perform well for removing oil dirt or contaminants because lower acoustic field produces greater bubbles, and therefore, more jet force.

CHAPTER 2 MATERIALS AND METHODS

In this chapter, experimental protocols, materials and methodologies are described. In section 2.1, the details of emulsion preparation are laid out in detail followed by the protocols used for preparing fresh and rev dust contaminated emulsions in sections 2.2 and 2.3. The prepared fluid is used as the base fluid thereafter and contaminated with rev dust under different experimental conditions. In section 2.4, a description of the method is provided for studying the impact of a number of physical parameters (e.g. pH, temperature, etc.) on the emulsion stability.

The techniques used for the emulsion stability measurements are described in section 2.5. A description of dilution test is given in section 2.6 to find out whether the emulsions still remain invert after undergoing different physical conditions. Sections 2.7 and 2.8 explain the protocols used in microwave and ultrasound treatments respectively. A short description of the statistical analysis used in Chapter 3 is presented in 2.9. Randomized block design is used to study the significance of the parameters' effect on the drilling fluid.

2.1 Preparing Invert Emulsions

A standard protocol was used for preparing invert emulsion drilling fluid for reproducible results in subsequent experiments.

Composition: Invert emulsion ingredients and drilling fluid additives were supplied by Marquis Alliance Inc. Invert emulsions were prepared with Neodril base oil by mixing 9:1 oil-brine volume ratio (excluding the volume of emulsifier) and 8 L/m³ MF emulsifier. The 10 % brine portion consisted of water with 30 % w/w CaCl₂, 10 kg/m³ of lime and 25 kg/m³ organophilic clay were added shortly thereafter. Three different amounts of rev dust¹² particles (i.e. 0.05, 0.1, 0.15 and 0.2 g/ml) were used to contaminate invert emulsions. The size of the rev dust particles is given as d₅₀ of 14.52 μm and standard deviation of 24.45 μm. Fluid was mixed for 5 min with a commercial Hamilton mixer (Model 950) each time after a supplement of additives.

Invert emulsion was prepared as follows:

¹² Rev dust is a trademarked friction reducing material composed of crystoballite silica and crystalline quartz and is used in lab tests to simulate mud cutting fines.

1. Base oil and primary emulsifier (i.e. 8 L/m³ MF) were mixed for 5 minutes at 10,000 rpm and room temperature at 25°C.
2. Lime was added to the container and mixed at 10,000 rpm for 5 minutes.
3. Brine was added and mixed at 10,000 rpm for 5 minutes.
4. Organophilic clay was added and mixed at 17,000 rpm for 5 minutes.
5. The emulsions were stored at the room temperature (25°C) for 24 h.
6. Prepared emulsions were visually observed for any phase separation.
7. The emulsions were mixed at 10,000 rpm for 5 minutes prior to each experiment.

2.2 Fresh Invert Emulsion Stability

Several techniques were used to evaluate the stability of the prepared invert emulsions. The primary purpose of this experiment is to find out whether the prepared emulsions need further treatment (i.e. microwave and ultrasound) to become separated. The stability of the prepared emulsions was first analyzed with different shearing time after 24 h of aging. 10 ml aliquot of invert emulsion was agitated with a VMR analog mini mixer (model number 58816-121) for four to six min and speed range of 900 to 3200 rpm. A 20 to 25 mm tube holder was used to mix up (8) 50 ml of centrifuge tubes. Emulsions' stability was visually observed after agitation for phase separation. The agitated emulsions were aged for 24 h, placed in a 50 ml polyethylene tube, closed with a tight-fitting closure and centrifuged for 20 min and 3000 RCF (4150 rpm) with a benchtop centrifuge (Thermo Electron Corporation, Model CL3R) to separate the phases.

A 20 min centrifugation time was chosen as the optimum time because no significant phase separation was observed for periods longer than 20 min. To determine the optimum centrifugation time, a base sample (no rev dust particles) was centrifuged and visually observed every 5 min intervals for separation. It was observed that phase separation did not change after the fourth (i.e. 20 min) interval.

2.3 Stability of the Contaminated Invert Emulsions

The stability of the contaminated emulsions was analyzed using centrifugation as described in section 2.2. Several researchers have shown that fine particles stabilize the nano emulsion by diffusing into the oil-water interface [47 – 50]. The aim of this experiment is to find out whether fine particles reduce the stability of the emulsion in drilling fluid.

2.3.1 Emulsion Contamination with Rev Dust Particles

The next step is to contaminate the invert emulsion with rev dust particles and study the mechanisms responsible for fine particles stability in invert emulsions. Rev dust particles were used to simulate drill cuttings in the invert emulsion. The principal objective of the subsequent sections is to build a suspension of rev dust particles in invert emulsion that remains stable after 3000 RCF centrifugation for 20 min. Emulsions were contaminated with rev dust particles as follows:

1. Four different concentrations of rev dust (**50, 100, 150** and **200** g/ml) were added to 5 ml deionized water.
2. The vial was mixed with an analog VMR mini mixer at 3200 rpm and aged for 24 h.
3. 10 ml aliquot of Neodrill emulsions was added to the vial and agitated with the mini mixer at 3200 rpm for 5 min and aged for 24 h.
4. The vial was centrifuged at 3000 RCF for 20 minutes; the phase separation was visually observed afterwards and quantified with a digital caliper (see section 2.5).
5. The caliper measurements were converted to volume fraction and given in Table 3.2 of Chapter 3.

As a part of this study, a selected number of invert emulsions was prepared with Envirodrill base oil. This base oil supposedly contains relatively lower amount of aromatic components than Neodrill base oil. The invert emulsion was prepared with the above recipe set out for Neodrill invert emulsion.

2.4 The Effect of Physical Parameters on the Stability of the Contaminated Emulsion

Several pertinent physical factors (e.g. pH and temperature, electrolyte, etc.) were changed when preparing the invert emulsions. The principal aim of these experiments is to build invert emulsions that remain stable and unseparated after conventional treatments such as centrifugation and chemical treatments. If the conventional treatments fail to separate the prepared emulsion, further treatments will be investigated (i.e. microwave and ultrasound) to destabilize the emulsion and separate the fine particles.

2.4.1 pH Effects on the Emulsion Stability

Sodium Hydroxide was added to deionized water to increase its pH to 7.5 and 12.5. Four different concentrations (i.e. 50, 100, 150 and 200 g/L) of rev dust were added to a 5 ml aliquot of the water with the increased pH of 7.5 and 12.5. These samples are mixed with the analog VMR mini mixer at 3200 rpm and aged for 24 h. 10 ml aliquot of Neodrill emulsions was added to the vial and agitated with the mini mixer at 3200 rpm for 5 min and aged for 24 h. The vial was centrifuged at 3000 RCF for 20 minutes; the phase separation was visually observed and quantified with a digital caliper afterwards.

2.4.2 Temperature Effects on the Emulsion Stability

Deionized water was pre-heated to 55°C in a water bath for 5 min before hydrating rev dust. Rev dust was added to the heated water in different concentrations and mixed with the analog mini mixer at 3200 rpm and aged for 24 h. 10 ml aliquot of Neodrill invert emulsion was added to the vial and agitated the mini mixer at 3200 rpm for 5 min and aged for 24 h. The vial was centrifuged at 3000 RCF for 20 minutes; the phase separation was visually observed and quantified with a digital caliper afterwards.

2.4.3 Electrolytes Effects on the Emulsion Stability

The effect of electrolytes was studied by running three different screening tests. First, deionized water was used in preparing emulsion to study the effect of ions on the emulsion stability. Second, Calcium Chloride was replaced with Sodium Chloride to observe the effect of ions valence on the emulsion stability. At last, lime content was reduced in the emulsion to investigate the impact of Calcium on the emulsion stability.

The invert emulsion was prepared with deionized water instead of brine (30% w/w CaCl_2) to study the fluid's behavior when it contains no calcium. To study the effect of ion valence on emulsion stability, invert emulsion was also prepared with Sodium brine (30% w/w NaCl), aged for 24 h and centrifuged at 3000 RCF for 20 min. The phase separation was measured with the digital caliper and converted to volume fraction as shown in section 2.3.1.

Hydrated lime--composed of calcium hydroxide and crystalline silica-- is another source of calcium in the invert emulsion widely used to activate emulsifiers in the invert emulsion; however, it may inhibit the hydration of clay particles. Hydrated lime content was once halved to 5 kg/m^3 and eliminated another time from the recipe while all other parameters remained constant. Emulsions were aged for 24 h and centrifuged at 3000 RCF for 20 min.

2.4.4 Hot Rolling Effects on the Emulsion Stability

Neodrill invert emulsions were hot-rolled at high temperature in a pressurized cell to simulate the fluid under drilling conditions. High temperature aging is conducted to evaluate the impact of temperature on drilling fluid's performance.

1. Four different concentrations of rev dust (**50, 100, 150 and 200 g/L**) were added to 200 ml of invert emulsions.
2. 300 ml of the contaminated emulsions were placed in the oven roller and hot-rolled at 121°C for 16 h.
3. 50 ml of the hot-rolled fluid was centrifuged at 3000 RCF for 20 min, and phase separation was observed and quantified by the caliper measurement.
4. The emulsions' stability was analyzed with respect to their phase separation and ES measurements.

2.4.5 Organophilic Clay Content Effects on the Emulsion Stability

Drilling fluid cutting capacity increases with increasing stress yield point. To increase the stress yield point of the fluid, organophilic clay was added to the prepared invert

emulsion in 5 kg/m³ increments (until the clay content reaches 45 kg/m³) and mixed for 30 min. Rev dust was added to the clay laden emulsion in four different concentrations (**50, 100, 150 and 200 g/L**). Emulsions then were centrifuged at 3000 RCF for 20 min and the phase separation was quantified with a digital caliper to observe emulsions' stability.

2.4.6 Wettability Effects on the Emulsion Stability

1. Four different concentrations of rev dust (**50, 100, 150 and 200 g/L**) were added to a centrifuging vial with 5 ml of Neodrill base oil.
2. The vial was mixed with an analog VMR mini mixer at 3200 rpm for 2 min and aged for 24 h.
3. 10 ml aliquot of Neodrill emulsions was added to the vial and agitated with the mini mixer at 3200 rpm for 5 min.
4. The vial was centrifuged at 3000 RCF for 20 minutes, the phase separation was visually observed afterwards, and the volume of sedimentation and supernatant oil were measured indirectly with a digital caliper.

Sediment fraction (shown in Figure 2.2) was compared to that of hydrated rev dust with deionized water to find whether oil wetting the particles have an impact on the emulsion stability.

To enhance particles oil wettability, a certain volume of MF oil-wet surfactant was used.

1. The emulsion was prepared as set out in section 2.1.
2. Organophilic clay was added and mixed at 17,000 rpm for 5 minutes.
3. The surfactant was added thereafter in 2 ml/ 50 g solid and 10 ml/ 50 g solid.
4. Rev dust was added in different concentrations (**50, 100, 150 and 200 g/L**) and mixed at 10,000 rpm for 5 min.
5. Electrical stability of the emulsions was measured using a commercial ES meter, Fann Model 22C, and averaged over three independently repeated tests.

2.5 Phase Separation Measurements

Several methods were used to evaluate the stability of the emulsions and efficiency of treatments: caliper (in volume), rheology measurements and electrical stability. A description of the techniques is given below to quantify and measure the phase separation after centrifugation. Caliper and optical density measurements were used in virtually all experiments to measure the phase separation. Rheological and electrical stability tests were only conducted for the samples prepared with the Hamilton mixer in large quantities because these tests require a minimum of 300 ml of a sample.

2.5.1 Caliper Measurements

A digital caliper was used to measure the phase separation in millimeter. For certain samples, separated layers were not distinguishable and became difficult to measure causing uncertainty in the measurements. The height of sedimentation and supernatant oil were measured with a digital caliper in mm and were converted to ml using the formulas:

If $h < 17.23$

$$V = \left[\frac{0.362 \times \pi \times h \times (h + 4.04)^2 - \pi \times h \times r_1^2}{3} \right] \times 10^{-3} \quad (2.1)$$

Otherwise,

$$V = \left[\pi \times (h - 17.23) \times r_0^2 \right] \times 10^{-3} + V_0 \quad (2.2)$$

where, r_0 (mm) is the tube radius, h (mm) is the height of the separated layer, r_1 is cap radius (mm) of the truncated cone, V_0 is the volume of the truncated cone (ml) as shown in Figure 2.1.

The values from caliper measurements were converted to volume because the centrifuging tubes are not cylindrical. In other words, fraction height scale of separated phases is not a suitable index for the phase separation evaluation; sediment fraction is overcalculated when fraction height scale is used as a phase separation index because the

volume of the conical part of the centrifuging tube is lower than a cylinder with equivalent height.

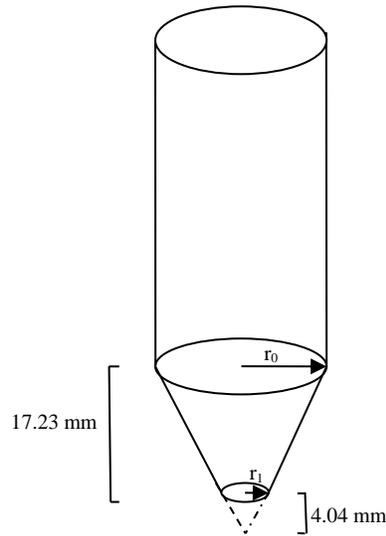


Figure 2.1 The Schematic representation of the parameters and values used in the volume calculation

A typical result of the phase separation experiments is shown in Figure 2.2. Generally, a clear oil layer is observed at the top of the sample. Transition 1 is the invert emulsion below the supernatant oil layer, and Transition 2 is the unseparated emulsion, which contains organoclay. Sediment is assumed to be mostly rev dust due to its dark color settled down at the bottom of the tube. Both layers may contain both phases; however, the fraction is not known. Some measurements are given in a range because the separated layer's surface was not smooth and flattened, so the caliper measurements have been averaged in the observation range. The converted volumes were substituted in the following formulas to be computed for fractions according to:

$$R_{oil} = \frac{\text{Total of the separated oil (ml)}}{\text{Total Volume - Sediment (ml)}} \quad (2.3)$$

$$R_{Sediment} = \frac{\text{Volume of the sediment (ml)}}{\text{Dry rev dust volume (ml)}} \times 0.263 \quad (2.4)$$

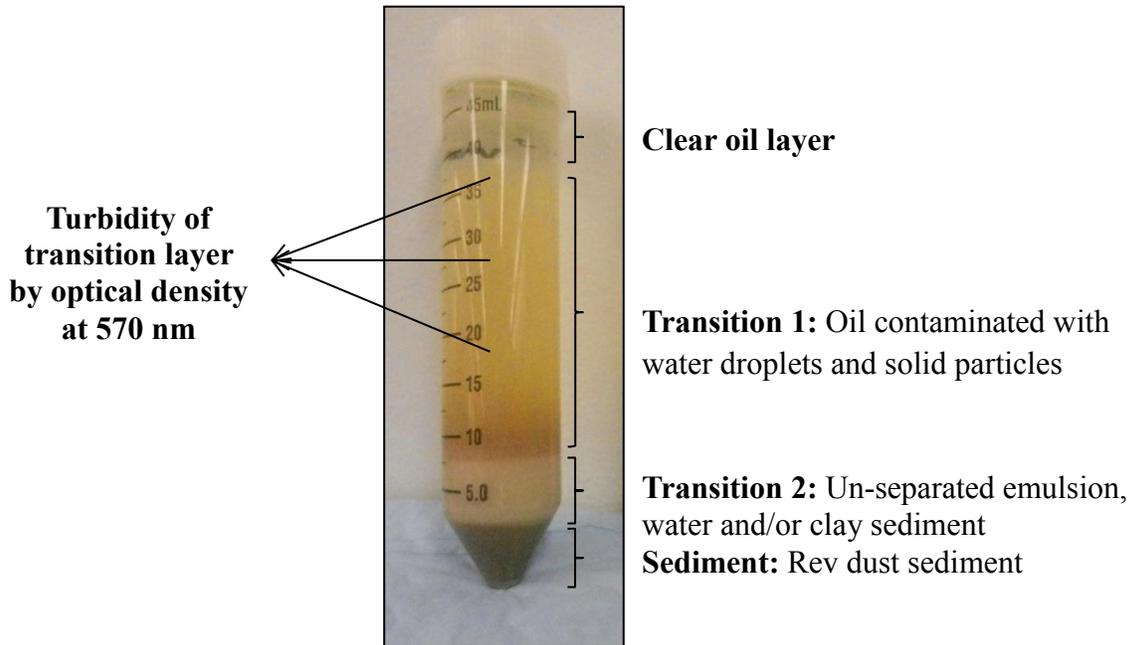


Figure 2.2 Two Phase separation for sample of Neodrill emulsion after centrifuging.

On the denominator of oil ratio (i.e. Equation 3), volume of sediment was subtracted from the total volume, since total volume varies with the amount of added rev dust; for instance, if certain volume of rev dust is added to 300 ml of Neodrill emulsion, the volume of separated sediment for higher rev dust concentration is more than lower rev dust concentration. Rev dust fractions were also calculated by dividing the sediment volume by powdered rev dust volume. The ratio represents the fraction of rev dust settled down to the initial added rev dust. The ratio has been rescaled by a constant (i.e. the fraction of sediment for 50 g/L) to be well suited for graphical representation.

2.5.2 Optical Density Measurements

The optical density or absorbance is a quantitative expression defined as the ratio of the radiation falling on a material to the radiation transmitted through a material, and is reported in “Absorbance Units”. An increase in optical density indicates an increase in particle size. 200 μm of the supernatant oil after centrifuging was taken for optical density measurements. Optical density was measured using a spectrophotometer (i.e. SpectraMax Plus384 Absorbance Microplate Reader) at 590 nm to read the turbidity.

Darley et al. (1957) studied the onset of flocculation/ aggregation of particles by measuring gel strength, clay volume and optical density. When aggregation of particles occurs, optical density rapidly increased indicating the presence of larger particles. Studies have also shown that the transparency of emulsions increases with decreasing droplet size [77] [78]. As a result, an increase in optical density of supernatant oil could be caused by greater amount of total suspended particles or smaller emulsion droplet size. The conclusion on optical density measurements is explained by either of these hypotheses depending on the conditions; for instance, when fine particles are not present in the emulsion, an increase in optical density of invert emulsion is explained by smaller emulsion droplet. On the other hand, when emulsion is contaminated with fine particles, an increase in the optical density of the emulsion is explained by greater amount of total suspended particles.

2.5.3 Rheological Measurements

Rheological properties of drilling fluid indicate the character of deformation and flow of drilling fluids. Bingham plastic and power law models are two common models to describe the behavior of shear dependent fluids like drilling fluids. The invert emulsion in this study behaves as a non-Newtonian fluid and exhibits a Bingham plastic behavior. The shear stress vs. shear rate plot demonstrated a linear trend with an intercept indicating the fluid to be Bingham. The fluid's behavior is defined with only two points for the consistency curve. A Fann Model 35 viscometer was used to measure the rheological parameters including Apparent (μ_a) and Plastic Viscosity (μ_p). The sample is added to the stainless steel sample cup up to the sample fill line (350 ml) and placed under the sleeve. The cup is lifted up using the locking knob to the scribed line on the rotor for the proper immersion depth. The desired speed is selected with the speed switch on the right side of the base.

$$\mu_a = \theta_{600}/2 \text{ (Pa}\cdot\text{s)} \quad (2.5)$$

$$\mu_p = \theta_{600} - \theta_{300} \text{ (mPa}\cdot\text{s)} \quad (2.6)$$

The viscometer is also used to determine the gel strength (in lb/100 sq. ft. or kg/ m²) of drilling fluids. The gel strength indicates the inter-particle forces and the degree of

gelation when the fluid is at static conditions. Sample is stirred at 600 rpm for about 15 sec and left at rest for 10 sec. The viscometer is then switched to 3 rpm (gel position) and dial reading is recorded.



Figure 2.3 Fann Model 35 viscometer is a direct reading instrument used to measure rheological properties in six-speed designs. The sample is added to the steel cup and placed under the sleeve.

2.5.4 Electrical Stability

Electrical stability (ES) of an oil based mud is considered a measure of its emulsion stability. Crittendon conjectured that emulsion is more stable at higher ES values [79]. The electrical stability of the invert emulsion was measured using an OFITE Electrical Stability Meter (ES). The probe was immersed in the sample and hand stirred for 10 seconds to create a uniform composition and temperature. The display value displays the voltage at which the emulsion breaks down. There may be a great variation in readings when measuring the electrical stability. According to American Petroleum Institute procedure [80], the two ES values should not differ by more than 50 g/L. If they differ by more than 50 g/L, the meter or electrode should be checked. The chemical composition

and shear history of a drilling fluid dictate the absolute magnitude of the ES. As a result, only trends in Electrical Stability, not exact values, in ES should be used in interpretations [81].

2.5.5 Microscopic Analysis

A Carl Zeiss AxioVert S100 microscope was used to visually analyze the supernatant oil and sediment layers taken after centrifuging.

2.5.6 Retort Analysis

The OFITE retort kit was used as a means of separating and measuring the volumes of water, oil, and solids contained in a sample of drilling fluid. 50 ml of sample is heated to vaporize the liquid components which are then condensed and collected in a graduated cylinder. The retort was allowed to run for a minimum of 45 minutes. Liquid volumes are determined from reading the water and oil phases on the graduated cylinder. The total volume of solids, both suspended and dissolved, is obtained by noting the difference of the total sample volume versus the final liquid volume collected.

2.6 Dilution Test

In order to ascertain that adding 5 ml of aqueous rev dust does not convert emulsions from invert to direct, a dilution test was carried out. A drop of the emulsions was added to a beaker of deionized water and observed for its dispersion behavior. If the droplet is not dispersed in water, we can conclude that the emulsion is invert.

2.7 Microwave

A commercial microwave (BP-110 manufactured by Microwave Research and Applications, Inc) was used to heat samples at the fixed frequency of 2.45 GHz. Even though this is a laboratory microwave, it operates like most of household microwave ovens in that power and time are set. Mode stirrer system provides uniform heating within cavity. Domestic microwaves have certain limitations which render their use unsafe and hazardous for laboratory experiments. Fifty (50) ml of invert emulsion was poured into a beaker and microwaved at different power levels. The

location of the beaker was marked to place the sample in the same spot for each run. Microwaved samples were left to cool down and then poured into centrifuging tubes to age for 24 h. After aging, samples were centrifuged for 20 min and 3000 RCF to allow phase separation. The same methodology was used to study the effect of viscosity on the separation efficiency. 35 kg/m³ organophilic clay was added to the invert emulsion, and thereafter, contaminated with different rev dust loads. Samples were aged for 24 h and centrifuged for 20 min and 3000 RCF. Phase separation was quantified using caliper and density measurements.

