Non-Aqueous Emulsions

Introduction

The origin of non-aqueous drilling fluids can be traced to the 1920s when crude oil was used as a drilling fluid. The advantages of oil as a drilling and completion fluid were obvious even then:

- Clays do not hydrate and swell.
- Wellbore stability is improved.
- Production is improved from sandstones containing clays.
- Problems are reduced when drilling evaporites (salts, anhydrite, etc).
- Wellbore enlargement is reduced.
- Mud properties are more stable.
- Contamination resistance is increased.

Oils also have certain characteristics that are undesirable. They are flammable and may contain compounds that cause the failure of rubber goods such as hoses, O-rings, gaskets and Blowout Preventer (BOP) elements. Oils lack gel structure and are difficult to viscosify so they can be weighted. Many oils contain toxic or hazardous compounds that cause Heath, Safety and Environmental (HSE) concerns. They have high gas solubility for many of the gases encountered when drilling wells (natural gas, carbon dioxide and hydrogen sulfide). This can interfere with kick detection and well-control procedures. Oils may not degrade readily under certain conditions. Oils also float on water and can migrate a significant distance from their source.

Several different approaches have been taken to use oil in drilling fluids while minimizing the associated problems. Water-base “oil emulsion” muds were developed that contained 10 to 20% emulsified oil. Chemicals were used to emulsify the oil in the water as small droplets that would remain dispersed in the water rather than floating to the surface. This emulsified oil lowered fluid loss and reduced friction between the drillstring and wellbore. These water-base “oil emulsion” systems are rarely used today because they led to the same hole problems in water-sensitive shales and became contaminated like any other water-base mud system.

Improvements in the performance of non-aqueous drilling fluids (primarily crude oil) came with the development and use of asphaltic additives to increase viscosity and reduce fluid loss. However, these oil muds had a poor tolerance of water contamination.

In the 1940s, diesel-base muds were developed that not only tolerated water, but used emulsified water to control and maintain properties. Emulsified water droplets lowered fluid loss and raised viscosity. The continuous oil phase of these muds made them act as oil muds — wetting with an oil film and preventing emulsified water from interacting with water-sensitive shales and cuttings to provide good wellbore stability. The muds were tolerant of salt and anhydrite contamination. These muds were emulsions in every sense and were called “invert emulsion” muds to distinguish them from the water-base “oil emulsion” muds that were in use at the time. Today, an invert emulsion mud is a fluid with diesel oil, mineral oil or synthetic fluid as the continuous phase and water or brine as an emulsified phase. The emulsified water or brine is dispersed within the oil (see Figure 1). This is the internal phase. Calcium chloride salt is used to increase the emulsified water phase salinity to a level where it does not influence (soften or swell) water-sensitive formations and cuttings.

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Non-Aqueous Emulsions

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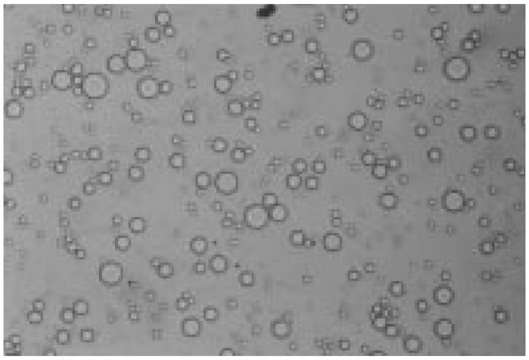

Figure 1: Dispersed water droplets in oil.

Invert emulsion muds should be used when conditions justify their application. Environmental acceptability, disposal, initial makeup cost, daily maintenance cost, anticipated hole problems, formation evaluation and formation damage issues should all be considered.

Oil muds have shown special economic advantages when used for:

- Troublesome shales.
- Salt, anhydrite, carnallite and potash zones.
- Deep, hot wells.
- Drilling and coring sensitive productive zones.
- Extended-reach drilling projects.
- Difficult directional wells.
- Slim-hole drilling.
- Corrosion control.
- Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) bearing formations.
- Perforating and completion fluids.
- Casing pack or packer fluids.
- Workover fluids.
- Spotting fluids to free stuck pipe.

Environmental concerns during the 1980s led to the use of mineral oils, highly refined oils that were less toxic and more environmentally acceptable than diesel. Mineral oils contain lower concentrations of aromatic compounds than diesel. Although not as toxic as diesel, mineral oils still may not be acceptable for use in certain environmentally sensitive locations, depending on local environmental regulations.

Driven by the need for the performance of oil-base muds while meeting increasingly strict environmental regulations for offshore locations, other “synthetic” non-aqueous liquids were introduced as alternative-base fluids. They are referred to as “synthetic fluids” because they are synthesized or manufactured from other compounds instead of being highly refined from crude oil. Synthetic fluids can be selected that have much lower toxicity and better HSE characteristics than either diesel oil or mineral oil. Esters, acetals, ethers, olefins and other synthetic solvents are among the compounds that have been used for synthetic-base muds. Synthetic-base drilling fluids are more expensive than water-, diesel-oil- or mineral-oil-base muds but the improved drilling performance of synthetic-base muds usually offsets this higher cost in offshore operations.

Diesel oil, mineral oils and the synthetic fluids are all nonpolar, non-aqueous liquids. They will not conduct electricity nor dissolve ionic compounds such as salt or anhydrite and are insoluble in water. They are used as the base or continuous fluid phase in invert emulsion muds. The mechanics of formulating, building, testing and maintaining an invert emulsion mud built with any of these base fluids is essentially the same. This chapter presents an overview of these non-aqueous fluids, systems and the fundamentals of emulsions. Other chapters will address specific products and systems.

The choice of which oil or synthetic will be used for a specific application is a matter of selecting a formulation that will provide a reasonable balance between environmental acceptability, waste disposal cost, mud cost, performance and availability.

Emulsion Fundamentals

Invert emulsion drilling fluids are mixtures of two immiscible liquids: oil...and water.

Invert emulsion drilling fluids are mixtures of two immiscible liquids: oil (or synthetic) and water. They may contain 50% or more water. This water is broken up into small droplets and uniformly dispersed in the external non-aqueous phase. These droplets are kept suspended in the oil (or synthetic) and prevented from coalescing by surfactants that act between the two phases.

Figure 2 compares two water-in-oil emulsions of substantially different water content. Provided the droplets are equal size, the system with the least water would be more stable due to the greater distance between droplets, thereby reducing the chance of coalescence.

...the smaller the droplet, the more stable the emulsion...

As shown in Figure 2, simply emulsifying the two phases causes a tremendous increase in the contact surface area between the two phases (oil-water interface). For example, if the containers in Figure 2 were a 2.72 cm cubes with a volume slightly over 20 cm^3, and 10 cm^3 of water were added to 10 cm^3 of oil then allowed to separate (as shown in the upper right corner of Figure 2), the contact surface area of the interface between the oil and water would be only 7.4 cm^2. Assuming this water is then emulsified into spherical droplets having a radius of 1 micron, the interfacial contact surface area would increase to 300,000 cm^2 (2.38×10^{12} spheres, each with 1.26×10^{-7} cm^2 surface area). This represents a 40,550 times increase in interfacial contact area just by forming the emulsion. In an emulsion, the huge number of droplets cause an increase in viscosity and act much like fine solids added to a water-base mud, increasing the plastic viscosity.

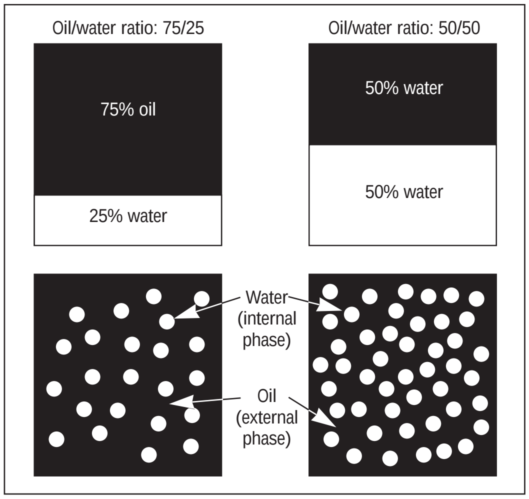

Figure 2: Effect of water content on water-in-oil emulsion.

To adequately emulsify the water in oil, there must be sufficient chemical emulsifier to form a film around each water droplet. The emulsion will be unstable if there is not sufficient emulsifier. As the water content increases, the required concentration of emulsifier increases.

From the standpoint of stability, the smaller the droplet, the more stable the emulsion since large droplets will coalesce more easily than smaller droplets (see Figure 3). Uniform droplet size also makes the emulsion more stable. To obtain small droplets of uniform size, energy or work must be applied in the form of shear. Sufficient shear to form a stable emulsion is often difficult to achieve in mud pits and in liquid mud plants. Sufficient shear can be achieved through turbulent agitation by specialized high-shear devices or when circulating through the bit jets, mud guns or

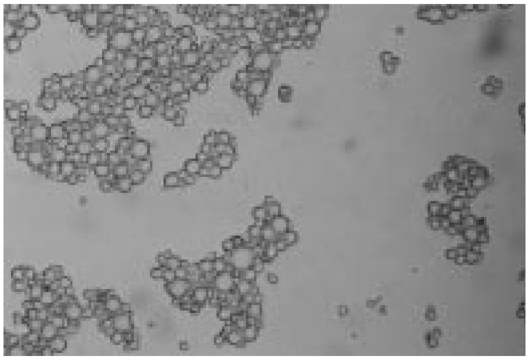

Figure 3: Coalescence of poorly emulsified water droplets.

The importance of sufficient shear and small droplet size and their relationship to mud stability cannot be overemphasized.

with some centrifugal pumps. The importance of sufficient shear and small droplet size and their relationship to mud stability cannot be overemphasized. Small, uniform water droplets generate viscosity and gel strengths that help support weight material and aid in the reduction of fluid loss by becoming trapped in the filter cake.

Increasing water content (internal phase) of an invert emulsion:

- Increases the size of water droplets.
- Increases the chances of water droplets coalescing.
- Increases the emulsion plastic viscosity.
- Increases the amount of emulsifier required to form a stable emulsion.
- Decreases the emulsion stability.

When oil (continuous phase) is added, the emulsion becomes more stable because the distance between water droplets is greater and the viscosity is reduced. To obtain the desired viscosity, gel strength and filtration control, the oil- (or synthetic-) to-water ratio must be balanced to meet specific needs.

The incorporation of solids into a water-in-oil or synthetic emulsion can have either a positive or negative effect on mud properties, depending upon the manner in which they are wetted. As long as the solids are maintained in an oil-wet condition and do not coalesce or deplete the required surfactant concentration, they will form a stable emulsion.

Wettability is determined by examining the angle of contact formed between each liquid and the surface of the solid. Figure 4 illustrates the three principal states of wetting that can occur in a three-phase system (solids in a mixture of two immiscible liquids) such as an oil or synthetic mud. By definition, if the angle formed by a liquid and a solid is less than 90° the solid is said to be preferentially wetted by that liquid. The low-contact angle promotes the liquid to spread out and coat the solid. A high-contact angle shows that the liquid prefers to ball up and not spread out over the surface. When a solid is preferentially wetted by a liquid, it has an affinity to be coated by that liquid only, even though two liquids are present in the emulsion. In Case 1, the angle formed by the water and solid surface is <90°, showing that the solid is preferentially water-wet (also indicated by the contact angle of the oil being >90°). Alternatively in Case 3, the angle formed by the oil and solid surface is <90° making it preferentially oil-wet, meaning that the solids are coated with a film of oil. For Case 2, the contact angle of both oil and water at the solid surface is 90° so that it is not preferentially wetted by either oil or water. If the contact angle, ever becomes 0°, the solid is said to be totally wetted by that liquid.

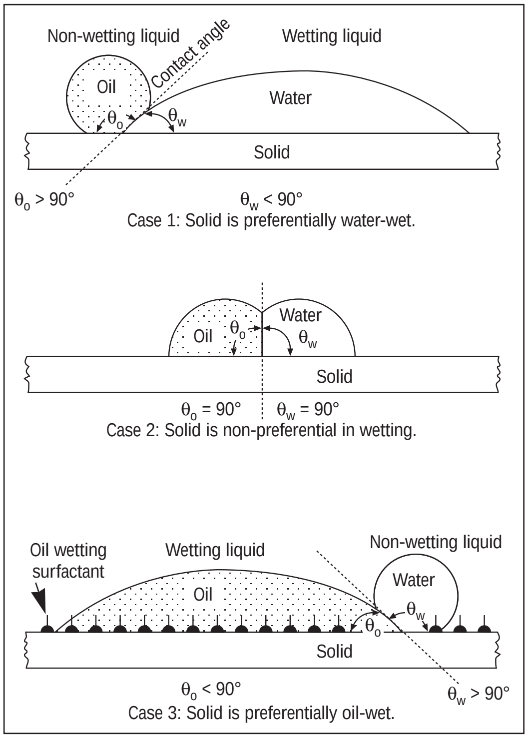

Figure 4: Contact angle and wettability.

Contact angles can be used to explain the theory of wetting. They are difficult to measure even in the laboratory, and trying to do so under field conditions is impractical. Several simple tests have been developed that indicate whether water-wetting is occurring. These tests will be described later in this chapter.

Surfactants have a hydrophilic polar head and an organophilic non-polar tail...

