Drilling Muds

According to the American Petroleum Institute (API), a drilling fluid is defined as a circulating fluid, used in rotary drilling to perform any or all of the various functions required in drilling operations.

Drilling fluids are mixtures of natural and synthetic chemical compounds used to cool and lubricate the drill bit, clean the hole bottom, carry cuttings to the surface, control formation pressures, and improve the function of the drill string and tools in the hole. They are divided into two general types: water-based drilling muds (WBMs) and oil-based drilling muds (OBMs). The type of fluid base that is used depends on drilling and formation needs, as well as the requirements for disposing of the fluid after it is no longer needed. Drilling muds are a special class of drilling fluids used to drill most deep wells. The term *mud* is used because of the thick consistency of the formulation.

Drilling fluids serve several fundamental functions (Brazzel, 2009; Melbouci and Sau, 2008):

- Control of downhole formation pressures,
- Overcoming the fluid pressure of the formation,
- Avoiding damage to the producing formation,
- Removal of cuttings generated by the drill bit from the borehole, and
- Cooling and lubricating the drill bit.

In order to perform their fundamental functions, drilling fluids should possess several desirable characteristics, which greatly enhance the efficiency of the drilling operation.

These include desired rheological properties (plastic viscosity, yield value, low-end rheology, and gel strengths), fluid loss prevention, stability under various temperature and pressure operating conditions, stability against contaminating fluids, such as salt water, calcium sulfate, cement, and potassium contaminated fluids (Melbouci and Sau, 2008).

The drilling fluid should also have penetration enhancement characteristics that wet the drill string and keep the cutting surfaces of the drill bit clean (whether it is a roller cone or other configuration).

Wetting ability is at least in part a function of the surface tension of the fluid. The fluid should also have a high degree of lubricity and to minimize friction between the drill string and the wall of the borehole to minimize of differential sticking. In this situation, the hydrostatic pressure of the drilling fluid column must be sufficiently higher than the formation pressure so that the drill string is forced against the wall of the borehole and stuck.

It should also prevent the solids of the formation, primarily shales and clays, from swelling, so reducing the incidence of drill sticking, undergauge holes etc.

CLASSIFICATION OF MUDS

The classification of drilling muds is based on their fluid phase alkalinity, dispersion, and the type of chemicals used in their formulation. The classification according to (Lyons, 1996) is reproduced in Table 1.1.

Drilling muds are usually classified as either WBMs or OBMs, depending upon the continuous phase of the mud. However, WBMs may contain oil and OBMs may contain water (Guichard et al., 2008).

OBMs generally use hydrocarbon oil as the main liquid component, with other materials such as clays or colloidal asphalts being added to provide the desired viscosity together with emulsifiers, polymers, and other additives including weighting agents. Water may also be present, but in an amount not usually greater than 50% by volume of the entire composition. If more than

TABLE 1.1 Classification of Drilling Muds

Class	Description
Fresh water muds[d]	pH from 7–9.5, include spud muds, bentonite-containing muds, phosphate-containing muds, organic thinned muds (red muds, lignite muds, lignosulfonate muds), organic colloid muds
Inhibited muds[d]	Water-based drilling muds that repress hydration of clays (lime muds, gypsum muds, sea water muds, saturated salt water muds)
Low-solids muds[n]	Contain less than 3–6% of solids. Most contain an organic polymer
Emulsions	Oil in water and water in oil (reversed phase, with more than 5% water)
OBMs	Contain less than 5% water; mixture of diesel fuel and asphalt

d) Dispersed systems
n) Nondispersed systems

about 5% of water is present, the mud is often referred to as an invert emulsion, i.e., a water-in-oil emulsion.

WBMs conventionally contain viscosifiers, fluid loss control agents, weighting agents, lubricants, emulsifiers, corrosion inhibitors, salts, and pH control agents. Water makes up the continuous phase of the mud, and is usually present as at least 50 volume percent of the entire composition. Oil is also usually present in small amounts, but will typically not exceed the amount of the water, so that the mud will retain its character as a water-continuous-phase material.

Potassium muds are the most widely accepted water mud system for drilling water sensitive shales. K^+ ions attach to clay surfaces and lend stability to the shale that is exposed to drilling fluids by the bit. The ions also help to hold the cuttings together, minimizing its dispersion into finer particles. Potassium chloride, KCl is the most widely used source of potassium, with others being potassium acetate, potassium carbonate, potassium lignite, potassium hydroxide, and potassium salt of partially hydrolyzed polyacrylamide (PHPA).

For rheological control, different types of polymers are used, such as xanthan gum and PHPA. For fluid loss control, mixtures of starch and polyanionic cellulose (PAC) are often used. Carboxymethyl starch, hydroxypropyl starch, carboxymethyl cellulose (CMC), and sodium polyacrylate are also used. PHPA is widely used for shale encapsulation.

Salt water muds contain varying amounts of dissolved sodium chloride (NaCl) as a major component. Undissolved salt may also be present in saturated salt muds to increase density or to act as a bridging agent over permeable zones. Starch and its derivatives for fluid loss control, and xanthan gums for hole cleaning are among the few additives that are effective for salt water muds.

Sea water mud is a WBM designed for offshore drilling whose make-up water is taken from the ocean. Sea water has relatively low salinity, containing about 3–4% of NaCl, but has a high hardness because of the presence of Mg^{+2} and Ca^{+2} ions. This hardness is removed from sea water by adding NaOH (sodium hydroxide), which precipitates Mg^{+2} as $Mg(OH)_2$ (magnesium hydroxide) and by adding Na_2CO_3 (sodium carbonate), which removes Ca^{+2} as $CaCO_3$ (calcium carbonate). The additives are the same as those used in fresh water muds (Guichard et al., 2008), namely

- Bentonite clay,
- Lignosulfonate,
- Lignite,
- CMC, or
- PAC, and
- Caustic soda.

Xanthan gum may be used in place of bentonite. Silicate-mud is a type of shale-inhibitive water mud that contains sodium or potassium silicate as the inhibitive component. If this material is used, then a high pH is a necessary characteristic of silicate muds in order to control the amount and type of polysilicates

that are formed. This is achieved by the addition of NaOH (or KOH) and the appropriate silicate solution. Silicate anions and colloidal silica gel combine to stabilize the wellbore by sealing microfractures, forming a silica layer on shales and possibly acting as an osmotic membrane, which can produce in-gauge holes through troublesome shale sections that otherwise might require an oil mud.

Lime mud is a type of WBM that is saturated with lime $(Ca(OH)_2)$, and has excess, undissolved lime solids maintained in reserve. Fluid loss additives include starch, hydroxypropyl starch, CMC, or PAC (Guichard et al., 2008).

Dispersed Noninhibited Systems

Drilling fluids used in the upper hole sections are referred to as *dispersed noninhibited systems*. They are formulated from fresh water and may contain bentonite. The classification of bentonite-based muds is shown in Table 1.2. The flow properties are controlled by a flocculant or thinner, and the fluid loss is controlled with bentonite and CMC.

Phosphate-treated Muds

Phosphates are only effective in small concentrations, and the mud temperature must be less than 55°C. The salt contamination must be less than 500 ppm sodium chloride. The concentration of calcium ions should be kept as low as possible. The pH should be between 8 and 9.5. Some phosphates may decrease the pH, so more NaOH must be added.

Lignite Muds

Lignite muds are temperature resistant up to 230°C. Lignite can control viscosity, gel strength, and fluid loss. The total hardness must be lower than 20 ppm.

TABLE 1.2 Classification of Bentonite Fluid Systems

Solid–solid Interactions	Inhibition Level	Drilling Fluid Type
Dispersed	Noninhibited	Fresh water clay NaCl < 1%, $CaCl_2$, < 120 ppm
Dispersed	Inhibited	Saline fluids, Na^+, Ca^{2+} salt, saturated salt, gypsum, lime)
Nondispersed	Noninhibited	Fresh water low-solids muds
Nondispersed	Inhibited	Salt and polymer fluids

Quebracho Muds

Quebracho is a natural product extracted from the heartwood of the Schinopsis trees that grow in Argentina and Paraguay. It is a well-characterized polyphenolic, readily extracted from the wood by treatment with hot water, and is widely used as a tanning agent. It is also used as a mineral dressing, as a dispersant in drilling muds, and in wood glues. Quebracho is commercially available as a crude hot water extract, either in lump, ground, or spray-dried form, or as a bisulfite-treated, spray-dried product that is completely soluble in cold water. It is also available in a bleached form, which can be used in applications where the dark color of unbleached quebracho is undesirable (Shuey and Custer, 1995).

Quebracho-treated fresh water muds were originally used at shallow depths. It is also referred to as *red mud* because of the deep red color. Quebracho acts as a thinner. Polyphosphates are also added when Quebracho is used. Quebracho is active at low concentrations and consists of tannates.

Lignosulfonate Muds

Lignosulfonate fresh water muds contain ferrochrome lignosulfonate for viscosity and gel strength control. These muds are resistant to most types of drilling contamination because of the thinning efficiency of the lignosulfonate in the presence of large amounts of salt and at extreme hardnesses.

Lime Muds

Lime muds contain caustic soda, an organic thinner, hydrated lime, and a colloid for filtrate loss. From this a pH of 11.8 can result, with calcium ions at a concentration of 3–20 ppm in the filtrate. Lime muds exhibit low viscosity, low gel strength, and good suspension of weighting agents. They can carry a larger concentration of clay solids at lower viscosities than other types of mud. At high temperatures, lime muds present a danger of gelation.

Sea Water Muds

The average composition of sea water is shown in Table 1.3. Most of the hardness in sea water is caused by magnesium. Sea water muds have sodium chloride concentrations above 10,000 ppm. They also contain bentonite, thinner (lignosulfonate or lignosulfonate with lignite), and an organic filtration control agent.

Nondispersed Noninhibited Systems

In nondispersed systems no special agents are added to deflocculate the solids in the fluid. The main advantages of these systems are the higher viscosities and the higher yield point-to-plastics viscosity ratio. These altered flow properties

TABLE 1.3 Composition of Sea Water

Component	Concentration/[ppm]
Sodium	10,500
Potassium	400
Magnesium	300
Calcium	400
Chloride	19,000
Sulfate	3,000

provide a better cleaning of the borehole, allow a lower annular circulating rate, and minimize the washout of the borehole.

Low-solids Fresh Water Muds

Clear fresh water is the best drilling fluid in terms of penetration rate. Therefore, it is desirable to achieve a maximal drilling rate using a minimal amount of solid additives. Originally, low-solids mud formulations were used in hard formations, but they now also tend to be used in other formations. Several types of flocculants are used to promote the settling of drilled solids by flocculation.

Variable Density Fluids

Variable density fluids are those that have a density which varies as a function of the pressure in the subterranean formation. Such a fluid comprises a base fluid and a proportion of elastic particles.

These elastic particles allow the density of the variable density fluid to vary as a function of pressure. For instance, as the elastic particles encounter higher downhole pressures, they become compressed, thereby decreasing the volume and in turn increasing the density of the fluid that contains them. When the elastic particles are fully compressed, the density increases considerably.

The increase in volume of the elastic particles in turn reduces the overall density of the variable density drilling fluid. The resulting change in density may be sufficient to permit the return of the variable density fluid through the riser to the surface without the need for any additional pumps or subsurface additives (Ravi et al., 2009).

The elastic particles are usually either a copolymer of styrene and divinylbenzene, a copolymer of styrene and acrylonitrile, or a terpolymer of styrene, vinylidene chloride, and acrylonitrile (Ravi et al., 2009).