2.8 Ultrasound

An ultrasonic cleaner with 40 KHz frequency and 5.7 L capacity was used to separate invert emulsion drilling fluids. A beaker with 50 ml invert emulsion was placed inside the water bath and sonicated for 5 minutes. The sample was poured into a centrifuging tube and centrifuged for 20 min and 3000 RCF. The phase separation was visually observed afterwards, and the volume of sedimentation and supernatant oil were measured indirectly with a digital caliper. Water level inside the ultrasonic bath plays a key role to transmit pressure waves to the sample. When water level in the tank changes, the generator electrically matches with the mechanical load and provides an optimum output. As a result, it is recommended to maintain water in the tank at a fixed level for all experiments.

2.9 Statistical Analysis

Standard deviation and mean were calculated for three replicates and indicated in figures by vertical error bars to describe the distribution of the measurements. To study the significance of the results, two statistical tests are used based on the experimental design.

2.9.1 Single Factor Analysis of Variance (ANOVA)

To compare a different levels (treatments) of a single factor, an analysis of variance is used to test hypotheses about the treatment means and estimate the treatment effects. Testing the equality of the a treatment means $\mu_1, \mu_2, \dots, \mu_a$. (null hypothesis) which is equivalent to testing the hypotheses.

$$H_0 = \mu_1 = \mu_2 = \dots = \mu_\alpha \quad (\text{Null hypothesis})$$

$$H_1 = \mu_i \neq \mu_j \text{ for at least one } i \text{ and } j \quad (\text{Alternative hypothesis})$$

If the null hypothesis is true, each observation consists of the overall mean μ plus a realization of the random error ϵ_{ij} . Therefore, if the null hypothesis is true, changing the levels of the factor has no effect on the mean response.

The ANOVA partitions the total variability in the sample data into two component parts. The test of above hypothesis is based on a comparison of two independent estimates of the population variance. The total variability in the data is described by the total sum of squares

$$SS_T = \sum_{i=1}^a \sum_{j=1}^n (y_{ij} - \bar{y}_{..})^2 \quad (2.7)$$

in which, a is the number of treatments (e.g. rev dust concentration, pH or temperature), n is the total number of observations, y_{ij} represents the response (i.e. phase separation), \bar{y}_i is the average of i^{th} row. And $\bar{y}_{..}$ is the average of all responses.

The partition of the total sum of squares is given in the following definition.

$$\sum_{i=1}^a \sum_{j=1}^n (y_{ij} - \bar{y}_{..})^2 = n \sum_{i=1}^a (\bar{y}_i - \bar{y}_{..})^2 + \sum_{i=1}^a \sum_{j=1}^n (y_{ij} - \bar{y}_i)^2 \quad (2.8)$$

Or symbolically,

$$SS_T = SS_{Treatments} + SS_E \quad (2.9)$$

The above equation indicates that the total variability in the data, measured by the total corrected sum of squares SS_T , can be partitioned into a sum of squares of differences between treatment means and the grand mean, denoted $SS_{Treatments}$, and a sum of squares of differences of observations within a treatment from the treatment mean denoted SS_E . Differences between observed treatment and the grand means measure the differences between treatments, while differences of observations within a treatment from the

treatment mean can be due only to random error. The sums of squares computing formulas for the ANOVA with equal sample sizes in each treatment are

$$SS_T = \sum_{i=1}^a \sum_{j=1}^n y_{ij} - \frac{\bar{y}_{..}}{N} \quad (2.10)$$

$$SS_{Treatments} = \sum_{i=1}^a \frac{y_i^2}{n} - \frac{\bar{y}_{..}}{N} \quad (2.11)$$

There is also a partition of the number of degrees of freedom that corresponds to the sum of squares identity in Equation (6). That is, there are $an - N$ observations; thus, SS_T has $an - 1$ degrees of freedom. There are a levels of the factor, so $SS_{Treatments}$ has $a - 1$ degrees of freedom. Finally, within any treatment there are n replicates providing $n - 1$ degrees of freedom with which to estimate the experimental error. Since there are a treatments, we have $a(n - 1)$ degrees of freedom for error. Therefore, the degrees of freedom partition is

$$an - 1 = a - 1 + a(n - 1) \quad (2.12)$$

The mean square for treatments and error are calculated as the ratio of the sum of squares of treatments and error by their corresponding degree of freedom as below

$$MS_{Treatments} = \frac{SS_{Treatments}}{(a - 1)} \quad (2.13)$$

$$MS_E = \frac{SS_E}{a(n - 1)} \quad (2.14)$$

If the null hypothesis is true, the ratio

$$F_0 = \frac{MS_{Treatments}}{MS_E} \quad (2.15)$$

has an F -distribution with $a - 1$ and $a(n - 1)$ degrees of freedom. Under the alternative hypothesis, the expected value of the numerator of the test statistic is greater than the expected value of the denominator. Consequently, we should reject H_0 if the statistic is large. This implies an upper-tail, one-tail critical region. Therefore, we would reject H_0 if $f_0 > f_{\alpha, a-1, 1(n-1)}$ where f_0 is the computed value of F_0 from Equation 15.

2.9.2 Randomized Block Design

The randomized block design is used to find out if there is a significant difference between treatments. The randomized block design is an extension of the paired t -test where the factor of interest has more than two levels (i.e. more than two treatments must be compared). The technique was used to find out if physical factors (e.g. pH, temperature and rev dust content) have any significant effect on the phase separation. If we wish to compare α different level of a single factor (treatment), an analysis of variance can be used to test for equality of treatment effects. We are interested in testing the equality of α treatment means (e.g. phase separation of four different rev dust content). We assume that factors do not interact; for instance, the pH effect remains unchanged regardless of temperature and rev dust content. We find that this is equivalent to testing the below hypotheses:

$$H_0 = \mu_1 = \mu_2 = \dots = \mu_\alpha \quad (\text{Null hypothesis})$$

$$H_1 = \mu_i \neq \mu_j \text{ for at least one } i \text{ and } j \quad (\text{Alternative hypothesis})$$

Therefore, if the null hypothesis is true, changing the levels of the factor has no effect on the mean response.

The sum of squares identity is extended to the randomized block design as the analysis of variance:

$$\sum_{i=1}^a \sum_{j=1}^b (y_{ij} - \bar{y}_{..})^2 = b \sum_{i=1}^a (\bar{y}_{i.} - \bar{y}_{..})^2 + a \sum_{j=1}^b (\bar{y}_{.j} - \bar{y}_{..})^2 + \sum_{i=1}^a \sum_{j=1}^b (y_{ij} - \bar{y}_{.j} - \bar{y}_{i.} + \bar{y}_{..})^2 \quad (2.16)$$

In which, a and b are the number of rows (treatments) and columns (blocks), y_{ij} represents the response (i.e. phase separation), $\bar{y}_{i.}$ and $\bar{y}_{.j}$ are the averages of i th row and j th column respectively and $\bar{y}_{..}$ is the average of all responses.

The degrees of freedom corresponding to the sum of squares are
 $(a-1) + (b-1) + (a-1)(b-1)$ (2.17)

For the randomized block design, the relevant mean squares are

$$MS_{Treatments} = \frac{SS_{Treatments}}{a-1} \quad (2.18)$$

$$MS_{Blocks} = \frac{SS_{Blocks}}{b-1} \quad (2.19)$$

$$MS_E = \frac{SS_E}{(a-1)(b-1)} \quad (2.20)$$

To test the null hypothesis, we use the ratio, $F_0 = \frac{MS_{Treatments}}{MS_E}$, which has an F -distribution with $a-1$ and $(a-1)(b-1)$ degrees of freedom if the null hypothesis is true.

We reject the null hypothesis at the α -level of significance if the calculated value of $F_0 > F_{\alpha, a-1, (a-1)(b-1)}$. P value is computed from the F_0 ratio and ANOVA table. If the P value obtained from ANOVA table with $df_1 = (a-1)$ and $df_2 = (a-1)(b-1)$ is smaller than α (significance level), then we reject the null hypothesis. In other words, if $P\text{-value} \leq \alpha$, then reject H_0 and if $P\text{-value} > \alpha$, then do not reject H_0 .

CHAPTER 3

RESULTS AND DISCUSSIONS

In this chapter, results of the experiments—as per the methodology described in Chapter 2—are presented and discussed. The aim of this section is to study the parameters which play a significant role in emulsion gelation and stability. The results are utilized to build the most stable physical conditions for the succeeding sections (i.e. treatment methods). It is intended to prepare an invert emulsion which remains stable after conventional mechanical treatments such as centrifugation. In other words, the results of this section serve as the basis for preparing the most stable emulsions to be treated by microwave and ultrasound.

Caliper measurement, microscopic analysis and Electrical Stability were three principal techniques used for invert emulsion stability analysis. Randomized block design was used to statistically assess the significance of the parameters. In section 3.1, the stability of fresh emulsion under different physical conditions is presented graphically and numerically. Fresh invert emulsion is prepared under basic physical conditions (e.g. room temperature (25 °C) and no added alkalinity to the deionized water) with no rev dust contamination as laid out in section 2.1. The impact of the physical parameters on the fresh emulsion stability is addressed in sections 3.2 to 3.6. The most suitable physical conditions (i.e. pH, temperature and rev dust content) for emulsion stability were selected for formulating the emulsion to be tested using microwave and ultrasound. Microwave and ultrasound treatment results are given and discussed in sections 3.7 and 3.8.

3.1 Fresh Invert Emulsion Stability

Neodrill emulsion was prepared as laid out in section 2.1. Neodrill base oil was used for the most of screening tests. In a few tests, Neodrill base oil was replaced with Envirodrill base oil to study the impact of the base oil on the particles' suspension capacity. Ten (10) ml aliquot of the prepared emulsion was left at the room temperature (25 °C) and observed for the phase separation and emulsion stability. Next, a wide range of speed (from 900 to 3200 rpm) was used with the VMR vortex mini mixer (model number 58816-121) to shear the emulsions to study the impact of shearing rate on the emulsions stability. Observations were

made based on the color and visual characteristics (e.g. flow behavior) of the separated phases.

As shown in Figure 3.1, no immediate separation was observed for Neodrill invert emulsions after shearing and the samples remained stable after three weeks aging. The invert emulsion before centrifugation (Figure 3.1, left) is uniform in color; indicating the emulsion stability. Table 3.1 gives the speed range, shearing time and observation for the sheared invert emulsion. The test was replicated for 4 min and 6 min shearing time, but no separation was observed for any of the replicates (mixing more than 5 min is not recommended with the given device). Therefore, it is concluded that the vortex mixer does not exert sufficient force to break the emulsion.

Table 3.1 Speed range for agitating Neodrill invert emulsions with the VMR mini mixer. No separation was observed for all sheared samples with the speed range of 900 to 3200 rpm.

Speed Range (rpm)	Shearing Time	Observation
900	5 min	No separation
1500	5 min	No separation
3200	5 min	No separation

Samples were then centrifuged at 3000 RCF¹³ for 20 min to separate into three phases (i.e. oil, water and solid) and measure the sediment. Figure 3.1 (right) shows a typical sample after centrifuging. Oil (transparent) has been separated at the top, and organophilic clay (beige color) settled down at the bottom of the centrifuging tube.

The sediment at the bottom of the tube is assumed to be organophilic clay due to the color resemblance to the dry clay particles. The results indicated that the prepared emulsions are stable at room conditions (25°C and 90 kPa), but separated under 3000 RCF centrifugation force. Consequently, to differentiate the impact of physical parameters on the emulsion stability, all samples would be centrifuged thereafter with 3000 RCF for 20 min to break the emulsion into three distinct phases (i.e. pure oil, emulsion and sediment) as shown in Figure 3.1 (right).

¹³ Relative Centrifugal Force

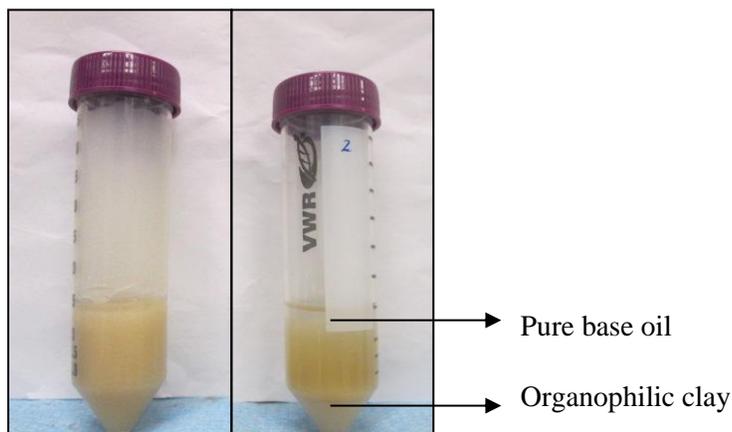


Figure 3.1 Neodrill invert emulsions before (left) and after centrifuging (right) for 20 min. The emulsions remained stable after three weeks of aging. Oil (transparent) has been separated at the top, and organophilic clay settled down at the bottom of the tube after 20 min of centrifuging with 3000 RCF.

3.2 Effect of pH, Temperature and Rev Dust Content on Rev Dust Hydration¹⁴

Several pertinent physical factors (e.g. pH and temperature, rev dust content) were changed when preparing the invert emulsions. These factors are assumed to be the most important parameters affecting the stability of invert emulsion drilling fluids. These parameters are tested in order to study the degree of which they affect the suspension of rev dust particles. The corresponding physical conditions (i.e. pH, temperature and rev dust content) of the most stable emulsions were selected to prepare a new formulation of drilling fluid to be tested using microwave and ultrasound.

3.2.1 pH Effect on the Rev Dust Hydration

The pH of deionized water was increased to 7.5 and 12.5 using Sodium Hydroxide and rev dust was added to the water in different concentrations as laid out in section 2.4.1. Figure 3.2 shows the aqueous solution of rev dust with pH of 7.5 and 12.5 before adding invert emulsion. It was observed that increasing pH diminished the supernatant water at the top and improved the hydration of rev dust particles in 5 ml of deionized water. As

¹⁴ Hydration is the mechanism in which clay particles incorporate water molecules directly into the crystalline structure.

shown in Figure 3.2 (left), rev dust particles did not fully absorb all the 5 ml water (partial hydration). Figure 3.2 (middle) shows a partial hydration for 200 g/L rev dust and pH of 7.5. A turbid water layer is observed at the top, but rev dust has not fully absorbed all the water. In Figure 3.2 (right), rev dust has hydrated to its fullest extent (i.e. complete hydration) inasmuch as no free water is visible.

At high pH, OH^- ions interact with the edges of the clay particles making them negatively charged. Particles, therefore, disperse much more effectively at higher pH range because of the developed negative charge. At higher rev dust loads, the sample did not ooze out of vials when held upside down which indicates a high degree of gelation. In other words, higher alkalinity demonstrated a higher degree of hydration for rev dust particles. In conclusion, rev dust particles better hydrate in higher pH before the addition of invert emulsion; the impact of pH on the emulsion's stability is given in section 3.3.

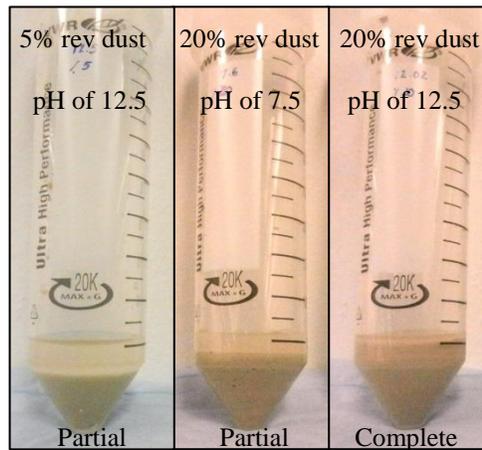


Figure 3.2 Hydration of rev dust particles in deionized water: 5% rev dust and pH of 12.5 (left), 20% and pH of 7.5 (middle), and 20% and pH of 12.5 (right) in which all the deionized water has been absorbed in rev dust particles. It is observed that rev dust particles have relatively better hydrated in higher pH (right) than lower alkalinity (middle) because 5 ml deionized water has not been fully absorbed into rev dust particles (complete hydration).

3.2.2 Temperature Effect on the Rev Dust Hydration

Increasing temperature favored hydration of rev dust particles and produced more gelled solution. As discussed in Chapter 1, at elevated temperatures, the zeta potential becomes more negative and leads to increased gelation of the fluid. Figure 3.3 shows 200 g/L rev dust content hydrated at the room temperature (25°C) and 55°C. Unfortunately, the picture does not clearly reflect the difference between two samples; however, the 55 °C hydrated rev dust sample could be observed (visually) to be slightly thicker as it flows slowly when tilting the tube. As per section 3.2.1, all the observations are made visually before adding invert emulsion. To conclude, higher temperature slightly affected the hydration of rev dust particles. The impact of temperature on the emulsion's stability is discussed further in section 3.3.

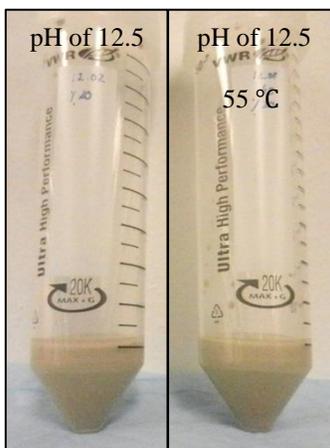


Figure 3.3 Hydration of rev dust particles in deionized water. 200 g/L rev dust and pH of 12.5 (left), and 200 g/L rev dust and pH of 12.5 and preheated to 55°C (right). The difference is not visually noticeable; however, the 55 °C hydrated rev dust sample flowed more slowly when tilting the centrifuging tube.

3.3 The Effect of pH, Temperature and Rev Dust Content on the Emulsion Stability

Having added 10 ml aliquot of Neodrill invert emulsion to the hydrated rev dust and mixed for 5 min with the mini mixer, the samples were aged for 24 h and centrifuged at 3000 RCF for 20

min¹⁵. The sequence of adding Neodrill invert emulsion to the hydrated rev dust was not practical to reverse (i.e. adding 5 ml of hydrated rev dust to 10 ml of Neodrill invert emulsion) since hydrated rev dust is typically stiff to flow into another container. As a result, Neodrill invert is added to the hydrated rev dust hereafter. Figure 3.4 shows invert emulsion samples after centrifuging for pH 7.5 and 12.5 at the room temperature (25°C) and 55°C. The separation is reported in average volume fraction of the contaminated emulsion in Table 3.2 and presented graphically in Figure 3.5. The first row of Table 3.2 reports the phase separation for the base Neodrill invert emulsion with no rev dust contamination (it contains no rev dust, and consequently, zero sediment).

At first glance, the sediment (charcoal grey sediment at the bottom assumed to be hydrated rev dust) and Transition 1 (assumed to be emulsion because of its beige color, see Figure 3.1) fractions for 100 and 150 g/L rev dust concentration are the lowest and highest, respectively, regardless of pH and temperature. Thus, the 100-150 g/L rev dust content stabilized the invert emulsion the most. Optical density values gradually decreased with increasing rev dust content as it is shown in Table 3.2. It is postulated that rev dust particles at higher concentrations enmesh the suspended particulates, form aggregates and settle down gravitationally resulting in a lower optical density.

Clay particles (such as rev dust) have the tendency to entrap and agglomerate the surrounding suspended solids very efficiently. During this stage, some Pozzolanic reactions also occur, in which, a cementitious particles settles down to the bottom of the reaction vessel. In other words, higher rev dust content serves to enmesh particulate material, thus effecting destabilization essentially by a sweeping mechanism. As a result, as it is shown in Table 3.2, rev dust content as high as 200 g/L has led to instability in the suspension.

Adding rev dust to the invert emulsion imparted turbidity to the Transition 1 suggesting rev dust particle suspension in the liquid phase. The results in Table 3.2 indicate that Transition 1 greatly reduced from 0.787 to 0.216 volume fraction for 50 g/L rev dust. In contrast, Transition 2

¹⁵ It should be noted that the inverse addition (i.e. adding hydrated rev dust to 10 ml of Neodrill invert emulsion) was not practical since rev dust particles became very stiff when hydrated that did not allow the flow of hydrated particles into centrifugation tube.

(mostly composed of organophilic clay and water, see Figure 3.1 (right) for the sediment color) dramatically increased from 0.086 to 0.466 for 50 g/L rev dust. As per Table 3.2, the same pattern is observed for 100 to 200 g/L rev dust content. A noticeable decrease is observed in the optical density of 200 g/L rev dust content and a slight increase in the separated oil and sediment volume. The significance of these parameters will be determined with the statistical analyses.

In summary, rev dust particles increased the volume of the separated oil, reduced Transition 1 and increased Transition 2. In other words, hydrated rev dust has further destabilized the invert emulsion. Thus, the 100-150 g/L rev dust concentrations seemingly produce the most stable suspension of rev dust particles. The author conjectures that pre-hydration of rev dust particles has disturbed the stability of the emulsion by particle enmeshment. The trend of pH and temperature impact on the emulsion stability does not have a consistent pattern as shown in Table 3.2. No conclusion, therefore, can be reached firmly based on the volume fractions in Table 3.2. However, the supernatant oil volume has slightly decreased from pH of 7.46 to 12.48 and increased for Transition 1 indicating more emulsion stability. To assess the conclusion, a statistical analysis was conducted. The results of this analysis are shown in Tables 3.3 to 3.5 and discussed next.

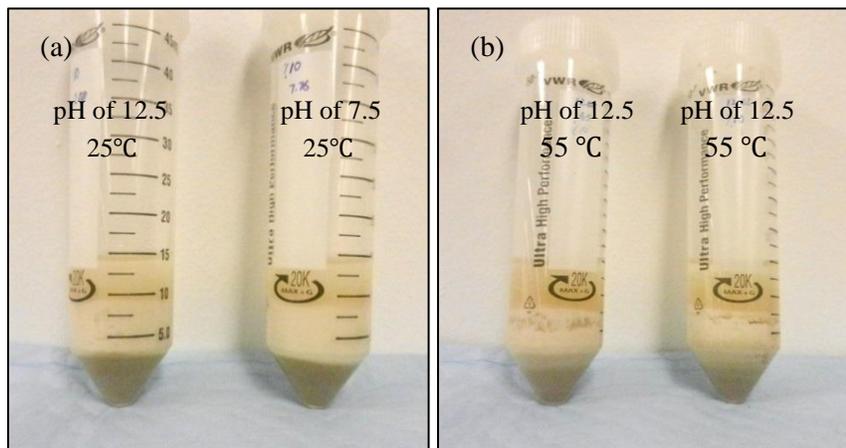


Figure 3.4 The effect of temperature and pH on the phase separation (50 g/L rev dust contamination);
a. pH 12.5 (left), 7.5 (right) at room temperature (25°C) , and
b. pH 12.5 at 55 °C (left) and room temperature (25°C) (right)

Phase separation was measured with a digital caliper (mm) and converted to volume by some basic mathematic calculations. Typically invert emulsions separate into four distinct layers: clear oil, transition 1 and 2, and sediment.

Table 3.2 Phase separation in volume fractions (no physical dimension) for different pH/ rev dust concentrations/ temperature.