Non-aqueous drilling fluids are formulated using additives based on a broad group of chemicals called surface-active agents or surfactants. These chemicals include emulsifiers, soaps and wetting agents. They act by reducing the interfacial tension between two liquids or between a liquid and a solid. Surfactants have a hydrophilic (water-loving) polar head and an organophilic (oil-loving or lipophilic) non-polar tail, as shown in Figure 5.

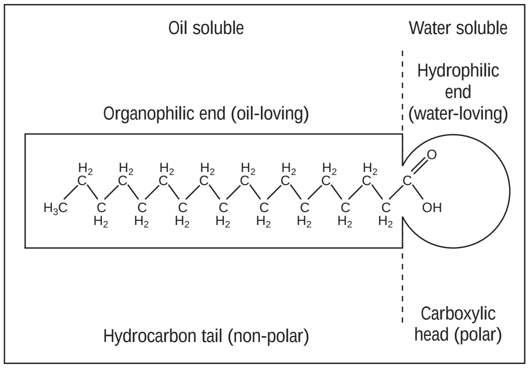

Figure 5: Surfactant structure (stearic acid).

Non-aqueous systems contain wetting agents that coat surfaces and solids to alter the contact angle...

The balance between the strength and character of the hydrophilic end and lipophilic end can be measured using the Hydrophilic-Lipophilic Balance (HLB) range. The HLB number can characterize the functionality of a surfactant. As shown in Figure 6, oil-in-water emulsifiers have higher HLB values and water-in-oil emulsifiers have lower HLB numbers, with wetting agents in the middle.

The main difference between emulsifiers, soaps and wetting agents is the surfaces they are designed to act upon and their HLB number. These differences may not be sharply defined. Most emulsifiers also have wetting properties. Wetting agents also act as emulsifiers to some degree and are categorized by their primary function in a particular formulation or by their chemistry.

Non-aqueous systems contain wetting agents that coat surfaces and solids to alter the contact angle (wettability) of the solid-liquid interfaces, as shown in Figure 7. These materials allow preferentially wetting of solids by the oil or synthetic. If a fluid is overtreated with wetting agents so that solids are totally wetted, the solids may tend to settle or sag. Solids must be maintained in the preferentially oil-wet condition to maintain a stable fluid.

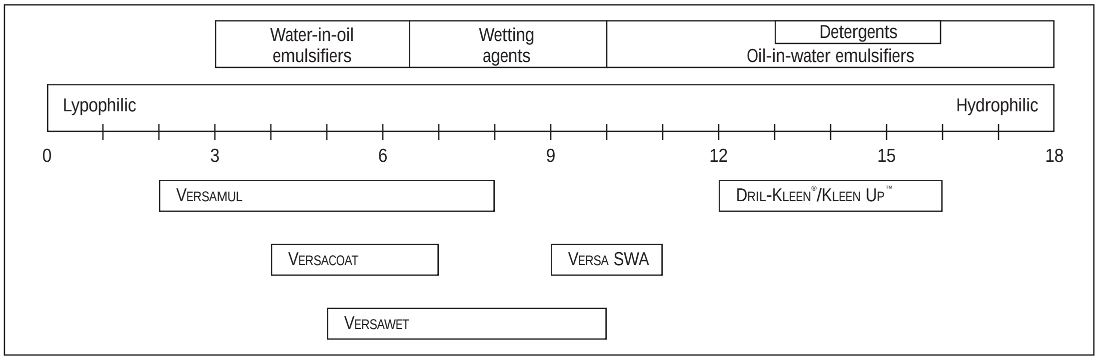

Figure 6: HLB range, function and products.

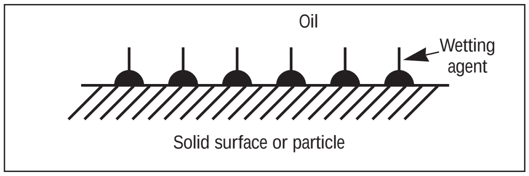

Figure 7: Orientation of wetting agent on surface or particle.

The preferential oil-wet condition can be disrupted by contamination with water, increased solids loading and insufficient treatments of wetting agents.

When water-wet solids occur:

- Solids tend to adhere to shaker screens.
- The appearance of the mud becomes "grainy," losing its glossy sheen.
- The Electrical Stability (ES) will decrease.
- The rheology will increase.
- Barite settling will be observed in mud cup, heat cup and pits.
- The High-Temperature, High-Pressure (HTHP) fluid loss will increase and may contain free water.

Weight material and solids that become water-wet will aggregate or cluster together and will settle or become separated from the system by shakers or other solids-control equipment. Settling of water-wet solids is characterized by soft deposits or "sag" as it is sometimes described. Treatments with wetting agents, such as VERSACOAT,® VERSAWET® or VERSA SWA® will restore the oil-wet condition and disperse these clusters of water-wet solids into more easily suspended individual particles.

Additives

Emulsifiers are surfactants that reduce the surface tension between the water droplets and oil...

Emulsifiers. Emulsifiers are surfactants that reduce the surface tension between the water droplets and oil (or synthetic). They stabilize the mixture by being partially soluble in water and partially soluble in oil, as shown previously in Figure 5. They are usually long-chain alcohols, fatty acids or polymers and can be anionic, cationic or non-ionic. One end of the emulsifier molecule has an affinity for water while the rest of the molecule has an affinity for oil or synthetic fluid. Emulsifier particles form a coating around the water droplets to keep them from coalescing, as shown in Figure 8.

Soaps. Some emulsifiers are soaps that are formed by the reaction of a fatty acid ester with an alkali (such as lime) where the hydrogen on the fatty acid is replaced by a metal, such as calcium from lime. Soaps made with sodium are water-soluble and form oil-in-water emulsions. Sodium hydroxide is the alkali used in many household soaps.

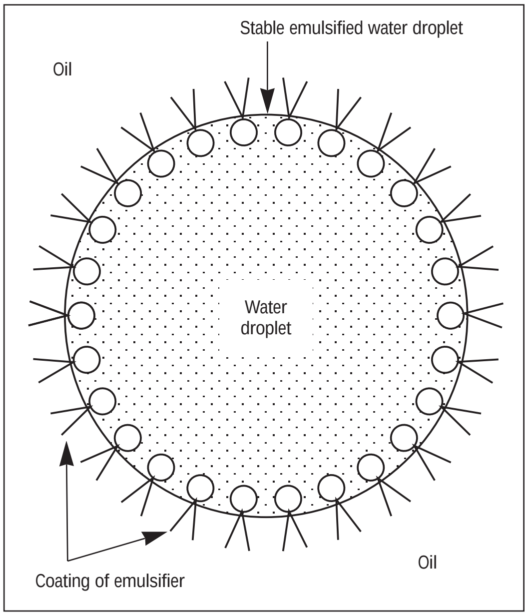

Figure 8: Arrangement of emulsifier around a water droplet.

Water-insoluble soaps are formed when metals heavier than sodium (such as calcium) are substituted for the hydrogen of the fatty acid. These water-insoluble soaps are used in greases, gel thickeners, paints and oil-muds. Calcium soaps are used extensively as the primary emulsifier in invert emulsion muds. Most calcium soap emulsifiers are formed by adding fatty acid (usually a liquid) and lime or quicklime (as an alkaline source of calcium) to the base oil of the mud, where they react to form the calcium soap.

Actually, to have a stable emulsion, there must not only be sufficient emulsifier to stabilize all of the water droplets, plus wetting agent, to coat all of the solids, but there must be an excess amount of emulsifier and wetting agent in the formulation to coat new solids and emulsify any additional water which may be encountered. This condition of well-emulsified brine, coated solids and an excess of treating agents is shown in Figure 9.

A wetting agent is a surface-active agent that reduces the interfacial tension and contact angle between a liquid and a solid.

Wetting agents. A wetting agent is a surface-active agent that reduces the interfacial tension and contact angle between a liquid and a solid. This causes the liquid to spread over the surface of the solid, as shown previously in Figure 4. Wetting agents have one end that is soluble in the continuous-phase liquid and the other that has a strong affinity for solid surfaces, as shown previously in Figure 7. In non-aqueous fluids, wetting agents cause solids to be wet with oil or synthetic liquid. The solids (barite, clays and drill solids) must be wetted by the continuous liquid phase of the drilling fluid or they will aggregate and settle. Most solids naturally have a preferentially water-wetting tendency and require wetting agents to wet them with either oil or synthetic fluid.

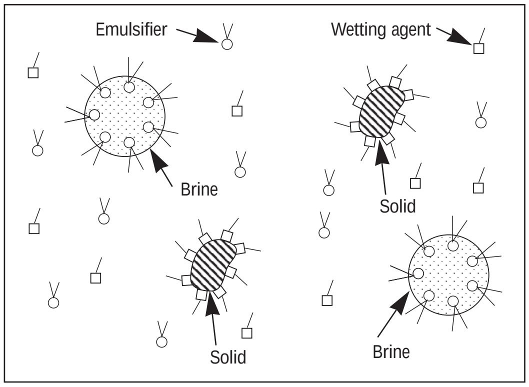

Figure 9: Schematic of stable emulsion.

Viscosifiers. Although emulsified water increases viscosity, viscosifiers and gelling agents are also required. Untreated clays cannot be used as viscosifiers because they do not hydrate and yield in oil or synthetic fluid. If the clays are first coated with an amine, so that they are organophilic, then they will yield and viscosify in oil and synthetic fluids. VG-69® is an organophilic bentonite clay. Organophilic clay still needs a polar activator (water or alcohol) to produce the maximum yield. Therefore, their yield decreases as the oil- or synthetic-to-water ratio increases. These clays yield faster with increased shear and temperature. However, if the amine is not temperature-stable, and decomposes, the clay will become an inert solid. High-temperature organophilic clays may be needed for high-temperature applications.

Alternative non-clay viscosifiers are available to increase viscosity. They include asphaltic materials, fatty acid gellants and polymers. Developing viscosity is a particular problem when mixing new fluids in mud plants where low shear mixing and low temperatures do not allow amine-treated clays to yield. However, freshly prepared muds should not be treated with more organophilic clay than will be required when drilling. Overtreatment with clay leads to excessive viscosity once the fluid is exposed to shear and temperature in the well. Alternative viscosifiers such as VERSA-HRP,® an oil-soluble polymer, should be used to provide additional suspension while mixing and transporting new muds. Many polymer viscosifiers, such as VERSA-HRP, degrade with increased exposure to temperature and shear. In freshly prepared fluids this is counteracted by the corresponding activation or yield of organophilic clay under these conditions.

Barite is the most common weight material used in oil- and synthetic-base muds.

Weight material. Barite is the most common weight material used in oil- and synthetic-base muds. Calcium carbonate is also used, particularly in lower-density packer fluids, where it is easier to suspend than either barite or hematite. Hematite may be used in high-density muds where its high specific gravity helps minimize the total solids content of the mud. Alternative weight materials may require different wetting agents.

Filtration-control additives. HTHP filtration control of invert emulsion muds is affected by the viscosity of the continuous fluid phase, the oil- or synthetic-to-water ratio, the tightness of the emulsion, water-wetting of the solids, the solids content, and the amount of amine-treated clay in the system. Many synthetic systems do not require special filtration-control additives in formulations designed for use at temperatures less than 300°F (149°C). At temperatures above this, most systems require a filtration-control additive. Gilsonite (VERSATROL® I) or asphalt, amine-treated lignite (VERSALIG®) and polymers are the most common filtration-control additives.

Gilsonite, a naturally occurring hydrocarbon or asphaltic mineral, is an efficient and cost-effective additive for controlling filtration in oil muds. Different grades are available, as distinguished by their melting points. Some operators prefer not to use gilsonite because of concerns regarding formation plugging and damage. Gilsonite may contain hydrocarbons that will be considered contaminants in synthetic-base muds. It should be determined if the use of gilsonite is forbidden by existing or impending regulations before adding it to synthetic fluids.

VERSALIG (amine-treated lignite) is often used in cases when VERSATROL I or asphalt is not acceptable. This may occur if gilsonite is not allowed due to concerns about formation damage, when temperatures exceed the melting point of gilsonite, or when asphalt is restricted due to environmental regulations. Although often used in synthetic systems, amine-treated lignite may be considered to be objectionable for use in synthetic fluids because it will discolor the fluid. M-I's "F"-type polymeric filtration-control additive is preferable to amine-treated lignite in some synthetic muds, as it will provide good filtration control without discoloring a mud.

Systems

Oil and synthetic liquids can be used to formulate three different types of systems:

1. **All-oil systems.** These systems do not contain water in their formulation. In practice, while drilling they incorporate small amounts of water from the formation and cuttings. Most will tolerate only very little water and rarely contain more than 5% water. Quite often these systems, such VERSACORE,™ are used to core productive intervals.
2. **Invert emulsions.** These contain oil (or synthetic) as the external or continuous phase and water (brine) as the internal phase of the emulsion. They can be subclassified in two separate categories:
   a) **Conventional.** These are "tight" and very stable emulsions that have zero API (100 psi) fluid loss. They usually have high electrical stability and a controlled HTHP fluid loss less than 10 cm^3 at 500 psi (3,447 kPa) and 300°F (149°C), with no water in the filtrate.
   b) **Relaxed-filtrate.** These are slightly less stable emulsions purposefully run with higher HTHP filtrates than conventional invert emulsion muds. It is normal for them to have some water in the HTHP filtrate. They may also have measurable API (100 psi) filtrate. The emulsions are loose, and the electrical stability will be lower than that of conventional invert emulsion muds. Relaxed systems use surfactant emulsifiers that do not require lime. Relaxed filtrate, invert emulsion mud systems can be converted to conventional invert-emulsion mud systems, *but conventional systems cannot be converted to relaxed systems*. Relaxed-filtrate systems are generally used on land wells where Rates of Penetration (ROP) are relatively low. They provide higher ROP with some bit types as compared to conventional systems.