Gas-based Muds

Although natural gas (methane) exhaust or other combustion gases can be used, air is the most common gas to be used in such drilling fluids. It is used to produce so-called foam muds, in which air bubbles are surrounded by a film of water containing a foam-stabilizing substance or film-strengthening material, such as an organic polymer or bentonite.

This type of mud is not recirculated and is often used for reduced-pressure drilling to improve the hole stability in caving formations. However, this type of mud has some limitations, since the drilling water produces wet formations, and it has a limited salt tolerance.

Drill-in Fluids

After drilling a well to the total depth, it is a normal practice to replace the drilling mud with a completion fluid. This fluid is a clean, solids-free, or acid soluble, non-damaging formulation, intended to minimize reductions in permeability of the producing zone. Prior to producing from the formation, it is usually necessary to clean up what is left by the original mud and the completion fluid, by breaking and degrading the filter cake with an oxidizer, enzyme, or an acid solution.

Nowadays, many wells exploit the pay-zone formations for long distances horizontally. It is no longer practical in these wells to drill the pay-zone with conventional, solids-laden muds, as the extended clean-up process afterwards is much more difficult. Consequently, the current generation of drill-in fluids was developed.

Drill-in fluids are completion fluids, but they also act as drilling muds. As the pay-zone is penetrated horizontally, these fluids must provide the multifunctional requirements of drilling fluids in addition to the non-damaging attributes of completion fluids. In practice, the normal drilling mud is replaced with a drill-in fluid just before the pay-zone is penetrated, and used until the end of the operation.

MUD COMPOSITIONS

Commercial products are listed in the literature. The additional components include bactericides, corrosion inhibitors, defoamers, emulsifiers, fluid loss and viscosity control agents, and shale control additives (Anonymous, 1991a,b,c, 1992, 1996).

Inhibitive Water-based Muds

Minimizing the environmental impact of the drilling process is a highly important part of drilling operations, in order to comply with environmental regulations which have become stricter throughout the world. In fact, this is a

mandatory requirement for the North Sea sector. The drilling fluids industry has made significant progress in developing new fluids and ancillary additives to fulfill the increasing technical demands for drilling oil wells. Additives now have very little or no adverse effects on the environment or on drilling economics.

New drilling fluid technologies have been developed to allow the continuation of oil-based performance with regard to formation damage, lubricity, and wellbore stability aspects and thus penetration rates. These aspects were greatly improved by incorporating polyols or silicates as shale inhibitors in the fluid systems.

Polyol-based fluids contain a glycol or glycerol as a shale inhibitor, commonly used in conjunction with conventional anionic and cationic fluids to provide additional inhibition of swelling and dispersing of shales. They also provide some lubrication properties.

Sodium or potassium silicates are known to provide levels of shale inhibition comparable to that of OBMs. This type of fluid is characterized by a high pH (>12), for optimum stability of the mud system. The inhibition properties of such fluids are due to the precipitation or gelation of silicates that occurs on contact with divalent ions and lower pH in the formulation, providing an effective water barrier that prevents hydration and dispersion of the shales.

Water-based Muds

These muds have water as the continuous phase, which may contain several dissolved substances such as alkalies, salts and surfactants, organic polymers in colloidal state, droplets of emulsified oil, and various insoluble substances, such as barite, clay, and cuttings in suspension.

The mud composition that is selected for use often depends on the dissolved substances present in the most economically available make-up water, or on the soluble or dispersive materials in the formations to be drilled. Several mud types or systems are recognized and described in the literature such as:

- Spud muds,
- Dispersed/deflocculated muds,
- Lime muds,
- Gypsum muds,
- Salt water muds,
- Nondispersed polymer muds,
- Inhibitive potassium muds,
- Cationic muds, and
- Mixed metal hydroxide muds.

Despite their environmental acceptability, conventional WBMs exhibit major deficiencies relative to OBMs/pseudo oil-based drilling muds (POBMs)

TABLE 1.4 Water-based Drilling Muds

Compound	References
Glycol-based	Lee et al. (1997)
Alkali silicates	Mullen and Gabrysch (2001), Urquhart (1997)
Polyacrylamide, carboxymethyl cellulose	Kotelnikov et al. (1996)
Carboxymethyl cellulose, zinc oxide	Gajdarov and Tankibaev (1996)
Acrylamide copolymer, polypropylene glycol (PPG) (water-based mud)	Patel and Muller (1996)

because of their relatively poor shale inhibition, lubricity, and thermal stability characteristics. To overcome these deficiencies, specific additives may be added to the WBM compositions to bring their properties close to that of OBMs/POBMs while minimizing their environmental impact.

Components of WBMs are shown in Table 1.4. Various methods for the modification of lignosulfonates have been described in the literature, for example, condensation with formaldehyde (Martyanova et al., 1997) or modification with iron salts (Ibragimov et al., 1998). It has been found that chromium-modified lignosulfonates, as well as mixed metal lignosulfonates of chromium and iron, are highly effective as dispersants. They are therefore useful for controlling the viscosity of drilling fluids and reducing their yield point and gel strength. Because chromium is potentially toxic, its release into the natural environment is continuously being reviewed by various government agencies around the world.

Therefore, less toxic substitutes are desirable. These can be prepared by combining tin or cerium sulfate with an aqueous solution of calcium lignosulfonate, thereby producing a solution of tin or cerium sulfonate and a calcium sulfate precipitate (Patel, 1994b).

Compositions with Improved Thermal Stability

To avoid the problems associated with viscosity reduction in polymer-based aqueous fluids, formates, such as potassium formate and sodium formate, are commonly added to enhance their thermal stability, but this is very expensive, and thermal stabilities of polymer-based aqueous fluids can be improved by other means (Maresh, 2009).

The stability of a wellbore treatment fluid may be maintained up to temperatures of 135–160°C (275–325°F) by introducing various polysaccharides into the fluid. The apparent viscosities of some drilling fluids containing xanthan gum and polyacrylamide (PAM) before and after rolling at 120°C are shown in Table 1.5.

TABLE 1.5 Apparent Viscosity Before and After Rolling (Maresh, 2009)

Composition	Before $\eta/$[cP]	After $\eta/$[cP]
Brine/XC	13	3
Brin/PA	8.5	6
Brine/Filtercheck	4	4
Brine/FLC/XC	16	10.5
Brine/FLC/PA	14.6	9
Brine/XC/CLAYSEAL	12.5	3
XC/PA	30	28.5
XC/PA/FLC	38.5	16.5
XC/PA/FLC/CLAYSEAL	34	28
XC/PA/FLC/CLAYSEAL/Barite	38.5	38.5
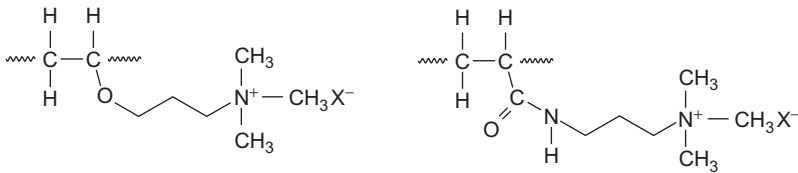
FIGURE 1.1 Quaternized etherified polyvinyl alcohol and quaternized polyacrylamide (Patel et al., 2009).

Shale Encapsulator

A shale encapsulator is added to a WBM in order to reduce the swelling of the subterranean formation in the presence of water. It must be at least partially soluble in the aqueous continuous phase in order to be effective.

A conventional encapsulator is a quaternary PAM, preferably a quaternized polyvinyl alcohol. Useful anions include halogen, sulfate, nitrate, and formate (Patel et al., 2009).

By varying the molecular weight and the degree of amination, a wide variety of products can be produced. It is possible to create shale encapsulators for use in low salinity conditions, including fresh water (Patel et al., 2009). The repeating units of quaternized, etherified polyvinyl alcohol and quaternized PAM are shown in Figure 1.1.

Membrane Formation

In order to increase wellbore stability, formulations for water-based drilling fluids can be provided that form a semi-permeable osmotic membrane over a specific shale formation (Schlemmer, 2007). This membrane allows the comparatively free movement of water through the shale, but significantly restricts the movement of ions across the membrane and thus into the shale.

Membrane formation involves the application of two reactants to form a relatively insoluble Schiff base in situ, which deposits the shale as a polymer film. This Schiff base coats the clay surfaces as a polymer membrane.

The first reactant is a soluble monomer, oligomer, or polymer with ketone, aldehyde, aldol functionalities, or precursors to those. Examples are carbohydrates, such as dextrin and linear or branched starch. The second reactant is a primary amine. These compounds react via a condensation reaction to form an insoluble crosslinked polymer. The formation of a Schiff base is shown in Figure 1.2.

Figure 1.2 shows the reaction of a dextrine with a diamine, but other primary amines and polyamines will of course react in the same way. Long chain
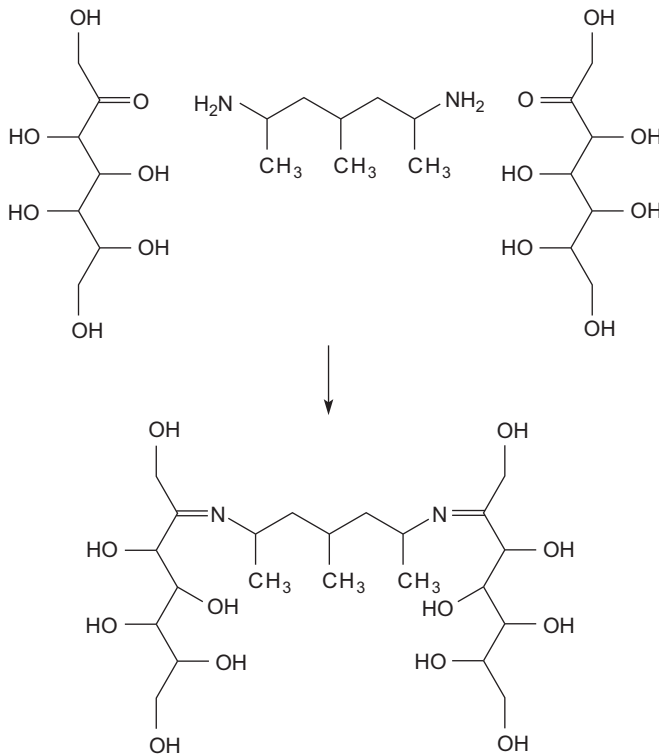

FIGURE 1.2   Formation of a Schiff base (Schlemmer, 2007).

amines, diamines, or polyamines with a relatively low amine ratio may require pH adjustment, using materials such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, or calcium hydroxide (Schlemmer, 2007). The Schiff base formed in this way must be essentially insoluble in the carrier brine in order to deposit a sealing membrane on the shale during the drilling of a well.

By carefully selecting the primary polymer and the crosslinking amine, their relative concentrations, and the pH, the required degree of crosslinking, polymerization, and precipitation of components occurs, effectively forming an osmotically effective membrane on or within the face of the exposed rock.

Oil-based Drilling Muds

These materials have oil as their continuous phase, usually diesel oil, mineral oil or low toxicity mineral oil. Because some water will always be present, the OBM must contain water-emulsifying agents. Various thickening and suspending agents as well as barite are added. The emulsified water may contain alkalies and salts. If water is purposely added (for economical reasons), the OBM is called an invert emulsion mud.

Due to the character of their continuous phase, OBMs provide unequaled performance attributes with respect to the rate of penetration, shale inhibition, wellbore stability, high lubricity, high thermal stability, and high salt tolerance. However, they are subjected to strict environmental regulation regarding their discharge and recycling.

OBMs are now being replaced by synthetic muds. Diesel oil is harmful to the environment, particularly the marine environment in offshore applications. The use of palm oil derivatives could be considered as a harmless alternative (Yassin and Kamis, 1990), or hydrated castor oil can be used as a viscosity promoter instead of organophilic quaternized clays (Mueller et al., 1991).