Rev Dust (g/L)	Oil layer (v/v) / Turbidity (AU)	Transition 1 (v/v)	Transition 2 (v/v)	Sediment (v/v)
	0.128/ 1.162*	0.787	0.086	0
pH = 7.5/ T = 25°C				
50	0.318/ 1.854	0.216	0.466	0.215
100	0.353/ 1.514	0.184	0.463	0.192
150	0.365/ 1.589	0.175	0.460	0.167
200	0.248/ 1.581	0.295	0.457	0.210
pH = 12.5/ T = 25°C				
50	0.310/ 2.016	0.270	0.420	0.351
100	0.275/ 1.817	0.289	0.436	0.180
150	0.261/ 1.823	0.282	0.457	0.185
200	0.248/ 1.789	0.295	0.457	0.210
pH = 12.5/ T = 55°C				
50	0.236/ 2.025	0.309	0.455	0.382
100	0.259/ 2.246	0.300	0.441	0.208
150	0.255/ 2.019	0.297	0.448	0.185
200	0.290/ 1.768	0.301	0.408	0.242

* Turbidity before centrifugation was 2.134 AU.

The randomized block technique was used to statistically describe the behavior of the data. Table 3.3 shows the results of randomized block technique for rev dust and pH. It was concluded that pH had a significant effect on the optical density of the supernatant oil; however, there is not sufficient evidence to conclude that it also impacted the phase separation. As shown in Table 3.4, the P value is less than the significance level ($P < 0.05$) indicating that **pH** (at constant temperature) had a significant effect on the **optical density**. An increase in optical density indicates an increase in particle size or a decrease in droplet size. As a result, for 10% and 15% rev dust concentrations, we postulate that more solids have been accumulated in Transition 1. The conclusion could be substantiated by the corresponding sediment volume of 100 and 150 g/L rev dust samples. The sediment for these two concentrations is comparatively the lowest indicating more suspension of particles in the Transition phases. There is a decrease in optical

density at higher rev dust concentration (i.e. 200 g/L) mostly because of the particles' enmeshment by the larger aggregates due to the gravity settling.

Table 3.3 Optical Density (AU) values for pH of 7.5 and 12.5 and different rev dust contents.

pH/ Temp	Rev Dust Content (g/L)			
	50	100	150	200
7.46/ 25°C	1.854	1.514	1.589	1.581
12.48/ 25°C	2.016	1.817	1.823	1.789

Table 3.4 ANOVA Two Factor without replicates for optical density of pH 7.5 and 12.5; pH has a significant effect on the optical density of the supernatant oil because $P < 0.05$.

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Rev dust	0.095	3	0.032	18.254	0.020	9.277
pH	0.103	1	0.103	59.264	0.005	10.128
Error	0.005	3	0.002			
Total	0.203	7				

Temperature did not have a significant effect on the optical density nor phase separation ($P > 0.05$). It was concluded that only the **rev dust** content significantly impacted the amount of **sediment** because $P < 0.05$. The optical density of supernatant oil varies within 1.5 to 1.9 for the pH of 7.5 and 1.8 to 2.2 for the pH of 12.5 at room temperature and 55°C. Since both P-values (for rev dust rows) given in Tables 3.4 and 3.6 are less than the significance level ($P < 0.05$), it is concluded that rev dust content has caused a significant difference in the optical density of the supernatant oil and sediment of the contaminated emulsions.

Table 3.5 Optical Density (AU) values for 25 °C and 55°C and different rev dust contents.

pH/ Temp	Rev Dust Content (g/L)			
	50	100	150	200
12.48/ 25°C	2.016	1.817	1.823	1.789
12.48/ 55°C	2.025	2.246	2.019	1.768

Table 3.6 ANOVA Two Factor without replicates for sediment at two different temperatures (i.e. 25 and 55°C); Temperature did not have a significant effect on the optical density nor phase separation ($P > 0.05$).

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Rev dust	0.043	3	0.014	120.234	0.001	9.277
Temperature	0.001	1	0.001	8.661	0.060	10.128
Error	0	3	0			
Total	0.044	7				

To summarize, adding hydrated rev dust particles reduced the stability of Neodrill invert emulsion. pH and rev dust content had a significant effect on the optical density of the supernatant oil. Higher rev dust contents lead to instability in particles suspension in the liquid phase due to the sweeping mechanism of the flocculated clay particulates. It was observed that 100-150 g/L rev dust content is the most optimum concentration that the fluid was able to suspend. Higher alkalinity exhibited a higher degree of gelation and particle suspension. pH of 12.5 was, therefore, selected for the wettability analysis.

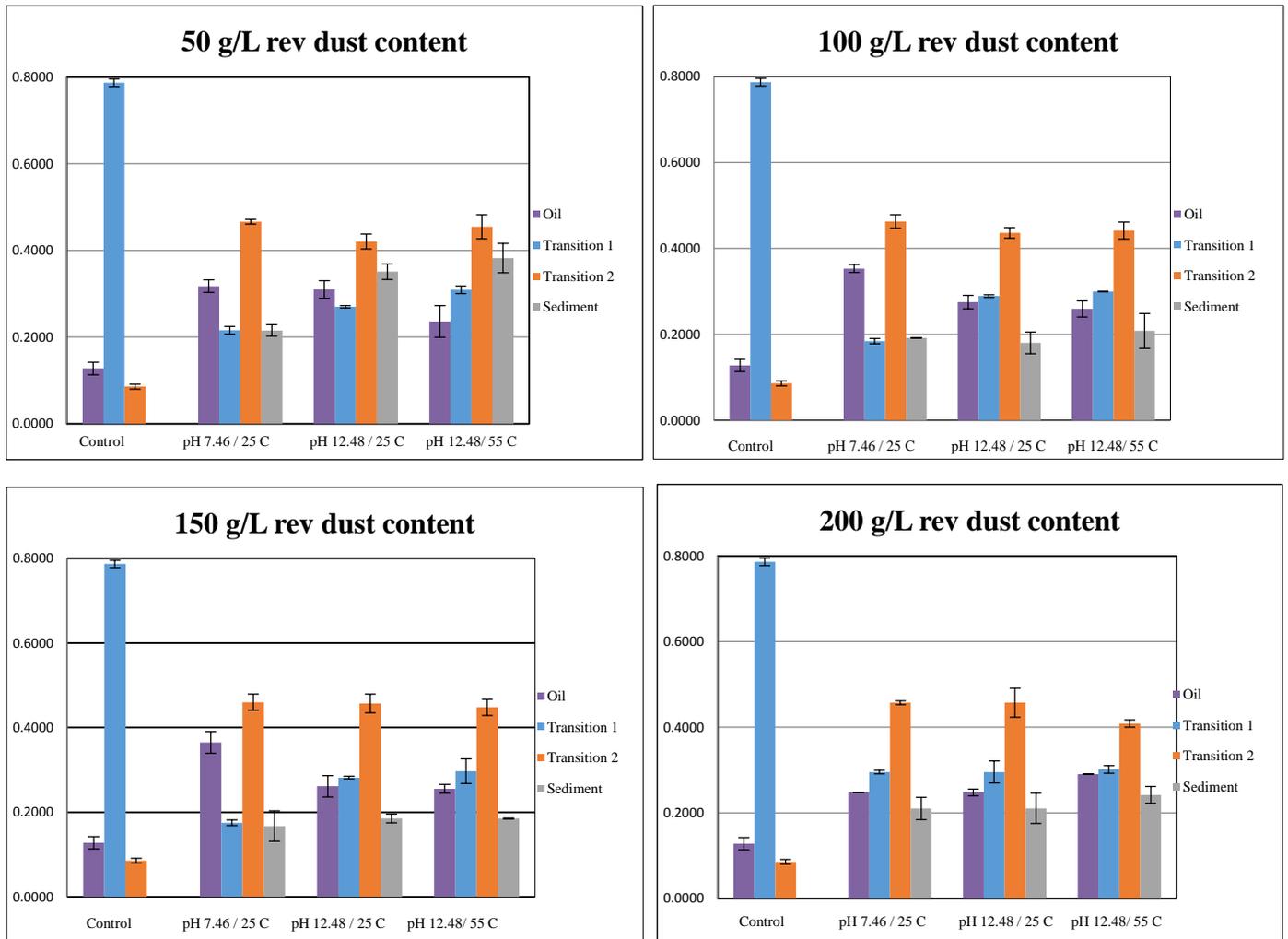


Figure 3.5 The graphical representation of the volume fractions (no physical dimension) with different pH, rev dust content and temperature after 20 min centrifugation with 3000 RCF. Based on the blue (Transition 1, volume fractions) and red bars (Transition 2, volume fractions) in Figure 3.5, it is evident that virtually for all samples adding hydrated rev dust has greatly increased the Transition 2 and reduced Transition 1. It is assumed that the hydrated rev dusts entraps other droplets and solid particles inside the network of clay platelets and settle gravitationally.

3.4 The Effect of Wettability on the Emulsion Stability

In the previous section, it was determined that adding hydrated rev dust destabilized the invert emulsion. In this section, dry rev dust was added to the Neodrill invert emulsion with no pre-hydration to visually compare with the emulsion contaminated with hydrated rev dust in water with the pH of 12.5. First, 50 g/L rev dust content added to 5 ml of Neodrill shown in Figure 3.6(a) (left) and water with the pH of 12.5(right) and aged for 24 h. Figure 3.6(a) (left) shows 5

ml of Neodrill oil mixed with 50 g/L rev dust. Having aged the samples for 24 h, 10 ml of Neodrill invert emulsion was added to each tube and mixed with the vortex mixer for 5 min and aged for 24 h. It can be observed in Figure 3.6(a) (right) that rev dust particles added to the deionized water has produced more turbidity indicating that more solids have been suspended in water than oil.

As discussed in the preceding paragraph, the particle suspension capacity greatly differed in deionized water and Neodrill base oil (see Figure 3.6). In order to find out how the rev dust particles react to the Neodrill invert emulsion, additional tests were conducted. Ten (10) ml of Neodrill invert emulsion was added to the tubes of Figure 3.6(b) (left), mixed with the vortex mixer for 5 min and aged for 24 h. Figure 3.6(b) shows the tubes after 20 min centrifugation with 3000 RCF. It can be seen that adding 5 ml deionized water (right) increased the Transition 2 (milky color) mostly composed of organophilic clay. Figure 3.6(b) (left) also indicates that adding Neodrill base oil by itself for the given mixing speed cannot stabilize the emulsion, as expected.

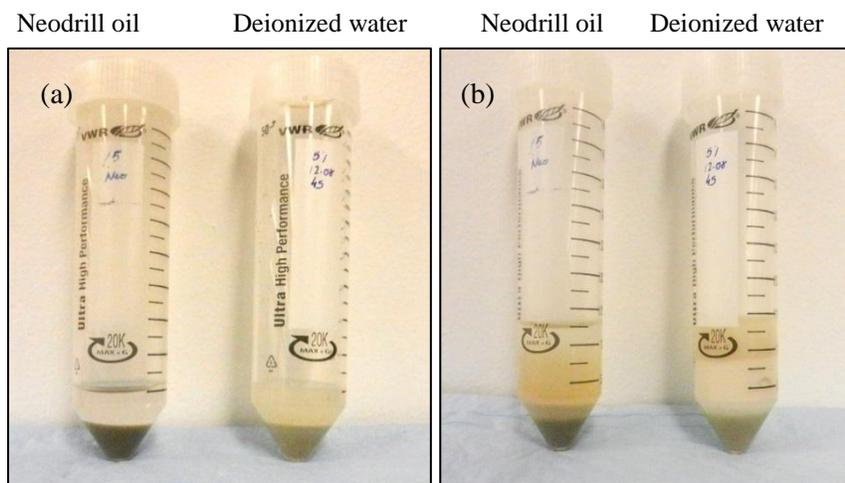


Figure 3.6

- a. 50 g/L rev dust added to 5 ml of Neodrill (left) and deionized water with the pH of 12.5 at room temperature 25 °C (right);
- b. 10 ml of Neodrill invert emulsion added to 5 ml Neodrill oil contaminated with 50 g/L rev dust (left) and deionized water with the pH of 12.5 contaminated with 50 g/L of rev dust at room temperature 25 °C (right).

The rev dust particles are better dispersed in deionized water (more turbidity in the liquid phase) than Neodrill base oil both because they have an affinity to water. Adding deionized water to the Neodrill invert emulsions greatly increased Transition 2 in Figure 3.6(b) (right). Figure 3.6(b) shows that adding Neodrill base oil by itself cannot oil wet the rev dust particles and needs additional mechanisms to suspend fine particles.

Figure 3.7 shows the images of contaminated Neodrill invert emulsion with hydrated and un-hydrated rev dust particles. It is inferred that rev dust particles preferably have absorbed water molecules onto their surface. Microscopic images corroborated this assumption as shown in Figure 3.7(d). Rev dust particles have an affinity for water and hydrate when immersed in water. Microscopic images show that rev dust particles disperse more effectively when not hydrated as per Figure 3.7(a). The samples were taken from Transition and Sediment layers (see Figure 2.2 in Chapter 2). The clay particles show up as dark, irregularly shaped (rounded, but not spherical) against a grey background [82]. Particle size in sediment for hydrated rev dust is greater than that of un-hydrated sample. In other words, microscopic images of the Transition oil indicate that

particles' dispersion in dry blending process is relatively higher than contamination with hydrated rev dust (see Figure 3.7-a).

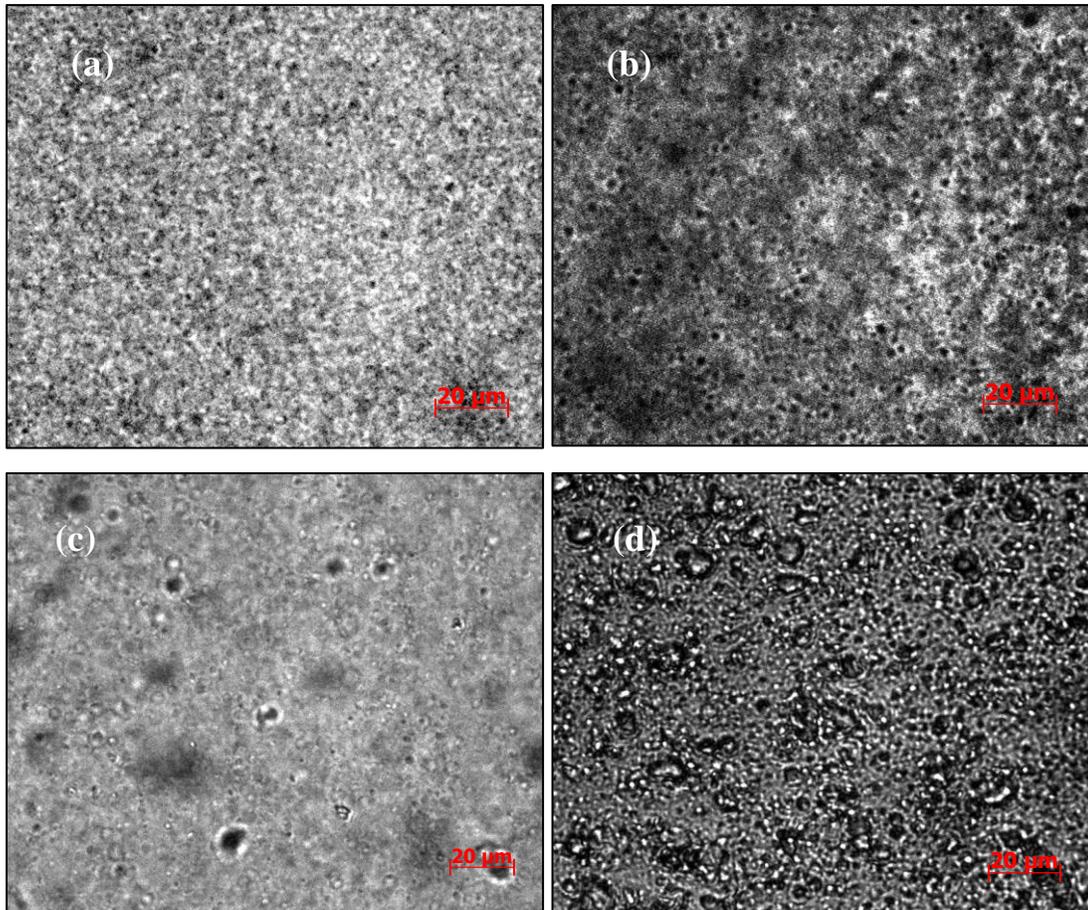


Figure 3.7 Microscopic images (50 g/L rev dust contamination) for

- a. Un-hydrated rev dust for Transition layer with 10,000 rpm mixing
- b. Un-hydrated rev dust for Sediment layer with 10,000 rpm mixing
- c. Hydrated rev dust for Transition layer with pH of 7.5 and 3,200 rpm mixing
- d. Hydrated rev dust for Sediment layer with pH of 7.5 and 3,200 rpm mixing

As it is shown in Figures (a) and (c), particles have been better dispersed in Un-hydrated rev dust (a) than (c). The sediment images (b) and (d) indicate that rev dust particles have absorbed water molecules onto their surface after pre-hydration. As expected, particle size is relatively larger in sediment layers than Transition because larger particles settle down due to the centrifugal force.

In summary, adding dry rev dust particles (un-hydrated) with high mixing speed better disperse the particles in the Neodrill invert emulsion. As a result, the contaminant (i.e. rev dust) is added

to the invert emulsion without pre-hydration and mixed with high shear rate to disperse the particles hereafter.

3.5 Dilution Test for Neodrill Invert Emulsions Contaminated with Hydrated and Un-hydrated Rev Dust Particles

In the previous experiments, Neodrill invert emulsion was added to 5 ml of deionized water. A dilution test was conducted to ascertain that emulsions have not been converted to direct emulsion. Figure 3.8 shows the dilution test for emulsions contaminated with rev dust. In either hydrating or dry blending the rev dust particles, prepared emulsions were observed to be invert emulsions because they were not dispersed in water.



Figure 3.8 Dilution test for emulsions where rev dust initially was added to Neodrill oil (left) water with pH 12.5 (right) and. The test indicated that emulsions are still invert even though 5 ml of deionized water was added.

3.6 The Effect of Adding Oil Wet Surfactant on the Emulsion Stability

As discussed in section 3.4, rev dust particles did not suspend in Neodrill base oil by mixing. An oil wet surfactant was added to the emulsion contaminated with 50 g/L as described in 2.4.6 to oil wet the particles to test whether an oil wet surfactant can improve the particle suspension capacity. The emulsion then was aged for 24 h and centrifuged for 20 min and 3000 RCF. It is believed that adding oil wet surfactant coats the particles with hydrophobic compounds and reduces the surface tension between particulates and oil phase. Material considerations limited testing to 50 g/L rev dust contamination.

An additional test with Envirodrill base oil was conducted to assess the stability of the emulsions. Envirodrill base oil was used because it presumably contains lower aromatic compounds which mostly consist of two atoms with different electronegativity, or polarity. Invert emulsion with more polar base oil (such as diesel) relatively produce more stable drilling fluid.

Two (2) ml of MF surfactant per 50 g solid (2 ml/ 50 g solid) was added to the invert emulsions as laid out in section 2.4.6. Figure 3.9 shows the phase separation (i.e. Transition and Sediment volume fractions) of Envriodrill and Neodrill invert emulsions with and without adding MF surfactant. Table 3.6 gives the caliper and optical density measurements for two types of base oil contaminated with 50 g/L rev dust and centrifuged for 20 min and 3000 RCF. Figure 3.9 graphically represents the phase separation of Neodrill and Envirodrill emulsions with MF oil surfactant contaminated with 50 g/L rev dust. A clear oil film has been separated for Envirodrill invert emulsion indicating the lower stability of the Envirodrill invert emulsion. Ngai et al. (2006) found that the absorption of the water-swollen microgel particles to the oil water interface is substantially reduced when the polarity of the oil is decreased [39]. The higher stability of Neodrill invert is presumed due to higher aromaticity of the base oil. Sediment in Envirodrill invert emulsion is comparatively less indicating more rev dust suspension in Transition 1 (see Table 3.6 or Figure 3.9). Adding MF surfactant slightly increased the Transition regardless of the base oil (Figure 3.10). Furthermore, adding the surfactant increased the sediment for hot-rolled (dynamically aged in the rolling oven) sample, however, slightly reduced for the not-hot rolled samples.

Electrical Stability of the emulsions was measured with an OFITE Electrical Stability Meter to analyze the relative stability of the prepared emulsions. The test was replicated three times and average values are given in Table 3.7. From Table 3.7, the ES values have increased for the hot-rolled fluid and decreased for Envirodrill samples. Turbidity of the the Envirodrill invert emulsion is relatively lower because of lower emulsion stability, and consequently, lower ability to suspend particles when compared to the Neodrill invert emulsion. Adding the surfactant slightly increased the Electrical Stability of both Neodrill and Envirodrill invert emulsions. Electrical Stability of Envirodrill invert emulsion contaminated with 50 g/L rev dust slightly increased from 629.7 (see Table 10) to 667.8 V and Neodrill emulsion (AHR) increased from

1113 to 1173 V. The author postulates that the particles become slightly more oil wet and increases the ES of the emulsion.

Table 3.7 Phase separation (volume fractions) and optical density measurements the contaminated emulsion with MF oil surfactant after 20 min centrifuging with 3000 RCF. It is concluded that Envirodrill invert emulsion is less stable than Neodrill invert either because of the base oil or lower organoclay content.

50 g/L Rev Dust	Oil	Transition 1/ Turbidity	Transition 2	Sediment	Electrical Stability* (V)
Neodrill (BHR)	0	0.861/ 1.423	0.139	0.301	513.3
Neodrill (AHR)	0	0.869/ 1.812	0.132	0.332	1173
Envirodrill	0.1906	0.680/ 0.501	0.130	0.203	667.8

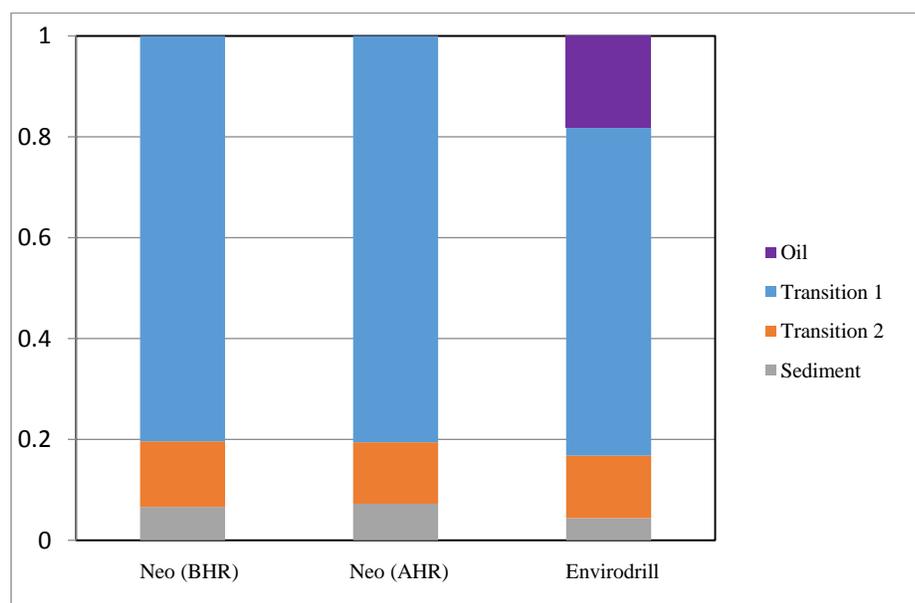


Figure 3.9 The graphical representation of the volume fractions for the emulsions with MF oil surfactant contaminated with 50 g/L rev dust; a clear oil layer was separated indicating lower stability of Envirodrill invert emulsion.