Synthetic fluids are almost always conventional systems.

Synthetic fluids are almost always conventional systems. They are often formulated with the lowest synthetic-to-water ratio that is consistent with stable properties to reduce the cost per barrel. Most synthetic muds have low HTHP filtration rates without the use of special filtration-control additives at temperatures below 300°F (149°C).

Properties

The composition, viscosity characteristics, density and properties of the base liquid... have a significant effect...

The composition, viscosity characteristics, density and properties of the base liquid used in oil and synthetic fluids have a significant effect on properties, viscosity at wellbore temperatures, and overall performance of oil and synthetic drilling fluids.

Density. Non-aqueous liquids used to formulate oil-base and synthetic systems are much more compressible than water. Their density increases with increased pressure. Fortunately, these liquids also expand (reducing density) with increased temperature so that the two effects (temperature and pressure) somewhat counteract each other. The density will change with temperature and pressure so that the equivalent density downhole will be different from the surface-measured density. There will even be a difference in density between the Equivalent Circulating

Base Fluid	Specific Gravity	Viscosity (CST at 104°F)	Flash Point (°F)	Pour Point (°F)	Aniline Point (°F)
Diesel oil	0.85	3 - 4	150	14	149
Ultra-low-tar mineral oil	0.81	3.5	>239	-10	~190
Mineral oil	0.80	2 - 3	212	-0.4	169
Ester	0.85	5 - 7	354	-22	77
Poly Alpha Olefin (PAO)	0.80	5 - 7	347	-85	225
Ether	0.83	5 - 6	330	14	104
Linear Alpha Olefin (LAO)	0.78	2 - 3	237 - 295	10 - 32	156 - 178
Internal Olefin (IO)	0.78	2 - 3	279	-11	~180
Linear Paraffin (LP)	0.77	2.5	>212	14	>200

Table 1: Typical properties oils and synthetic liquids

…there are considerable differences in the viscosity and pour point of base oils and synthetic fluids.

Density (ECD) while drilling and Equivalent Static Density (ESD) while tripping due to these temperature and pressure effects. An estimate of the downhole density can be calculated with M-I's VIRTUAL HYDRAULICS® software. The actual density of these fluids is dependent on the base liquid properties and the temperature and pressure profiles of the well being drilled.

Rheology. As shown in Table 1, there are considerable differences in the viscosity and pour point of base oils and synthetic fluids. The viscosity of the base fluids directly influences the Plastic Viscosity (PV). Base fluids with high viscosities make drilling fluids with higher PVs. The viscosity of all the oil and synthetic fluids is temperature-sensitive — the viscosity decreases as the temperature increases, as shown for the funnel viscosity of a typical oil-base mud in Figure 10.

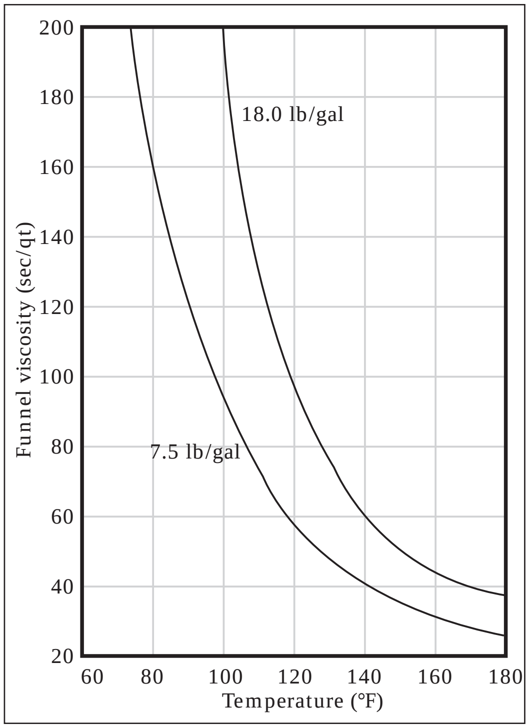

Figure 10: Effect of temperature on funnel viscosity of oil-base mud.

For rheology to be meaningful, it must be checked at the same temperature each time. A heat cup is used to heat the sample to the desired temperature, usually 120 or 150°F (49 or 65.5°C), before the rheology is checked. Base liquids with high pour points may have unacceptably high viscosity at cold temperatures.

When a drilling fluid is compressed, the effect on the viscosity is even greater than the effect on the base fluid alone.

Compression raises the viscosity of the base fluid, as shown for diesel in Figure 11. When a drilling fluid is compressed, the effect on the viscosity is even greater than the effect on the base fluid alone. The effect of compression

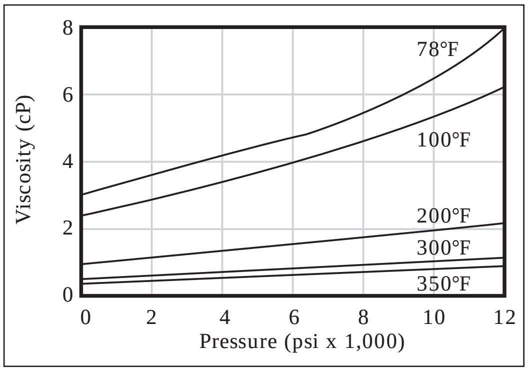

Figure 11: Effect of temperature and pressure on diesel-oil viscosity.

is greatest in high-pressure wells — deep wells drilled with heavyweight mud and high pump pressures.

For situations where it is critical to know the exact hydrostatic and circulating pressures in the well, the rheology of these fluids should be tested under temperature and pressure using a Fann Model 70 HTHP rheometer. With this information and M-I's VIRTUAL HYDRAULICS software, the effect of temperature and pressure can be predicted to optimize the hydraulic conditions.

> ***…the effect of temperature and pressure can be predicted to optimize the hydraulic conditions.***

The emulsified water droplets in invert emulsions act like solids. This causes the plastic viscosity to increase as the water concentration is increased. The oil (or synthetic) and water content may need to be changed at times to help adjust the rheological properties.

Acceptable ranges for the rheology of oil- and synthetic-base drilling fluids are determined in part by the base fluid's properties. In all cases, the plastic viscosity should be kept as low as economics permit. The yield point and gels should then be adjusted for optimum performance depending on the required density, annular geometry, hole angle, flow rate and well temperature.

The basic concepts of rheology apply to oil and synthetic drilling fluids:

1. Plastic viscosity is the theoretical viscosity of a fluid at an infinite shear rate. It should be kept as low as possible. It is a good approximation of the viscosity through the bit. Plastic viscosity increases with base-fluid viscosity; water content; and with the concentration, size, shape and distribution of the solids.
2. Yield point is often used as an indicator of a drilling fluid's shear thinning characteristics and ability to suspend cuttings and weight material. The yield point is determined from the viscometer 300- and 600-RPM readings and may not be indicative of a drilling fluid's low-shear-rate rheology. Other rheological measures may be better indicators of shear thinning and low-shear-rate behavior. These include the low-shear yield point (2 x 3 RPM minus 6 RPM), yield stress in the modified power law model and the "n" value of the power law model. The "n" value usually increases with treatments of wetting agents and emulsifiers that "thin" the mud and reduce the yield point. The "n" value can be decreased by treatments of low-shear-rate rheology modifiers (VERSAMOD™ and NOVAMOD™) and amine-treated clay that "thicken" the mud, thus increasing the yield point.
3. Initial gel strength above 5 lb/100 ft^2 is usually required to suspend weight material. This is not an absolute value because of the effects of temperature on oil and synthetic fluids. Oil and synthetic fluids should always be monitored for settling which can indicate either one of two different serious problems: settling because of inadequate gel strengths or water-wet solids.

The (P_{OM}) of an oil- or synthetic-base mud is a measure of the excess lime content.

ALKALINITY P_{OM}

The phenolphthalein alkalinity (P_{OM} or V_{SA}) of an oil- or synthetic-base mud is a measure of the excess lime content. Conventional invert emulsion systems use the primary emulsifier and calcium from lime to form calcium soaps for the emulsion. The excess lime content can be calculated by:

Excess lime (lb/bbl) = P_{OM} x 1.295

The P_{OM} of conventional systems should be maintained above 2.5 cm^3 of 0.1 N sulfuric acid, with typical values being 5 to 10. If the P_{OM} of a conventional system falls below 2.5 for an extended period of time, the emulsion may become unstable. Generally, high alkalinity produces a more stable water-in-oil emulsion. Relaxed filtrate systems use surfactant emulsifiers that do not require lime to maintain stable emulsions. In relaxed-filtrate systems, the P_{OM} is normally maintained at approximately 1 to 2 cm^3 of 0.1 N sulfuric acid to buffer against acid gases.

...high fluid loss may lead to differentially stuck pipe and formation damage...

Lime is added to oil- and synthetic-base drilling fluids for alkalinity and calcium to treat carbon dioxide (CO_2) or hydrogen sulfide (H_2S) contamination. Most oil- and synthetic-base drilling fluids have a relatively high tolerance for lime. Ester-base synthetic systems are an exception. Lime can react with esters and cause serious problems. The excess lime content of ester-base drilling fluids must be monitored and controlled carefully within acceptable ranges, especially when drilling cement. Ester-base drilling fluids are not the best choice for drilling zones with high concentrations of carbon dioxide or hydrogen sulfide.

NOTE: M-I bases all recommendations concerning alkalinity treatments on the API V_{SA} or P_{OM} method. If the operator desires, we will determine the P_{OM} by both the API method and the "Back Titration" method. However, all treatment recommendations will be based on the API V_{SA} (direct titration) method.

FLUID LOSS

Although the filtrate of an oil or synthetic fluid mud will not cause hole and formation problems associated with clay swelling, filtrate should be controlled because high fluid loss may lead to differentially stuck pipe and formation damage in some formations. The HTHP fluid loss (300°F and 500 psi) of conventional formulations is normally controlled at less than 10 cm^3. The base fluid and formulation determine the amount and type of fluid-loss-control additives.

Generally, gilsonite (VERSATROL I) is the most widely used filtration control additive in oil-base systems although any of the other fluid-loss additives can also be used. VERSALIG should be used if the operator has a policy against using asphaltic materials and gilsonite for filtration control.

Relaxed fluid-loss systems normally do not require the use of VERSATROL I or VERSALIG, because high fluid loss is desirable. Filtration can be reduced through the use of additional emulsifiers and wetting agents. Relaxed systems may contain water in the HTHP fluid loss.

Synthetic fluids normally do not require additional additives to meet HTHP fluid-loss requirements. Frequently, additional emulsifier will reduce fluid loss. M-I "F," a polymeric material, can be used in synthetic-base muds when a fluid-loss additive is needed. VERSALIG, an amine-treated lignite, is generally compatible with these systems, but it will discolor synthetic muds. VERSATROL I and asphaltic materials should not be used as they may contaminate synthetic fluid base systems with hydrocarbons that reduce their environmental value to that of common oil mud.

ELECTRICAL STABILITY

The electrical stability is an indication of how well...the water is emulsified in the oil or synthetic phase.

The electrical stability is an indication of how well (or tightly) the water is emulsified in the oil or synthetic phase. Higher values indicate a stronger emulsion and more stable fluid. Oil and the synthetic fluids do not conduct electricity. In the electrical stability test, the voltage (electrical potential) is increased across electrodes on a fixed-width probe until the emulsified water droplets connect (i.e., coalesce) to form a continuous bridge or circuit. The stronger the emulsion, the higher the voltage required to break down the emulsion completing the electrical circuit to conduct electricity. The unit of measure for recording the electrical stability is volts.

Some of the most important factors that influence electrical stability are:

1. **Water content.** Higher water content decreases electrical stability because the distance between water droplets decreases. This allows for easier electrical circuit completion through coalescence and a reduction in the electrical stability.
2. **Water-wet solids.** Water-wet solids reduce emulsion stability. Water-wet solids act as water droplets with respect to electrical conductivity. Clusters of water-wet solids conduct electricity, producing the effect of larger water droplets and a reduction in electrical stability.
3. **Emulsion strength.** Water droplets are larger and more weakly emulsified in new and unstable mud systems, causing these fluids to have significantly lower emulsion stability values. Increased shear and temperature and the incorporation of some drill solids significantly increase emulsion stability in freshly prepared fluids. In existing fluids, increasing the emulsifier and wetting agent concentration improves emulsion strength. Water droplet size and emulsifier concentration governs this aspect of emulsion stability.
4. **Temperature.** The temperature at which the electrical stability measurement is made changes the emulsion stability and electrical conductance. The electrical stability should be measured at the same temperature (120°F or 49°C) to provide relevant data.
5. **Salt concentration.** The electrical conductivity of water increases with increasing salt concentration. Increasing the salt concentration will usually cause a slight decrease in electrical stability. In addition, adding powdered salt can cause temporary instability until the salt becomes solubilized into the water phase.
6. **Saturation.** When the water phase becomes salt saturated, especially with calcium chloride, salt will precipitate from solution as a water-wet solid that reduces emulsion stability. In addition, when drilling salt sections careful attention to the amount and types of salts is critical

The electrical stability of an oil- or synthetic-base fluid should be used to indicate trends.