An OBM can be made more viscous with maleated ethylene-propylene elastomers (Jones and Acker, 1999). The elastomers are ethylene-propylene copolymers or ethylene-propylene-diene terpolymers. These compounds are far more effective oil mud viscosifiers than the organophilic clays orginally used. However, specific organophilic clays can provide a drilling fluid composition that is less sensitive to high temperatures (Dino and Thompson, 2001).

Poly-α-olefins (PAOs) are biodegradable and non-toxic to marine organisms. They also meet viscosity and pour point specifications for OBM formulations (Ashjian et al., 1995). The hydrogenated dimer of 1-decene (Mercer and Nesbit, 1992) can be used instead of conventional organic fluids, as can n-1-octene (Lin, 1996).

Polyethercyclicpolyols

Polyethercyclicpolyols possess molecular properties and characteristics that permit the preparation of enhanced drilling fluids, which inhibit the formation of

gas hydrates, prevent shale dispersion, and reduce the swelling of the formation to enhance wellbore stability, reduce fluid loss, and reduce filter cake thickness.

Drilling muds that incorporate these compounds are substitutes for OBMs in many applications (Blytas and Frank, 1995; Blytas et al., 1992; Blytas et al., 1992; Zuzich and Blytas, 1994; Zuzich et al., 1995). Polyethercyclicpolyols are prepared by thermally condensing a polyol, for example glycerol, to oligomers and cyclic ethers.

Emulsifier for Deep Drilling

Two major problems are encountered when using OBMs for drilling very deep wells (Dalmazzone, 2007). The first is a problem with the stability of the emulsions at elevated temperatures. The emulsion must be stable up to temperatures of 200°C. If the emulsion coalesces, the fluid loses its rheological properties.

The second problem is their environmental impact. The emulsification agents must not only be effective, but also as non-toxic as possible.

Fatty acid amides consisting of *N*-alkylated polyether chains are used as emulsifiers. For those the term 'polyalkoxylated superamides' has been coined (Le Helloco et al., 2004). As a cosurfactant, tall oil fatty acids or their salts can be used.

Biodegradable Composition

Some oil-based drilling fluids are biodegradable. The main oil phase component of these materials is a mixture of methyl esters from biodegradable fatty acids. A typical formulation of a biodegradable drilling fluid is shown in Table 1.6.

Electric Conductive Nonaqueous Mud

A wellbore fluid has been developed that has a nonaqueous continuous liquid phase and exhibits an electrical conductivity that is a factor of 10^4 to 10^7 greater than a conventional invert emulsion. 0.2–10% by volume of carbon black particles and emulsifying surfactants are used as additives. Information from electrical logging tools, including measurements while drilling, can be obtained (Sawdon et al., 2000).

Water Removal

Water can be removed from OBMs by the action of magnesium sulfate (Smith and Jeanson, 2001).

Synthetic Muds

Synthetic muds are expensive. Two factors influence the direct cost, namely the costs per barrel and mud losses. Synthetic muds are the technical equivalent of OBMs when drilling intermediate hole sections. They are technically superior to all water-based systems when drilling reactive shales in directional wells.

TABLE 1.6 Biodegradable Drilling Fluid (Goncalves et al., 2007)

Compound	Amount/[%]			Function
Soybean methylate	55	to	70	Oil component
D-Limonene	1	to	5	Pour point depressant
2,6-Di-*tert*-butyl-*p*-cresol	0.1	to	0.5	Antioxidant
Hydrogenated castor oil	0.3	to	1	Oil component
Fatty acid salts	3	to	6	Puffer
Magnesium oxide	1	to	3	In situ soap former
NaCl Brine	26	to	30	Aqueous component
Organophilic clay	0.5	to	1	Viscosifier
Succinimide copolymer	0.1	to	0.5	Fluid loss agent
Sodium polyacrylate	0.1	to	0.5	Fluid loss agent
Citric acid	0.1	to	1.5	Puffer
Barium sulfate	0.1	to	25	Weighting agent

With efficient solids-control equipment, optimized drilling, and good house-keeping practices, the cost of the synthetic mud can be brought to a level that is comparable to OBM (Munro et al., 1993).

POBMs or synthetic oil-based drilling muds are made on the same principle as OBMs. They have been developed to maintain the performance characteristics of OBMs while reducing their environmental impact. The objective behind the design of these drilling fluids is to exchange the diesel oil or mineral oil base with an organic fluid that has a lower environmental impact. The organic fluids used are esters, polyolefins, acetal, ether, and linear alkyl benzenes. As with OBMs, POBMs may contain various ingredients, such as thickening and suspending agents and emulsifying agents as well as weighting agents.

POBMs were developed to maintain the technical performance characteristics of OBMs and reduce their environmental impact. They are, however, not as stable as OBMs depending upon the continuous phase present. From an environmental perspective, legislation is becoming as strict for POBMs as for OBMs. The mud selection process is based on the mud's technical performance and environmental and financial impact.

Skeletally isomerized linear olefins exhibited a better high-temperature stability in comparison to a drilling fluid prepared from a conventional PAO. Fluid loss properties are good, even in the absence of fluid loss additives (Gee et al., 1992, 1998, 2000; Williamson et al., 1995). Although normal α-olefins are not

generally useful, mixtures of mostly linear olefins are minimally toxic and are highly effective as the continuous phase of drilling fluids (Gee et al., 1995, 1992).

Acetals as mineral oil substitutes exhibit good biodegradability and are less toxic than mineral oils (Hille et al., 1992, 1998). Acrylic acid (AA) salts are formed by the neutralization reaction of AA in aqueous solution (Shimomura et al., 1990).

Alginates are hydrocolloids, which are extracted from brown marine microalgae. Water-soluble alginates are prepared as highly concentrated, pumpable suspensions in mixtures of propylene glycol and water by using hydroxypropylated guar gum in combination with carboxymethylated cellulose, which is used as a suspending agent (Kehoe and Joyce, 1993).

Inverted Emulsion Drilling Muds

Inverted emulsion muds are used in 10–20% of all drilling jobs. Historically, first of all crude oils, then diesel oils and mineral oils were used to formulate invert drilling fluids. Considerable environmental damage may occur when the mud gets into the sea. Drilling sludge and the heavy mud sink to the seabed and partly flow with the tides and sea currents to the coasts. All of these hydrocarbons contain no oxygen and are not readily biodegraded (Hille et al., 1998).

Because of problems of toxicity and persistence, alternative drilling oils have been developed. Examples of such oils are fatty acid esters and branched chain synthetic hydrocarbons such as PAOs. Fatty acid ester-based oils have excellent environmental properties, but drilling fluids made with these esters tend to have lower densities and are prone to hydrolytic instability.

PAO-based drilling fluids can be formulated to high densities with good hydrolytic stability and low toxicity. They are, however, somewhat less biodegradable than esters and they are expensive. The fully weighted, high-density fluids tend to be too viscous (Lin, 1996).

Esters

Esters of C_6 to C_{11} monocarboxylic acids (Müller et al., 1990; Mueller et al., 1990a,b, 1994), acid-methyl esters (Mueller et al., 1990a), and poly-carboxylic acid esters (Mueller et al., 1991), as well as oleophilic monomeric and oligomeric diesters (Mueller et al., 1991), have all been proposed as basic materials for inverted emulsion muds. Natural oils are triglyceride ester oils (Wilkinson et al., 1995) and are similar to synthetic esters. Diesters also have been proposed (Mueller et al., 1991, 1992, 1993, 1995; Muller et al., 1993).

Acetals

Acetals and oleophilic alcohols or oleophilic esters are suitable for the preparation of inverted emulsion drilling muds and emulsion drilling muds. They

may replace the base oils, diesel oil, purified diesel oil, white oil, olefins, and alkyl benzenes (Hille et al., 1996, 1998). Examples are isobutyraldehyde, di-2-ethylhexyl acetal, dihexyl formal. Also mixtures with coconut alcohol, soya oil, and α-methyldecanol are suitable. Some aldehydes are shown in Figure 1.3.

Inverted emulsion muds are more useful in stable, water sensitive formations and in inclined boreholes. They are stable up to very high temperatures and provide excellent corrosion protection. Their disadvantages are their higher price, the greater risk if gas reservoirs are bored through, the more difficult handling for the team at the tower, and their greater environmental problems.

The high setting point of linear alcohols and the poor biodegradability of branched alcohols limit their use as an environment-friendly mineral oil substitute. Higher alcohols, which are slightly water-soluble, are eliminated for use in offshore muds because of their high toxicity to fish.

Esters and acetals can be degraded anaerobically on the seabed. This possibility minimizes the environmentally damaging effect on the seabed. When such products are used, rapid recovery of the ecology of the seabed takes place after the end of drilling. Acetals, which have a relatively low viscosity and in particular a relatively low setting point, can be prepared by combining various aldehydes and alcohols (Hille et al., 1998; Young and Young, 1994).

Anti-settling Properties

Ethylene-AA copolymer, neutralized with amines such as triethanol amine or N-methyl diethanol amine, enhances anti-settling properties (McNally et al., 1999; Santhanam and MacNally, 2001).

Glycosides

If glycosides are used in the internal phase, then much of the concern over the ionic character of the internal phase is not necessary. If water is limited in the system, then the hydration of the shales is greatly reduced.

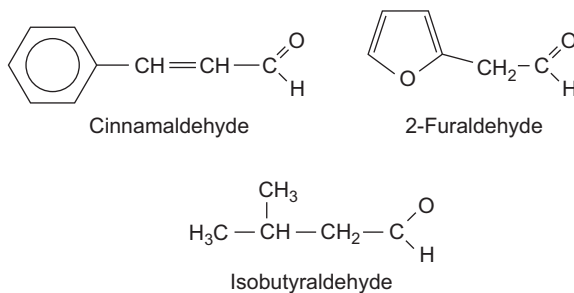Cinnamaldehyde   2-Furaldehyde

Isobutyraldehyde

FIGURE 1.3   Aldehydes.

The reduced water activity of the internal phase of the mud and the improved efficiency of the shale is an osmotic barrier if the glycoside interacts directly with the shale. This helps to lower the water content of the shale, thus increasing rock strength, lowering effective mean stress, and stabilizing the wellbore (Hale and Loftin, 1996).

Methyl glucosides also could find applications in water-based drilling fluids and have the potential to replace OBMs (Headley et al., 1995). The use of such a drilling fluid could reduce the need for the disposal of oil-contaminated drilling cuttings, minimize health and safety concerns, and minimize adverse environmental effects.

Miscellaneous

Other proposed base materials are listed in Table 1.7. Quaternary oleophilic esters of alkylolamines and carboxylic acids improve the wettability of clay (Ponsati et al., 1992, 1994). Nitrates and nitrites can replace calcium chloride in inverted emulsion drilling muds (Fleming and Fleming, 1995).

Reversible Phase Inversion

Invert emulsion fluids, in which the emulsion can be readily and reversibly converted from a water-in-oil type emulsion to an oil-in-water type emulsion, have been developed. The essential ingredient is an amine-based surfactant, which

TABLE 1.7 Other Materials for Inverted Emulsion Drilling Fluids

Base material	References
Ethers of monofunctional alcohols	Mueller et al. (1990)
Branched didecyl ethers	Godwin and Mathys (1993), Godwin and Sollie (1993)
α-Sulfofatty acids	Mueller et al. (1996)
Oleophilic alcohols	Mueller et al. (1990b), Muller et al. (1990)
Oleophilic amides	Mueller et al. (1990c)
Hydrophobic side chain polyamide from N,N-didodecylamine and sodium polyacrylate or polyacrylic acid	Monfreux et al. (2000)
Polyether amine	Wall et al. (1995)
Phosphate ester of a hydroxy polymer	Brankling (1994)

may be diethoxylated tallow amine, diethoxylated soya amine, or *N*-tallow-1,3-diaminopropane (Patel, 2008).