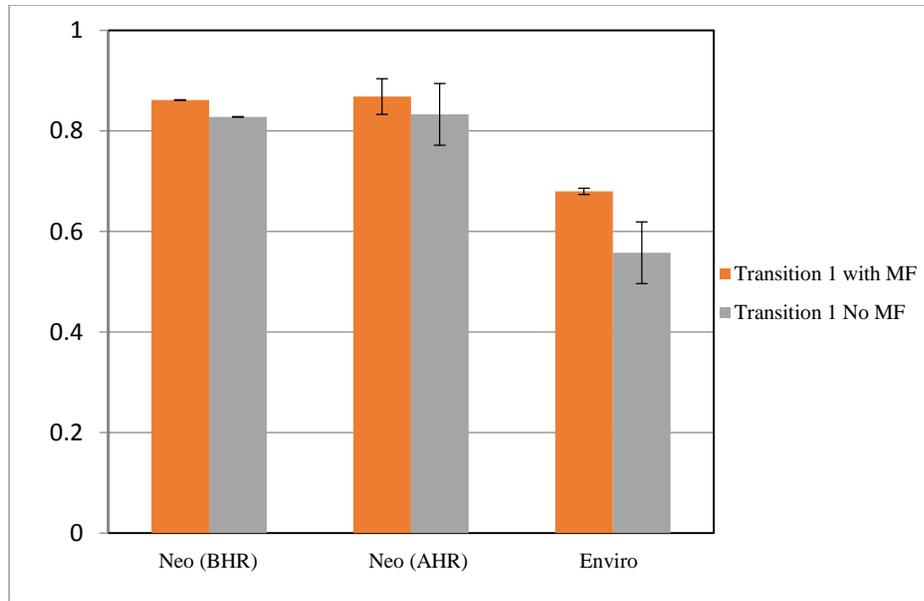


Figure 3.10 Transition 1 for 50 g/L contaminated emulsion with and without MF oil surfactant; Transition 1 for samples with no surfactant is relatively lower than those with surfactant.

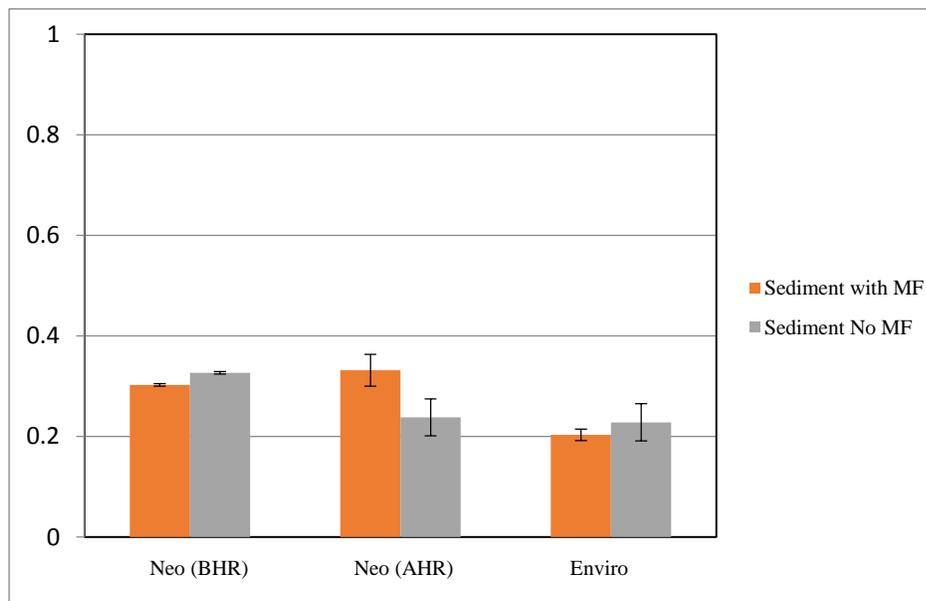


Figure 3.11 Sediment for 50 g/L contaminated emulsion with and without MF oil surfactant. Sediment for samples does not conform to the same Transition pattern.

Table 3.9 and 3.10 give the results of ANOVA test for optical density with and without surfactant. It is concluded that adding the surfactant had a significant effect on the optical density

of the supernatant oil since both P-values are less than the significance level ($P < 0.05$). In other words, adding a surfactant to the invert emulsions suspended more rev dust particles in the liquid phase. As mentioned in section 3.3, optical density of the separated liquid is contingent upon the particle size of the suspended solid and emulsion droplet size. Adding oil wet surfactant slightly reduced the sediment volume indicating more suspended solids into the liquid phase. As a result, an increase in optical density demonstrated an increase in particle size and more total suspended solid in the liquid. In other words, in a 200 g/L contaminated emulsion, there is a higher probability that particles suspend in the liquid phase, and therefore, increase the optical density of the supernatant liquid.

Table 3.8 Optical density measurements (three replicates) of Neodrill and Envirodrill invert emulsions.

50 g/L Rev Dust	Turbidity (AU)		
Neodrill			
BHR	1.361	1.431	1.477
AHR	1.666	1.811	2.228
Envirodrill			
BHR	0.504	0.501	0.499

Table 3.9 ANOVA Single Factor for optical density of the contaminated emulsions with and without MF surfactant (AHR); since $P < 0.05$, it is concluded that adding surfactant had a significant effect on the optical density of the supernatant oil after hot rolling.

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.248	1	0.248	23.382	0.003	5.987
Within Groups	0.064	6	0.011			
Total	0.312	7				

Table 3.10 ANOVA Single Factor for optical density of the contaminated emulsions with and without MF surfactant (BHR); since $P < 0.05$, it is concluded that adding surfactant had a significant effect on the optical density of the supernatant oil after hot rolling.

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.066	1	0.066	43.107	0.003	7.709
Within Groups	0.006	4	0.002			
Total	0.073	5				

3.7 Electrolyte Effects on the Emulsion Stability

The brine in oil emulsion acts as a semi-permeable barrier that prevents water molecules to be in direct contact with the water-sensitive shale. Rev dust particles—composed of silica and quartz—extremely hydrate in aqueous medium and form rigid networks of clay platelets. These particles play the role of shale particles in the real drilling operation. In bench scale testing, calcium chloride is added (30% w/w) to deionize water to prepare brine to be used in invert emulsion preparation; however, calcium is a primary source of electrolyte that inhibits the clay hydration, and consequently, fluid capacity to suspend solids. In this section, the level of calcium concentration in the system was changed to study the effect of electrolyte on the emulsion stability and contaminant (i.e. rev dust) suspension.

These results discussed below suggest that the amount of calcium chloride in the brine had a great impact on the rheological properties of the fluid. When brine was replaced by deionized water and used to prepare the invert emulsions, the fluid was greatly thickened after adding organophilic clay inasmuch as shearing was no longer effective.

Hydrated lime—composed of calcium hydroxide and crystalline silica—is another source of calcium widely used to activate emulsifiers in the invert emulsion. Hydrated lime was halved when preparing invert emulsion so as to study the impact of calcium hydroxide on both rheological properties and emulsions stability. Lime is added to the mixture of base oil and emulsifier to activate emulsifiers in the invert emulsion as described in section 2.1. Table 3.11 gives the rheological properties of Neodrill invert emulsion drilling fluids with 35 kg/m^3 and two different lime contents.

The particle suspension capacity is best reflected in the rheological properties of the fluid such as gel strength. Rheological properties of the prepared fluid, therefore, were measured to enable us to quantify the degree of gelation and particles suspension. Rheological properties were all measured at the temperature range between $35 - 38^\circ\text{C}$. Based on the consulting curve, the viscosity model best describes the Bingham plastic since after the yield point has exceeded, changes in shear stress are proportional to changes in shear rate with a constant of proportionality as shown in Figure 3.13. The regression coefficient for the linear model indicates

a high level of confidence. As it is shown in Table 3.12, regression coefficients for 5 g/L and 10 g/L lime contents are 0.989 and 0.991 respectively. In addition, as it is shown in Table 3.11, time (i.e. calcium hydroxide) content was not a significant factor in the rheological behavior of the fluid.

Table 3.11 Rheological measurements for Neodrill invert emulsion with 35 kg/m³ and two different lime contents. Rheological properties have not been significantly changed when lime content was halved to 5 g/L.

Lime At 38 – 35 °C	θ_{600}	θ_{300}	θ_{200}	θ_{100}	θ_6	θ_3	10-sec gel strength (Ib/100 ft ²)	Electrical Stability (V)
5 g/L	48	31-32	25	17	10	9	5-6	1266.75
10 g/L	50	33	26	19	11	10	8	1221.5

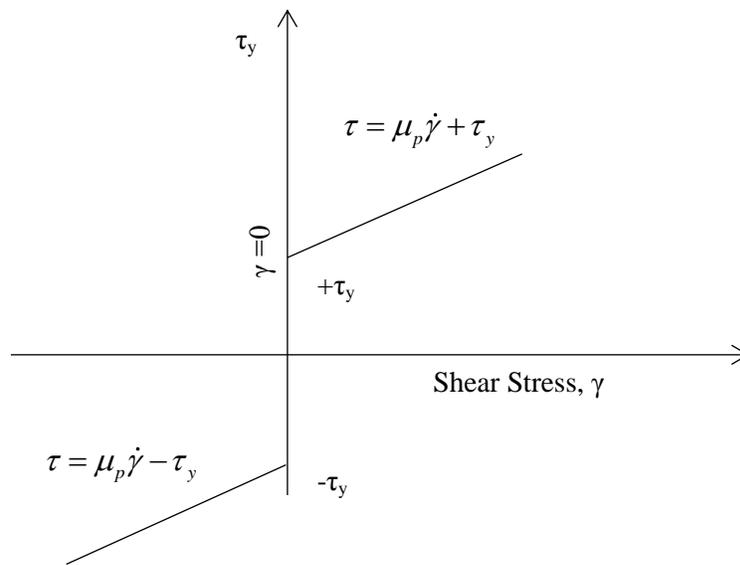


Figure 3.12 Shear stress vs. shear rate for a Bingham plastic fluid.

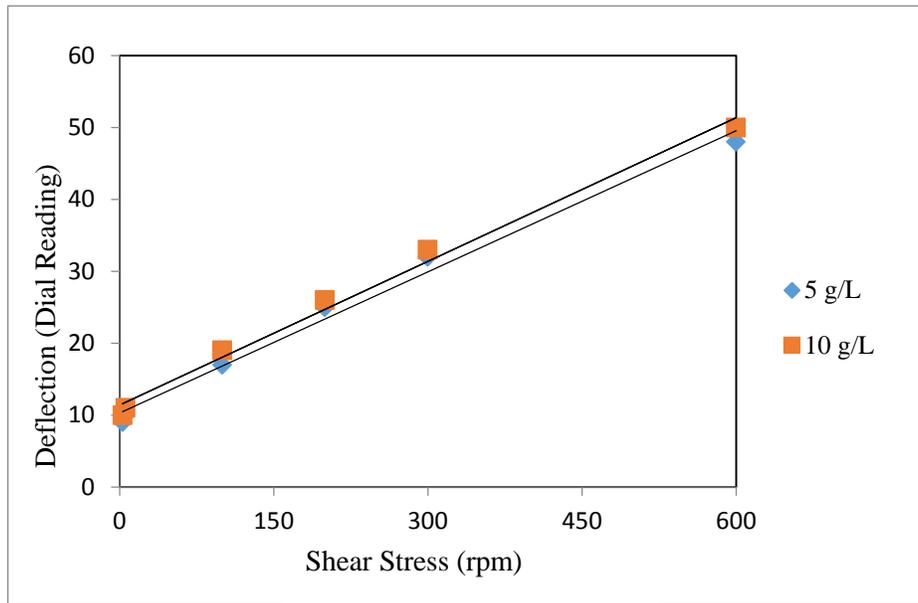


Figure 3.13 Shear stress vs. shear rate for the rheological measurements given in Table 11. A simple linear regression was used to correlate the shear stress values to shear rate.

Table 3.12 Linear regression models for the rheological data in Table 3.11. The regression coefficient for the linear model indicates a high level of confidence.

Lime Content	Linear Regression	R^2	Rheological Model
5 g/L	$y = 0.0654x + 10.318$	0.989	Bingham
10 g/L	$y = 0.0666x + 11.418$	0.991	Bingham

Table 3.11 indicates that the rheological properties of the fluid have not dramatically changed for 5 g/L lime content. Hydroxide ions are believed to cancel out the impact of compressing the diffuse layer by calcium, and hence, render clay particulates dispersed. On the other hand, the calcium chloride present in the brine greatly changed the rheological properties of the drilling fluid. The author postulates that the presence of electrolytes in the water phase has larger impacts than oil phase because clay particles (i.e. rev dust) absorb water molecules into their crystalline structures (see Figure 3.7-d). The calcium ions, therefore, compress the diffusive electrical double layer and inhibit the hydration of rev dust particles.

3.8 Hot Rolling Effects on the Neodrill Invert Emulsion Stability

A series of Neodrill invert emulsion was hot-rolled (AHR) at 121.11 °C (250°F) for 16 h and contaminated with rev dust particles as described in part 2.4.4. The phase separation (in volume fraction) of Neodrill invert emulsions is given in the first two rows of Table 3.13. A series of Neodrill invert emulsions was hot rolled for 16 h at 121.11°C. It is believed that hot rolling (dynamically aged in the rolling oven) reduces the emulsion droplet size and greatly influences the emulsion rheology (gel strength and particle suspension capacity) due to several factors: (1) a decrease in the mean distance of separation between the droplets, (2) a decreases in the thickness of the absorbed surfactant layer with respect to the droplet size (3) a decrease in the width of particle size distribution, or polydispersity [83]. Hot rolling generally increases the gel strength, which is the measurement of suspension properties of a drilling fluid.

Prepared Neodrill invert emulsion was hot rolled to increase the capacity of the fluid to suspend fine particles. Figure 3.14 shows the phase separation after centrifugation. Based on the Transition bars (blue) in Figure 3.14, it can be seen that there is no significant difference between samples before and after hot-rolling. Surprisingly, in none of these tests, hot rolling reduced the phase separation or the capacity of fluid to suspend fine particles. Hot rolling significantly increased the Electrical Stability of the invert emulsion as expected. As mentioned in section 3.6, a screening test with lower centrifugal force (i.e. 900 rpm and 1500 rpm) was conducted because it was presumed that centrifugal force was overly aggressive; however, the results of the screening test indicated that, even at lower centrifugal force, no significant difference could be visually observed between samples before and after hot-rolling.

Table 3.13 shows the volume fractions of the separated phases and optical density of the supernatant oil. First two rows of Table 3.13 are the samples with no rev dust contamination and zero sediment. Sediment volume is the lowest for 100 g/L rev dust content as shown in Figure 3.15; however, Transition 1 is the highest for 50 g/L rev dust content. Optical density values slightly increased with rev dust content indicating more turbidity of the Transition 1. This indicates that higher rev dust content has boosted the light absorbance, and therefore, optical density because there are more particles suspended into the emulsion. Hot rolling the fluid both increased the Electrical Stability and optical density of the supernatant oil; however, adding more

rev dust slightly reduced the Transition 1 and Electrical Stability. A decrease in Electrical Stability of invert emulsion with higher rev dust content is attributed to forming a conductive bridge composed of rev dust particles.

Since the solid load is different in these samples; for instance, the amount of solid and invert emulsion fluid in 150 g/L sample differs from that of 50 g/L. As a result, these fractions were normalized by using Equations (1) and (2) (see Chapter 2) and are shown in Figure 3.15.

Table 3.13 Phase separation and optical density measurements for Neodrill drilling fluid contaminated with dry rev dust; Electrical Stability values decreased and turbidity increased as rev dust content increased.

Centrifuging 20 min	Transition 1/ Turbidity	Transition 2	Sediment	Electrical Stability* (V)
Invert (BHR)	0.842/ 1.254	0.158	0	1385
Control (AHR)	0.837/ 1.480	0.163	0	1764.8
50 g/L (AHR)	0.833/ 1.401	0.167	0.238	1113
100 g/L (AHR)	0.799/ 1.474	0.201	0.127	814.3
150 g/L (AHR)	0.796/ 1.477	0.202	0.174	677

* Before centrifuging

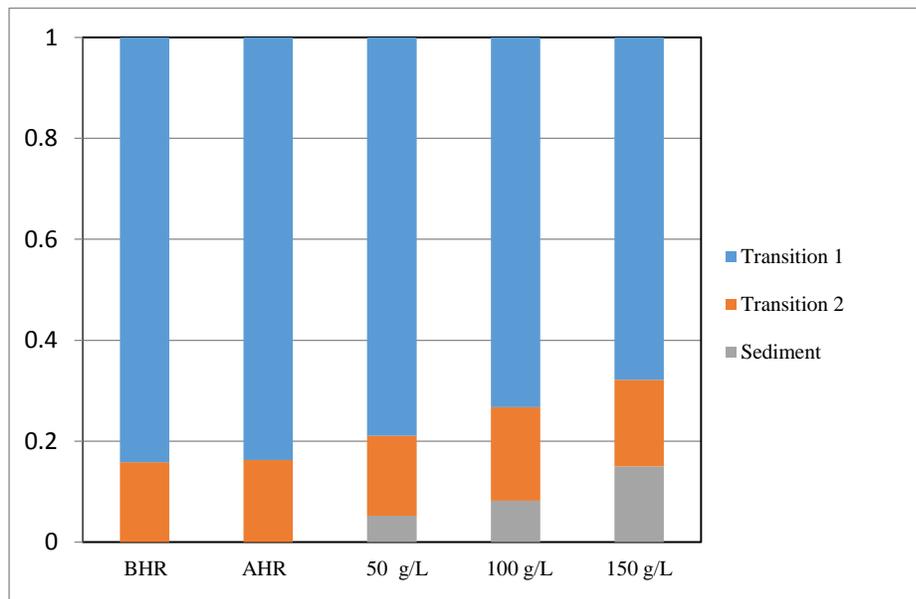


Figure 3.14 Neodrill drilling fluid contaminated with dry rev dust.

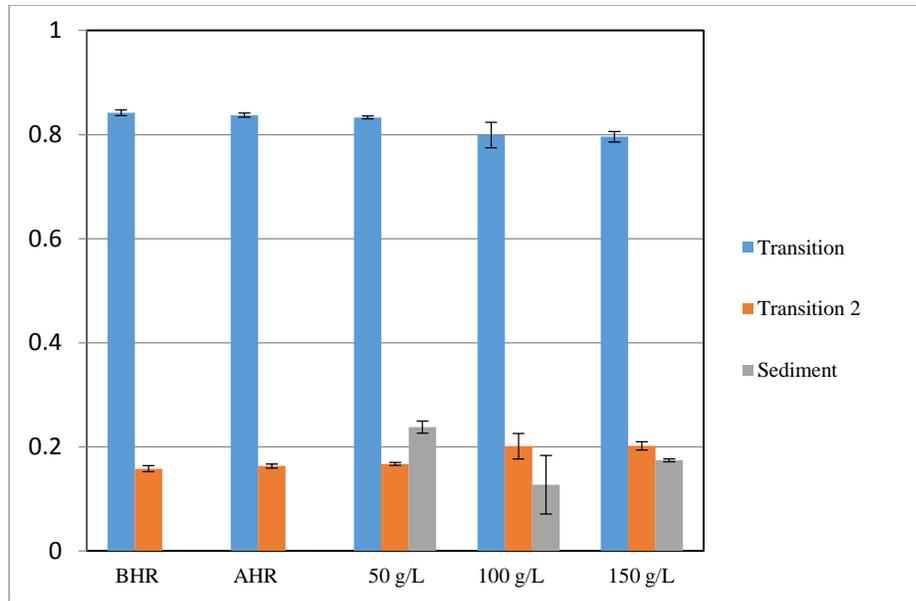


Figure 3.15 Neodrill drilling fluid contaminated with dry rev dust after 20 min of centrifugation with 3000 RCF; Transition bar is almost identical for all samples; however, invert emulsion with 100 g/L rev dust has the lowest Sediment among three concentrations.

The randomized block technique was used to statistically describe the behavior of the data. Normalized data were used in a single factor ANOVA to find out if rev dust content has a significant effect on the phase separation. The total variability in the data is measured by the sum of squares SS_T , can be partitioned into a sum of squares of differences between treatment means and the grand mean denoted $SS_{Treatments}$ and a sum of squares of differences of observations within a treatment from the treatment mean denoted SS_E . Differences between observed treatment means and the grand mean measure the differences between treatments, while differences of observations within a treatment from the treatment mean can be due only to random error. The P-values from Tables 3.14 and 3.15 are less than the 0.05 significance level ($P < 0.05$), so we can conclude that **rev dust content** had significantly affected the **Sediment** and **Transition** (i.e. phase separation) after centrifugation. In virtually all preceding experiments, rev dust content played a significant role in the Sediment and Transition volume. Prepared emulsion is capable of carrying and suspending fine particles up to a certain level. As the rev dust content increases, sweeping mechanism of clay particles become dominant and lead to a gravitational settling of solids in the fluid.

Table 3.14 ANOVA Single Factor for sediment of three rev dust content; rev dust content had significantly affected the Sediment after 20 min centrifugation with 3000 RCF.

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.019	2	0.009	8.452	0.018	5.143
Within Groups	0.007	6	0.001			
Total	0.025	8				

Table 3.15 ANOVA Single Factor for transition of three rev dust content; rev dust content had significantly affected the Transition after 20 min centrifugation with 3000 RCF.

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.003	2	0.001	5.397	0.046	5.143
Within Groups	0.001	6	0			
Total	0.004	8				

In conclusion, hot rolling did not have an impact on the cuttings capacity of the fluid (or phase separation), even though it greatly increased the ES of the emulsion. Therefore, even though ES can partly indicate the stability of emulsion, it does not represent the cutting capacity of the fluid. 100-150 g/L contaminant (i.e. rev dust) relatively is the highest (most optimum) rev dust concentration that the fluid is able to suspend.

3.9 Rev Dust Effect on the Envirodrill Emulsion Stability

Envirodrill invert emulsion was contaminated with different rev dust loads (i.e. 50 g/L to 200 g/L) and centrifuged at 3000 RCF and 20 min to figure out the impact of rev dust particles on the Envirodrill invert emulsion. Table 3.16 gives the caliper and optical density measurements for phase separation after 20 min centrifugation with 3000 RCF. Based on Figures 3.16 and 3.17, it is evident that Envirodrill emulsion is less stable than Neodrill because of the greater degree of phase separation (i.e. oil separation). The optical density and ES results in Table 16 were plotted in Figures 3.18 and 3.19. Optical density measurements show a steady decrease as rev dust increases both for Neodrill and Envirodrill emulsions (see Figures 3.18 and 3.19). Electrical Stability, in contrast, decreased when rev dust increased. As it is shown in Figure 3.14,

Transition 1 is the highest and sediment is the lowest for 100 g/L rev dust sample indicating 100 g/L rev dust content to be the most optimum concentration to be formulated for future studies.