...flake particles do not readily dissolve in oil and synthetic muds.

to preventing this unstable situation (see binary salt calculation). Small additions of freshwater to reduce saturation and dissolve the salt will solve this problem.

7. **Weight material.** High-density muds weighted with hematite or other special minerals often have lower electrical stabilities than muds weighted with barite.

Freshly mixed, invert-emulsion muds usually have low electrical stabilities when shipped from the liquid mud plant, even though they are adequately treated with emulsifiers. The emulsions of these systems will tighten as they are exposed to downhole temperatures and sheared through the bit. Sufficient shear will actually form a "mechanical" emulsion with little emulsifier or wetting agent. Once drilling has commenced, barite, organophilic clay and drill solids will aid in further stabilizing the emulsion as these oil-wet fine solids are adsorbed at the water interface.

The electrical stability of an oil- or synthetic-base fluid should be used to indicate trends. An electrical stability of 800 in one mud may indicate a perfectly stable emulsion if the electrical stability has remained constant for several days. But an electrical stability of 1,200 in another mud might indicate major problems if previous values had been significantly higher. A well-defined downward trend or a rapid drop in electrical stability indicates the emulsion is weakening.

Electrical stability measurements should be made and recorded routinely. These values should be plotted so that trends can be easily seen. Trends upward or downward indicate changes in the system. An analysis of sequential mud checks will indicate possible causes of the change.

$CaCl_2$ CONTENT

Calcium chloride is added to increase the emulsified water phase salinity to provide inhibition of shales and reactive solids. The range for calcium chloride content is usually 25 to 35% by weight. The $CaCl_2$ content should be determined by titration and can be calculated by:

$$\% \, CaCl_2 \, (wt) = \left(\frac{Ag \times 1.565}{(Ag \times 1.565) + \% H_2O} \right) \times 100$$

Where:

Ag = cm^3 0.282 N silver nitrate per cm^3 of mud

% H_2O = Volume % water from retort

The concentration can be adjusted by adding powdered calcium chloride over several circulations. Powdered $CaCl_2$ is preferred over flake $CaCl_2$, because the larger flake particles do not readily dissolve in oil and synthetic muds. Flaked salts must first be dissolved in water before being added to a non-aqueous system. The powdered form is generally available as 94 to 97% active material. The $CaCl_2$ content should be maintained at a concentration lower than saturation (40% wt).

Alternatives to $CaCl_2$ include sodium chloride, potassium chloride, organic non-chlorides salts and other water-soluble liquids.

Controlled Activity

Water activity is a measure of the chemical potential for water to be transferred between mud and shales.

Water activity (A_W) is a measure of the chemical potential for water to be transferred between mud and shales. Activity is measured using the vapor pressure (relative humidity) of shale or mud. Activity can also be estimated based on the chemical composition of the brine (salinity). Pure water has an A_W of 1.0. Calcium chloride brines used in most non-aqueous emulsion muds have an A_W between 0.8 (22% wt) and 0.55 (34% wt). Lower values for activity are more inhibitive.

Procedures for calculating the amount of salt or water to add to adjust activity are covered in the Calculations section at the end of this chapter.

Clay-containing formations and shales swell and are weakened by the adsorption of water. The possibility exists that the water from an emulsion mud can alter shales if the A_W of the shale is lower than the activity of the mud. The key to inhibition is to "balance" the activity of the mud with that of the shale, so that the adsorption of water onto the shales is theoretically reduced to zero.

The transfer of water between an emulsified brine and a shale is often compared to osmosis. In osmosis, a solvent (water) diffuses through a semi-permeable membrane from a low concentration of solute or salt, to a high concentration of solute or salt, to equalize the concentrations. The theory of controlled activity describes the oil or synthetic fluid and emulsifiers surrounding the water droplets as a semi-permeable membrane. Shale control using this controlled (or balanced) activity is limited mainly to oil- and synthetic-emulsion muds. Water-base muds containing additives (such as glycols and silicates) exhibit only weak semi-permeable membrane characteristics.

Calcium chloride ($CaCl_2$) is normally used to obtain activities from 1.0 to 0.40 (see Table 2 in the Calculations section at the end of this chapter). Sodium chloride (NaCl) may be used to obtain activities from 1.0 to 0.75 (saturated NaCl) (see Table 3 in the Calculations section at the end of this chapter). A wide variety of alternative internal-phase chemicals can be used to reduce activity. However, many alternative materials do not provide sufficiently low activity to achieve adequate inhibition. When calcium chloride ($CaCl_2$) is added to a saturated sodium chloride (NaCl) brine, the activity is reduced but the effect is not cumulative. Activity is based on mutual solubility. Since $CaCl_2$ has a greater solubility than NaCl, sodium chloride will precipitate as fine solids at conditions above saturation.

Oil or Synthetic Ratio (O/W or S/W)

Generally, higher mud weights require higher ratios.

The oil- or synthetic-to-water (O/W or S/W) ratio relates only to the liquid portion of the mud and is not affected by the solids content. The oil- or synthetic-to-water ratio relates the oil and water fractions to the total liquid fraction. Generally, higher mud weights require higher ratios. However, different conditions favor the use of different ratios, so there is no ratio that must be used for any set of conditions.

The calculation of the oil-to-water ratio requires retort values as follows:

Oil ratio (O) =

$$\left(\frac{\text{vol \% oil}}{\text{vol \% oil + vol \% water}}\right) \text{ x } 100$$

Water ratio (W) = 100 – oil ratio

Factors that affect the oil-to-water or synthetic-to-water ratios are:

1. **Base fluid cost.** Oils and synthetic fluids are expensive. Lower oil- and synthetic-to-water ratios reduce the price of the final formulation.
2. **Residual oil or synthetic fluid on cuttings.** In some offshore areas, the permissible residual oil or synthetic fluid on discharged cuttings is regulated. Low oil- and synthetic-to-water ratios reduce the amount of oil or synthetic residue on the cuttings, making it easier to meet specified limits. Invert emulsions with O/W or S/W ratios of 50:50 have been run in the North Sea to meet these specifications.
3. **Residual brine on cuttings.** In some locations, the amount of residual brine on cuttings may be restricted due to environmental considerations. All-oil or high-O/W or -S/W formulations can be used to reduce the amount of brine discharged on cuttings. Alternative internal-phase chemicals can be used to replace chloride salts and still obtain a low water-phase activity.
4. **Rheology.** The emulsified water in an invert emulsion acts like a solid and increases the plastic viscosity as the O/W or S/W ratio decreases. The emulsified water also helps organophilic clays and fatty acid rheological modifiers (VERSAMOD and NOVAMOD) yield. Special clays and alternative viscosifiers may be required for all-oil or high-ratio fluids (>90:10).
5. **Fluid loss.** The emulsified water in invert emulsions acts like a solid and lowers the fluid loss. Muds with low O/W or S/W ratios tend to have lower fluid losses than muds with high ratios.
6. **Mud weight.** The weight material in an oil or synthetic mud must be wet with the oil or synthetic fluid. As the density of the mud is increased, the liquid phase volume decreases and the O/W or S/W ratio must be increased to provide additional base fluid to wet the weight material. The higher the mud weight, the more difficult it is to run low-ratio (high-water) fluids.
7. **Temperature.** Emulsion stability decreases with temperature. Higher O/W or S/W ratios are run in high-temperature formulations to achieve greater emulsion stability.

Procedures for calculating the amount of water or oil to add to adjust the O/W activity are covered in the Calculations section at the end of this chapter.

The O/W ratio remains constant when the mud is weighted up or solids are incorporated into the mud, even though the volume percent liquid is decreased significantly. A rapid decrease in the O/W or S/W ratio indicates an influx of saltwater from the formation, and a pit volume increase should have been observed. When using oil or synthetic muds, all water hoses on the pits should be disconnected or plugged to prevent accidental contamination with water. Heavy rains may also contaminate the system with water. Contamination with water from any source will decrease the oil- or synthetic-to-water ratio and require that chemicals and oil or synthetic fluid be added to maintain the properties.

An increase in the O/W or S/W ratio is unusual unless base oil or synthetic is added to the system. If this is observed, carefully monitor pit volumes to be sure that formation liquids, such as crude, are not intruding and contaminating the mud system. Evaporation of the water phase has been reported with high flow line temperatures. This will increase O/W or S/W ratios. After the trend of increasing ratio is confirmed with more than one retort analysis, water should be added to the system to maintain a stable oil- or synthetic-to-water ratio. If the oil- or synthetic-to-water ratio is allowed to increase too high from evaporation of water, the salt in the water phase may reach saturation, precipitate and destabilize the emulsion.

The viscosity and HTHP filtrate will change with changes in the oil- or synthetic-to-water ratio. Changing the ratio is not used to alter either of these properties. What would appear to be a relatively minor change can involve significant increases in volume and cost. For example, if the O/W ratio of a 14.4 lb/gal mud containing 30% solids is increased from 70:30 to 75:25, the oil plus the barite required to maintain the weight at 14.4 will increase the volume by 19%.

Gas Solubility

Oil and synthetic fluids are soluble to methane and other gases encountered while drilling.

Oil and synthetic fluids are soluble to methane and other gases encountered while drilling. They have high gas solubility to natural gas, carbon dioxide and hydrogen sulfide, as shown in Figure 12. This can interfere with kick detection and well-control procedures. This soluble gas does not begin to come out of solution until the pressure is reduced as the mud is circulated up the annulus. The majority of the gas expansion occurs in the last 1,000-ft interval below the surface. For this reason, extra care should be taken to monitor pit levels with these systems and when handling the influx of wellbore fluids. It is impor-

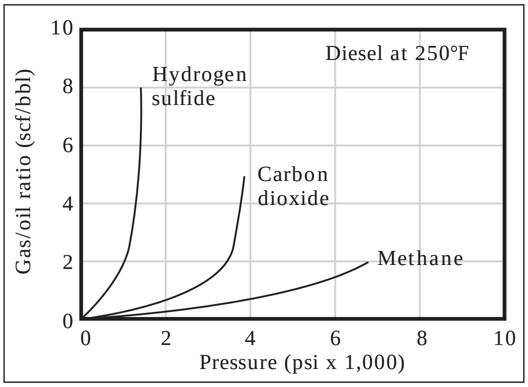

Figure 12: Gas solubility in diesel oil.

Gas Stripping of Barite

tant to be able to monitor and detect kicks to a level of about 5 bbl.

Although gas stripping of barite is not common, the problem can exist and can be demonstrated in the laboratory. Symptoms of gas stripping may include: unexpected settling in a localized area of the wellbore, slight to moderate flowing of the well and gas-cut mud upon returning to circulation. Under static conditions, the liquefied gases downhole become completely miscible in the external or diesel phase. Either an intrusion due to underbalance or the density difference will allow these low-density hydrocarbons to migrate upward, mixing and diluting the mud, and reducing viscosity. The dilution from these liquids may sufficiently weaken gel strengths to the point of causing barite to settle out.

Water-Wet Solids

When oil-wet, the solids will not adhere to one another or to other surfaces.

The concentration of wetting agent... must be maintained at adequate levels at all times.

It is obvious that increasing mud density is the only cure for this problem.

When exposed to mixtures of water and oil or synthetic fluid, most solids (drill solids, salts and weight materials) will preferentially water-wet unless surfactant wetting agents are used to make them oil- or synthetic-wet. Water-wet solids in emulsion muds adhere to each other and aggregate so that they may settle and sag, adhere to metal surfaces and destabilize the emulsion. As discussed earlier, wetting agents coat the solids and cause them to oil- (or synthetic-) wet. When oil-wet, the solids will not adhere to one another or to other surfaces.

The concentration of wetting agent decreases with time and use as it is carried off on cuttings. If the wetting agent concentration falls below a certain level, the solids will water-wet. When weight material is added to a mud, additional wetting agent is needed to coat these high surface area solids so that they do not become water-wet. If salt (especially calcium chloride) is precipitated from the brine phase of an invert emulsion, it will require large amounts of wetting agent to act on the tremendous surface area of the ultra-fine solids.

The concentration of wetting agent in non-aqueous emulsion fluids must be maintained at adequate levels at all times. Unfortunately, there are no quantitative field tests for determining the concentration of wetting agents. Pilot testing with added solids (clay or barite) can be done as a qualitative indication of reserve wetting agent. A number of indications of water-wetting can be observed along with changes in mud properties to anticipate a water-wetting problem. The following parameters can help determine the need for increasing wetting agent concentration before problems arise.

1. **Cuttings integrity.** Cuttings that are preferentially oil-wet are firm and possess an angular form. Water-wet cuttings are gummy, sticky (especially to metal parts) and soft with rounded smooth corners. Due to their gummy, sticky nature, water-wet solids tend to coalesce and “piggy-back” across a shaker screen.
2. **Sticky solids or “sag.”** Water-wet solids may coat or blind the shaker screens and prevent mud from passing through the screen. This should not be confused with plugging the screens with sand or bridging materials. Water-wet solids also settle and sag, so a build up of settled solids in

the mud pits or barite sag observed when testing the mud can be an indication of water-wet solids.