The invert emulsion is admixed with an acid that can protonate the amine surfactant. When sufficient quantities of the acid are present, the invert emulsion is converted so that the oleaginous fluid becomes the discontinuous phase and the non-oleaginous fluid becomes the continuous phase.

The phase inversion is reversible, so that on addition of a base capable of deprotonating the protonated amine surfactant, a stable invert emulsion is formed, where the oleaginous liquid becomes the continuous phase and the non-oleaginous fluid become the discontinuous phase (Patel, 2008).

In other words, when the drilling fluid is converted into an oil-in-water type emulsion, solids, now substantially water-wet, may now be separated from the fluid, by gravity or mechanical means, for further processing or disposal. The fluid may then be mixed with a base, which can deprotonate the protonated amine surfactant, and so converts the oil-in-water type emulsion back to a water-in-oil emulsion. The resulting water-in-oil emulsion may then be used as it is, or may be reformulated into a drilling fluid that is suitable for use in another well (Patel, 2008).

Foam Drilling

Drilling low-pressure reservoirs with nonconventional methods can use low-density dispersed systems, such as foams, to achieve underbalanced conditions. Selection of an adequate foam formulation, requires not only the reservoir characteristics but also the foam properties to be taken into account.

Parameters such as stability of foam, and the interactions between rock-fluid and drilling fluid-formation fluid are among the properties to consider when designing the drilling fluid (Aguilar et al., 2000).

A composition with a specific pH, an ionic surfactant, and a polyampholytic polymer whose charge depends on the pH, is circulated in a well. By varying the pH, it is possible to destabilize the foam in such a way as to more easily break it back at the surface, and potentially to recycle the foaming solution (Argillier and Roche, 2000).

Chemically Enhanced Drilling

Chemically enhanced drilling offers substantial advantages over conventional methods in carbonate reservoirs. Coiled tubing provides the perfect conduit for chemical fluids that can accelerate the drilling process and provide stimulation while drilling (Rae and Di Lullo, 2001). The chemical fluids are mainly acidic in order to dissolve or disintegrate the carbonate rock.

Supercritical Carbon Dioxide Drilling

The efficiency of drilling operations can be increased using a drilling fluid material that exists as supercritical fluid, or a dense gas at temperature and pressure conditions occurring in the drill site, such as carbon dioxide.

A supercritical fluid exhibits physiochemical properties intermediate between those of liquids and gases. Mass transfer is rapid with supercritical fluids, and their dynamic viscosities are nearer to those of normal gaseous states.

In the vicinity of the critical point, the diffusion coefficient is more than 10 times that of a liquid. Carbon dioxide can be compressed readily to form a liquid, and under typical borehole conditions, it is a supercritical fluid.

The viscosity of carbon dioxide at its critical point is only 0.02 cP. This value increases with pressure to about 0.1 cP at 70 MPa (about 10,000 psi). Because the diffusivity of carbon dioxide is so high, and the rock associated with petroleum-containing formations is generally porous, the carbon dioxide is effective in penetrating the formation.

Carbon dioxide therefore is often used to stimulate the production of oil wells, because it tends to dissolve in the oil, reducing the oil viscosity while providing a pressure gradient that drives the oil from the formation.

Carbon dioxide can be used to reduce mechanical drilling forces, to remove cuttings, or to jet erode a substrate. Supercritical carbon dioxide is used with coiled-tube drilling equipment. The very low viscosity of supercritical carbon dioxide provides efficient cooling of the drill head and efficient cuttings removal.

Furthermore, the diffusivity of supercritical carbon dioxide within the pores of petroleum formations is significantly higher than that of water, making jet erosion much more effective than water. Supercritical carbon dioxide jets can be used to assist mechanical drilling, for erosion drilling, or for scale removal. Spent carbon dioxide can be vented to the atmosphere, collected for reuse, or directed into the formation to aid in the recovery of petroleum (Kolle, 2002).

ADDITIVES

Thickeners

A variety of compounds that are useful as thickeners is shown in Table 1.8 and the individual compounds are explained in detail in the following sections.

Polymers

Thickener polymers include polyurethanes (PUs), polyesters, PAMs, natural polymers, and modified natural polymers (Doolan and Cody, 1995).

TABLE 1.8 Thickeners

Compound	References
A water-soluble copolymer of hydrophilic and hydrophobic monomers, acrylamide (AAm)-acrylate of silane or siloxane	Meyer et al. (1999)
Carboxymethyl cellulose, polyethylene glycol	Lundan et al. (1993), Lundan and Lahteenmaki (1996)
Combination of a cellulose ether with clay	Rangus et al. (1993)
Amide-modified carboxyl-containing polysaccharide	Batelaan and van der Horts (1994)
Sodium aluminate and magnesium oxide	Patel (1994a)
Thermally stable hydroxyethyl cellulose (HEC) 30% ammonium or sodium thiosulfate and 20% HEC	Lukach and Zapico (1994)
AA copolymer and oxyalkylene with hydrophobic group	Egraz et al. (1994)
Copolymers acrylamide-acrylate and vinylsulfonate–vinylamide	Waehner (1990)
Cationic polygalactomannans and anionic xanthan gum	Yeh (1995)
Copolymer from vinyl urethanes and AA or alkyl acrylates	Wilkerson et al. (1995)
2-Nitroalkyl ether–modified starch	Gotlieb (1996)
Polymer of glucuronic acid	Courtois-Sambourg et al. (1993)
Ferrochrome lignosulfonate and carboxymethyl cellulose	Kotelnikov et al. (1992)
Cellulose nanofibrils[a]	Langlois (1998, 1999)
Quaternary alkyl amido ammonium salts	Subramanian et al. (2001)
Chitosan[b]	House and Cowan (2001)

a) Stable up to temperatures of about 180°C
b) Solubilized in acidic solution

pH Responsive Thickeners

The viscosity of ionic polymers is dependent on their pH. In particular, pH responsive thickeners can be prepared by copolymerization of acrylic or methacrylic acid ethyl acrylate or other vinyl monomers and tristyrylpoly(ethyleneoxy)$_x$ methyl acrylate. Such a copolymer provides a stable, aqueous, colloidal

dispersion at a pH lower than 5.0, but becomes an effective thickener for aqueous systems on adjustment to a pH of 5.5 to 10.5 or higher (Robinson, 1996, 1999).

Mixed Metal Hydroxides

By addition of mixed metal hydroxides, typical bentonite muds are transformed to an extremely shear-thinning fluid (Lange and Plank, 1999). At rest, these fluids exhibit a very high viscosity but are thinned to an almost water-like consistency when shear stress is applied.

The shear thinning rheology of mixed metal hydroxides and bentonite fluids is due to the formation of a three-dimensional, fragile network of mixed metal hydroxides and bentonite.

The positively charged, mixed metal hydroxide particles attach themselves to the surface of negatively charged bentonite platelets. Typically, magnesium aluminum hydroxide salts are used as mixed metal hydroxides.

Mixed metal hydroxides demonstrate the following advantages in drilling (Felixberger, 1996):

- High cuttings removal,
- Suspension of solids during shutdown,
- Lower pump resistance,
- Stabilization of the borehole,
- High drilling rates, and
- Protection of the producing formation.

Mixed metal hydroxide drilling muds have been used successfully in horizontal wells; in tunneling under rivers, roads, and bays; for drilling in fluids; for drilling large-diameter holes; with coiled tubing; and to ream out cemented pipe.

Mixed metal hydroxides can be prepared from the corresponding chlorides by treatment with ammonia (Burba and Strother, 1991). Experiments with various drilling fluids showed that the mixed metal hydroxides system, coupled with propylene glycol (Deem et al., 1991), caused the least skin damage of the drilling fluids tested.

Thermally activated mixed metal hydroxides, made from naturally occurring minerals, especially hydrotalcites, may contain small or trace amounts of metal impurities besides the magnesium and aluminum components, which are particularly useful for activation (Keilhofer and Plank, 2000).

Mixed hydroxides of bivalent and trivalent metals with a three-dimensional spaced-lattice structure of the garnet type ($Ca_3Al_2[OH]_{12}$) have been described (Burba et al., 1992; Mueller et al., 1997).

Lubricants

Bit lubricants are dealt with in detail in Chapter 4. During drilling, the drill string may develop an unacceptable rotational torque or, in the worst case, become

stuck. When this happens, the drill string cannot be raised, lowered, or rotated. Common factors leading to this situation include:

- Cuttings or slough build-up in the borehole,
- An undergauge borehole,
- Irregular borehole development embedding a section of the drill pipe into the drilling mud wall cake, or
- Unexpected differential formation pressure.

Differential pressure sticking occurs when the drill pipe becomes embedded in the mud wall cake opposite a permeable zone.

The difference between the hydrostatic pressure in the drill pipe and the formation pressure holds the pipe in place, resulting in a sticking pipe. Differential sticking may be prevented, and a stuck drill bit may be freed by using an OBM, or an oil-based, or water-based surfactant composition.

Such a composition reduces friction, permeates drilling mud wall cake, destroys binding wall cake, and reduces the differential pressure. Unfortunately, many such compositions are toxic to marine life.

Bacteria

Bacterial contamination of drilling fluids contributes to a number of problems. Many of the muds contain sugar-based polymers in their formulation that provide an effective food source for bacterial populations. This can lead to direct degradation of the mud.

In addition, the bacterial metabolism can generate deleterious products. Most notable among these is hydrogen sulfide, which can lead to the decomposition of mud polymers, the formation of problematic solids such as iron sulfide, and corrosive action on drilling tubes and drilling hardware (Elphingstone and Woodworth, 1999). Moreover, hydrogen sulfide is a toxic gas.

Many polymers are used in drilling fluids as fluid loss control agents or viscosifiers. Because of the degradation of these polymers by bacteria in drilling fluids, an increase in fluid loss can occur. All naturally occurring polymers are capable of being degraded by bacterial action, but some are more susceptible than others. One solution, besides using bactericides, is to replace the starch with low viscosity PAC, polyanionic lignin, or other enzyme-resistant polymer (Hodder et al., 1992).

Certain additives are protected from biodegradation while drilling deep wells by quaternary ammonium salts (Rastegaev et al., 1999), which considerably reduces consumption of the additives needed.

Bacterial control is important not only in drilling fluids, but also for other oil and gas operations. The topic is treated more extensively in Chapter 5. Some bactericides especially recommended for drilling fluids are summarized in Table 1.9 and sketched out in Figure 1.4.