Table 3.16 Phase separation and optical density measurements for Envirodrill drilling fluid contaminated with dry rev dust; unlike Neodrill invert emulsion which there was no oil separation, a clear oil phase appeared at the top for Envirodrill samples indicating lower stability of Envirodrill emulsions.

Rev Dust Content	Oil	Transition 1/ Turbidity	Transition 2	Sediment	Electrical Stability* (V)
BHR	0	0.870/ 0.281	0.130	0	885.7
50 g/L	0.3019	0.558/ 0.419	0.140	0.228	629.7
100 g/L	0.1486	0.704/ 0.454	0.148	0.134	513.3
150 g/L	0.1570	0.690/ 0.537	0.153	0.154	371.7

*Before centrifugation

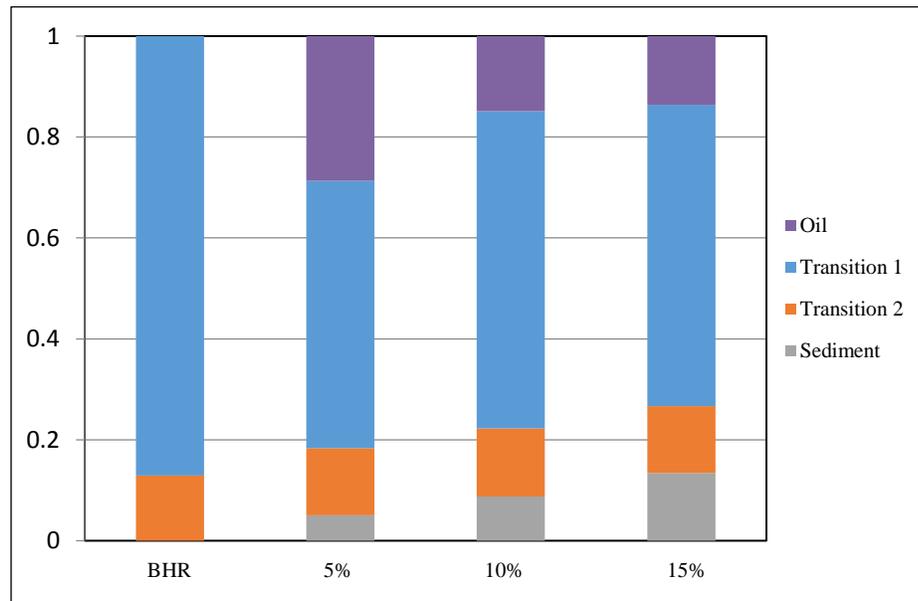


Figure 3.16 The graphical representation of the volume fraction with different rev dust contents for Envirodrill invert emulsion after 20 min centrifugation with 3000 RCF.

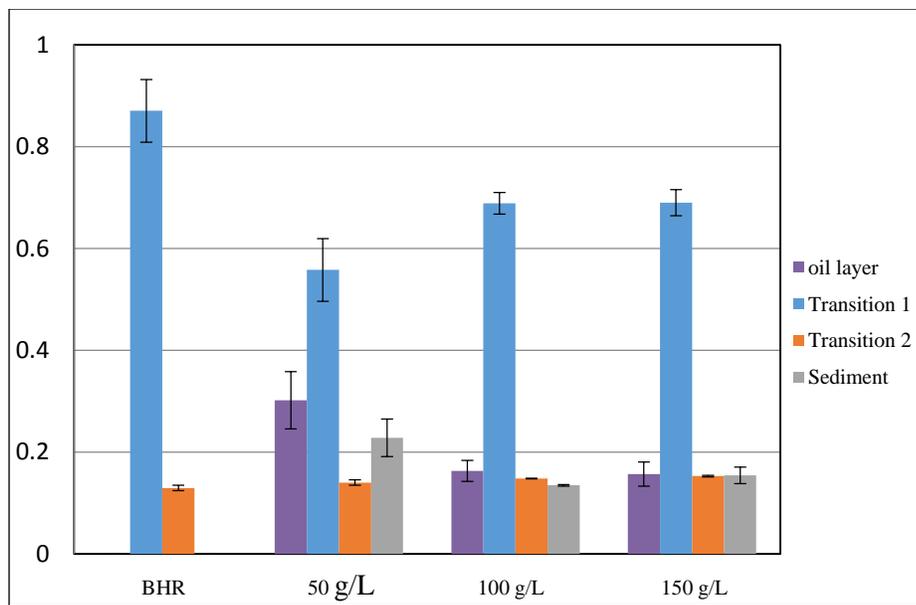


Figure 3.17 The graphical representation of the normalized volume fraction with different rev dust contents for Envirodrill invert emulsion after centrifugation; Transition significantly reduced after the addition of rev dust, but increased for 100 g/L rev dust content indicating higher stability of invert emulsion for 100 g/L and 150 g/L rev dust contents.

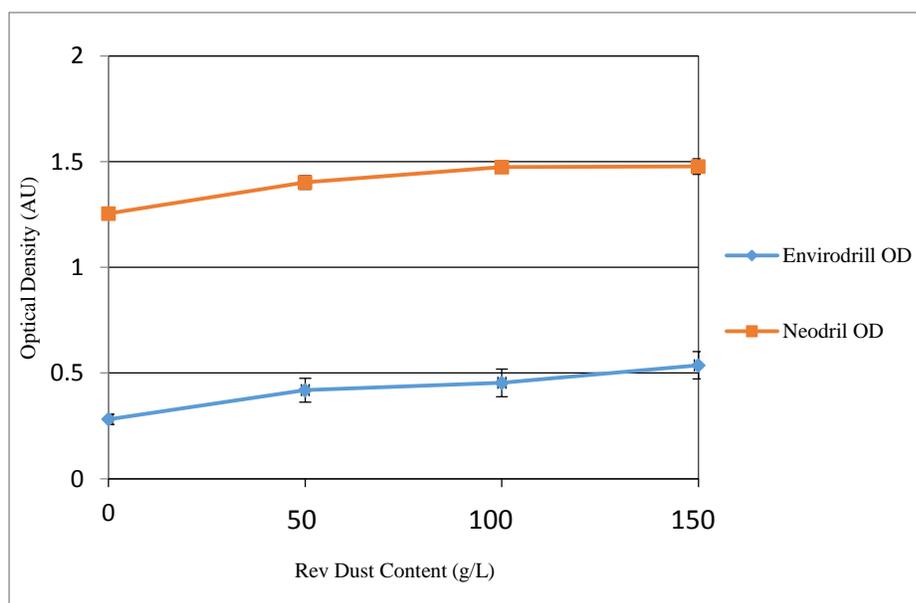


Figure 3.18 Optical Density vs. rev dust content for Neodril and Envirodrill emulsions; regardless of the type of base oil, optical density values increase with increasing rev dust content.

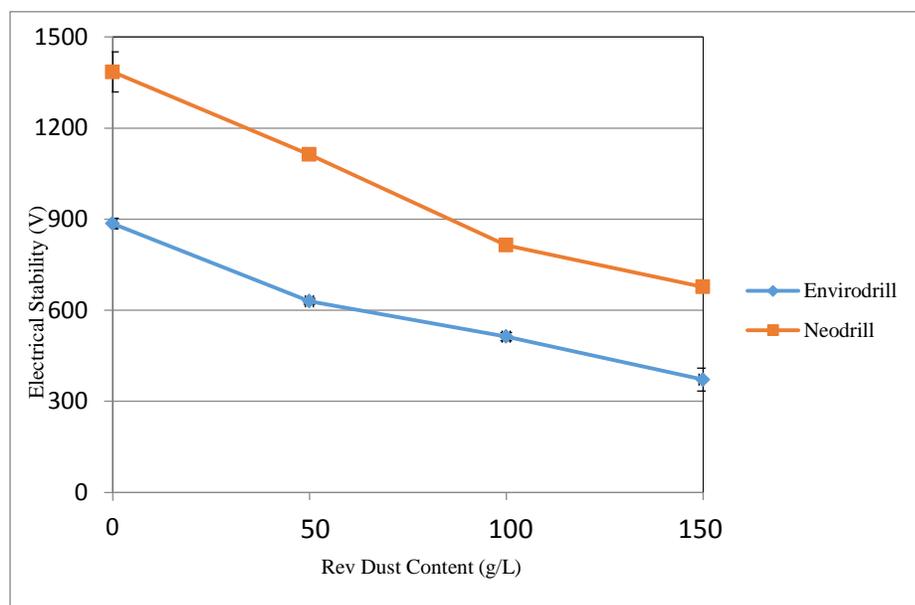


Figure 3.19 Electrical Stability vs. rev dust content for Neodrill and Envirodrill emulsions; regardless of the type of base oil, Electrical Stability values decrease with increasing rev dust content.

ANOVA single factor results are given in Tables 3.17 to 3.19 for the Oil, Transition, and the sediment with different rev dust content. It is concluded that adding rev dust has made a significant difference in the **Sediment** and **Oil** layers of invert emulsion after centrifugation. As mentioned earlier in this section, optical density of the separated liquid is contingent upon the particle size of the suspended solid and emulsion droplet size. Adding more rev dust particles has led to an increase in the optical density of the liquid phase probably due to the larger amount of suspended particle in Transition 1.

Table 3.17 ANOVA Single Factor for sediment of three rev dust content; rev dust content had significantly affected the oil separation for Envirodrill invert emulsion after 20 min centrifugation at 3000 RCF.

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.007	2	0.004	39.049	0.007	9.552
Within Groups	0	3	0			
Total	0.007	5				

Table 3.18 ANOVA Single Factor for transition of three rev dust content; rev dust content **did not** have significantly affected the Transition for Envirodrill invert emulsion after 20 min centrifugation at 3000 RCF.

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.010	2	0.005	4.473	0.126	9.552
Within Groups	0.003	3	0.001			
Total	0.014	5				

Table 3.19 ANOVA Single Factor for oil of three rev dust content; rev dust content had significantly affected the sediment for Envirodrill invert emulsion after 20 min centrifugation at 3000 RCF.

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.028	2	0.014	10.567	0.044	9.552
Within Groups	0.004	3	0.001			
Total	0.032	5				

To conclude, Neodrill invert emulsion was proven to be more stable than Envirodrill emulsion. Neodrill invert supposedly contains more aromatic compounds than Envirodrill base oil. Aromatic compounds mostly consist of bonds with imbalanced charge distribution (i.e. polar molecules). Polarity of the base oil in drilling fluids plays a role in the absorption of the water-swollen microgel particles. Adding oil wet surfactant slightly improved the emulsion stability by increasing the volume of Transition 1. The surfactant coats the particles and makes them more oil wet. The film of surfactant around the particles reduces the electrical conductivity and increases the voltage at which emulsion break-down occurs. Sediment volume was observed to be comparatively lower for Envirodrill invert emulsion than its Neodrill counterparts. Such an observation is still recondite and needs further studies on the chemistry of the base oil and its interactions with rev dust particles. Rev dust particles have an affinity for water molecules and better disperse in water medium. This may be why the rev dust particles are not stable in invert emulsion and settle down as a result of centrifugation. Electrical Stability of the invert emulsion decreased as rev dust content increased. Rev dust forms a conductive bridge composed of aqueous medium which acts as a carrier of water.

3.10 Organophilic Clay Content Effects on the Emulsion Stability

The principal aim of this experiment is to find out whether organophilic clay increases the solid suspension capacity of the fluid. As per section 2.4.5, organoclay was added to the Neodril invert emulsion in 5 kg/m³ increment and mixed for 5 minutes between each interval. As it is shown in Table 3.20, increasing organoclay content increased the gel strength and yield point of the fluid. Table 3.20 gives the dial readings of different clay content. Figure 3.20 validates the assumption of Bingham plastic model for the rheological measurements given in Table 3.20. A simple linear regression model was used to fit all the rheological data given in Table 3.20. As organophilic content in the fluid increases, apparent viscosity as well as yield point of the fluid increased.

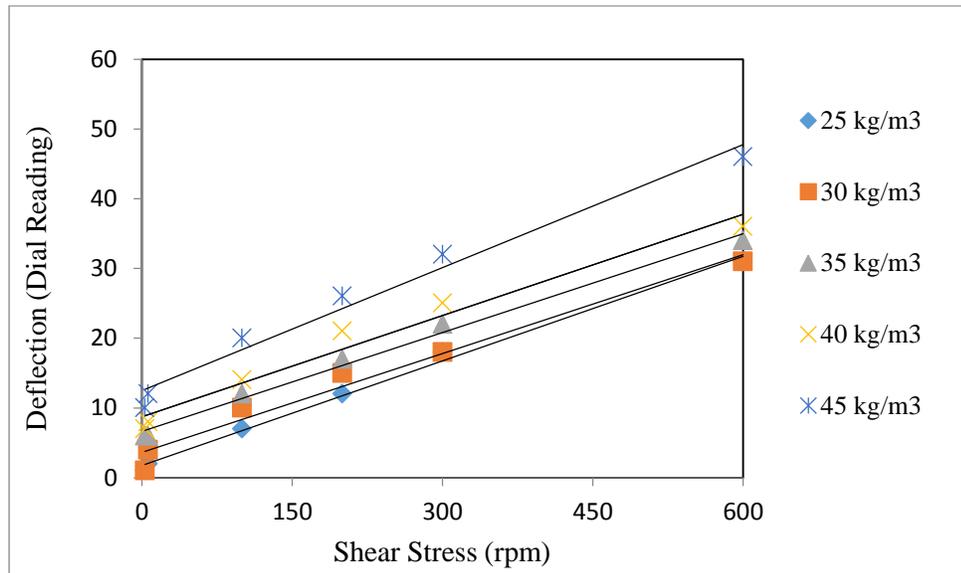


Figure 3.20 Shear stress vs. shear rate for the rheological measurements given in Table 20. A simple linear regression was used to correlate the shear stress values to shear rate.

Table 3.20 Linear regression models for the rheological data in Figure 3.20. All the samples behaved as a Bingham plastic fluid.

Clay Content	Linear Regression	R^2	Rheological Model
25 kg/m ³	$y = 0.0499 x + 1.769$	0.995	Bingham
30 kg/m ³	$y = 0.0472 x + 3.652$	0.974	Bingham
35 kg/m ³	$y = 0.0472 x + 6.652$	0.991	Bingham
40 kg/m ³	$y = 0.0484 x + 8.754$	0.971	Bingham
45 kg/m ³	$y = 0.0588 x + 12.481$	0.978	Bingham

Table 3.21 Rheological measurements for Neodrill invert emulsion with different organophilic clay contents; adding organophilic clay increased both the yield point and Electrical Stability of the invert emulsion.

Clay Content At 38 – 35 °C	θ_{600}	θ_{300}	θ_{200}	θ_{100}	θ_6	θ_3	10-sec gel strength
25 kg/m ³	31	18	12	7	2	1	2
30 kg/m ³	31	18	15	10	4	1	4
35 kg/m ³	34	22	17	12	6	6	5
40 kg/m ³	36	25	21	14	8	7	7
45 kg/m ³	46	32	26	20	12	10	11

Prepared invert emulsion was contaminated with 100 g/L rev dust (because 100 g/L was selected in the previous section as the optimum contaminant concentration), mixed for 5 minutes with Hamilton mixer and aged for 24 h. The samples were then centrifuged for 20 min with 3000 RCF. As it is shown in Figure 3.21, adding more organoclay led to a more viscose fluid (see Table 3.21) and lower phase separation. Transition 1 for 45 kg/m³ organoclay content is relatively darker than its lower clay content counterparts indicating more solid suspension in the liquid phase. As a result, higher organoclay content produced a more gelled fluid which is more capable of suspending rev dust particles. Transition 2 (milky color) is visually lower for higher organophilic indicating more organoclay particles in Transition 1. Caliper measurements were not practical herein since the separated phase interfaces are not sharp and distinguishable.

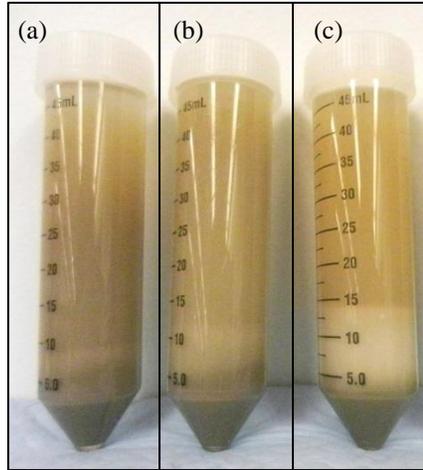


Figure 3.21 The effect of organophilic clay content on the Neodrill invert emulsion stability:

- a. Invert emulsion laden with 45 kg/m^3 organoclay and centrifuged for 20 min and 3000 RCF.
- b. Invert emulsion laden with 35 kg/m^3 organoclay and centrifuged for 20 min and 3000 RCF.
- c. Invert emulsion laden with 25 kg/m^3 organoclay and centrifuged for 20 min and 3000 RCF.

Samples with higher organophilic clay content produced more particle suspension capacity. Transition 1 in Figure 3.21-a (45 kg/m^3 organoclay) is relatively more opaque indicating more suspension of rev dust particulates.

Adding organoclay slightly increased the Electrical Stability of the emulsions. The ES increased from 1385 for 25 kg/m^3 to more than 1999 for 35 and 45 kg/m^3 . Since Electrical Stability of emulsion is a relative measure of its oil wetness, an increase in Electrical Stability of invert emulsions with higher organophilic clay (more oil wet particles) can be explained.

3.11 Microwave

Fifty (50) ml of Neodrill invert emulsion contaminated with different rev dust loads (50 to 150 g/L) was microwaved for 5 min to enhance the phase separation before centrifugation. Microwaved samples were left to cold down under fume hoods for a few minutes and visually observed for phase separation. Low (180 watts) and Medium Low (360 watts) power levels almost did not have any impact on the phase separation. The emulsions remained stable after 5 min of microwaving with Low and Medium Low power levels. The author postulates that heat conduction is the dominant mechanism in low power radiation. The steady heating of the sample

does not result in emulsion break down and causes heat loss to the surrounding media. In contrast, Medium High (775 watts) and High (1000 watts) power levels greatly destabilized the emulsions by evaporating water molecules.

Table 3.22 presents the rheological properties of the contaminated Neodrill invert emulsion with 25 kg/m³ clay content before centrifugation. Based on Table 3.22, it is evident that apparent viscosity of the fluid has slightly increased when the rev dust content increased from 50 to 150 g/L. Figure 3.22 shows the Neodrill emulsion contaminated with 50 g/L rev dust after 5 min of microwaving. Bubbles, depending on the constituents and clay content, appeared to the surface after a few minutes of microwaving (see Figure 3.22-a).

Color difference of the microwaved sample indicates the destabilization of the invert emulsion. Phase separation (in volume fraction) of Neodrill emulsions after 5 min of microwaving and 20 min centrifugation at 3000 RCF are given in Table 3.23 and graphically presented in Figure 3.24. Total volume of the sample after microwaving indicates that a volume of liquid (mostly water) has been evaporated. In addition, the volume of sediment increased as higher power level was used regardless of the rev dust content. Interestingly, Transition 1 almost disappeared from the separated phases and Transition 2 (milky color) was highly solidated. As it is shown in Figure 3.24, the volume of the separated oil is relatively higher for the Medium High power level; however, the Transition 2 volume is larger for the High power level. It was not possible to accurately measure the Sediment volume with the digital caliper because the phase interface was not distinguishable. In samples with no rev dust contamination, phase separation by microwave is not so much effective as those contaminated with rev dust. We postulate that rev dust particles have a high dielectric loss enhancing selective heating, and consequently, demulsification.

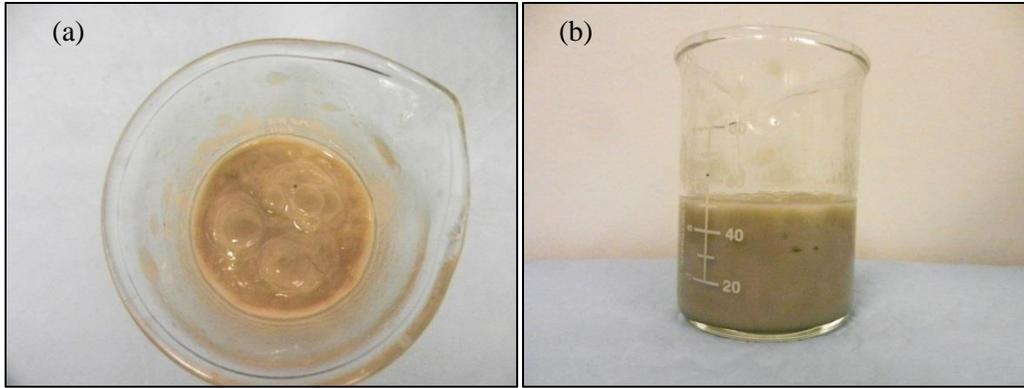


Figure 3.22 Neodrill emulsion contaminated with 50 g/L rev dust after microwaving:

- Bubbles begin to show up to the surface after a few minutes of microwaving
- Color difference of the microwaved sample indicates the destabilization of the invert emulsion.

Table 3.22 Rheological properties and Electrical Stability of Neodrill emulsions contaminated with rev dust particles before centrifugation. Apparent viscosity of the fluid has slightly increased when the rev dust content increased from 50 to 150 g/L.

Rev dust (g/L)	θ_{600}	θ_{300}	θ_{200}	θ_{100}	θ_6	θ_3	10-sec gel strength	Electrical Stability (V)
50	32	18	12	7	1-2	1-2	2	1138.67
100	35	20	14	8	2	2	2	783.33
150	38	21	15	9	2-3	2-3	3	706.67
Field Neodrill	162	96	68	43	12	10	12	

Table 3.23 Phase separation in volume fraction for Neodrill drilling fluid contaminated with dry rev dust after microwaving for 5 min and centrifugation for 20 min with 3000 RCF.

Rev Dust (g/L)	Oil	Transition	Transition 2	Total (ml)
50				
Control	0.051	0.710	0.240	49.939
M-HI	0.071	0.666	0.264	44.969
HI	0.185	0.479	0.336	43.924

100				
Control	0.093	0.600	0.3076	50.336
M-HI	0.486	0.107	0.4069	42.511
HI	0.488	0	0.513	41.193
150				
Control	0.159	0.519	0.322	49.939
M-HI	0.545	0	0.455	39.412
HI	0.494	0	0.506	40.552

Relatively more oil volume has been recovered with Medium High power level and sediment is greater for higher power level. In addition, increasing rev dust content improved the phase separation. Figure 3.22 shows the microscopic images for invert emulsions contaminated with different rev dust contents (i.e. 50, 100 and 150 g/L). Visually the invert emulsions have been destabilized and particle size has greatly increased under microwave. As rev dust content increased, larger aggregates were visibly formed in microscopic images. When the water in a smectile solution slowly evaporates, cation concentration of water increases, and therefore, cations tend to diffuse away less from the clay surfaces, and as a result, the Stern layer becomes compressed and clay lattices approach to eventually aggregate and settle out.