3. **Pump pressure.** "Gummy/sticky" water-wet solids tend to adhere to metal parts. When water-wet solids adhere and build up in the bore of the drillstring, the restriction in flow will quickly increase the pump pressure.
4. **Fine cuttings.** The surface of the cuttings must be oil-wet. The amount of wetting agent required to oil-wet the surface of the cuttings increases as the surface area of the cuttings increases. Finely ground cuttings have a greater surface area than coarse cuttings. Cuttings when drilling siltstone, lignite, salt and limestone are naturally small. The cuttings when drilling with conventional diamond bits are very fine. Formations and bits that produce fine cuttings will increase the requirements for wetting agents.
5. **Dull, grainy appearance.** Much can be determined by observing the appearance of invert-emulsion fluids. Systems that are stable, well emulsified and oil-wet are shiny and glossy. Water-wet solids will give an oil mud a dull, flat, grainy appearance. In extreme cases, free water may collect on the surface of the fluid.
6. **Water in HTHP filtrate.** One of the first indications of instability is an increase in the HTHP fluid loss and "free" water in the filtrate. Relaxed systems that normally contain water in the HTHP filtrate cannot be diagnosed using this technique.
7. **Saturated brine phase.** Salt solubility varies with temperature changes so that when a fluid is cooled, salt may precipitate as fine, troublesome solids. All emulsion muds should be monitored for saturation and treated to limit salt precipitation. In addition, when drilling salt, the calcium chloride brine becomes saturated so that salt is constantly being precipitated. When drilling salt, the binary salt titrations and calculations must be done. Precipitated salt crystals are difficult to wet and often act as water-wet solids. The affinity for water is stronger if the salt is divalent such as calcium or magnesium chloride. The salt concentration should be kept below saturation for the lowest temperature in the circulating system. If the salt saturation level is exceeded, the mud should be treated with water to reduce brine salinity. Increased treatments of wetting agent will be required any time saturated brine conditions are encountered.
8. **Red rag test.** The wet "red rag" test may appear unscientific, but it can provide a simple confirmation of water wetting. In the test, an oil or synthetic mud covered spatula is wiped on a water-wet red shop rag. If the mud (solids) stay on top of the rag, the mud solids are water-wet. If the solids soak into and pass through the rag surface leaving only a dark stain, the fluid is oil- or synthetic-wet.
9. **Mixer impeller test.** Stir a sample of the oil mud in a Hamilton Beach-type mixer for a period of 30 min at 2,000 to 4,000 RPM. Raise the blade out of the sample and spin dry (do not wipe dry). If gummy solids adhere to the blades, the sample is water-wet. The mixer blade should always appear to be clean and oil-wet.
10. **Glass jar tests.** There are two variations of this test, one using a Hamilton Beach-type mud mixer and one a Waring-type blender. The mud mixer test uses a glass jar and the blender method uses the glass blender jar. Both tests use the appearance of the glass after mixing the mud for a period of time. Water-wet solids will adhere to the glass and form an opaque film if

severe water-wetting is occurring. A slight film will be observed if minor wetting problem is present. **Mud mixer test**: Place 350 ml mud in a 16-ounce jar and stir at 70 volts (using a rheostat) for 1 hr. Pour out mud and rinse (by hand or with slight shake) first with the base liquid (oil or synthetic) then with an emulsion breaking solvent (like xylene/IPA). Turn the jar upside down on a rag and allow to dry. Observe film on jar. **Blender test**: Stir 350 ml of mud at high speed in a glass blender jar for 30 min. Pour the mud out and rinse the blender jar with xylene/IPA or a similar solvent. Air-dry the jar without wiping. Observe film on glass.

11. **Electrical stability test.** A single electrical stability reading (numerical value) of an oil mud will not indicate if a fluid has oil-wet or water-wet solids. However, a plot of the electrical stability readings over several days can reveal fluctuations that suggest a decline in the stability of the system and the possibility of the onset of a water-wet solids problem.

These tests should be used with observed trends in the other mud properties to determine the need for additional wetting agent.

Treatment: There is no exact method to determine the quantity of wetting agent that will be required to completely correct any given water-wet problem. However, it is recommended to begin with a treatment of 0.5- to 1.0-lb/bbl wetting agent. *NOTE: The most important thing is to begin treatments immediately once the problem has been identified!*

When possible, pilot testing can indicate a need for wetting agent before it becomes apparent. Five samples should be hot rolled for 16 hr at 160°F. One sample should be hot rolled without being treated with additional wetting agent. The remaining four samples should be treated with 0.5, 1.0, 1.5 and 2.0 lb/bbl of wetting agent. If the base sample has adequate wetting agent, there should be only very small incremental differences in the electrical stability, rheology and HTHP of the samples with increased concentration of wetting agent. If the base fluid needs wetting agent, there will be a significant difference in the properties of the untreated base and the other samples. Another pilot-testing method for water-wetting and overall mud stability involves a similar method incrementally weighting up samples 2 or more lb/gal.

Whenever oil- or synthetic-fluid muds are hot rolled, adequate ventilation, safety equipment and fire extinguishers should be available. To minimize the likelihood of leaking or breaking, the bombs/jars should be tightly sealed and the sample should be given “head” room for expansion (see Pilot Testing section of Testing chapter).

Hydrogen Sulfide

Hydrogen sulfide is a poisonous and dangerous acidic gas...

Hydrogen sulfide (H_2S) is a poisonous and dangerous acidic gas encountered in many formations and produced fluids. It can quickly deaden senses and can be fatal even at low concentrations. Personal protection and the appropriate safety measures should be taken any time hydrogen sulfide is suspected.

Oil and synthetic muds provide good protection from hydrogen sulfide corrosion and hydrogen embrittlement. The continuous oil or synthetic phase of the mud is non-conductive and does not provide an electrolyte for the corrosion process. If the mud has adequate wetting agents, the drill pipe will be preferentially oil- or synthetic-wet. However, if the emulsion becomes unstable, and the mud water-wets the drillstring and casing, the corrosion protection provided by oil and synthetic muds will be lost.

High lime content emulsion muds are best for drilling in known hydrogen sulfide formations.

Hydrogen sulfide is an acid gas. High lime content emulsion muds are best for drilling in known hydrogen sulfide formations. Hydrogen sulfide contamination can reduce alkalinity (P_{OM}) and destabilize the emulsion of oil and synthetic muds. This can lead to water-wetting of the drill pipe, sulfide corrosion and hydrogen embrittlement.

Oil- and synthetic-fluid muds offer corrosion protection from hydrogen sulfide, but no increase in protection for personnel. Hydrogen sulfide is just as toxic and dangerous to personnel when oil and synthetic muds are used as when water-base muds are used. Use personal safety protection and the utmost caution if hydrogen sulfide is encountered. *NOTE: When hydrogen sulfide is expected or encountered, the oil mud alkalinity (P_{OM}) should be maintained at >5.0 cm^3 of 0.1 N H_2SO_4 at the flow line with additions of lime.* In addition to forming calcium soaps that are essential for a stable emulsion in

Lost Circulation

conventional oil muds, lime reacts with hydrogen sulfide to form calcium sulfide and convert hydrogen sulfide gas to soluble sulfides.

Although lime is essential to safely drilling zones that contain hydrogen sulfide, it does not render the sulfides completely inert. A zinc-base scavenger, like SULF-X,® should be used to precipitate the sulfides as zinc sulfide. Lime, SULF-X and adequate mud weight provide the basis for safely drilling zones containing hydrogen sulfide. These precautions can still be overwhelmed by a large “bubble” or hydrogen sulfide kick. *NOTE: When drilling hydrogen sulfide zones, no drilling fluid product or system is an adequate substitute for training, preparation and caution on the part of all personnel involved with the drilling operation.*

When hydrogen sulfide is encountered, the mud may require large additions of lime, emulsifier and wetting agents to stabilize its properties. The mud should be watched for indications of water-wetting.

Hydrogen sulfide may turn the mud black. It may be detectable by its rotten egg odor and through the use of “sniffers” or detectors. The alkalinity (P_{OM}) will decrease, but this can be an indication of carbon dioxide (CO_2) contamination as well as hydrogen sulfide (H_2S) contamination. The electrical stability and rheology may drop. The modified garrett gas train is the most reliable test method for determining if an oil or synthetic mud is contaminated with hydrogen sulfide. The procedure for this test can be found in the Testing chapter of this manual. When hydrogen sulfide is expected, the gas from drilling breaks, connections and trips should be tested with the modified garrett gas train in addition to the regularly scheduled mud checks.

Lost circulation… can quickly become intolerable due to the high cost of the fluids.

The buildup of solids is unacceptable and the increase in viscosity may increase the ECD…

Lost circulation with oil and synthetic muds can quickly become intolerable due to the high cost of the fluids. The compressibility of these fluids makes the density and rheological properties of the mud higher downhole. This makes the likelihood of losing circulation with oil and synthetic muds greater than with water-base mud having similar density and rheology. To minimize lost circulation, the mud density and rheological properties should be kept at the minimum values consistent with safety and good drilling practices. M-I’s VIRTUAL HYDRAULICS computer program can model and optimize the performance of oil and synthetic fluids under downhole conditions to minimize the possibility of lost circulation.

Another reason for the increased risk of losing returns with oil and synthetic muds is their low leak-off (fluid-loss) values. The properties of these fluids make them excellent fracturing fluids, as they tend to propagate fractures better than water-base fluids. This characteristic, combined with the fact that they oil- or synthetic-wet the fractured formation, prevents it from softening and healing as readily as with water-base. For this reason, oil and synthetic muds are not recommended for testing casing shoes and fracture pressures. Because of their compressibility, the actual hydrostatic pressure cannot be known with certainty, and even Formation Integrity Tests (FIT) can pose a significant risk of fracturing the formation.

In the event of lost circulation, the procedures used to regain circulation are similar to those used with water-base mud systems. A more thorough discussion of lost circulation and remedies is covered in the Lost Circulation chapter. Lost circulation can be divided into two basic situations: (1) losses into an active fracture (usually in a shale near the last casing shoe), and (2) whole mud losses to porous and permeable zones (that can range from matrix sandstones to vugular and cavernous carbonate formations). The types of materials and techniques used need to be applied according to the suspected mode of loss.

Lost-Circulation Material (LCM) pills containing from 30 to 50 lb/bbl (86 to 143 kg/m^3) of LCM is a recommended standard. These pills should be spotted at the thief zone and should be left undisturbed for a period of time. Generally, a blend of several different types of LCM works better than a single product. For instance, a blend of granular, fibrous and flake materials often works best. The particle size of the LCM used should be matched with the rate of mud losses. Medium or fine grades of mica or NUT PLUG® are recommended for LCM pills. A blend of sized calcium carbonate particles has been used successfully in many areas, especially where losses are to high-permeability-matrix formations. Losses to active fractures have been shown to be slowed or stopped with an adequate concentration of larger-granule LCM additives. Be aware that flake cellophane, cedar bark, cane fiber, saw dust, cotton seed hulls, grain hulls, shredded newspaper and other shredded fibrous materials can destabilize emulsions. These materials should not be used in oil or synthetic muds, if there are other options.

While it is a common practice with water-base muds containing LCM to bypass the shale shakers, this should not be done with oil- and synthetic-base muds. The buildup of solids is unacceptable and the increase in viscosity may increase the ECD and may actually increase mud losses.

In instances of severe lost circulation, specially formulated high-fluid-loss diatomaceous earth slurry squeezes (DIASEAL™ M type), reverse gunk squeezes (200 to 250 lb/bbl of VG-69 per barrel of water with no cement) or cement squeezes are often more effective than LCM pills. Again, the materials and techniques should be matched to the rate of mud loss. In the most severe cases of lost circulation where the normal procedures have failed to bring about total returns and cost is a problem, oil and synthetic systems should be displaced with a water-base mud system.

Solids Control

High drill solids increase plastic viscosity by crowding.

Shale shakers are the primary method of controlling drill solids in oil- and synthetic-base muds.

Efficient solids control is essential to the economic use of oil and synthetic systems due to their relatively high cost and disposal considerations. Although drill solids do not hydrate in oil and synthetic muds as they do in water-base muds, solids control is critical in these muds. High drill solids increase plastic viscosity by crowding. Drill solids must be treated with wetting agents to keep them from destabilizing the emulsion. Excessive solids in oil- and synthetic-base muds not only reduce hydraulic efficiency, but they may reduce the stability of the emulsion as well. The cost of the base fluid and chemicals in these systems make correcting solids contamination through dilution more expensive than using adequate solids-control equipment to minimize drill solids accumulation.

A well-designed solids-control program is preferred to relying on dilution to keep drill solids at an acceptable level. Dilution creates a second problem in addition to cost, because the increased volume generated must be transported, stored and/or disposed of.

Dilution and centrifuges are the only effective means of reducing the fine solids content...

The solution is to mechanically remove the solids before they have the opportunity to accumulate and degrade in size. Proper solids-control management and maintenance allows oil and synthetic muds to be reused almost indefinitely. If drill solids accumulate in an oil or synthetic mud they will cause problems on subsequent wells.

Good primary solids-control equipment (shale shakers and centrifuges) is critical to the success of oil- and synthetic-base mud systems. Their importance increases in direct proportion to the cost of the base fluid.