TABLE 1.9 Bactericides for Drilling Fluids

Bactericide	References
Bis[tetrakis(hydroxymethyl) phosphonium] sulfate[a]	Elphingstone and Woodworth (1999)
Dimethyl-tetrahydro-thiadiazine-thione	Karaseva et al. (1995)
2-Bromo-4-hydroxyacetophenone[b]	Oppong and King (1995)
Thiocyanomethylthio-benzothiazole[c]	Oppong and Hollis (1995)
Dithiocarbamic acid,	Austin and Morpeth (1992)
Hydroxamic acid[c]	Austin and Morpeth (1992)
1,2-Benzoisothiazolin-3-one	Morpeth and Greenhalgh (1990)
3-(3,4-Dichlorophenyl)-1,1-dimethylurea	Morpeth and Greenhalgh (1990)
Di-iodomethyl-4-methylphenyl sulfone[d]	Morpeth and Greenhalgh (1990)
Isothiazolinones	Downey et al. (1995), Hsu (1990, 1995), Morpeth (1993)

a) Absorbed on solid
b) Synergistically effective with organic acids
c) Synergistically effective with organic acids
d) Algicide

Pyrazol   Isooxazol   Isothiazol   1,2-Benzoisothiazolin-3-one

4,5-Dichloro-2-N-octyl-isothiazolin-3-one
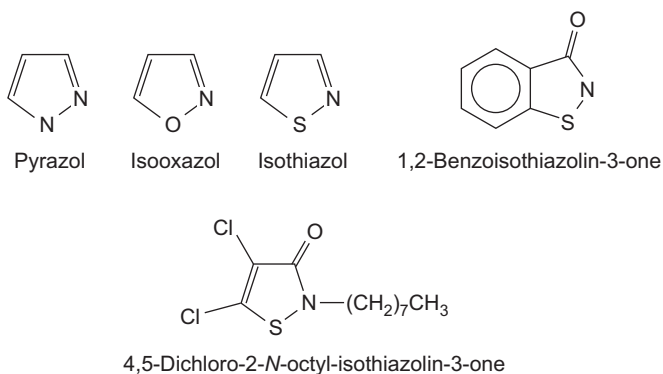
FIGURE 1.4   Components for biozides.

Corrosion Inhibitors

Corrosion inhibitors are the subject of several topics in petroleum industries, such as transport and completion. They are detailed in Chapter 6.

Viscosity Control

Bentonites are highly colloidal and swell in water to form thixotropic gels. This property results from their micaceous sheet structure. Because of these viscosity-building characteristics, bentonites are used as viscosity enhancers or builders in such areas as drilling muds and fluids, concrete and mortar additives, foundry and molding sands, and compacting agents for gravel and sand, as well as cosmetics. Most bentonites that are found in nature are in their sodium or calcium form.

The performance of a calcium bentonite as a viscosity builder can often be enhanced by conversion to the sodium form. Crude bentonite can be upgraded to a range of solutions with unusually high aqueous viscosities (Bauer et al., 1993). The crude material is sheared and dried. Sodium carbonate is then dry-blended with the material and pulverized. The resulting bentonite clays are self-suspending, self-swelling, and self-gelatinizing when mixed with water.

The modification of bentonite with alkylsilanes also improves their dispersing properties (Kondo and Sawada, 1996). Incorporation of phosphonate-type compounds in bentonites for drilling mud permits the removal of free calcium ions in the form of soluble and stable complexes, and the preservation or restoration of the initial fluidity of the mud (Michelson and Vattement, 1999). The phosphonates also have dispersing and fluidizing effects on the mud.

Clay Stabilization

Selected clay stabilizers are shown in Table 1.10. Thermally treated carbohydrates are suitable as shale stabilizers (Sheu and Bland, 1992). They may be formed by heating an alkaline solution of the carbohydrate, and the reaction product may be reacted with a cationic base. The inversion of non-reducing sugars may be first effected on selected carbohydrates, with the inversion catalyzing the browning reaction.

Formation Damage

Polyacrylates are often added to drilling fluids to increase their viscosity and limit formation damage. The filter cake is critical to preventing reservoir invasion by mud filtrate. Polymer invasion of the reservoir has been shown to have a great impact on permeability reduction (Audibert et al., 1999). The invasion of filtrate and solids in drilling in fluid can cause serious reservoir damage.

Shale Stabilizer

Swelling due to shale hydration is one of the most important causes of borehole instability. Three processes are known to contribute to shale instability (Bailey et al., 1994):

1. Movement of fluid from the wellbore into the shale,
2. Changes in stress and strain, which occur during the interaction of shale and filtrate, and
3. Softening and erosion, caused by invasion of mud filtrate and consequent chemical changes in the shale.

Adding a shale stabilizer to drilling fluids is an effective way to control clay swelling (Fu and Hu, 1997). A copolymer of AAm and acrylonitrile has been found to be effective in this regard. Experimental results show that the inhibitors are effective in inhibiting shale hydration swelling, especially their quaternized product. 2-Hydroxybutyl ether and polyalkyl ether modified polygalactomannans have been described as useful shale hydration inhibitors (Dino, 1997).

TABLE 1.10 Clay Stabilizers for Drilling Fluids

Additive	References
Modified poly-amino acid[a]	Bruton and McLaurine (1993)
Polyacrylamide	Ballard et al. (1994)
Amphoteric acetates and glycinates	Jarrett (1997a)
Capryloamphoglycinate	Alonso-Debolt and Jarrett (1995)
Cocoamphodiacetate	Alonso-Debolt and Jarrett (1995)
Disodium cocoamphodiacetate	Alonso-Debolt and Jarrett (1995)
Lauroamphoacetate	Alonso-Debolt and Jarrett (1995)
Sodium capryloamphohydroxypropyl sulfonate	Alonso-Debolt and Jarrett (1995)
Sodium mixed C_8 amphocarboxylate	Alonso-Debolt and Jarrett (1995)
Alkylamphohydroxypropyl sulfonate	Alonso-Debolt and Jarrett (1995)
Polyvinylpyrrolidone	
Polyvinyl alcohol	
Starches	
Cellulosic material	Patel et al. (1995)
Partially hydrolyzed polyacrylamide and PPG, or a betaine	Patel et al. (1995)
Quaternized trihydroxyalkyl amine	Patel et al. (1995)
Polyfunctional polyamine	McGlothlin and Woodworth (1996)

a) Water sensitive smectite or illite shale formations

TABLE 1.11 Surface Active Agents for Drilling Muds

Compound	References
Alkylpolyglycosides	Lecocumichel and Amalric (1995)
Amphoteric surfactants	Dahanayake et al. (1996)
Acetal or ketal adduct hydroxy polyoxyalkylene ether[a]	Felix (1996)
Amphoteric anion ethoxy and propoxy units	Hatchman (1999)
Alkanolamine	Hatchman (1999)

a) *Controlling foam formation, drilling muds*

A copolymer of styrene and maleic anhydride (MA) with alkylene oxide based side chains is effective as a shale stabilizer (Smith and Balson, 2000), as are a variety of polyoxyalkylene amines. It was found that polyoxypropylene-diamine $H_2N-CH(CH_3)CH_2[-OCH_2CH(CH_3)]_x-NH_2$ (Patel et al., 2001) is the best, with $x < 15$. Surfactants are used to change the interfacial properties. Suitable surfactants are given in Table 1.11.

Fluid Loss Additives

Filtration control is an important property of a drilling fluid, particularly when drilling through permeable formations, where the hydrostatic pressure exceeds the formation pressure. It is important for a drilling fluid to quickly form a filter cake to effectively minimize fluid loss, but which also is thin and erodable enough to allow product to flow into the wellbore during production (Jarrett and Clapper, 2010). Fluid loss additives are detailed in Chapter 2. Here a few fluid loss additives are summarized for quick reference.

There are a number of methods that have been proposed to help prevent the loss of circulation fluid (Messenger, 1981). Some of these methods use fibrous, flaky, or granular materials to plug the pores as the particulate material settles out of the slurry.

Other methods use materials that interact in the fissures of the formation to form a plug of increased strength. Lost circulation additives are summarized in Table 1.12.

Water Swellable Polymers

Certain organic polymers absorb comparatively large quantities of water, for example, alkali metal polyacrylate or crosslinked polyacrylates (Green, 2001). Such water-absorbent polymers, insoluble in water and in hydrocarbons, can be

TABLE 1.12 Lost Circulation Additives

Material	References
Encapsulated lime	Walker (1986)
Encapsulated oil-absorbent polymers	Delhommer and Walker (1987a)
Hydrolyzed polyacrylonitrile	Yakovlev and Konovalov (1987)
Divinylsulfone, crosslinked	
Poly(galactomannan) gum	Kohn (1988)
PU foam	Glowka et al. (1989)
Partially hydrolyzed polyacrylamide 30% hydrolyzed, crosslinked with Cr^{3+}	Sydansk (1990)
Compound	**References**
Oat hulls	House et al. (1991)
Rice products	Burts Jr (1992, 1997)
Waste olive pulp	Duhon (1998)
Nut cork	Fuh et al. (1993), Rose (1996)
Pulp residue waste	Gullett and Head (1993)
Petroleum coke	Whitfill et al. (1990)
Shredded cellophane	Burts Jr (2001)

injected into the well so that they encounter naturally occurring or added water at the entrance to and within an opening in the formation. The resultant swelling of the polymer forms a barrier to the continued passage of the circulation fluid through that opening into the formation.

The hydrocarbon carrier fluid initially prevents water from contacting the water-absorbent polymer until such water contact is desired. Once the hydrocarbon slug containing the polymer is properly placed at the lost circulation zone, water is mixed with it so that the polymer will absorb the water and substantially increase in size to close off the lost circulation zone (Bloys and Wilton, 1991; Delhommer and Walker, 1987b; Walker, 1989). The situation is similar to an oil-based cement. The opposite mechanism is used by a hydrocarbon-swellable elastomer (Wood, 2001).

Anionic Association Polymer

Another type of lost circulation agent is a combination of an organic phosphate ester and an aluminum compound, for example, aluminum isopropoxide.

The alkyl phosphate ester becomes crosslinked by the aluminum compound to form an anionic association polymer, which serves as a gelling agent (Reid and Grichuk, 1991), hence preventing fluid loss.

Fragile Gels

A fragile gel is one that can be easily disrupted or thinned under shear stress, etc, but can quickly return to a gel when the stress is alleviated or removed, such as when the circulation of the fluid is stopped. Fragile gels may be disrupted simply by a pressure or a compression wave during drilling. They break instantaneously when disturbed, turning from a gel back into a liquid with minimum pressure, force, and time.

Metal crosslinked phosphate esters impart a fragile progressive gel structure to a variety of oil and invert emulsion-based drilling fluids, both at neutral or acidic pH.

The amount of phosphate ester and metal crosslinker that is used in a drilling fluid depends on the oil type and the desired viscosity of the product. Generally, however, more phosphate ester and metal crosslinker is used for gelling or enhancing the viscosity of the fluid for transport than is used for imparting fragile progressive gel structure to the drilling fluid (Bell and Shumway, 2009).

Aphrons

Other lost-circulation additives can be present in an encapsulated form. The encapsulation is then dissolved and the material swells to close fissures. Microbubbles in a drilling fluid can be generated by certain surfactants, and polymers known as *aphrons* are a different approach to reduce the fluid loss (Ivan et al., 2001).

An aphron drilling fluid is similar to a conventional drilling fluid, but the drilling fluid system is converted to an energized air-bubble mud system before drilling (Kinchen et al., 2001).

Permanent Grouting

Lost circulation also can be suppressed by grouting permanently, either with cement or with organic polymers that cure in situ (Allan and Kukacka, 1995; Cowan and Hale, 1994).

Scavengers

Oxygen Scavengers

Oxygen corrosion is often underestimated, but studies have shown that the corrosion can be limited when proper oxygen scavengers are used. Hydrazine leads the group of chemicals that are used for oxygen removal. Because of its special properties, it is used for corrosion control in heating systems and in drilling operations, well workover, and cementing (Sikora, 1994).

Hydrogen Sulfide Removal

It is sometimes necessary to remove hydrogen sulfide from a drilling mud. Techniques using iron compounds that form sparingly soluble sulfides have been developed, for example, the use of iron (II) oxalate (Sunde and Olsen, 2000) and iron sulfate (Prokhorov et al., 1993), where the sulfur is precipitated out as FeS. Alternatively, ferrous gluconate is an organic iron-chelating agent, stable at pH levels as high as 11.5 (Davidson, 2001).