No separation was observed for 50 and 100 g/L rev dust content when the organophilic clay was increased to 35 kg/m³. The nature of the organoclay (i.e. hydrophobicity) hinders the selective heating of microwave because these particles have a low dielectric loss. In addition, it becomes more difficult for water molecules to escape in a gelled medium. As mentioned in section 3.9, increasing organophilic clay increases the gel strength and cuttings capacity of the fluid, and consequently, reduces the phase separation by microwave treatment.

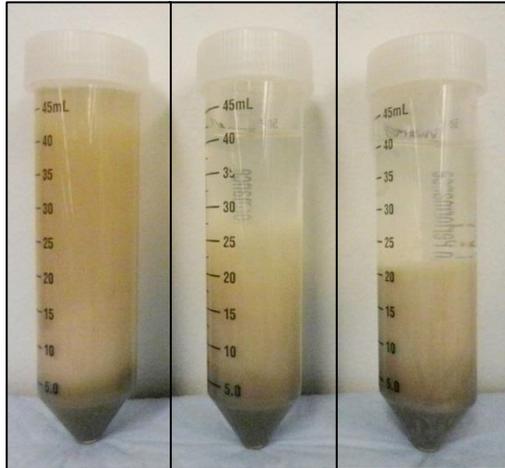


Figure 3.23 Phase separation for Neodrill invert emulsion with 50 (left) 100 (middle) and 150 (right) rev dust contamination (g/L) after 5 min of microwaving and 20 min of centrifugation at 3000 RCF. Relatively more oil volume has been recovered with Medium High power level and sediment is greater for higher power level.

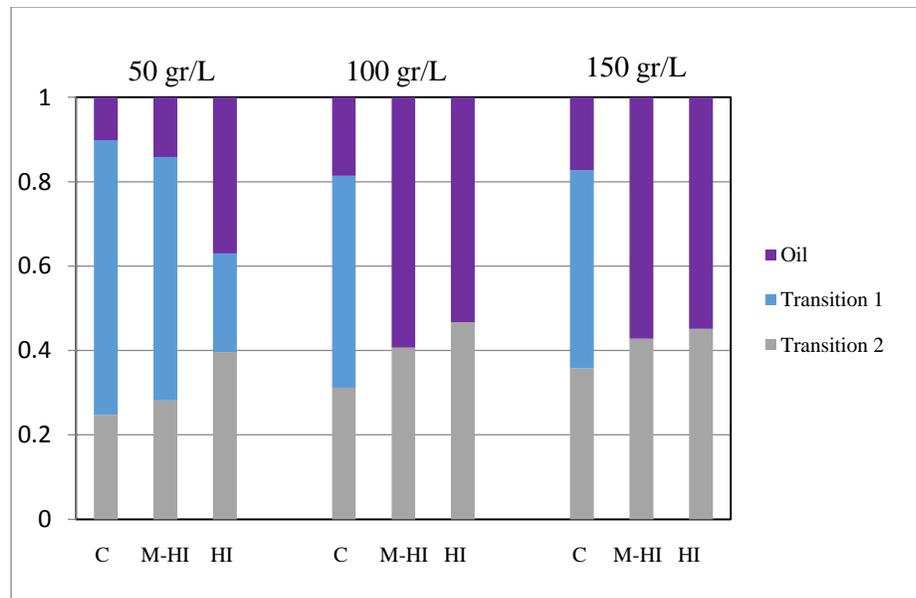


Figure 3.24 The graphical representation of the caliper measurements with different rev dust contents for Neodrill invert emulsion after 5 min of microwaving and 20 min of centrifugation at 3000 RCF. Sediment is the thick particle settling mostly consists of organophilic clay and rev dust.

Table 3.24 gives the weight loss after microwaving samples for 5 min. It is concluded that weight loss was because of water evaporation from the emulsion under microwave effect. The results in Table 3.24 points to the reason why samples visually became thicker when microwaved since water phase evaporates under microwave heating. As it is shown in Table

3.24, higher power level and rev dust content increased the weight loss of the emulsions after 5 min microwaving. Table 3.24 indicates a range of 3 to 8 gr weight loss after microwaving depending on the power and rev dust content. Assuming that most of the evaporated liquid is water with the density of 1.141 g/ml (including CaCl₂), approximately 3 ml or 60% of the total brine has been evaporated for the microwaved invert emulsion with 50 g/L rev dust content. As rev dust concentration increased, the amount of evaporated liquid increased as well. Evaporation of water has caused compression of the emulsion, and consequently, coalescence of the droplets.

Table 3.24 Weight loss calculation after 5 min of microwaving; It is concluded that weight loss was because of water evaporation from the emulsion. In addition, weight loss of the microwaved samples increased as the rev dust content and microwave power level increased.

	Power Level	Before (gr)	After (gr)	Weight Loss (gr)
50 g/L rev dust	M-HI	95.802	92.390	3.412
	HI	96.636	91.812	4.824
100 g/L rev dust	M-HI	98.392	93.973	4.419
	HI	98.113	91.935	6.178
150 g/L rev dust	M-HI	98.838	93.204	5.634
	HI	101.042	92.577	8.465

To summarize, microwave greatly enhanced the phase separation by selective heating. The weight loss of the invert emulsion indicates that water presumably has been evaporated after microwaving. As expected, the composition of the fluid has a great impact on the phase separation; for instance, rev dust and organophilic clays totally had different effects on the phase separation even though they both are the subgroups of one family. Microwave radiation seemingly had a noticeable on the physical and chemical properties of the invert emulsion. Power level played a key role in the phase separation. As mentioned before, lower power level does not have an impact on the phase separation because heat is gradually conducted and lost to the medium. As a result, it is important that adequate power level is applied to selectively heat polar molecules.

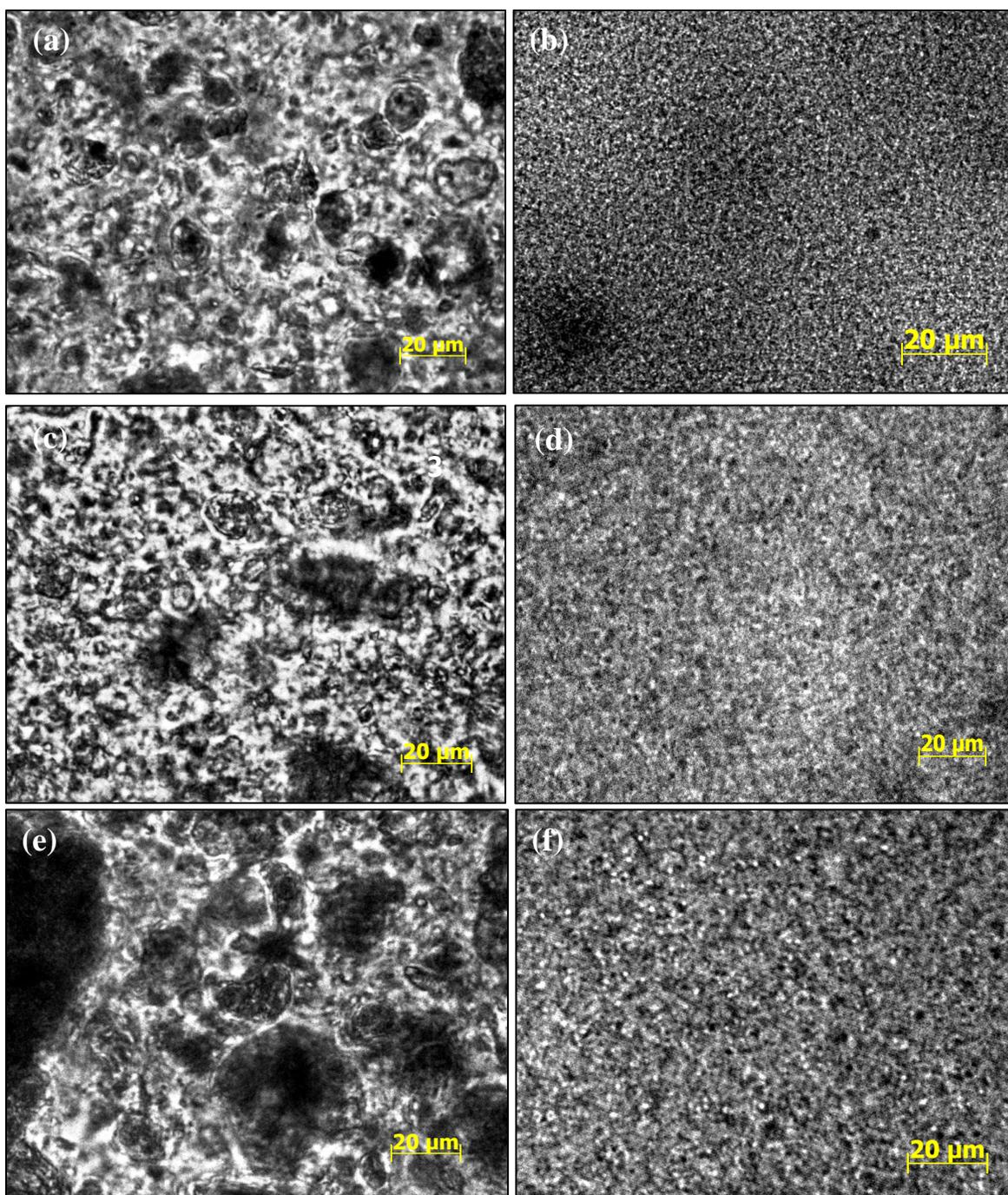


Figure 3.25 Microscopic images (Neodrill invert emulsion) for: 50 g/L rev dust content after microwaved for 5 min with M-HI power level (a) and before microwave (b). 100 g/L rev dust content microwaved for 5 min with M-HI power level (c) and after microwave (d). 150 g/L rev dust content microwaved for 5 min with M-HI power level (e) and before microwave (f).

As rev dust content increased in microscopic images, larger aggregates were visibly formed compared to their initial condition (right hand side images).

3.12 Ultrasound

Fifty (50) ml of Neodrill invert emulsion contaminated with different rev dust loads (50 to 150 g/L) was sonicated for 5 min to enhance the phase separation before centrifugation. Figure 3.26 shows a typical sample of Neodrill invert emulsion with 100 g/L rev dust content after 5 min of sonication. Cavitation bubbles appeared at the surface after a minute and aggregates were visually observed after 5 min of sonication. The microbubbles are created because of degasing and phase change to vapor.

Table 3.24 shows the weight measurements before and after sonication. The calculated weight loss was negligible (see Table 3.25). In other words, heating was not a significant factor in particles aggregation. The caliper measurements for three different rev dust contents are given in Table 3.26. No separation was observed for the invert emulsion without rev dust contamination. Furthermore, phase separation greatly reduced when organophilic content increased to 35 kg/m³ because the velocity of inter-particle collisions, and hence particles agglomeration, is reduced. It is evident that sonication has destabilized the emulsion inasmuch as solid aggregates were clearly visible straight after sonication. As it is shown in Figure 3.26, sediment volume has not been significantly changed after sonication; however, it is observed that sonication has created a clear oil layer at the top for all the samples.

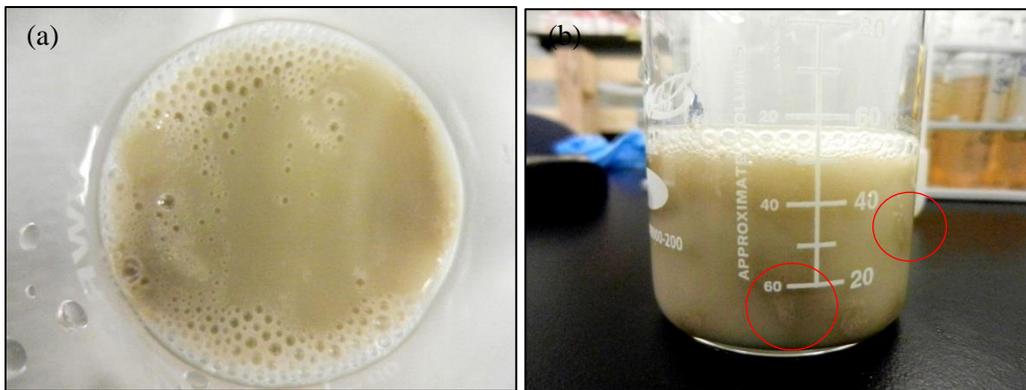


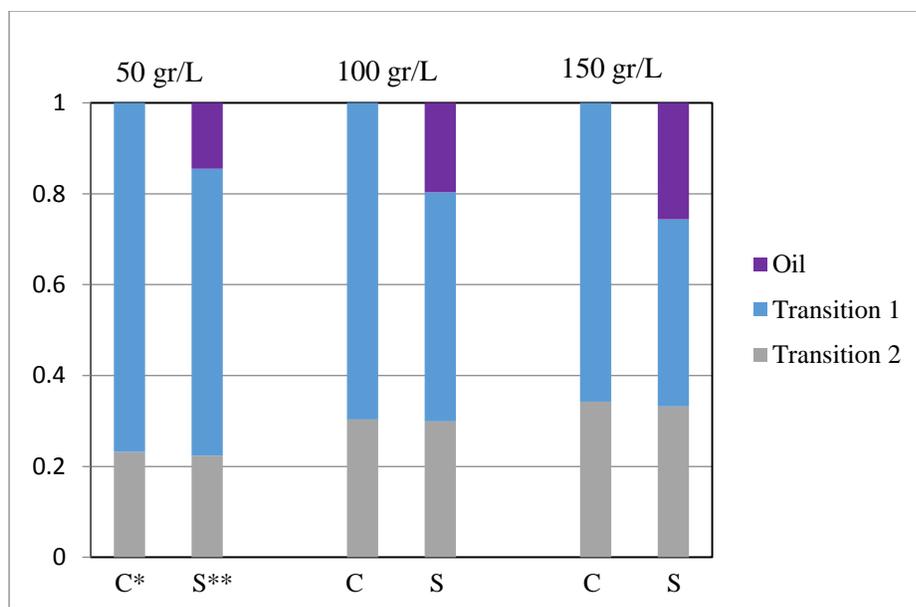
Figure 3.26 Invert emulsion contaminated with 100 g/L rev dust in the ultrasonic bath (a) and after treatment (b). Cavitation bubbles are visible after a minute of sonication in the ultrasonic bath. After 5 min of sonication, particle aggregates were visually observed in the beaker.

Table 3.25 Weight measurements after 5 min of sonication. The calculated weight loss was negligible and might not be due to sonication effect.

	Before (gr)	After (gr)
50 g/L rev dust	97.307	97.303
100 g/L rev dust	98.616	98.616
150 g/L rev dust	102.182	102.177

Table 3.26 Phase separation in volume fraction for Neodrill drilling fluid contaminated with dry rev dust after sonication and centrifugation.

Rev Dust (g/L)	Oil	Transition	Sediment	Total
50				
Control	0	0.768	0.232	50.390
Ultrasound	0.145	0.631	0.224	44.904
100				
Control	0	0.697	0.303	50.390
Ultrasound	0.196	0.504	0.299	42.308
150				
Control	0	0.657	0.343	50.390
Ultrasound	0.256	0.412	0.332	42.135



*Control
 **Sonicated

Figure 3.27 The graphical representation of the caliper measurements with different rev dust contents for Neodrill invert emulsion after 5 min of sonication and 20 min of centrifugation. Sonication has destabilized the invert emulsion and created supernatant oil at the top of the tube.

To conclude, even though clay agglomerates were visually observable in the beaker after sonication, centrifuging could not increase the volume of the sediment as much as microwave treatment. Increasing rev dust content enhanced the phase separation similar to the microwave treatment.

CHAPTER 4

CONCLUSIONS

Today there is a greater need for drilling waste management to ensure maximum reliability and minimal risk to the environment and reduce the operation costs since millions of barrels of waste drilling fluid are disposed without any treatment. Recycling and recovery of the waste fluid would cut drilling and disposal costs and enhance the drilling efficiency.

Invert emulsion drilling fluids have been widely used since 1980's due to their higher performance and wellbore stability during drilling operation. As drilling fluid is reused for the drilling of multiple wells, it accumulates low gravity solids and fine particles, which adversely affects the drilling efficiency by viscosity build-up, enhancing torque and drag, increasing the risk of pipe sticking, etc. The aim of this research is to find a remedy to remove fine particles from invert emulsion drilling fluid. This study was split into two principal parts: first, invert emulsion drilling fluids were studied for the parameters which play a significant role in emulsion gelation and stability when contaminated with fine particles. Invert emulsions were prepared under diverse conditions (e.g. different alkalinity and temperature) and then contaminated with fine particles. In the second part, two novel technologies (i.e. microwave and ultrasound) were used to remove the fine particles and recycle the base oil. The efficiency of these two techniques was assessed based on the phase separation and emulsion stability.

4.1 Conclusions

The principal aim of the first part was to study the impact of physical parameters on the stability and particle suspension capacity of invert emulsion drilling fluids. The following conclusions were reached after a careful analysis of the results of this study.

1. pH and temperature played a significant role in rev dust particle hydration. Increasing the alkalinity and temperature of the deionized water improved the rev dust particle hydration. At higher alkalinity and elevated temperature, clay particles become dispersed and deflocculated.

2. An increase in pH and temperature leads to a better rev dust hydration; however, final stability of the particles after the addition of the invert emulsion was not greatly impacted (P value < 0.05). This could be attributed to several factors:
 - The mixing speed is not sufficient to mix the hydrated rev dust particles into fresh invert emulsion, and therefore, large aggregates settle down due to the gravity force.
 - Alkalinity and temperature only play a role in water based drilling fluid where Stern/diffuse layer exist. In other words, Stern layer only is formed by water molecules because of ionization.
 - An increase in alkalinity or temperature increases the zeta potential of particles which impedes particle's absorption on the oil-water interface.
 - Rev dust particles have an affinity for water molecules and better disperse in water medium. Hydration of rev dust particles precipitates their settling because of the gravity force and leads to an instable solid network that coalesces, and ultimately, settles in the tube after centrifuging.

The last might explain why only rev dust content had an impact on the Sediment. The clear supernatant oil may suggest that particle enmeshment has occurred by adding hydrated rev dust. Upon flocculation, since particles are loosely associated, a large amount of water is enclosed, which form a voluminous sediment. It is also possible that rev dust particles lack any surfactant to make it oil wet and must absorb and remove emulsifier from the bulk mud, thereby reducing its stability [113].

3. Adding the oil wet surfactant slightly increased the Electrical Stability of the emulsion from 1113 to 1173 (V). The surfactant coats the particles and makes them more oil wet. The film of surfactant around the particles reduces the electrical conductivity and increases the voltage at which emulsion break-down occurs. Rev dust forms a conductive bridge composed of aqueous and acts as a carrier of water.
4. The presence of an **electrolyte** in **water phase** greatly inhibits clay hydration; for instance, sodium ions produce a net negative edge surface, and hence, prevent positive

edge to negative basal surface of gel structures. The degree of inhibition, however, depends upon the valance of the dissolved salt; for instance, the inhibitive impact of sodium chloride was not as high as calcium chloride. On the other hand, Calcium hydroxide (lime) did not influence the dispersion of clays because OH⁻ ions interact with the edges of the clay particles making them neutral or negatively charged. As a result, hydroxide ions cancel out the effect of double layer compression and further disperse the clay platelets.

5. In virtually all experiments, Neodrill invert emulsion showed to be more stable than Envirodrill. The higher stability of Neodrill invert could be put down to, first, higher aromaticity of the base oil, and second, higher clay content of the invert emulsion. Invert emulsion with higher clay content demonstrated higher gel strength and plastic viscosity.
6. Hot rolling had a great impact on the properties of the invert emulsion in terms of increasing optical density of the separated oil phase and Electrical Stability. Hot rolling reduces the emulsion droplet size and greatly influences the emulsion rheology. The observed increase in viscosity could be due to (1) a decrease in the mean distance of separation between the droplets, (2) a decreases in the thickness of the absorbed surfactant layer with respect to the droplet size (3) a decrease in the width of particle size distribution, or polydispersity [114]. Having said that, hot-rolling did not have a significant impact on the phase separation after centrifugation (P value<0.05). The author conjectures that hot rolling temperature might not be adequately high to affect the properties of the invert emulsion or rev dust particles should have been added to the invert emulsion before hot rolling.
7. An increase in optical density indicates an increase in particle size. The increase in optical density of supernatant oil could be caused by greater amount of total suspended particles or smaller emulsion droplet size. The optical density of the invert emulsion increased after hot rolling indicating a decrease in droplet size (with no rev dust). Optical density of the invert emulsion increased after adding rev dust to a certain concentration,

however, decreased above 150 g/L rev dust content. Since droplet size remains constant when adding rev dust, the increase is only explained by rev dust particle size.

8. Microwave showed very encouraging results in terms of phase separation. It is believed that microwave dehydrate the bound water surrounding the colloidal particles, and therefore, allow them to come into contact. Weight measurement indicates the water evaporation by microwaving and thus why samples became thicker. The thick Sediment indicates that particles are highly dehydrated and do not enclose a large amount of interlayer water. Assuming water to be the evaporated liquid, more than 60% of the initial brine was evaporated and 50% of Neodrill base oil was recovered for the microwaved invert emulsion with 50 g/L rev dust content.
9. It should be noted that low microwave power level does not have an impact on the separation because heat is gradually conducted and lost to the medium. Since rev dust is by nature water wet, it absorbs water film, and consequently, is heated by microwave. To conclude, as the rev dust concentration increases, phase separation is enhanced. On the other hand, increasing organophilic content reduced the phase separation because it becomes more difficult for water to escape in a compacted medium. The phase separation largely depends on the composition of the fluid to be microwaved.
10. Microwave did not achieve the desired effect on phase separation of Neodrill field sample. Since the composition of the field sample is not known, no firm conclusion could be reached to explain the difference. It is conjectured that particles in the field sample are highly oil wet or have low dielectric loss. Under this condition, heat conduction is dominant rather than selective heating.
11. Ultrasound was proven to be highly effective in terms of agglomerating rev dust particles. The aggregated particles were visible with naked eyes after sonication. Several mechanisms are known to be responsible for particle' collision: orthokinetic, acoustic wake effect and mutual radiation pressure interaction mechanisms. Microbubbles also play a significant role in causing considerable agitation in the liquid and raising the possibility of particles' collisions. Adding more clay particles reduced the separation

because the velocity of inter-particle collisions, and hence particles agglomeration, is reduced.

12. Both microwave and ultrasound are novel physical techniques that do not have the drawbacks of chemical treatment techniques such as susceptibility to changes in influent quality and larger volumes of waste, customization at every site to determine the type and the quantity of chemicals required, etc; either microwave or ultrasound technique aids in the phase separation of invert emulsion drilling fluids. These technologies can be installed in the solid removal facilities or before distiller or centrifuge inlet to enhance solid removal and phase separation. To scale up the technology, a close liaison is required between microwave engineering to optimize the frequency and power output.