SHALE SHAKERS

Shale shakers are the primary method of controlling drill solids in oil- and synthetic-base muds. The shakers should use the finest mesh screens that will not discharge liquid mud off the end of the shaker or discard excessive amounts of weight material. In practice, this means mud should travel ⅔ to ¾ the length of the shale shaker. With good shakers, the screen mesh may be limited by the amount of barite they discard. Three percent of recently added API grade barite may be large enough to be discarded by a 200-mesh screen. It is more economical to screen out small amounts of barite than it is to dilute the drilled solids that would accumulate if larger mesh screens were used. Mud should never be allowed to bypass the screens, since the cuttings will be ground finer and finer with each subsequent circulation to a point where they can not be removed mechanically. Also, the increased concentration of larger particles will reduce the efficiency of any additional solids-control equipment.

For weighted muds, a dual-centrifuge (tandem) system is often used.

Shale shakers are critical for economically maintaining oil and synthetic systems. If high penetration and flow rates are anticipated, scalping shakers should be used to remove the larger cuttings. The underflow of the scalping shakers should then be routed to high capacity fine-screen shakers capable of handling the highest flow rate. Ideally, the screens on these shakers should be 200 mesh or finer.

Wet cuttings from the primary shale shakers are often passed over “drying” shakers to reduce the residual fluid on the cuttings to a minimum. These drying shakers tend to mechanically degrade the cuttings and return liquids high in fine solids. If a centrifuge is being used, the underflow from the drying shakers should be centrifuged before it is returned to the active system. Although the value of the synthetic fluid recovered by drying shakers can be significant, the primary use of these shakers is to reduce the quantity of waste that must be disposed of and the residual liquid discharged with the waste.

MUD CLEANERS

Mud cleaners have been used to control solids in oil muds with limited success. The mud cleaner is designed to remove large particles from the mud system by processing the underflow from a desilter through a shaker screen. Thus, the cut from a mud cleaner is governed by the screen size. High capacity, high G-force shale shakers can process the entire mud flow over the fine mesh screens, making a mud cleaner unnecessary. Even if the mud cleaner used ultrafine-mesh screens, the mechanical degradation of the particles through its centrifugal feed pump would be detrimental and the unit would most likely be removing more barite than drill solids. There is little or no justification for using mud cleaners on rigs equipped with efficient shale shakers.

CENTRIFUGES

Dilution and centrifuges are the only effective means of reducing the fine solids content of oil and synthetic muds. Centrifuges reduce the amount of dilution needed to control mud properties.

Centrifuges can be used on unweighted oil and synthetic muds to remove fine drill solids and recover the expensive fluid phase. In this process, the discharge containing drill solids is discarded while the effluent is returned to the active system. The weight of the fluid being returned to the active system should be monitored daily. If the returning fluid weight exceeds liquid phase density, usually ~7.0 lb/gal, by an appreciable amount, too many ultrafine solids are being returned to the system. If this occurs, adjustments should be made to the centrifuge to lower its cut point.

For weighted muds, a dual-centrifuge (tandem) system is often used. The system is designed to remove only the undesirable solids and retain both the expensive fluid phase and the weight material. A primary low-G-force centrifuge is used to recover most of the weight material, returning it directly to the active system. The overflow or effluent (liquid with fine solids) is then processed through a secondary higher-G-force centrifuge that makes a finer cut, removing as many of the fine solids as is possible. The solids removed by the secondary centrifuge are discarded and the expensive liquid effluent is either returned to the active system or used for dilution on the primary centrifuge. The weight of the effluent from the secondary centrifuge must be monitored regularly to determine if fine solids are accumulating and if it will be detrimental to the active system.

A rule of thumb can be used to evaluate the efficiency of the dual-centrifuge system. A sample of the effluent from the second centrifuge should be weighted up to that of the active mud system. The mud rheology should then be measured and evaluated against the desired properties of the drilling fluid. If the rheology is not acceptable, adjustments should be made in the processing system to decrease the weight of the effluent.

Unfortunately, no mechanical processing system will eliminate the need for fresh dilution of oil or synthetic liquids while drilling. Downhole filtration, weight material additions and fine solids accumulation require fresh oil additions, regardless of the mechanical equipment used. The efficiency of centrifuges is decreased because of the increased viscosity of the emulsion as compared to water-base mud. Therefore, a series of high-G-force shakers with fine mesh screens continue to be the most effective means of controlling drilled solids in oil and synthetic muds.

Solids control is a major concern in maintaining optimum mud performance and minimizing downtime. Correct use of solids-control equipment can minimize the expensive process of dilution by controlling the build-up of undesirable solids while minimizing the loss of expensive fluid.

Cementing in Non-Aqueous Muds

Cementing... requires the use of specially designed spacer fluids to prevent mixing...

Cementing in oil and synthetic muds requires the use of specially designed spacer fluids to prevent mixing of the cement and oil or synthetic mud. These spacers are designed to be compatible with both the cement and the mud while providing other necessary functions for cementing. In addition to obtaining a good displacement of oil or synthetic muds, spacers also need to contain surfactants that will return the oil- or synthetic-wet surfaces back to a water-wet condition so that an effective

Packer Muds

cement bond can be achieved. Most cement companies will provide their own spacers for this purpose.

Mixtures of oil or synthetic mud and cement may form a viscous mass that cannot be pumped, resulting in cement channeling, lost circulation and poor cement bonding. In addition, an oil or synthetic mud will wet the casing and the borehole, causing poor cement bonding. The use of specially designed spacers not only eliminates the problems associated with mixing, but can also effect a change in the wettability of the casing and borehole. Water-wetting the casing and borehole will lead to proper bonding of the cement. If specially designed spacers are not available, the use of multiple spacers will be required. These consist of water and oil or synthetic fluid placed so they are in contact with the fluid with which they are compatible (i.e., cement/water, diesel oil/mud, synthetic fluid/mud). It is recommended that specially designed spacers be used when possible due to their added advantages.

...packer fluids should be formulated so that they do not settle.

The formulation of spacers varies widely. The formulation used is dependent on the personal preference of whoever is specifying or designing the spacer and cement job. However, there is one philosophy or technique common to all spacer design — *The fluid being displaced should be as thin as possible, while the displacing fluid should be as thick as possible.*

This approach promotes thinning of the fluid in the hole so that it does not channel, improves filter-cake removal and generates a “piston-type” action of the displacing fluid, forcing the displaced fluid out of the hole in the most efficient manner.

A packer fluid is the fluid that is left above the packer in the annular space between the tubing and casing or liner when a well is completed and ready for production. Packer fluids are usually designed to provide hydrostatic pressure equal to the pressure of the producing formation. Most wells experience tubing failures or packer failures during their producing life and require remedial operations or stimulation. These procedures become unnecessarily expensive and complicated if the weight material from the packer fluid settles on the packer. Consequently, packer fluids should be formulated so that they do not settle. Packer fluids should be thermally stable at the bottom-hole temperature. They should also protect tubing OD and casing ID from corrosion.

VERSADRIL® and VERSACLEAN® systems can be formulated to be excellent packer muds. These packer muds provide (1) excellent temperature stability over long periods of time, (2) excellent weight-material suspension characteristics and (3) lasting protection of the metal goods from corrosion. Water-base muds do not offer the same level of performance as packer fluids.

The following procedures can be used to formulate a stable oil or synthetic packer fluid without a specific formula or test procedure.

1. The fluid to be used should be formulated from an existing used mud or should contain as much previously used fluid as possible. Muds that have been used for drilling are more stable due to the previous heat cycling and shear through the bit. These actions reduce and stabilize the water droplet size and possibly reduce the size of the solids. Some colloidal solids are beneficial in packer fluids as they help prevent sag. If new mud must be used, it should be circulated and sheared through the well and a bit for 2 to 3 circulations or more, if possible.
2. The mud system should be screened to remove large particles that are difficult to suspend. This is a critical step in the proper construction of a packer mud and should be done without exception. Screen size should be as small as possible, up to 200 mesh.

Casing-Pack Fluids

It is common practice to use the drilling fluid as the casing-pack fluid.

3. Another critical issue is to be sure that the fluid does not contain any water-wet solids. Water-wet solids tend to form large conglomerates that settle more easily. Severe water-wetting may also prevent organophilic clays from building adequate gel strengths. Before an oil or synthetic mud is used for a packer fluid, it should be pilot tested with suitable wetting agents and emulsifiers to assure that water-wetting does not exist. However, care must be taken not to overtreat with wetting agent, as this can thin the fluid and cause barite settling from insufficient viscosity.
4. The mud system MUST be treated with lime until the alkalinity (P_{OM}) stabilizes in the proper range. A minimum of 2 lb/bbl of excess lime is required for ALL oil and synthetic packer muds. A new mud system will require large additions of lime to accomplish this because they

consume lime during the calcium soap formation process before they become completely stable. Large treatments of lime may cause water wetting, that MUST be avoided and corrected. It is recommended that treatments of VERSACOAT or VERSAMUL® accompany any large treatment with lime.

5. Packer fluids must be designed to meet different specifications from drilling fluids. The packer fluid's rheology must be high enough to prevent weight material from settling for extended periods, years in some cases. The rheological requirements for this will vary with the oil- or synthetic-to-water ratio of the packer fluid, its density, the specific gravity of the weight material used and the bottom-hole temperature of the well. The 10-min gel strength of weighted packer fluids will generally need to be in a range of 25 to 60 lb/100 ft^2. Packer fluids weighing 10 to 13 lb/gal do not contain sufficient weight material to gain suspension from particle crowding. They will need higher gel strengths than heavier-weight packer fluids, and may need to be formulated with bentonite or a low-yield clay to build body with colloidal-size solids.

Workover Fluids

6. When pilot testing packer fluids, mix enough volume of each formulation to static age at least six samples. Depending on the size of the static aging bombs, this will probably require more than six-barrel equivalents. Use a sample of the actual liquid mud that will be used in the packer fluid to mix these samples. The properties of the packer fluid should be checked and recorded before static aging. Six samples of the packer fluid should be pressured and static aged at the bottom-hole temperature of the well. Check the static shear and properties of two samples after being static aged for one, seven and 30 or more days. Check the samples for settling after the static shear rates are taken. If both samples fail because of settling, excessive shear rates, or instability of the mud properties, the other samples should be discarded and a new formulation should be developed and tested.

Oil mud is the fluid of choice for "washing over" and retrieving casing.

A casing pack is the fluid that is pumped ahead of the cement and left in the annulus above the cement on the outside of the casing being cemented. It is common practice to use the drilling fluid as the casing-pack fluid. When an oil or synthetic fluid casing pack is needed, the hole should be drilled with the system to eliminate the time needed for displacing and stabilizing the well with the casing pack. The purpose of oil or synthetic casing packs is:

- To stabilize the wellbore.

Troubleshooting Oil Muds

	Primary Emulsifier	Wetting Agent
Conventional system	VERSAMUL	VERSACOAT
Relaxed system	VERSACOAT	VERSAWET

A. PROBLEM: INSUFFICIENT VISCOSITY

Cause	Treatment
Undertreatment of viscosifier Lack of proper particle size distribution	Add organophilic clay, VG-69 Add VERSA-HRP Add VERSAMOD
Low water content	Add water (brine)
New mud, lack of shear	Shear through bit or shear unit
Gas stripping	Increase mud weight Add wetting agent Add primary emulsifier and lime

B. PROBLEM: EXCESSIVE VISCOSITY

Cause	Treatment
High water content (saltwater flow)	Dilute with oil Add primary emulsifier and lime Add wetting agent* Add VERSATHIN ®
Incorporated drill solids	
1. High solids (% volume)	Centrifuge/solids control Use dilution Add wetting agent* Add VERSATHIN*
2. Fines solids problem	Centrifuge/solids control Use dilution Add wetting agent* Add VERSATHIN*
3. Water-wet solids	Add wetting agent and primary emulsifier Add VERSA SWA*
High-temperature instability	Add wetting agent and primary emulsifier Decrease water content Reduce solids content
Acid gases	Add lime (conventional system) Add primary emulsifier and wetting agent Increase mud weight
Overtreatment	Dilute with oil

C. PROBLEM: INCREASE IN HTHP FILTRATION

Cause	Treatment
Weak emulsion	Add primary emulsifier Add lime (conventional system)
Lack of proper particle size distribution	Add VERSATROL I Add VERSALIG Add VG-69 Add weight material or bridging agent
High-temperature instability	Add primary emulsifier and wetting agent Add lime (conventional system) Add VERSATROL I or VERSALIG

D. PROBLEM: WATER IN HTHP FILTRATE (IF UNDESIRABLE)

Cause	Treatment
Weak emulsion	Add primary emulsifier and wetting agent Add lime (conventional system)
High-temperature instability	Add primary emulsifier Add lime (conventional system) Add VERSATROL I or VERSALIG

E. PROBLEM: WATER-WET SOLIDS

Cause	Treatment
Super-saturation	Add emulsifier and wetting agent Add VERSA SWA* Add water sparingly
Excessive solids	Use solids control and dilution Add wetting agent Add VERSA SWA*
Undertreatment	Add primary emulsifier and wetting agent Add VERSA SWA*

*VERSA SWA should be used sparingly and only when other treatments and methods are ineffective.

F. PROBLEM: SHALE SHAKER SCREEN BLINDING

Cause	Treatment
Water-wet solids	Add wetting agent Add primary emulsifier Add VERSA SWA*

*VERSA SWA should be used sparingly and only when other treatments and methods are ineffective.