Zinc compounds have a high reactivity with regard to H_2S and therefore are suitable for the quantitative removal of even small amounts of hydrogen sulfide (Wegner and Reichert, 1990). However, at high temperatures they may negatively affect the rheology of drilling fluids.

Surfactants

Surfactant in Hydrocarbon Solvent

Methyl-diethyl-alkoxymethyl ammonium methyl sulfate has high foam extinguishing properties (Fabrichnaya et al., 1997).

Biodegradable Surfactants

Alkylpolyglucosides (APGs) are highly biodegradable surfactants (Nicora and McGregor, 1998). The addition of APGs, even at very low concentrations, to a polymer mud can drastically reduce fluid loss even at high temperatures. Moreover, both fluid rheology and temperature resistance are improved.

Deflocculants and Dispersants

Deflocculants have a relatively low molecular weight. Complexes of tetravalent zirconium with organic acids, such as citric, tartaric, malic, and lactic acids, and a complex of aluminum and citric acid have been claimed to be active as dispersants.

Polymers composed of sodium styrene sulfonate, MA, and a zwitterionic functionalized MA (Grey, 1993; Peiffer et al., 1991, 1992, 1993) are also suitable. The dispersant is especially useful in dispersing bentonite suspensions (Burrafato and Carminati, 1994).

Polymers with amine sulfide terminal moieties are synthesized by using aminethiols as chain transfer agents in aqueous addition polymerization reactions. The polymers are useful as mineral dispersants (McCallum and Weinstein, 1994).

Shale Stabilizing Surfactants

There are special shale stabilizing surfactants consisting of non-ionic alkanolamides (Jarrett, 1997b), for example, acetamide monoethanolamines and diethanol amines. Acetone and ethanolamine are shown in Figure 1.5.
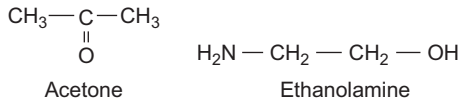
$$CH_3 - \underset{\underset{O}{\overset{\|}{}}}{C} - CH_3 \qquad H_2N - CH_2 - CH_2 - OH$$

Acetone   Ethanolamine

FIGURE 1.5   Acetone, ethanolamine.

Toxicity

Alkyl phenol ethoxylates are a class of surfactants that have been used widely in the drilling fluid industry. The popularity of these surfactants is based on their cost effectiveness, availability, and range of obtainable hydrophilic-lipophilic balance values (Getliff and James, 1996).

However, studies have shown that alkyl phenol ethoxylates exhibit oestrogenic effects and can cause sterility in some male aquatic species. This may have subsequent human consequences, and such possibilities have led to their use being banned in some countries, and agreements to phase out their use have been drawn up. Alternatives are available, and in some cases they show an even better technical performance.

Defoamers

Defoamers are covered in Chapter 22.

Hydrate Inhibitors

Hydrate inhibitors for drilling fluids are summarized in Chapter 13.

Weighting Materials

There are many weighting materials, including barite and iron oxides, which are used to increase the specific weight of a slurry. Conversely, the specific weight can be reduced by foaming or by the addition of hollow glass particles.

Barite

Barite has been used as a weighting agent in drilling fluids since the 1920s. It is preferred over other materials because of its high density, low production costs, low abrasiveness, and ease of handling. Other weighting materials have been used, but they are problematic or costly. Finished barite producers sometimes blend ores from different sources to obtain the desired average density to meet API specifications.

Some barite ores contain alkaline-soluble carbonate minerals that can be detrimental to a drilling fluid, such as iron carbonate (siderite), lead carbonate (cerussite), and zinc carbonate (smithsonite) (Kulpa et al., 1992). Details of how to characterize barite have been worked out (Recommended practice for chemical analysis of barite, 1996). Barite can be modified to become oleophilic (Shen et al., 1998, 1999).

To recover barite from drilling muds, a direct flotation without prior dewatering and washing of the drilling muds has been described (Heinrich, 1992). An alkyl phosphate is used as a collecting and frothing reagent.

Ilmenite

Environmental considerations suggest replacing barite with ilmenite. However, the use of this as weighting material can cause severe erosion problems. Using ilmenite with a narrow particle size distribution around $10\,\mu$ can reduce the erosion to a level experienced with barite (Saasen et al., 2001).

Carbonate

It is possible to replace barite and iron-based weighting material with carbonate if a high degree of weighting is not required. Besides being cheaper than barite, such materials are less abrasive, which is especially important when drilling is performed in producing formations. It is also readily soluble in hydrochloric acid. The main shortcomings of carbonate powders are due to the presence of a coarsely divided fraction, and also of noncarbonate impurities (Lipkes et al., 1996).

Zinc Oxide, Zirconium Oxide, and Manganese Tetroxide

Zinc oxide (ZnO), is a particularly suitable material for weighting because it has a high density; $5.6\,\mathrm{g\,ml^{-1}}$ versus $4.5\,\mathrm{g\,ml^{-1}}$ for barite. It is soluble in acids (e.g., HCl), and its particle size can be set so that it does not invade the formation. Acid solubility is particularly useful because dissolved ZnO can be pass through a production screen without plugging it. A high density means less weighting material is needed per unit mud volume to achieve a desired density.

The particle size, around $10\,\mu$, is such that the ZnO particles do not invade the formation core with the filtrate. On the other hand, the particle size is not large enough to settle out of suspension.

Zirconium oxide possesses similar properties to ZnO. It has a density of $5.7\,\mathrm{g\,ml^{-1}}$ and is soluble in nitric acid and hot concentrated hydrochloric, hydrofluoric, and sulfuric acids. Therefore, a filter cake formed from zinc or zirconium oxide can be dissolved. The high solubility of ZnO in acids makes it particularly suitable as weighting material (Lau et al., 1997). On the other hand, manganese tetroxide (Mn_3O_4) is so fine that it invades the formation with the filtrate.

Hollow Glass Microspheres

Initially, glass microspheres were used in the 1970s to overcome severe lost circulation problems in the Ural Mountains. The technology has subsequently been used in other sites (McDonald et al., 1999). Hollow glass beads reduce the density of a drilling fluid and can be used for underbalanced drilling (Medley Jr. et al., 1997, 1995). Field applications have been reported (Arco et al., 2000).

Organoclay Compositions

It has long been known that organophilic clays can be used to thicken a variety of organic compositions. Such clays are prepared by the reaction of an organic cation with a clay. If this cation contains at least one alkyl group of at least 8–10 carbon atoms, then the clays produced have the property of increasing the viscosity of organic liquids and thus imparting desired rheological properties to a wide variety of such liquids, including paints, coatings, adhesives, and similar products.

It is also well known that such organoclays may function to thicken polar or nonpolar solvents, depending on the organic salt. Their efficiency in non-aqueous systems can be further improved by adding a polar organic material of low molecular weight to the composition. Such materials have been called *dispersants*, *dispersion aids*, and *solvating agents*. Low molecular weight alcohols and ketones, particularly methanol and acetone, have been found to be the most efficient.

Organophilic clays are generally prepared by reacting a hydrophilic clay with an organic cation, usually a quaternary ammonium salt compound produced from a fatty nitrile. Examples of hydrophilic clays include bentonite, attapulgite, and hectorite.

Native clay surfaces have negatively charged sites and cationic counter ions such as sodium and calcium cations. Thus, they may be treated with a cationic surfactant to displace the cations that are naturally present at the clay surfaces. The cationic surfactant becomes tightly held to the surfaces through electrostatic charges. In this manner, the hydrophilic nature of the clay is reversed, making it more soluble in oil. Bentonite, when treated with sodium cations, is known as sodium bentonite. Those monovalent sodium cations may be easily displaced from the clay, making a large number of anionic sites available (Miller, 2009).

Quaternary ammonium compounds contain nitrogen moieties in which one or more of the hydrogen atoms attached to the nitrogen are substituted by organic radicals. One of the most popular quaternary ammonium compounds for organophilic clays is dimethyl dihydrogenated tallow ammonium chloride. Tallow contains unsaturated and saturated fatty acids, including oleic acid, palmitic acid, stearic acid, and other minor fatty acids.

The hydrocarbon structure of this compound and the two long chain alkyl groups makes it very oil-soluble. Further, the presence of two methyl groups prevent steric interference, thus allowing close packing of the ammonium cation at the clay surface.

The dimethyl dihydrogenated tallow ammonium chloride surfactant, however, cannot be activated efficiently at relatively low temperatures. Improved cationic surfactants have been developed in which the ammonium compounds have greater numbers of alkyl groups. Inclusion of a benzyl group greatly enhances the performance of organophilic clays at low temperatures (Miller, 2009).

Two or more types of organic salts in the presence of an organic anion act synergistically. The combination of hydrophobic and hydrophilic organic salts and an organic anion produces an organophilic clay gellant, which exhibits improved gelling properties in nonaqueous systems (Nae et al., 1995).

Examples are dimethyl dihydrogenated tallow quaternary ammonium chloride and methyl bis-polyoxyethylene (15 units) cocoalkyl quaternary ammonium chloride, and the salts stearic, succinic, and tartaric acids (Mardis et al., 1997; Nae et al., 1993, 1999).

Biodegradable Organophilic Clay

Organophilic clays are treated with a quaternary ammonium surfactant having an amide linkage. Examples of such surfactants are shown in Figure 1.6.

The surfactants are based on stearamides. The benzyl group greatly enhances the performance of organophilic clays at temperatures near 7°C.

This type of cationic surfactant is substantially biodegradable, meaning that it is capable of being decomposed by natural biological processes. In particular, it undergoes aerobic biodegradation, which is the breakdown of organic chemicals by microorganisms when oxygen is present.

In this process, aerobic bacteria use oxygen as an electron acceptor and degrade organic chemicals into smaller compounds, producing carbon dioxide and water as the final product (Miller, 2009).

Clays treated in this way may therefore be used in drilling fluids without concern that the surfactant could accumulate in the environment. The surfactant will usually not reach toxic levels that could harm the surrounding environment and the life supported by it (Miller, 2009). The organophilic clay is suitable for both oil-based fluids and invert emulsions.

Polyvinyl neodecanoate

Organophilic clays have been considered as necessary for the suspension of drill cuttings. However, formulations have been developed recently that have
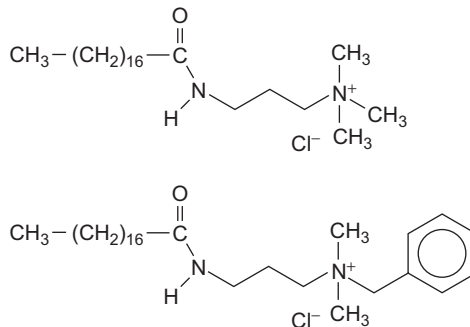

FIGURE 1.6   Quaternary ammonium surfactants (Miller, 2009).

improved suspension properties, without organophilic clays (Miller and Kirsner, 2009).

Additives for clayless formulations are emulsified copolymers of 2-ethylhexyl acrylate (EHA) and AA. However, at elevated temperatures it is likely that some acrylate will hydrolyze to AA, thus raising the level of AA moieties in the copolymer. For certain applications, vinyl neodecanoate may be substituted for EHA (Miller and Kirsner, 2009).

These drilling fluids do not need viscosifiers or additional suspension agents and generally do not need fluid loss control agents or filtration control additives. Their rheological properties remain stable over a broad temperature range, even after exposure to high temperatures (Miller and Kirsner, 2009).

Since space is limited at some well sites, such as offshore platforms, it may be advantageous to use efficient drilling fluid additives, which can be formulated using as few additives as possible.

Miscellaneous

Reticulated Bacterial Cellulose

Reticulated bacterial cellulose may be used in place of a conventional gellant, or in combination with conventional gellants to produce enhanced drilling muds (Westland et al., 1992). Only relatively small quantities of this material is needed to enhance their rheologic properties.