4.2 Recommendations

Based on the conclusions reached at the end of this chapter, the following recommendations for the future studies are made:

1. It is recommended to study the application of either Response Surface Method or non-linear mathematical modeling in optimization of chemicals in drilling fluid recycling or dewatering.
2. The aromaticity of the base oil plays a prominent role in swelling of organophilic clay. The aromaticity of the base oil was not known in this study. Further research to elucidate on the part played by oil aromaticity is suggested.
3. It is recommended to study to the dehydration impact of microwave on the organophilic clay and rev dust particles by x-diffraction or methylene blue adsorption and SEM analysis which may illuminate the dehydration and nature of phase separation.
4. The microwave device used in this study was not equipped with a temperature probe, and as a result, there is no data on the temperature profile of the samples. A temperature profile sensor or probe would clearly demonstrate the components which generate heat under microwave radiation.
5. Further research on the power requirement for phase separation would aid understanding the responsible heating mechanism of the invert emulsions.

6. The frequency of both microwave and ultrasound waves play a significant role in the phase separation. Finding the optimum frequency for drilling fluids is very difficult since drilling fluids consist of a variety of different chemicals. Further research on frequency optimization is recommended to pave the way for the commercialization of these technologies.
7. Several parameters such as volume, type of base oil, water-oil ratio and chemical additives of the sample (i.e. drilling fluid) need to be further studied under microwave and ultrasound treatments. The outcome would contribute substantially to our understanding of the separation mechanisms.
8. Karl Fisher method is highly recommended for the sediment layer of the microwaved sample to analyze the amount of water loss.
9. Chemical treatment is recommended to be used along with microwave and ultrasound to enhance the phase separation efficiency.

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APPENDIX A

PHASE SEPARATION MEASUREMENTS

Average caliper measurements (in mm) for different pH/ rev dust concentrations/ temperature (Table 3.2)

Rev Dust (g/L)	Oil layer (mm)	Transition 1 (mm)	Transition 2 (mm)	Sediment (mm)	Total (mm)
Invert	3.64	17.01	10.7		30.07
pH = 7.5/ T = 25°C					
50	8.7	6.1	15.42	10.77	41.39
100	9.17	5.13	13.62	13.68	42.11
150	8.83	4.76	12.84	15.41	42.66
200	8.53	4.21	12.78	18.3	42.68
pH = 12.5/ T = 25°C					
50	6.75	8.02	12.63	13.05	41.5
100	6.67	7.92	12.95	13.34	41.79
150	6.71	7.46	12.41	15.76	42.55
200	7.12	7.83	11.63	17.49	42.48
pH = 12.5/ T = 55°C					
50	5.86	8.34	13.22	13.71	41.43
100	7.04	8	12.51	14.08	41.52
150	6.72	7.83	11.93	15.75	42.27
200	7.32	7.72	10.29	18.08	42.55

Optical density (AU) measurements for different pH/ rev dust concentrations/ temperature (Table 3.2)

Rev Dust (g/L)	pH = 7.5/ T = 25°C	pH = 12.5/ T = 25°C	pH = 12.5/ T = 55°C
50			
	1.8541	1.5786	1.8251
	2.3335	2.3	1.9659
	1.9567	2.0131	2.2847
	1.1563	1.8682	
	1.9236	2.072	
	1.9003	2.262	
Average	1.854	2.016	2.025
100			
	0.9817	1.4046	1.3142
	1.8391	1.9635	1.9637
	1.7222	1.9899	2.1875
		1.3718	1.7832
		1.9136	2.0126
		2.2545	1.898
Average	1.514	1.817	2.246
150			
	1.9166	1.2384	1.6705
	1.9555	1.9249	1.8547
	1.7694	1.859	1.9222
	0.3268	1.7288	1.1387
	1.4605	2.0761	1.8714
	2.0999	2.1117	2.2734
Average	1.589	1.823	2.019
200			
	1.9166	1.6705	1.3078
	1.9555	1.8547	2.0074
	1.7694	1.9222	2.0491
	0.3268	1.1387	1.2672
	1.4605	1.8714	1.8417
	2.0999	2.2734	2.1328
Average	1.654	1.789	1.768

Caliper measurements (in mm) for Neodrill drilling fluid contaminated with dry rev dust (Table 3.13)

Replicate	Transition 1 (mm)	Transition 2 (mm)	Sediment (mm)	Total Emulsion (mm)
Invert (BHR)				
1	42.38	8.081	0	50.461
2	42.812	7.649	0	
3	42.285	8.176	0	
Control (AHR)				
1	42.453	8.008	0	50.461
2	42.221	8.24	0	
3	42.058	8.403	0	
50 g/L (AHR)				
1	39.889	7.83	2.742	41.476
2	39.873	8.09	2.498	
3	39.727	8.052	2.682	
100 g/L (AHR)				
1	37.336	11.086	2.039	36.613
2	36.896	8.55	5.015	
3	36.729	8.369	5.363	
150 g/L (AHR)				
1	34.713	8.307	7.441	34.058
2	34.143	8.704	7.614	
3	33.849	8.936	7.676	

Optical density (AU) measurements for for Neodrill drilling fluid contaminated with dry rev dust (Table 3.13)

Replicate	BHR	Control (AHR)	50 g/L (AHR)	100 g/L (AHR)	150 g/L (AHR)
1	1.277	1.527	1.431	1.451	1.446
2	1.249	1.580	1.384	1.437	1.474
3	1.281	1.413	1.403	1.492	1.438
4	1.216	1.381	1.430	1.475	1.525
5	1.224	1.553	1.347	1.510	1.518
6	1.278	1.429	1.414	1.477	1.460
Average	1.254	1.480	1.401	1.474	1.477

Caliper measurements (in mm) for Envirodrill drilling fluid contaminated with dry rev dust (Table 3.16)

Replicate	Oil layer (mm)	Transition 1 (mm)	Transition 2 (mm)	Sediment (mm)	Total Emulsion (mm)
Control					
1	0	81.69	23.58	0	104.17
50 g/L					
1	25.19	52.54	11.73	16.99	87.73
2	26.28	48.5	12.89	15.57	
3	25.74	50.52	12.31	16.28	
100 g/L					
1	13.77	56.88	12.53	19.77	78.54
2	13.92	59.5	12.47	19.64	
3	13.85	58.19	12.5	19.71	
150 g/L					
1	12.65	56.09	12.03	24.94	73.81
2	15.08	54.5	12.5	23.08	
3	13.87	55.30	12.27	24.01	

APPENDIX B
MATERIAL SAFETY DATA SHEETS

 <p>MARQUIS ALLIANCE <small>A Division of ENCLIFE</small> Suite 1800, 800-6th Ave SW Calgary, Alberta T2P 3G3 Phone: (403)264-1588 / Fax: (403)261-8015</p>	<p>MATERIAL SAFETY DATA SHEET</p>	<p>Page 1 of 5 BENTONE 150 OCTOBER 8, 2013</p>
1. IDENTIFICATION OF PRODUCT		
PRODUCT NAME:	Bentone 150	
SYNONYMS:		
PRODUCT USE:	Drilling Fluid Additive	
CHEMICAL FAMILY:	Organophilic Clay	
<u>WORKPLACE HAZARDOUS MATERIAL INFORMATION (WHMIS):</u>		
WHMIS CONTROLLED PRODUCT:	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO	
WHMIS CLASSIFICATION:	D2A Materials Causing Other Toxic Effects – Very Toxic	
		
<p>This product has been classified in accordance with the hazard criteria of the CPR and the MSDS contains all the information required by the CPR.</p>		
	<p>NFPA KEY:</p> <p>Health: </p> <p>Flammability: </p> <p>Instability: </p> <p>Special Hazard:</p>	<p>4 Severe Hazard</p> <p>3 Serious Hazard</p> <p>2 Moderate Hazard</p> <p>1 Slight Hazard</p> <p>0 Minimal Hazard</p>
2. COMPOSITION/INFORMATION ON INGREDIENTS		
<u>INGREDIENT NAME</u>	<u>CAS NUMBER</u>	<u>% (w/w)</u>
Crystalline Silica, Quartz	14808-60-7	<1.0%
3. HAZARDS IDENTIFICATION		
EYE CONTACT:	May produce mechanical irritation.	
SKIN CONTACT:	Cannot be absorbed through the skin. Not expected to cause irritation	
INGESTION:	Not expected to produce adverse effects.	
INHALATION:	May cause slight irritation.	
ADDITIONAL HAZARDS:	NA	
4. FIRST AID MEASURES		
EYE CONTACT:	Flush eyes with running water for at least 15 minutes, if adverse symptoms develop, seek medical attention.	
SKIN CONTACT:	Wash with soap and water.	
INGESTION:	Provide symptomatic treatment and seek medical attention.	
INHALATION:	Remove patient to fresh air, if breathing is difficult, administer oxygen. Administer artificial respiration if required, and seek medical attention.	
NOTES TO PHYSICIAN:	NA	
<p>NA: None available ND: Not determined NE: Not Established</p>		



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5. FIRE FIGHTING MEASURES

FLASH POINT: Not Applicable
FLASH POINT METHOD: Not Applicable
AUTOIGNITION TEMPERATURE: Not Applicable
FLAMMABLE LIMITS IN AIR (%): Upper Limit: Not Applicable Lower Limit: Not Applicable
EXTINGUISHING MEDIA: Dry chemical, CO₂, foam, water
SPECIAL EXPOSURE HAZARDS: NA
HAZARDOUS DECOMPOSITION / COMBUSTION MATERIALS (UNDER FIRE FIGHTING CONDITIONS): Avoid high dust concentrations, and ensure all equipment is properly grounded to prevent static discharges.
SPECIAL FIRE FIGHTING PROCEDURES: Firefighters must wear appropriate breathing apparatus and clothing
UNUSUAL FIRE AND EXPLOSION HAZARDS: NA

6. ACCIDENTAL RELEASE MEASURES

PERSONAL PRECAUTIONS: Use proper personal protective equipment as listed in section 8.
SPILL PROCEDURES: Use appropriate safety equipment. Small spills, sweep up and put into approved DOT containers for disposal or re-use. Large spills, do not allow to enter waterways, sweep or shovel into approved DOT containers for re-use or disposal.
ENVIRONMENTAL PRECAUTIONS: Do not allow to enter waterways.

7. HANDLING AND STORAGE

HANDLING: Avoid ingestion. Practice reasonable caution and personal cleanliness. Avoid skin and eye contact.
STORAGE: Store in a cool, dry, well ventilated place. Keep container tightly closed and away from incompatible materials.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

ENGINEERING CONTROLS / VENTILATION: Provide mechanical ventilation to prevent dust concentrations, and to reduce potential exposure.
PERSONAL PROTECTIVE EQUIPMENT: Chemical-resistant clothing is recommended, including gloves, apron, and goggles.
RESPIRATORY PROTECTION: Recommend NIOSH-approved dust respirator.
OTHER PROTECTIVE EQUIPMENT: NA

INGREDIENTS	ACGIH		OSHA	NIOSH	IDLH
	TLV-TWA	STEL	PEL	REL	
Crystalline Silica, Quartz	0.05 mg/m ³	NA	0.1 mg/m ³	NA	50 mg/m ³
Nuisance dust	10 mg/m ³	NA	15 mg/m ³ (total) 5 mg/m ³ (respirable)	NA	NA

NA: None available

ND: Not determined

NE: Not Established



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MATERIAL SAFETY DATA SHEET

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BENTONE 150

OCTOBER 8, 2013

9. PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL STATE: Solid (powder)
COLOUR: Off white
ODOUR: Odourless
ODOUR THRESHOLD: NA
pH: NA
SPECIFIC GRAVITY: 1.6 g/cm³
BOILING POINT: NA
FREEZING / MELTING POINT: NA
VAPOR PRESSURE: NA
VAPOR DENSITY: NA
% VOLATILE BY VOLUME: NA
EVAPORATION RATE: NA
SOLUBILITY: Insoluble
VOCs: NA
VISCOSITY: NA
MOLECULAR WEIGHT: NA

10. STABILITY AND REACTIVITY

CHEMICAL STABILITY: STABLE
HAZARDOUS POLYMERIZATION: WILL NOT OCCUR
CONDITIONS TO AVOID: NA
MATERIALS TO AVOID: None Known
HAZARDOUS DECOMPOSITION PRODUCTS: Possible emissions of carbon monoxide, carbon dioxide, ammonia
ADDITIONAL INFORMATION: NA

11. TOXICOLOGICAL INFORMATION

PRINCIPLE ROUTES OF EXPOSURE

INGESTION: YES NO
SKIN CONTACT: YES NO
INHALATION: YES NO
EYE CONTACT: YES NO
ADDITIONAL INFORMATION: NA

ACUTE TEST OF PRODUCT:

	LD50 (Oral: Rat)	LD50 (Dermal: Rabbit)	LC50 (Inhalation: Rat)
Crystalline Silica, Quartz	Not Available	Not Available	Not Available

EFFECTS OF ACUTE EXPOSURE: May cause slight irritations.

EFFECTS OF CHRONIC EXPOSURE: As with any nuisance dust, long-term exposure to concentrations above recommended guidelines

NA: None available

ND: Not determined

NE: Not Established



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OCTOBER 8, 2013

GENERAL IRRITANCY OF PRODUCT: may overload the lung clearance mechanism and cause adverse lung effects and shortness of breath. Long-term exposure to products containing crystalline silica may cause silicosis.
SENSITIZATION: None known
 Not Available

CARCINOGENICITY:

INGREDIENTS	IARC	ACGIH
Crystalline Silica, Quartz	Class 1	A2

CARCINOGENICITY: Contains crystalline silica, a known carcinogen to humans.
TERATOGENICITY: Not Applicable
REPRODUCTIVE TOXICITY: Not Applicable
MUTAGENICITY: Not Applicable
SYNERGISTIC PRODUCTS: Not Applicable

12. ECOLOGICAL INFORMATION

ECOTOXICOLOGICAL INFORMATION:

INGREDIENTS	FISH SPECIES	ACUTE CRUSTACEANS	FRESHWATER ALGAE
Crystalline Silica, Quartz	NA	NA	NA

ECOTOXICITY: NA
ENVIRONMENTAL FATE: NA
OTHER INFORMATION: NA

13. DISPOSAL CONSIDERATIONS

DISPOSAL OF WASTE METHOD: Dispose of waste in accordance with all government regulations.
CONTAMINATED PACKAGING: Clean containers and dispose of in accordance with all government regulations.

14. TRANSPORT INFORMATION

TRANSPORTATION OF DANGEROUS GOODS:

PROPER SHIPPING NAME:

CANADA

Not Regulated

UNITED STATES

Not Available

TDG CLASSIFICATION:

UN NUMBER (PIN):

PACKING GROUP:

NOTE:

DOT HAZARDOUS SUBSTANCES:

MARINE POLLUTANT:

DOT REPORTABLE QUANTITY (lbs)

NA: None available

ND: Not determined

NE: Not Established



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BENTONE 150

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15. REGULATORY INFORMATION

WORKPLACE HAZARDOUS MATERIAL INFORMATION (WHMIS):

WHMIS CONTROLLED PRODUCT: YES NO

WHMIS CLASSIFICATION: D2A Toxic effects



This product has been classified in accordance with the hazard criteria of the CPR and the MSDS contains all the information required by the CPR.

	Listed	Not Listed	Exempt
CANADIAN DSL INVENTORY STATUS:	X		X
U.S. TSCA INVENTORY STATUS:	X		X

U.S. REGULATORY RULES

CERCLA / SARA			Right to Know List			California Proposition 65
302	311/312	313	MA	NJ	PA	
NA	NA	NA	NA	NA	NA	NA

16. OTHER INFORMATION

ADDITIONAL INFORMATION: No additional information is available.

DISCLAIMER: To the best of our knowledge, the information contained herein is accurate. However, neither the above named supplier nor any of its subsidiaries assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of suitability of any material is the sole responsibility of the user. All materials may present unknown hazards and should be used with caution. Although certain hazards are described herein, we cannot guarantee that these are the only hazards that exist.

Marquis Alliance expressly disclaims all expressed or implied warranties of merchantability and fitness for a particular purpose with respect to the product provided.

NA: None available ND: Not determined NE: Not Established

PRODUCT DATA



PRODUCT NAME:

Calcium Carbonate (Calc carb 325)

DESCRIPTION:

Calcium Carbonate (CaCO₃) is a naturally occurring ground rock which is only slightly soluble in water and soluble in hydrochloric acid.

PROPERTIES:

Typical Analysis		Physical											
Calcium	37.0%	Poultry	3000	Coarse	1457 kg/m ³	Particle Size Distribution							
Magnesium	0.96%					Mesh	4	5	6	8	10	20	Pan
Silica	0.6%					% Retained	0	.6	15	77	6	1	0.4
Iron	0.07%	Super Cal	500	Medium	1444 kg/m ³	Mesh	16	20	30	40	60	100	Pan
Aluminum	0.11%					% Retained	.2	8.8	30	28	27	5.3	.7
Loss on Ignition	43.5%	"O" Grind	65	Fine	1282 kg/m ³	Mesh	30	60	100	200	325		
Acid Insolubles	1.7%					% Retained	0	1.4	9.2	35.4	54		
Typical pH (10% Aqueous)	8 - 11	325	44	Ultra Fine	950 kg/m ³	Mesh					325		
						% Retained					<95		

APPLICATION:

Supercal is a "medium grind" carbonate with a particle size larger than "325" or "0" grind, but less than "Poultry" grit. It can be used in combination with other sized carbonates to provide a wide spectrum of bridging agents for drilling fluids. Its acid solubility also makes it especially suitable as a weighting or bridging agent in completion/work over and stimulation operations.

Temporary Diverting Agent

Calcium carbonate can be used to divert stimulation fluids into other producing intervals. When used in fracturing, diverting agents are designed to bridge at the formation pores and prevent fluid from entering. By using this technique, stages of diverting material can be used to divert the stimulation fluid into other potential reservoirs. The temporary plug can then be removed with hydrochloric acid.

MIXING AND HANDLING:

Calcium Carbonate may be added directly through the hopper. To minimize settling in the surface tanks, the fluid should be of sufficient viscosity or the agitation such that the particles are kept in suspension. It is advisable to use a dust mask and eye protection while mixing all powdered products. For further handling precautions consult the Material Safety Data Sheet.

WHMIS: D2A (See MSDS)	TDG: Not Regulated	PACKAGING: 25 Kg sack / 56 Sacks per Pallet
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CALCIUM CARBONATE (ALL GRADES)

MARCH 23, 2011

1. IDENTIFICATION OF PRODUCT

PRODUCT NAME: CALCIUM CARBONATE (calcarb 325)
SYNONYMS:
PRODUCT USE: Drilling mud additive
CHEMICAL FAMILY: Alkaline

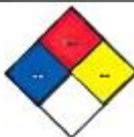
WORKPLACE HAZARDOUS MATERIAL INFORMATION (WHMIS):

WHMIS CONTROLLED PRODUCT: YES NO

WHMIS CLASSIFICATION: D2A Toxic effects- very toxic



This product has been classified in accordance with the hazard criteria of the CPR and the MSDS contains all the information required by the CPR.



NFPA KEY:		4	Severe Hazard
Health:		3	Serious Hazard
Flammability:		2	Moderate Hazard
Instability:		1	Slight Hazard
Special Hazard		0	Minimal Hazard

2. COMPOSITION/INFORMATION ON INGREDIENTS

INGREDIENT NAME	CAS NUMBER	% (w/w)
Calcium Carbonate	471-34-1	60 - 100%
Crystalline Silica, Quartz	14808-60-7	0.1 - 1%

3. HAZARDS IDENTIFICATION

EYE CONTACT: May cause irritation with discomfort or pain, local redness, and swelling of the conjunctiva.
SKIN CONTACT: Prolonged exposure may cause irritation.
INGESTION: May cause gastrointestinal irritation. If ingested in large quantities, may cause nausea, constipation and hypercalcaemia, hemorrhage.
INHALATION: If inhaled in form of dust, may cause respiratory tract irritation or inflammation. Exposure may cause coughing and sneezing. Large amounts may cause chemical pneumonitis.
ADDITIONAL HAZARDS: NA

4. FIRST AID MEASURES

EYE CONTACT: Flush eyes with water for at least 15 minutes. If adverse symptoms develop, seek medical attention.
SKIN CONTACT: Carefully and gently brush the contaminated body surfaces in order to remove all traces of calcium carbonate. Use a brush, cloth, or gloves. Remove all contaminated clothing. Rinse contaminated area with lukewarm water for 15 to 20 minutes. If irritation occurs or persists, seek medical attention.
INGESTION: If conscious, wash out mouth with water. Drink several glasses of water to dilute. Seek medical

NA: None available; ND: Not determined; NE: Not Established



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CALCIUM CARBONATE (ALL GRADES)

MARCH 23, 2011

INHALATION: attention
 Remove patient to fresh air. If breathing has stopped, administer artificial respiration, and seek medical attention.

NOTES TO PHYSICIAN: NA

5. FIRE FIGHTING MEASURES

FLASH POINT: NA- Does not burn or support combustion.

FLASH POINT METHOD: NA

AUTOIGNITION TEMPERATURE: NA

FLAMMABLE LIMITS IN AIR (%): Upper Limit: NA Lower Limit: NA

EXTINGUISHING MEDIA: NA

SPECIAL EXPOSURE HAZARDS: NA

HAZARDOUS DECOMPOSITION / COMBUSTION MATERIALS (UNDER FIRE FIGHTING CONDITIONS): Calcium carbonate is generally non-flammable but ignites on contact with fluorine. Wear adequate personal protection to prevent contact with material or its combustion products. Firefighters must wear appropriate breathing apparatus and clothing.

SPECIAL FIRE FIGHTING PROCEDURES: NA

UNUSUAL FIRE AND EXPLOSION HAZARDS: NA

6. ACCIDENTAL RELEASE MEASURES

PERSONAL PRECAUTIONS: Use proper personal protective equipment as listed in section 8.

SPILL PROCEDURES: Limit access to trained personnel. Sweep up and place in container. Use industrial vacuums for large spills. Avoid raising dust. Ventilate area.

ENVIRONMENTAL PRECAUTIONS: NA

7. HANDLING AND STORAGE

HANDLING: Avoid ingestion. Practice reasonable caution and personal cleanliness. Avoid skin and eye contact.

STORAGE: Store in a cool, dry, well ventilated place. Keep container tightly closed and away from acids.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

ENGINEERING CONTROLS / VENTILATION: Provide mechanical ventilation to prevent dust concentrations, and to reduce potential exposure.

PERSONAL PROTECTIVE EQUIPMENT: Chemical-resistant clothing is required, including gloves, apron, and goggles. Fully cover skin.

RESPIRATORY PROTECTION: Recommend NIOSH-approved dust respirator.