G. PROBLEM: WATER FLOW

Indicator	Treatment
Decrease in O/W ratio (water intrusion)	Increase mud weight
Decrease in mud weight	Increase mud weight Add primary emulsifier and wetting agent Add lime (conventional system) Add oil to adjust O/W ratio Add salt to adjust brine salinity

H. PROBLEM: CO_2 CONTAMINATION

Indicator	Treatment
P_{OM} decrease	Increase mud weight Add lime
Rheology increase	Add primary emulsifier and wetting agent Add oil for dilution Increase mud weight Add lime

I. PROBLEM: HYDROGEN SULFIDE CONTAMINATION

Indicator	Treatment
P_{OM} decrease	Increase mud weight Add lime Add primary emulsifier and wetting agent Add zinc-base hydrogen sulfide scavenger, SULF-X
Foul odor	Increase mud weight Add lime Add primary emulsifier and wetting agent Add zinc-base hydrogen sulfide scavenger, SULF-X
Mud turns black	Increase mud weight Add lime Add primary emulsifier and wetting agent Add zinc hydrogen sulfide scavenger, SULF-X
Drill pipe turns black	Increase mud weight Add lime Add primary emulsifier and wetting agent Add zinc-base hydrogen sulfide scavenger, SULF-X

J. PROBLEM: LOST CIRCULATION

Cause	Treatment
Overbalanced hydrostatic pressure	Reduce mud weight (if possible) Use LCM pills Set casing
Excessive annular pressure loss	Decrease rheology and gel strengths Decrease circulation rates
Surge pressures	Decrease rheology and gel strengths Stage and circulate tripping in/out of hole Reduce tripping speed Use LCM pills spotted in hole

Calculations

- To provide a stable fluid with good suspension over long periods of time.
- To keep the casing from sticking if there are plans to salvage it at a later date.

BRINE TABLES

% Weight $CaCl_2$	Density (kg/l)	Density (lb/gal)	Cl^- (mg/l)	$CaCl_2$ (lb/bbl)	Water (bbl)	Brine Activity (A_W)
2	1.015	8.46	12,969	7.1	0.995	0.989
4	1.032	8.60	26,385	14.5	0.990	0.980
6	1.049	8.75	40,185	22.0	0.986	0.971
8	1.066	8.89	54,496	29.9	0.981	0.960
10	1.084	9.04	69,190	37.9	0.975	0.948
12	1.101	9.19	84,459	46.3	0.969	0.932
14	1.120	9.34	100,175	54.9	0.963	0.914
16	1.139	9.50	116,403	63.8	0.957	0.892
18	1.158	9.66	133,141	72.9	0.950	0.867
20	1.178	9.82	150,455	82.4	0.942	0.837
22	1.198	9.99	168,343	92.2	0.934	0.804
24	1.218	10.16	186,743	102.3	0.926	0.767
26	1.239	10.33	205,781	112.7	0.917	0.726
28	1.260	10.51	225,395	123.5	0.907	0.683
30	1.282	10.69	245,647	134.6	0.897	0.637
32	1.304	10.87	266,474	146.0	0.886	0.590
34	1.326	11.06	288,004	157.8	0.875	0.541
36	1.349	11.25	310,237	170.0	0.863	0.492
38	1.372	11.44	333,109	182.5	0.851	0.443
40	1.396	11.64	356,683	195.4	0.837	0.395

% volume salt = 100 x (1.0 - bbl water).
Properties based on 20°C and 100% purity.

Table 2: Calcium chloride brine.

The calcium chloride concentration needed for the internal phase is dependent on the activity of the actual formation being drilled. Most muds use 25 to 35% by weight calcium chloride.

% Weight $NaCl_2$	Density (kg/l)	Density (lb/gal)	Cl^- (mg/l)	NaCl (lb/bbl)	Water (bbl)	Brine Activity (A_W)
2	1.013	8.44	12,254	7.1	0.992	0.989
4	1.027	8.56	24,932	14.4	0.986	0.977
6	1.041	8.68	37,914	21.9	0.979	0.964
8	1.056	8.81	51,260	29.6	0.971	0.950
10	1.071	8.93	64,970	37.5	0.964	0.935
12	1.086	9.05	79,044	45.6	0.955	0.919
14	1.101	9.18	93,481	53.9	0.947	0.902
16	1.116	9.31	108,344	62.5	0.938	0.883
18	1.132	9.44	123,570	71.3	0.928	0.862
20	1.148	9.57	139,282	80.4	0.918	0.839
22	1.164	9.71	155,357	89.6	0.908	0.815
24	1.180	9.84	171,858	99.2	0.897	0.788
26	1.197	9.98	188,843	109.0	0.886	0.759

% volume salt = 100 x (1.0 - bbl water).
Properties based on 20°C and 100% purity.

Table 3: Sodium chloride brine.

- To isolate the casing from corrosive formation fluids.
- To provide a non-conductive environment if cathodic protection will be used to protect the casing.

The properties recommended for casing packs are similar to those recommended for packer fluids. Somewhat higher rheologies may be recommended for casing packs than for packer fluids, in order to sweep the annulus. Casing packs will be exposed to formation fluids for the life of the well. To compensate for this, casing packs are often treated with additional emulsifiers and wetting agents. The steps recommended earlier for formulating and testing a packer fluid can be used to formulate casing packs.

Most oil or synthetic systems can be conditioned to meet even the most demanding properties required of casing packs and packer fluids. As with packer muds, the fluid must be stabilized by circulating it through the well, exposing it to heat and shear before final treatments and conditioning as a casing pack fluid.

Salt	Salt Constant (C)
Calcium chloride	1.565
Sodium chloride	1.648
Magnesium chloride	1.343
Potassium chloride	2.103

If an oil- or synthetic-base fluid was used as the packer fluid, a similar fluid will probably be used as the workover fluid. Oil and synthetic fluids may be used in extremely corrosive environments and as perforating fluids to prevent formation damage. Because of their good lubricity and low sticking tendencies, these fluids are especially suited for "wash over" operations where there is a high likelihood of sticking the wash pipe.

The preparation of wells in depleted fields for gas storage is an excellent application for oil muds containing VERSATROL I. If the existing wells' casing is corroded and leaking, it will usually be replaced rather than repaired. The casing strings must be washed over. Oil mud is the fluid of choice for "washing over" and retrieving casing. The oil muds used in these applications will require closer attention and more treating chemicals than a drilling operation. After working over the wells in a gas storage project with oil-base fluids, the fluids are usually used as the casing pack and packer fluids for completing the wells.

If the wells were originally drilled and completed with water-base fluids, the water-base mud and solids behind the casing will be incorporated in the oil mud as they are “drilled” with the wash pipe. The exposed shales will probably slough into the hole and add to the problem. Preparations should be made on each of these wells to deal with large quantities of water-wet solids. The volume of workover fluid required may be substantially greater than estimated based on the original hole diameter. Large quantities of base oil, emulsifiers and wetting agents will be required to treat the water and water-wet solids that will be incorporated into the workover fluid.

NOTE: In the following equations, % $CaCl_2$ and % NaCl stand for weight % unless labeled as % $CaCl_2$ (vol). Liquids like % H_2O and % Oil stand for volume % unless labeled otherwise.

BRINE CONVERSIONS

Density (lb/gal) = SG x 8.34
$CaCl_2$ (ppm) = % $CaCl_2$ x 10,000
Chlorides (ppm) = % $CaCl_2$ x 6,390
NaCl (ppm) = % NaCl x 10,000
Chlorides (ppm) = % NaCl x 6,065

Any salt % by weight calculation:

$$\text{Weight \% salt} = \left(\frac{(\text{Ag x C})}{(\text{Ag x C}) + \%\ H_2O}\right) \text{x } 100$$

Where:
Ag = cm^3 of 0.282 silver nitrate used in chlorides determination/cm^3 mud
C = Salt constant
% H_2O = Volume % water from retort

BRINE ACTIVITY (A_W) CURVE FIT EQUATIONS:

The following equations can be used to determine the water activity (A_W):

CALCIUM CHLORIDE:

$$A_W = 1 + 0.001264834\ (\%\ CaCl_2) - 0.0006366891\ (\%\ CaCl_2)^2 + 5.877758 \text{ x } 10^{-6}\ (\%\ CaCl_2)^3$$

SODIUM CHLORIDE:

$$A_W = 1 - 0.004767582\ (\%\ NaCl) - 0.0001694205\ (\%\ NaCl)^2$$

MAGNESIUM CHLORIDE:

$$A_W = 1 - 0.002444242\ (\%\ MgCl_2) - 0.0004608654\ (\%\ MgCl_2)^2$$

POTASSIUM CHLORIDE:

$$A_W = 1 - 0.003973135\ (\%\ KCl) - 7.47175 \text{ x } 10^{-5}\ (\%\ KCl)^2$$

ADJUSTMENT OF WATER ACTIVITY

The following technique should be used to determine the quantity of calcium chloride required to adjust (decrease) the water activity to a desired value by increasing brine salinity.

Increasing brine salinity:

1. Titrate chlorides and calculate initial salt concentration, weight % $CaCl_2$.
2. Estimate present A_W of the fluid using Table 2: Calcium chloride brine, relating activity to the salt concentration (% by weight) or use the curve-fit equations.
3. Using a retort, determine the water content, volume % water.
4. Calculate the initial concentration of $CaCl_21$ (lb/bbl whole mud).

Initial weight % $CaCl_2$: % $CaCl_2$
Volume % water: % H_2O

$$CaCl_21 \text{ (lb/bbl whole mud)} = \frac{\% CaCl_2 \times \% H_2O \times 3.5}{100 - \% CaCl_2}$$

5. From a measurement or value for shale activity, determine the desired salt concentration, % $CaCl_22$, using the brine table or curve-fit equation. Using the equation listed below, determine the $CaCl_2$ required to reduce the A_W to the desired value.

Desired weight % $CaCl_2$: % $CaCl_22$
% purity $CaCl_2$: % purity

$$CaCl_2 \text{ (lb/bbl whole mud) to add} = \left[\frac{\% CaCl_22}{100 - \% CaCl_22} - \frac{\% CaCl_21}{100 - \% CaCl_21}\right] \times \frac{350 \times \% H_2O}{\% \text{ purity}}$$

Example:

Initial weight % $CaCl_2$:	10
Volume % water:	20
Desired weight % $CaCl_2$:	25
% purity:	78

From 4. Initial $CaCl_21$ (lb/bbl whole mud):	7.78
From 5. $CaCl_22$ (lb/bbl whole mud) to add:	19.9

Occasionally, an increase in the activity (a decrease in the salt content) is desirable. This is most often done when drilling salt, when the salt concentration increases due to evaporation or when overtreatment has occurred. The following procedure can be used to determine the amount of water to add to adjust (increase) the water activity to the desired value.

Decreasing brine salinity

1. Titrate chlorides and calculate initial salt concentration, weight % $CaCl_2$.
2. Estimate present A_W of the fluid using Table 2: Calcium chloride brine, relating activity to the salt concentration (% by weight) or the curve-fit equation.
3. Using a retort, determine the water content, volume % water.
4. Calculate the initial concentration of $CaCl_21$ (lb/bbl whole mud).

Initial weight % $CaCl_2$: % $CaCl_2$
Volume % water: % H_2O

$$CaCl_21\ (\text{lb/bbl whole mud}) = \frac{\%\ CaCl_2 \times \%\ H_2O \times 3.5}{100 - \%\ CaCl_2}$$

5. Using the desired value for fluid activity, determine the desired salt concentration, % $CaCl_22$, using the brine table or curve-fit equation. Using the equation listed below, determine the amount of water required to increase the A_W to the desired value.

Desired weight % $CaCl_2$: % $CaCl_22$

Water to add (bbl/bbl) =

$$\frac{(100 \times CaCl_21) - (\%\ CaCl_22 \times CaCl_21) - (\%\ CaCl_22 \times \%\ H_2O \times 3.5)}{\%\ CaCl_22 \times 350}$$

Example:

Initial weight % $CaCl_2$: 22
Volume % water: 10
Desired weight % $CaCl_22$: 15

From 4. Initial $CaCl_21$ (lb/bbl whole mud): 9.87
From 5. Water to add (bbl/bbl): 0.0598

Oil-to-water ratios (O/W)

The calculation of oil-to-water and synthetic-to-water ratio requires retort values as follows:

$$\text{Oil ratio (O)} = \left(\frac{\%\ oil}{\%\ oil + \%\ H_2O}\right) \times 100$$

Water ratio (W) = 100 – oil ratio

or

$$\text{Water ratio (W)} = \left(\frac{\%\ H_2O}{\%\ H_2O + \%\ oil}\right) \times 100$$

NOTE: Adding the oil ratio and the water ratio always equals 100.

Example:

Volume % oil:	56
Volume % water:	24
Volume % solids:	20

$$\text{Oil ratio} = \left(\frac{56}{56 + 24}\right) \times 100 = 70\%\ \text{oil}$$

$$\text{Water ratio} = \left(\frac{24}{24 + 56}\right) \times 100 = 30\%\ \text{water}$$

Oil:water ratio (O/W) = 70:30 or 70/30

ADJUSTING O/W OR S/W RATIOS

Through simple calculations involving current retort data, a calculated increase or decrease in the oil- or synthetic-to-water ratio may be made. For a weighted mud, changing the oil- or synthetic-to-water ratio reduces mud weight. The added liquid and barite for reweighting will increase the system volume.