Scleroglucan

Scleroglucan is a polysaccharide secreted by the mycelia of certain microorganisms, produced by aerobic fermentation of D-glucose. It has been proposed as a better alternative to xanthan gum for drilling fluid compositions (Gallino et al., 1996).

For drilling fluid applications, scleroglucan can be used in unrefined form. It is an effective thickener for water (Vaussard et al., 1997) and enhances the lubricating and cleaning power of WBMs. In the drilling of deviated wells, scleroglucan permits better cleaning of the well (Donche et al., 1994; Vaussard et al., 1991). It can also be used in drilling jobs with large-diameter wells (Lacret and Donche, 1991; Ladret and Donche, 1991, 1996).

Uintaite

Uintaite is a naturally occurring, hydrocarbon mineral that is classified as an asphaltite. It is a natural product whose chemical and physical properties vary and depend strongly on the uintaite source. It is also called Gilsonite, which is a registered trademark of American Gilsonite Co., Salt Lake City, Utah.

General purpose Gilsonite brand resin has a softening point of about 175°C, Gilsonite HM has a softening point of about 190°C, and Gilsonite Select 300

and Select 325 have softening points of about 150°C and 160°C, respectively. The softening points of these natural uintaites depend primarily on the source vein that is mined when the mineral is produced.

Uintaite is described by Kirk-Othmer (Neel, 1980). The typical material used in drilling fluids is mined from an area around Bonanza, Utah, and has a specific gravity of 1.05 with a softening point ranging from 190–205°C, although a lower softening point (165°C) material is sometimes used. It has a low acid value, a zero iodine number, and is soluble or partially soluble in aromatic and aliphatic hydrocarbons, respectively.

For many years uintaite and other asphaltic-type products have been used in water-based drilling fluids as additives to assist in borehole stabilization. These additives can minimize hole collapse in formations that contain water sensitive, sloughing shales. Uintaite and asphalt-type materials have been used for many years to stabilize sloughing shales and to reduce borehole erosion. Other benefits derived from these products include borehole lubrication and reduction in the need for filtration.

Uintaite is not easily water-wet with most surfactants. Thus, stable dispersions of uintaite are often difficult to achieve, particularly in the presence of salts, calcium, solids, and other drilling fluid contaminants and in the presence of diesel oil. The uintaite must be readily dispersible and must remain water-wet; otherwise it will coalesce and be separated from the drilling fluid, along with cuttings at the shale shaker or in the circulating pits. Surfactants and emulsifiers are often used with uintaite drilling mud additives.

Loose or poor bonding of the surfactant to the uintaite will lead to it being washed off during use, possible agglomeration, and the removal of uintaite from the mud system with the drilling wastes. Thus, the importance of the wettability, rewettability, and storage stability criteria is evident.

A preferred product comprises about 2 parts Gilsonite HM, about 1 part Gilsonite Select, about 1 part causticized lignite, and about 0.1–0.15 part of a non-ionic surfactant (Christensen et al., 1991, 1993).

Sodium Asphalt Sulfonate

Neutralized sulfonated asphalt (i.e., salts of sulfonated asphalt and their blends with materials such as Gilsonite, blown asphalt, lignite, and mixtures of the latter compounds) are commonly used as additives in drilling fluids. These additives, however, cause some foaming in water or water-based fluids, and they are only partially soluble in the fluids.

Liquid additives have therefore been developed to overcome some of the problems associated with the use of dry additives. However, liquid compositions containing polyglycols can give rise to stability problems. Stable compositions can be obtained by special methods of preparation (Patel, 1996). In particular first the viscosifier is mixed with water, then the polyglycol, and finally the sulfonated asphalt is added.

Formation Damage by Gilsonite and Sulfonated Asphalt

Laboratory experiments have been conducted with a chromium lignite/ chromium lignosulfonate mud system both without and with solid lubricants. These studies looked at filtration loss, cake quality, and their impact on the formation.

A comparative evaluation has led to the conclusion that Gilsonite is a better additive compared with sulfonated asphalt, as it results in less filtration loss and compact cake formation, thereby reducing formation damage. Flow studies have indicated that the addition of these solid lubricants can be used in drilling fluids without adversely impacting the producing zones (Garg et al., 1995).

Multicomponent Additives

Multi-component additives for drilling fluids have been proposed, containing three primary components, namely a (Brazzel, 2009)

1. Rate of penetration enhancer,
2. Lubricant, and
3. Clay inhibitor or stabilizer.

Penetration enhancers are ester-based oils, which are potential carriers for other additives, such as surfactants. The lubricant is a chlorinated wax. The clay stabilizer is a polyglycol. The three components are premixed in a single container, for ease of use in adding to a drilling fluid system.

The pre-blended additive has significant advantages. Once a desired specific ratio is blended, then adding it at that ratio to a drilling fluid system is very much simplified and maintaining the desired volumetric concentrations in the system is much easier. Adding it to the overall system, is much quicker than adding each component singly (Brazzel, 2009).

CLEANING OPERATIONS

Cuttings Removal

When drilling deviated and horizontal wells, gravity causes deposits of drill cuttings and especially fines, or smaller sized cuttings, to build up along the lower side or bottom of the wellbore. Such deposits are commonly called *cuttings beds*. Buildup of cuttings beds can lead to undesirable friction, and possibly to sticking of the drill string.

Removing the drill cuttings from a deviated well, in particular when drilled at a high angle, can be difficult. Limited pump rate, eccentricity of the drill pipe, sharp build rates, high bottom hole temperatures, and oval-shaped wellbores can all contribute to inadequate hole cleaning.

Well treatments by circulating fluids that have been specially formulated to remove such cuttings beds are periodically necessary to prevent buildup to the point that the cuttings or fines interfere with the drilling apparatus.

Usually, the drilling operation must be stopped while such treatment fluids are swept through the wellbore to remove the fines. Alternatively, special viscosifier drilling fluid additives have been proposed to enhance the ability of the drilling fluid to transport cuttings, but such additives at best merely delay the buildup of cuttings beds and they can be problematic in themselves if they change the density of the drilling fluid. Removal of cutting beds has also performed mechanically wherein the drill string is pulled back along the well, pulling the bit through the horizontal or deviated section of the well.

Barium sulfate can be used as a sweep material. It should be ground and sieved to a size range that is sufficiently small to enable it to be suspended in the drilling fluid. After adding it to the drilling fluid, the fluid is circulated in the wellbore, where it removes the small cuttings or cuttings beds from the borehole and delivers them to the well surface.

The composition and the cuttings are then removed from the drilling fluid in a manner that prevents a significant change in its density. This is done by sieving or screening, preferably by the principal shale shaker of the drilling operation (West et al., 2001).

Junk Removal

Drilling equipment that is broken or stuck in the hole can be dissolved by means of nitric and hydrochloric acids mixed in a proportion of 1:3. To accelerate the dissolving of the metal, a mixture containing 1.1 parts of sodium nitrate and 1.0 part of monoethanolamine is added initially to the acids in the amount of 0.05–13.0 parts per 100 parts of acid mixture. The acidic residue in the hole is neutralized by addition of alkali and converted into drilling fluid by addition of polymer solution (Dolganskaya and Sharipov, 1992).

Filter Cake Removal

As the drilling fluid is circulated, a layer of solids, referred to as a filter cake, is usually formed on the walls of the wellbore. A certain degree of cake buildup usually is desirable to isolate formations from drilling fluids. Once the wellbore has been drilled to the desired depth, the drill string and bit are removed, and a pipe string, e.g., casing, liners, etc., are introduced into the wellbore.

Eventually, the wellbore may be conditioned by circulating the drilling fluid. The purpose of this conditioning is to remove as much of the filter cake and the gelled drilling fluid from the walls of the wellbore as possible. However, sometimes this is not enough to remove the undesired material completely. Problems with subsequent processing, e.g., in primary cementing operations may also arise, because in general, cement compositions are not compatible with the drilling fluid and the filter cake.

To mitigate these problems, a special chemical wash composition containing surfactants can be introduced, sometimes known as preflushes.
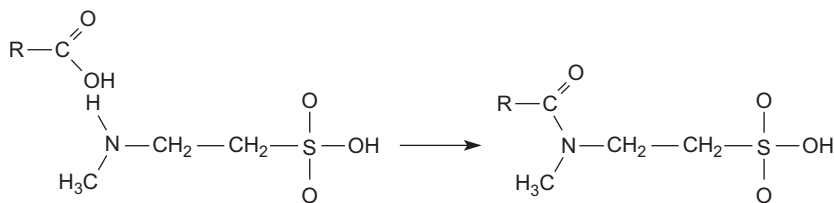
FIGURE 1.7   Acylation of *N*-Methyl-taurine.

An aqueous chemical wash solution contains sulfonated bisulfite lignin, and a taurate, present in amounts of 0.1– 5% (Dealy and Chatterji, 2010). The sulfonated lignin is produced by the bisulfite process, or by sulfomethylation of a lignosulfonate with formaldehyde.

Taurates, or taurides, are generally based on taurine, or 2-aminoethane-sulfonic acid. Taurine occurs naturally in food, being first isolated from ox bile in 1827. Taurine derivates have biological and medial roles (Azuma et al., 2009), and are used in cosmetics and as surfactants.

Examples of taurates useful for preflushes are *N*-methyl-*N*-cocoyl taurate, *N*-methyl-*N*-palmitoyl taurate, and *N*-methyl-*N*-oleyl taurate and their metal salts. They are obtained by the acylation of *N*-methyl taurine with the corresponding long chain acids (Walele and Syed, 1995), c.f., Figure 1.7.

Additional additives may be included in the chemical wash compositions, such as (Dealy and Chatterji, 2010):

- Viscosifying agents,
- Defoamers,
- Curing agents,
- Corrosion inhibitors,
- Scale inhibitors, and
- Formation conditioning agents.

Viscosifying agents may be clays, diatomaceous earth, starches, or polymers.

DRILLING FLUID DISPOSAL

Toxicity

Drilling fluids are known to be potentially toxic and are therefore environmentally damaging. They are composed, unlike other most toxic agents, of a wide variety of chemicals, thus making it difficult to predict the actual risk of a specific drilling mud, but methods for assessing this toxicity have been developed (Kanz and Cravey, 1985).

Studies under laboratory conditions revealed that in 9% of cases, drilling muds were acutely toxic at concentrations of 1,000–10,000 ppm. However, in

the natural environment, concentrations drop rapidly to background levels of around 200–1,000 ppm, hence low levels may be tolerated in the environment.

In a more recent study, soil samples from oil and gas drilling and production sites were analyzed for contaminating substances associated with drilling fluids and petroleum products. The results revealed that contamination of the soil was widespread and persistent. However, it is generally localized in the immediate vicinity of drilling and production activity. Most prominently, heavy metals, such as barium, chromium, lead, and zinc were detected. Further problems may be caused by salinity, pH, and petroleum hydrocarbons.

No discernible pattern of contamination between well sites was observed due to the variability of methods and materials used in the drilling of individual wells. It was considered that the levels of contaminating agents that were found do not represent an immediate environmental threat. However, the long-term cumulative effects are largely unknown (Carls et al., 1995).

The most consistently toxic bioassay phase is the suspended solid phase. This phase consists of bentonite, cuttings, and soluble components. The toxicity has been explained by specific chemical toxicity of a given mud component, or by physical toxicity generated by abrading or clogging epithelial tissue, i.e., respiratory or digestive body surfaces. In addition, the danger to marine animals from exposure to waste drilling muds may also originate from chemical toxicity. Further details are beyond the scope of this text and the reader is referred to the literature for more information (Kanz and Cravey, 1985, p. 329).