OTHER PROTECTIVE EQUIPMENT: NA

INGREDIENTS	ACGIH		OSHA	NIOSH
	TLV-TWA	STEL	PEL	REL
Calcium Carbonate	10 mg/m3 (Total dust)	--	15 mg/m3 (Total dust)	--
Crystalline Silica, Quartz	0.05 mg/m ³	--	0.1 mg/m3	--

NA: None available ND: No: determined NE: Not Established



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CALCIUM CARBONATE (ALL GRADES)

MARCH 23, 2011

9. PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL STATE: Solid
COLOUR: White-gray powder
ODOUR: Odourless
ODOUR THRESHOLD: NA
pH: 9.4
SPECIFIC GRAVITY: 2.65-2.75
BOILING POINT: NA
FREEZING / MELTING POINT: NA
VAPOR PRESSURE: NA
VAPOR DENSITY: NA
% VOLATILE BY VOLUME: NA
EVAPORATION RATE: NA
SOLUBILITY: 0.001% by weight
VOCs: NA
VISCOSITY: NA
MOLECULAR WEIGHT: NA

10. STABILITY AND REACTIVITY

CHEMICAL STABILITY: NO
HAZARDOUS POLYMERIZATION: WILL NOT OCCUR
CONDITIONS TO AVOID: Decomposes at 870C to form carbon dioxide and calcium oxide
MATERIALS TO AVOID: Fluorine, magnesium, aluminum, silicon, hydrogen, mercury, aluminum sulfate, ammonium salts, acids (violent reaction with generating heat and possible explosion in confined area)
HAZARDOUS DECOMPOSITION PRODUCTS: Decomposes at 870C to form carbon dioxide and calcium oxide
ADDITIONAL INFORMATION: NA

11. TOXICOLOGICAL INFORMATION

PRINCIPLE ROUTES OF EXPOSURE

INGESTION: YES NO
SKIN CONTACT: YES NO
INHALATION: YES NO
EYE CONTACT: YES NO

ADDITIONAL INFORMATION:

ACUTE TEST OF PRODUCT:

	LD50 (Oral: Rat)	LD50 (Dermal: Rabbit)	LC50 (Inhalation: Rat)
Calcium Carbonate	ND	ND	ND
Crystalline Silica, Quartz	NA	NA	NA

NA: None available ND: Not determined NF: Not Established



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MATERIAL SAFETY DATA SHEET

CALCIUM CARBONATE (ALL GRADES)

MARCH 23, 2011

EFFECTS OF ACUTE EXPOSURE: Not Available
EFFECTS OF CHRONIC EXPOSURE: May cause dermatitis.
GENERAL IRRITANCY OF PRODUCT: Eyes
SENSITIZATION: None

CARCINOGENICITY:

INGREDIENTS	IARC	ACGIH
Calcium Carbonate	NA	NA
Crystalline Silica, Quartz	Group 1	A2

CARCINOGENICITY: Contains traces of crystalline silica, a Group 1 carcinogen.
TERATOGENICITY: NA
REPRODUCTIVE TOXICITY: NA
MUTAGENICITY: NA
SYNERGISTIC PRODUCTS: NA

12. ECOLOGICAL INFORMATION

ECOTOXICOLOGICAL INFORMATION:

INGREDIENTS	FISH SPECIES	ACUTE CRUSTACEANS	FRESHWATER ALGAE
Calcium Carbonate	--	--	--
Crystalline Silica, Quartz	--	--	--

ECOTOXICITY: NA
ENVIRONMENTAL FATE: NA
OTHER INFORMATION: NA

13. DISPOSAL CONSIDERATIONS

DISPOSAL OF WASTE METHOD: Dispose of waste in accordance with all government regulations.
CONTAMINATED PACKAGING: Clean containers and dispose of in accordance with all government regulations.

14. TRANSPORT INFORMATION

TRANSPORTATION OF DANGEROUS GOODS:

	CANADA	UNITED STATES
PROPER SHIPPING NAME:	Not Regulated	Not Regulated
TDG CLASSIFICATION:		
UN NUMBER (PIN):		
PACKING GROUP:		
NOTE:		
DOT HAZARDOUS SUBSTANCES:		
MARINE POLLUTANT:		
DOT REPORTABLE QUANTITY (lbs)		

NA: None available ND: Not determined NE: Not Established



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CALCIUM CARBONATE (ALL GRADES)

MARCH 23, 2011

15. REGULATORY INFORMATION

WORKPLACE HAZARDOUS MATERIAL INFORMATION (WHMIS):

WHMIS CONTROLLED PRODUCT: YES NO

WHMIS CLASSIFICATION: D2A Toxic effects- very toxic



This product has been classified in accordance with the hazard criteria of the CPR and the MSDS contains all the information required by the CPR.

Listed Not Listed Exempt

CANADIAN DSL INVENTORY STATUS:

U.S. TSCA INVENTORY STATUS:

U.S. REGULATORY RULES

CERCLA / SARA			Right to Know List			California Proposition 65
NA	NA	NA	NA	NA	NA	NA

16. OTHER INFORMATION

ADDITIONAL INFORMATION: No additional information is available.

DISCLAIMER: To the best of our knowledge, the information contained herein is accurate. However, neither the above named supplier nor any of its subsidiaries assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of suitability of any material is the sole responsibility of the user. All materials may present unknown hazards and should be used with caution. Although certain hazards are described herein, we cannot guarantee that these are the only hazards that exist.

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NA - None available ND - Not determined NE - Not Established



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MATERIAL SAFETY DATA SHEET

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MA OILWET

APRIL 18, 2013

1. IDENTIFICATION OF PRODUCT

PRODUCT NAME: MA Oilwet
SYNONYMS:
PRODUCT USE: Water in oil emulsifier for oil-based drilling fluid
CHEMICAL FAMILY: Mixture

WORKPLACE HAZARDOUS MATERIAL INFORMATION (WHMIS):

WHMIS CONTROLLED PRODUCT: YES NO

WHMIS CLASSIFICATION: B-3 Combustible Liquid
 D-2-B Materials causing other toxic effects – skin and eye irritant



This product has been classified in accordance with the hazard criteria of the CPR and the MSDS contains all the information required by the CPR.

	NFPA KEY:	4 Severe Hazard
	Health:	3 Serious Hazard
	Flammability:	2 Moderate Hazard
	Instability:	1 Slight Hazard
	Special Hazard:	0 Minimal Hazard

2. COMPOSITION/INFORMATION ON INGREDIENTS

INGREDIENT NAME	CAS NUMBER	% (w/w)
Petroleum distillate	64741-44-2	40-70
Dipropyleneglycol methyl ether	34590-94-8	1-5

3. HAZARDS IDENTIFICATION

EYE CONTACT: May cause irritation.
SKIN CONTACT: May cause irritation. Prolonged or repeated exposure may cause dermatitis. Prolonged skin contact with petroleum products is associated with skin cancer.
INGESTION: May cause gastro-intestinal irritation, vomiting, and diarrhea.
INHALATION: Vapours or mists may cause respiratory tract irritation.
ADDITIONAL HAZARDS: NA

4. FIRST AID MEASURES

EYE CONTACT: Immediately flush with gently flowing warm water for 15 minutes or until irritation ceases. Hold eyelids open to ensure thorough flushing. When flushing is completed, obtain medical attention.

NA: None available. ND: Not determined. NE: Not Established.



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MA OILWET

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SKIN CONTACT: Wash contacted area thoroughly with soap and water. If irritation persists, obtain medical attention. Remove and launder contaminated clothing before reuse.

INGESTION: Do not induce vomiting or give liquids unless directed to do so by medical personnel. If vomiting occurs keep head below hips to prevent aspiration of vomitus. Obtain immediate medical attention. Never give anything by mouth if patient is unconscious, rapidly losing consciousness or convulsing.

INHALATION: Move to fresh air. Apply oxygen or artificial respiration if required. Obtain immediate medical attention.

NOTES TO PHYSICIAN: NA

5. FIRE FIGHTING MEASURES

FLASH POINT: 86°C (based on ingredients)

FLASH POINT METHOD: NA

AUTOIGNITION TEMPERATURE: NA

FLAMMABLE LIMITS IN AIR (%): Upper Limit: ND Lower Limit: ND

EXTINGUISHING MEDIA: Water fog, carbon dioxide, foam, dry chemical

SPECIAL EXPOSURE HAZARDS: NA

HAZARDOUS DECOMPOSITION / COMBUSTION MATERIALS (UNDER FIRE FIGHTING CONDITIONS): NA

SPECIAL FIRE FIGHTING PROCEDURES: Self-contained breathing apparatus required for fire fighting personnel.

UNUSUAL FIRE AND EXPLOSION HAZARDS: None known.

6. ACCIDENTAL RELEASE MEASURES

PERSONAL PRECAUTIONS: Use appropriate PPE as listed in section 8.

SPILL PROCEDURES: Evacuate area and eliminate ignition sources. Stop leak if possible to do so without risk. Dike to prevent spread of spilled material. Collect large spills with vacuum truck. Soak up small spills with absorbent material. Collect uncontaminated material for repackaging. Collect contaminated material and absorbents in approved containers for disposal.

ENVIRONMENTAL PRECAUTIONS: Keep out of sewers, storm drains, surface waters and soils.

7. HANDLING AND STORAGE

HANDLING: Avoid contact with eyes, skin and clothing. Avoid breathing vapours. Do not ingest. Wash hands after use. Launder contaminated clothing before reuse.

STORAGE: Store in a cool, dry well-ventilated place away from oxidizers and ignition sources. Keep container closed when not in use. Empty packages contain residual hazardous material and should be handled and stored as if full.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

ENGINEERING CONTROLS / VENTILATION: Use in a well-ventilated area. Use local exhaust ventilation in areas without good ventilation.

PERSONAL PROTECTIVE EQUIPMENT: Use neoprene or viton gloves. Wear chemical splash goggles.

RESPIRATORY PROTECTION: Wear an approved respirator with organic vapour cartridges or SCBA when handling this product.

OTHER PROTECTIVE EQUIPMENT: Ensure eyewash station and emergency shower are available.

NA: None available ND: Not determined NE: Not Established



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MA OILWET

APRIL 18, 2013

INGREDIENTS	ACGIH		OSHA	NIOSH	IDLH
	TLV-TWA	STEL	PEL	REL	
Petroleum distillate	10 mg/m3 (oil mist)	NA	NA	NA	NA
Dipropylene glycol methyl ether	NA	NA	NA	NA	NA

9. PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL STATE: Liquid
 COLOUR: Dark amber
 ODOUR: Mild hydrocarbon
 ODOUR THRESHOLD: NA
 pH: NA
 SPECIFIC GRAVITY: 0.93
 BOILING POINT: NA
 FREEZING / MELTING POINT: NA
 VAPOR PRESSURE: NA
 VAPOR DENSITY: NA
 % VOLATILE BY VOLUME: NA
 EVAPORATION RATE: NA
 SOLUBILITY: Insoluble
 VOCs: NA
 VISCOSITY: NA
 MOLECULAR WEIGHT: NA

10. STABILITY AND REACTIVITY

CHEMICAL STABILITY: STABLE
 HAZARDOUS POLYMERIZATION: WILL NOT OCCUR
 CONDITIONS TO AVOID: High temperatures and open flames.
 MATERIALS TO AVOID: Avoid contact with strong oxidizers.
 HAZARDOUS DECOMPOSITION PRODUCTS: Oxides of nitrogen, oxides of carbon and hydrocarbons.
 ADDITIONAL INFORMATION: NA

11. TOXICOLOGICAL INFORMATION

PRINCIPLE ROUTES OF EXPOSURE

INGESTION: YES NO
 SKIN CONTACT: YES NO
 INHALATION: YES NO
 EYE CONTACT: YES NO

ADDITIONAL INFORMATION:

NA: None available ND: Not determined NE: Not Established



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MA OILWET

APRIL 18, 2013

ACUTE TEST OF PRODUCT:

	LD50 (Oral: Rat)	LD50 (Dermal: Rabbit)	LC50 (Inhalation: Rat)
MA Oilwet	NA	NA	NA

EFFECTS OF ACUTE EXPOSURE: See section 3
EFFECTS OF CHRONIC EXPOSURE: NA
GENERAL IRRITANCY OF PRODUCT: Skin and eye irritant
SENSITIZATION: NA

CARCINOGENICITY:

INGREDIENTS	IARC	ACGIH
Petroleum distillate	NA	NA
Dipropylene glycol methyl ether	NA	NA

CARCINOGENICITY: NA
TERATOGENICITY: NA
REPRODUCTIVE TOXICITY: NA
MUTAGENICITY: NA
SYNERGISTIC PRODUCTS: NA

12. ECOLOGICAL INFORMATION

ECOTOXICOLOGICAL INFORMATION:

INGREDIENTS	FISH SPECIES	ACUTE CRUSTACEANS	FRESHWATER ALGAE
Petroleum distillate	NA	NA	NA
Dipropylene glycol methyl ether	NA	NA	NA

ECOTOXICITY: NA
ENVIRONMENTAL FATE: NA
OTHER INFORMATION: NA

13. DISPOSAL CONSIDERATIONS

DISPOSAL OF WASTE METHOD: Dispose of waste in accordance with all government regulations.
CONTAMINATED PACKAGING: Clean containers and dispose of in accordance with all government regulations.

14. TRANSPORT INFORMATION

TRANSPORTATION OF DANGEROUS GOODS:

	CANADA	UNITED STATES
PROPER SHIPPING NAME:	Not Regulated	Not Available
TDG CLASSIFICATION:		
UN NUMBER (PIN):		
PACKING GROUP:		
NOTE:		
DOT HAZARDOUS SUBSTANCES:		
MARINE POLLUTANT:		

NA: None available ND: Not determined NE: Not Established



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MATERIAL SAFETY DATA SHEET

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MA OILWET

APRIL 18, 2013

DOT REPORTABLE QUANTITY (lbs)

15. REGULATORY INFORMATION

WORKPLACE HAZARDOUS MATERIAL INFORMATION (WHMIS):

WHMIS CONTROLLED PRODUCT: YES NO

WHMIS CLASSIFICATION: B-3 Combustible liquid



D-2-B Materials causing other toxic effects – skin and eye irritant



This product has been classified in accordance with the hazard criteria of the CPR and the MSDS contains all the information required by the CPR.

	Listed	Not Listed	Exempt
CANADIAN DSL INVENTORY STATUS:	X		X
U.S. TSCA INVENTORY STATUS:	X		X

U.S. REGULATORY RULES

CERCLA / SARA			Right to Know List			California Proposition 65
302	311/312	313	MA	NJ	PA	
NA	NA	NA	NA	NA	NA	NA

16. OTHER INFORMATION

ADDITIONAL INFORMATION: No additional information is available.

DISCLAIMER: To the best of our knowledge, the information contained herein is accurate. However, neither the above named supplier nor any of its subsidiaries assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of suitability of any material is the sole responsibility of the user. All materials may present unknown hazards and should be used with caution. Although certain hazards are described herein, we cannot guarantee that these are the only hazards that exist.

Marquis Alliance expressly disclaims all expressed or implied warranties of merchantability and fitness for a particular purpose with respect to the product provided.

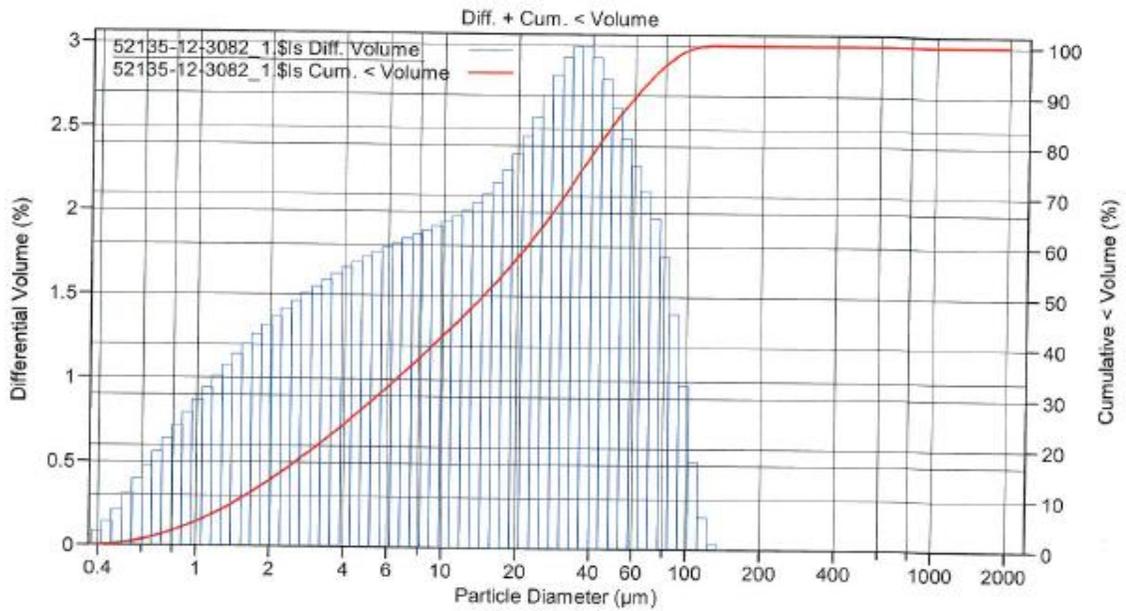
NA: None available ND: Not determined NE: Not Established



Beckman Coulter LS Particle Size Analyzer

CORE LABORATORIES - CANADA

File name: G:\2012\MARQUIS ALLIANCE ENERGY GROUP INC\12-3082\52135-12-3082_1.\$ls
 File ID: 52135-12-3082_1.\$ls
 Optical model: MADF 1274 #1
 Start time: Fraunhofer.rf780d
 9:01 6 Feb 2012



Volume Statistics (Arithmetic) 52135-12-3082_1.\$ls

Calculations from 0.375 µm to 2000 µm

Volume:	100%	S.D.:	24.45 µm
Mean:	23.66 µm	Skewness:	1.300 Right skewed
Median:	14.52 µm	Kurtosis:	1.106 Leptokurtic
Mode:	37.97 µm		

d_{50} : 14.52 µm

<10%	<25%	<50%	<75%	<90%
1.597 µm	4.165 µm	14.52 µm	36.29 µm	60.88 µm



Beckman Coulter LS Particle Size Analyzer

CORE LABORATORIES - CANADA

Interpolation from 0.375 µm to 2000 µm

Particle Diameter µm	52135-12 -2002_13% Volume %
0.375	7.99
1.3	4.84
1.9	3.87
2.8	3.68
3.9	3.86
5.6	3.36
7.8	2.95
11	2.33
16	1.83
22	1.40
31	1.11
44	0.86
75	0.52
125	0.32
180	0
250	0
355	0
500	0
710	0
1000	0

52135-12-2002_13%

Channel Number	Channel Diameter (Lower) µm	Diff. Volume %	Channel Diameter (Center) µm	Channel Diameter (Upper) µm	Cum. < Volume %	Channel Number	Channel Diameter (Lower) µm	Diff. Volume %	Channel Diameter (Center) µm	Channel Diameter (Upper) µm	Cum. < Volume %
1	0.375	0.081	0.393	0.412	0	53	47.84	2.83	50.23	62.03	83.7
2	0.412	0.15	0.432	0.452	0.081	54	52.83	2.45	55.14	57.77	85.3
3	0.452	0.22	0.474	0.496	0.23	55	57.77	2.28	60.63	63.42	87
4	0.496	0.31	0.520	0.545	0.44	56	63.42	2.13	66.45	68.62	91.0
5	0.545	0.40	0.571	0.598	0.75	57	69.82	1.97	72.84	76.43	93.2
6	0.598	0.48	0.627	0.657	1.15	58	76.43	1.74	80.67	83.90	95.1
7	0.657	0.56	0.688	0.721	2.38	59	83.90	1.40	87.90	92.10	96.9
8	0.721	0.64	0.755	0.791	3.98	60	92.10	0.98	94.49	101.1	98.3
9	0.791	0.72	0.822	0.860	2.82	61	101.1	0.52	105.9	111.9	99.2
10	0.860	0.79	0.910	0.954	3.54	62	111.0	0.19	116.3	121.8	99.8
11	0.954	0.87	0.990	1.047	4.34	63	121.8	0.026	127.7	133.8	99.96
12	1.047	0.84	1.097	1.149	5.21	64	133.8	0.0027	140.1	146.8	99.997
13	1.149	1.01	1.204	1.251	6.15	65	146.8	0	153.0	161.2	100
14	1.251	1.08	1.322	1.385	7.18	66	161.2	0	168.8	178.9	100
15	1.322	1.14	1.451	1.520	8.23	67	176.0	0	185.4	194.2	100
16	1.520	1.20	1.580	1.669	9.38	68	194.2	0	203.5	210.2	100
17	1.669	1.26	1.748	1.832	10.6	69	213.2	0	223.4	234.1	100
18	1.832	1.32	1.919	2.011	11.9	70	234.1	0	245.2	256.9	100
19	2.011	1.37	2.197	2.300	13.2	71	256.9	0	269.2	282.1	100
20	2.300	1.42	2.313	2.423	14.5	72	282.1	0	295.5	309.0	100
21	2.423	1.48	2.539	2.660	15.9	73	309.0	0	324.4	338.9	100
22	2.660	1.51	2.707	2.820	17.4	74	338.9	0	356.1	371.1	100
23	2.820	1.55	3.060	3.206	18.9	75	371.1	0	391.3	406.9	100
24	3.206	1.59	3.359	3.519	20.5	76	406.9	0	429.2	443.7	100
25	3.519	1.63	3.697	3.863	22.0	77	443.7	0	471.1	483.0	100
26	3.863	1.66	4.048	4.241	23.7	78	483.0	0	517.2	541.9	100
27	4.241	1.70	4.444	4.698	25.3	79	541.9	0	567.8	594.0	100
28	4.698	1.73	4.870	5.111	27.0	80	594.9	0	623.3	653.0	100
29	5.111	1.76	5.335	5.610	28.6	81	653.0	0	684.2	716.9	100
30	5.610	1.78	5.879	6.139	30.3	82	716.9	0	751.1	787.0	100
31	6.139	1.81	6.423	7.024	32.3	83	787.0	0	824.5	863.9	100
32	6.701	1.84	7.034	7.422	34.1	84	863.9	0	905.1	948.3	100
33	7.422	1.86	7.775	8.148	36.0	85	948.3	0	993.6	1041	100
34	8.148	1.89	8.537	8.944	37.8	86	1041	0	1091	1143	100
35	8.944	1.92	9.371	9.819	39.7	87	1143	0	1197	1255	100
36	9.819	1.94	10.28	10.78	41.8	88	1255	0	1314	1377	100
37	10.78	1.97	11.28	11.83	43.6	89	1377	0	1440	1512	100
38	11.83	2.01	12.60	12.90	45.5	90	1512	0	1584	1660	100
39	12.90	2.05	13.01	14.20	47.6	91	1660	0	1739	1822	100
40	14.20	2.11	14.94	15.65	49.8	92	1822	0	1909	2000	100
41	15.65	2.18	16.40	17.16	51.7		2000				100
42	17.16	2.26	18.00	18.86	53.9						
43	18.86	2.35	19.76	20.71	56.2						
44	20.71	2.45	21.76	22.73	58.5						
45	22.73	2.57	23.82	24.95	61.0						
46	24.95	2.70	26.15	27.39	63.5						
47	27.39	2.82	28.70	30.07	66.2						
48	30.07	2.93	31.61	33.01	69.0						
49	33.01	2.99	34.59	36.24	72.0						
50	36.24	2.99	37.97	39.78	75.0						
51	39.78	2.93	41.80	43.67	77.9						
52	43.67	2.80	45.75	47.94	80.9						