INCREASING OIL-TO-WATER RATIO

Oil or synthetic fluid must be added to the mud to raise the oil- or synthetic-to-water ratio. No water will be added to the system when this is done and the actual volume of water does not change.

To calculate the barrels of oil required to increase the O/W ratio:
A. Record the retort volume % oil as % oil.
B. Record the retort volume % water as % H_2O.
C. Record the water ratio of the desired O/W ratio as W_R.
D. Calculate the barrels of oil or synthetic fluid to add:

$$\text{Oil to add (bbl/bbl mud)} = \frac{\%\ H_2O}{W_R} - \frac{(\%\ \text{oil} + \%\ H_2O)}{100}$$

In this equation;

$$\text{New liquid volume (bbl/bbl mud)} = \frac{\%\ H_2O}{W_R}$$

$$\text{Original liquid volume (bbl/bbl mud)} = \frac{(\%\ \text{oil} + \%\ H_2O)}{100}$$

New liquid volume = Original liquid volume + oil to add

Example:

Volume % oil (retort):	51%
Volume % water (retort):	9%
Original O/W ratio:	85/15
Desired O/W ratio:	90/10 ($O_R = 90$, $W_R = 10$)

To increase the O/W ratio from 85/15 to 90/10, calculate how much oil must be added:

$$\text{Oil to add (bbl/bbl mud)} = \frac{\%\ H_2O}{W_R} - \frac{(\%\ \text{oil} + \%\ H_2O)}{100}$$

$$\text{Oil to add (bbl/bbl mud)} = \frac{9}{10} - \frac{(51 + 9)}{100} = 0.9 - 0.6 = 0.30 \text{ bbl oil per bbl of mud}$$

Therefore, to increase the O/W ratio from 85/15 to 90/10, 0.30 bbl of oil must be added for every barrel of mud.

DECREASING OIL-TO-WATER RATIO

Either water or brine must be added to the mud to lower the oil- or synthetic-to-water ratio. No oil or synthetic fluid will be added to the system and the oil or synthetic volume will not change.

DECREASING O/W RATIO USING WATER

To calculate the barrels of water (not brine) required to decrease the O/W ratio:
A. Record the retort volume % oil as % oil.
B. Record the retort volume % water as % H_2O.

C. Record the water ratio of the desired O/W ratio as O_R.
D. Calculate the barrels of water to add:

$$\text{Water to add (bbl/bbl mud)} = \frac{\%\ \text{oil}}{O_R} - \frac{(\%\ \text{oil} + \%\ H_2O)}{100}$$

DECREASING O/W RATIO USING BRINE

To calculate the barrels of brine (not water) required to decrease the O/W ratio, the volume of salt in the brine must be compensated for because it is a dissolved solid:

A. Record the retort volume % oil as % oil.
B. Record the retort volume % water as % H_2O.

$$\frac{\left[\text{MWt x 100}\right] - \left[\frac{SG_{WTMATL}}{0.12}\ \text{x \% Cor. Solids}\right] - \left[\frac{SG_{OIL}}{0.12}\ \text{x \% oil}\right] - \left[\text{Brine wt x (\% } H_2O + \%\ CaCl_2\ \text{(vol))}\right]}{(8.34\ \text{x}\ SG_{WTMATL}) - 21.67}$$

C. Record the water ratio of the desired O/W ratio as O_R.
D. Determine the brine volume % water (not decimal) % H_2O (brine). This is determined by taking the fractional number from the column listed as "Water (bbl)" in Tables 2 or 3 and multiplying by 100.
E. Calculate the volume of brine to add:

$$\text{Brine (bbl/bbl mud)} = \frac{100\ \text{x \% oil}}{\phantom{100\ \text{x \% oil}}} - (\%\ \text{oil} + \%\ H_2O)$$

Brine Salinity

$$\%\ H_2O\ \text{(brine) x}\ O_R \qquad \overline{\%\ H_2O\ \text{(brine)}}$$

NOTE: Raising or lowering the O/W ratio of a mud will change the mud density. Reweighting will not change the O/W ratio. Also note that in each of the above calculations, the values O_R and W_R must satisfy the following equation: $O_R + W_R = 100$.

SOLIDS ANALYSIS

Nomenclature:

MWt = Mud weight (lb/gal)
O_R = Oil ratio
W_R = Water ratio
Brine wt = Brine weight (lb/gal)
Ag = ml of $AgNO_3$ (0.282N) per cm^3 mud
% H_2O = Retort % H_2O
% oil = Retort % oil
% Cor. Solids = % Corrected Solids
% LGS = % Low-Gravity Solids (drill solids + VG-69)
% HGS = % High-Gravity Solids (weight material)
% $CaCl_2$ = % by weight calcium chloride
SG_{WTMATL} = Specific Gravity weight material
SG_{OIL} = Specific Gravity oil

$$1)\ O_R = \left(\frac{\%\ oil}{\%\ oil + \%\ H_2O}\right) \text{ x } 100$$

$$2)\ W_R = 100 - O_R$$

$$3)\ \%\ CaCl_2\ (wt) = \left(\frac{Ag \text{ x } 1.565}{(Ag \text{ x } 1.565) + \%\ H_2O}\right) \text{ x } 100$$

$$4)\ CaCl_2\ (lb/bbl\ whole\ mud) = Ag \text{ x } 5.4775$$

$$5)\ Brine\ wt\ (lb/gal) = 8.34 \text{ x } \{1 + [8.09 \text{ x } 10^{-3} \text{ x } (\%\ CaCl_2)] + [4.095 \text{ x } 10^{-5} \text{ x } (\%\ CaCl_2)^2] + \ldots [1.422 \text{ x } 10^{-7} \text{ x } (\%\ CaCl_2)^3]\}$$

$$6)\ SG_{BR} = Brine\ wt \div 8.34$$

$$7)\ \%\ CaCl_2\ by\ volume = \left[\left(\frac{834}{(SG_{BR} \text{ x } 8.34)(100 - \%\ CaCl_2)}\right) - 1\right] \text{ x } \%\ H_2O$$

$$8)\ \%\ Cor.\ Solids = 100 - \%\ H_2O - \%\ oil - \%\ CaCl_2\ (vol)$$

9) % LGS =

10) % HGS = % Cor. Solids – % LGS

11) LGS (lb/bbl) = 9.1 x % LGS

12) HGS (lb/bbl) = % HGS x SG_{WTMATL} x 3.5

NOTE: Equations 6 through 12 also apply to fluids containing sodium chloride; substitute the NaCl values for the $CaCl_2$ values.

NOTE: The API RP 13B-2 uses different calculations for some of the following situations. Refer to section 7 of the latest RP 13B-2 for an alternate calculation.

SINGLE-SALT SYSTEMS

If the brine phase of the oil mud contains only one salt, either $CaCl_2$ or NaCl, then the following equations will apply to determine percent (%) by weight, lb/bbl, specific gravity of the brine, mg/l, and ppm of the water phase of the respective salt. Also included are the total chlorides in the water phase. For salt systems, percent (%) by weight is the most common and most useful value for the conversion to various other concentration equivalents.

Brine salinity calculations require the following:

% H_2O = Retort % H_2O
Ag = ml of 0.282N $AgNO_3$ per cm^3 mud

From this data, we can calculate other concentration values using the following equations:

A) Calcium chloride
(Assuming that all the salt content is composed of calcium chloride.)

$$1)\ \%\ CaCl_2\ (wt) = \frac{Ag \text{ x } 1.565}{} \text{ x } 100$$

$$\left((\text{Ag x } 1.565) + \%\ H_20\right)$$

2) $CaCl_2$ (lb/bbl whole mud) = Ag x 5.4775

3) SG_{BR} = 1.000318525 + (8.0899459 x 10^{-3} x % $CaCl_2$) + …
(4.0944872 x 10^{-5} x [% $CaCl_2]^2$) + (1.4220309 x 10^{-7} x [% $CaCl_2]^3$)

4) Brine wt (lb/gal) = SG_{BR} x 8.34

5) $CaCl_2$ (mg/l) = 10,000 x % $CaCl_2$ x SG_{BR}

6) $CaCl_2$ (ppm) = % $CaCl_2$ x 10,000

7) Chlorides (mg/l) = % $CaCl_2$ x SG_{BR} x 6,393

Example:

% H_2O = 10
Ag = 2 ml of 0.282 N $AgNO_3$ per cm^3 mud

% $CaCl_2$ (wt) = 23.84
$CaCl_2$ (lb/bbl whole mud) = 11.0
SG $CaCl_2$ brine = 1.218
Brine weight (lb/gal) = 10.16
$CaCl_2$ (mg/l) = 290,440
$CaCl_2$ (ppm) = 238,385
Chlorides (mg/l) = 185,679

B) Sodium chloride
(Assuming that all the salt content is composed of sodium chloride.)

1) % NaCl (wt) = $\left(\dfrac{\text{Ag x } 1.649}{(\text{Ag x } 1.649) + \%\ H_20}\right)$ x 100

2) NaCl (lb/bbl whole mud) = Ag x 5.775

3) SG_{NaCl} = 1.000002116 + (7.1014067 x 10^{-3} x % NaCl) + …
(1.1917074 x 10^{-5} x [% $NaCl]^2$) + (3.7654743 x 10^{-7} x [% $NaCl]^3$)

4) Brine wt (lb/gal) = SG_{NaCl} x 8.34

5) NaCl (mg/l) = 10,000 x % NaCl x SG_{NaCl}

6) NaCl (ppm) = % NaCl x 10,000

7) Chlorides (mg/l) = % NaCl x SG_{NaCl} x 6,065

Example:

% H_2O = 15
Ag = 1.2 ml of 0.282 N $AgNO_3$ per cm^3 mud

% NaCl (wt) = 11.65
NaCl (lb/bbl whole mud) = 6.93
SG NaCl brine = 1.085
Brine weight (lb/gal) = 9.05
NaCl (mg/l) = 126,523
NaCl (ppm) = 116,608
Chlorides (mg/l) = 76,736

TWO-SALT (BINARY) SYSTEMS ($CaCl_2$/NaCl)

To determine the exact amounts of each salt present in an emulsion system containing both calcium chloride and sodium chloride, the calcium content must be titrated and a special calculation must be used as described below. The testing procedure for the whole mud calcium on an emulsion mud is described in the oil-base section of the Testing chapter.

Calcium content calculation

The calcium content can be determined from a calcium titration on the whole mud. It includes calcium from both lime and calcium chloride:

$$Ca_{mud} = \frac{4{,}000 \text{ (ml of 0.1m EDTA (Strong Versenate or equivalent))}}{\text{ml mud titrated}}$$

NOTE: Calcium determination utilizing 8N NaOH and Calcon Indicator.

BINARY SALT ($CaCl_2$/NaCl) CALCULATIONS

These calculations take into consideration the alkalinity effects of lime and determine how much, if any, sodium chloride is present. In the following procedure and equations, two possible situations can occur:

Situation 1: The fluid contains no measurable NaCl.
Situation 2: NaCl is present in significant quantities.

For Situation 1 use the single-salt calculations described previously for calcium chloride. For Situation 2 use the binary (two-salt) calculation that follows:

$$\text{“A” \% } CaCl_2 \text{ (wt) (using } Ca_{MUD} \text{ and } P_{OM}) = \left(\frac{[Ca_{MUD} - (0.5 \text{ x } P_{OM})] \text{ x } 11.1}{[(Ca_{MUD} - (0.5 \text{ x } P_{OM})) \text{ x } 11.1] + (10 \text{ x \% } H_2O)}\right) \text{ x } 100$$

$$\text{“B” \% } CaCl_2 \text{ (wt) (using } Cl_{MUD}) = \left(\frac{\text{Ag x } 1.565}{(\text{Ag x } 1.565) + \text{\% } H_2 0}\right) \text{x } 100$$

Situation 1: If A is greater than B, then no sodium chloride is present. Use the calculations given above for single-salt calcium chloride fluids.

Situation 2: If A is less than B, sodium chloride is present in significant amounts. Use the following calculations:

1) $CaCl_2$ (lb/bbl) = (Ca_{MUD} x 3.885) – (1.95 x P_{OM})

2) $\text{\% } CaCl_2 \text{ (wt)} = \dfrac{CaCl_2 \text{ (lb/bbl) x } 100}{[CaCl_2 \text{ (lb/bbl)} + (\text{\% } H_2O \text{ x } 3.5)]}$

3) $SG_{CACL2} = 1.000318525 + (8.0899459 \text{ x } 10^{-3} \text{ x \% } CaCl_2) + (4.0944872 \text{ x } 10^{-5} \text{ x } [\text{\% } CaCl_2]^2) + (1.4220309 \text{ x } 10^{-7} \text{ x } [\text{\% } CaCl_2]^3)$

4) $CaCl_2$ (mg/l) = 10,000 x % $CaCl_2$ x SG_{CACL2}

5) $CaCl_2$ (ppm) = % $CaCl_2$ x 10,000

6) Cl^- from $CaCl_2$ (mg/l) = % $CaCl_2$ x SG $CaCl_2$ x 6,393

7) NaCl (lb/bbl) = (5.775 x Cl_{MUD}) – (1.054 x $CaCl_2$ (lb/bbl))

8) $\text{\% NaCl (wt)} = \dfrac{\text{NaCl (lb/bbl) x } 100}{[\text{NaCl (lb/bbl)} + (\text{\% } H_2O \text{ x } 3.5)]}$