In a long-term study, the influence of increased levels of petroleum hydrocarbons upon soil and plants has been studied. Different doses of drilling fluids and crude oil were applied to clean soil, and the changes in some chemical parameters of the soil, plant density, and crop yields were measured. Drilling fluids showed a stronger impact on the chemical properties of the studied soil, while the plant density and yield were more strongly affected by the levels of crude oil. The soil levels of petroleum hydrocarbons, mineral oils, and polycyclic aromatic hydrocarbons were significantly reduced after the first trial year (Kisic et al., 2009).

For the reasons illustrated above, there is a need to take care in the waste management of drilling muds. Selected solutions for the waste management of these materials will now be discussed.

Conversion Into Cements

Water-based drilling fluids may be converted into cements using hydraulic blast furnace slag (Bell, 1993; Cowan and Hale, 1995; Cowan et al., 1994; Cowan and Smith, 1993; Zhao et al., 1996), a unique material that has low impact on the rheological and fluid loss properties of drilling fluids. It can be activated to set in drilling fluids that are difficult to convert to cements by other solidification technologies.

Hydraulic blast furnace slag has a more uniform and consistent quality than Portland well cements, and it is available in large quantities from multiple sources. Fluid and hardened solid properties of blast furnace slag and drilling fluids mixtures used for cementing operations are comparable with the properties of conventional Portland cement compositions.

Environmental Regulations

In response to effluent limitation guidelines promulgated by the Environmental Protection Agency for the discharge of drilling wastes offshore, alternatives to WBMs and OBMs have been developed. Thus, synthetic-based muds are more efficient than WBMs for drilling difficult and complex formation intervals, and they have lower toxicity and lower environmental impacts than diesel or conventional mineral OBMs.

Synthetic drilling fluids may present a significant pollution prevention opportunity, because they are recycled, and smaller volumes of metals are discharged with the cuttings. A framework for a comparative risk assessment for the discharge of synthetic drilling fluids has been developed that will help to identify potential impacts and benefits associated with the use of specific drilling muds (Meinhold, 1998).

CHARACTERIZATION OF DRILLING MUDS

Important parameters for characterizing the properties of a drilling mud are viscosity, specific weight, gel strength, and filtration performance.

Viscosity

Viscosity is measured by means of a Marsh funnel. The funnel is dimensioned so that the outflow time of 1 qt (926 ml) fresh water at 70°F (21°C) is 26 s.

Viscosity is also measured with a rotational viscometer. The mud is placed between two concentric cylinders. One cylinder rotates with constant velocity, while the other is connected by a spring. The torque on this cylinder results in a deviation of its position from rest, which may serve as a measure of viscosity.

Gel strength is measured by a rotational viscometer, if the maximal deflection of the pointer is monitored when the motor is turned on with low speed, the liquid being at rest for a prolonged time before, for example, for 10 min. This maximal deflection measurement is referred to as a 10-minute gel.

API Filtration

A filter press is used to determine the wall-building characteristics of a mud. This press consists of a cylindrical chamber, which is resistant to alkaline media. A filter paper is placed on the bottom of the chamber. The mud is placed into the chamber and a pressure of 0.7 MPa is applied. After 30 min the volume of

filtrate is reported. The filter cake is inspected visually and the consistency is noted as hard, soft, tough, rubbery, or firm.

There is another procedure suitable for OBMs under high-pressure and high-temperature conditions. Here, filtration is performed at 100 psi (7 MPa) and at temperatures of 200°F (93°C). It should be noted that research has shown that there may be significant differences between static and dynamic filtering.

Alkalinity and pH

Alkalinity is measured by acid-base titration, with methylorange or phenolphthalein as an indicator. Phenolphthalein changes color at pH 8.3, whereas methylorange changes color at pH 4.3. At pH 8 the neutralization of the strongly alkaline components such as NaOH is essentially complete.

Further reduction of the pH to 4 will also measure the levels of carbonates and bicarbonates that are present. Colorimetric tests and glass electrode systems are used to determine pH. Some indicators are shown in Figure 1.8.

Total Hardness

The sum of calcium and magnesium ions in the mud determines its total hardness. These ions are analyzed by complexometric titrations using ethylene diamine tetraacetic acid.

Roller Oven

The effects of temperature and various chemical additives on the rheological, filtration, and chemical properties of fluids and muds under simulated circulating conditions can be elucidated in a roller oven (Schroeder, 1987, 1992).
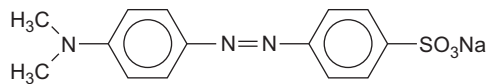
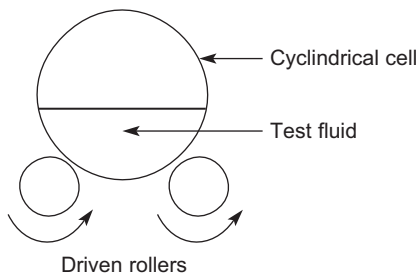Methylorange
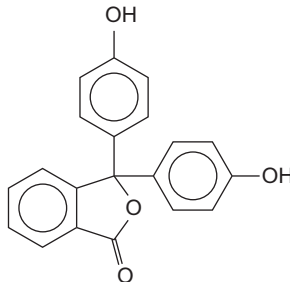
Phenolphthalein

FIGURE 1.8   pH Indicators.

FIGURE 1.9 Construction of a roller cell (schematically).

Its basic construction is shown in Figure 1.9. A more detailed view can be found in the literature (Schroeder, 1987).

In this oven, motorized rollers rotate a cylindrical cell, which contains the sample under investigation. A heating element is situated beneath the rollers, which heats the chamber to a predetermined temperature. A timer may be preset to start and end the test automatically without having an operator in constant attendance (Schroeder, 1987). The roller oven is a versatile tool to monitor ageing, and the change in properties of fluids used in the petroleum industry, as a function of temperature (Mueller et al., 2003).

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TRADENAMES

TABLE 1.13 Tradenames in References

Tradename Description	Supplier
Accolade® Drilling fluid (Bell and Shumway, 2009)	Halliburton Energy Services, Inc.
Adapta® Filtration control agent (Bell and Shumway, 2009; Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Aquagel® Sodium montmorillonite clay (Ravi et al., 2009)	Halliburton Energy Services, Inc.

TABLE 1.13 Tradenames in References–Cont'd

Tradename 　Description	Supplier
AquaPAC® 　Polyanionic cellulose 　(Melbouci and Sau, 2008)	Aqualon Corp.
BARABUF® 　Buffer (Ravi et al., 2009)	Halliburton Energy Services, Inc.
BARACARB® 　Ground marble (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
BARASIL® S 　Sodium silicate shale stabilizer 　(Ravi et al., 2009)	Halliburton Energy Services, Inc.
BARAZAN® 　Polysaccharide (Ravi et al., 2009)	Halliburton Energy Services, Inc.
BAROID® 41 　Ground barium sulfate 　(Bell and Shumway, 2009; 　Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
CELLEX 　Carboxymethyl cellulose 　(Ravi et al., 2009)	Halliburton Energy Services, Inc.
Celpol® (Series) 　Polyanionic cellulose 　(Melbouci and Sau, 2008)	Noviant, Nijmegen
Clay Sync™ 　Shale stabilizer (Maresh, 2009)	Baroid
ClaySeal® 　Shale stabilizer (Maresh, 2009)	Baroid Fluid Services
COLDTROL™ 　Fatty alcohol thinner 　(Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Disponil® 　Ether sulfonates (Emulsifyer) 　(Guichard et al., 2008)	Henkel
Driltreat™ 　Wetting agent (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
EDC95® 　*n*-Alkane cuts (Dalmazzone, 2007)	BHI

TABLE 1.13 Tradenames in References–Cont'd

Tradename Description	Supplier
EZMUD® Partially hydrolyzed polyacrylamide (Ravi et al., 2009)	Halliburton Energy Services, Inc.
FACTANT™ Concentrated emulsifier (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
FILTER-CHEK® Modified cellulose (Maresh, 2009; Ravi et al., 2009)	Halliburton Energy Services, Inc.
Geltone® (Series) Organophilic clay (Bell and Shumway, 2009; Miller, 2009; Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Grabber® Flocculant (Maresh, 2009)	Baroid
Hydro-Guard® Inhibitive water-based-fluid (Maresh, 2009)	Halliburton Energy Services, Inc.
IMPERMEX Pregelatinized cornstarch (Ravi et al., 2009)	Halliburton Energy Services, Inc.
Interdrill Emul HT® Emulgator (Dalmazzone, 2007)	Dowell Schlumberger
Interdrill® LORM Emulsification system (Dalmazzone, 2007)	Dowell Schlumberger
Invermul® Blends of oxidized tall oil and polyaminated fatty acids (Bell and Shumway, 2009; Ravi et al., 2009)	Halliburton Energy Services, Inc.
Kleemul® Emulsifier (Guichard et al., 2008)	BW Group
Kraton® Styrenic block copolymer (Guichard et al., 2008)	Shell
LE BASE™ Base drilling fluid (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
LE SUPERMUL™ Emulsifier (Bell and Shumway, 2009; Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.

TABLE 1.13 Tradenames in References–Cont'd

Tradename Description	Supplier
LIQUI-VIS Hydroxyethyl cellulose (Ravi et al., 2009)	Baroid
Lorm® Emulsifier (Dalmazzone, 2007)	Dowell Schlumberger
MICRO MATRIX® Cement (Dealy and Chatterji, 2010)	Halliburton Energy Services, Inc.
N-Dril™ HT Plus Filtration control agent (Maresh, 2009)	Baroid
PAC™ -L Filtration control agent (Maresh, 2009)	Baroid
PAC Polyanionic cellulose (Ravi et al., 2009)	Halliburton Energy Services, Inc.

PETROFREE® LV
  Ester-based invert emulsion
  (Miller and Kirsner, 2009)
	Halliburton Energy Services, Inc.

PETROFREE® SF
  Olefin-based invert emulsion
  (Miller and Kirsner, 2009)
	Halliburton Energy Services, Inc.

Plex® Acrylate resin (Guichard et al., 2008)	Rohm & Haas

Plioflex®
  Styrene butadiene rubber
  (Guichard et al., 2008)
	Goodyear Chemicals

Pliolite® DF01
  Styrene-butadiene copolymer
  (Guichard et al., 2008)
	Goodyear Tire & Rubber Co.

POLYAC® Polyacrylate (Ravi et al., 2009)	Halliburton Energy Services, Inc.
Resinoline® BD2 Tall oil fatty acid (Dalmazzone, 2007)	DRT-GRANEL

RHEMOD™ L
  Modified fatty acid
  (Bell and Shumway, 2009)
	Halliburton Energy Services, Inc.

Scotchlite™ Reflective glass (Ravi et al., 2009)	3M Comp.

TABLE 1.13 Tradenames in References–Cont'd

Tradename Description	Supplier
SF BASE™ Base drilling fluid (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Silwet® Ethyleneoxy surfactants (Patel, 2008)	O Si Specialities, Inc.
Staflo® PAC (Melbouci and Sau, 2008)	Akzo Nobel
Suspentone™ Attapulgite clay (Miller, 2009; Miller and Kirsner, 2009)	Diversity Technologies Corp.
Ultidrill® Hydrocarbon cuts (Dalmazzone, 2007)	Dowell Schlumberger
Versawet® NS Wetting agent (Patel, 2008)	M-I Drilling Fluids L.L.C.
XP07® n-Alkane cuts (Dalmazzone, 2007; Miller and Kirsner, 2009)	Baroid
X-VIS™ Suspension agent (Bell and Shumway, 2009; Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Zeogel® Attapulgite clay (Ravi et al., 2009)	Halliburton Energy Services, Inc.