DRILLING FLUIDS

1. Introduction

A range of specialty chemicals is used by the petroleum industry for oil and gas exploration, drilling and production, and for enhanced oil recovery. Broadly speaking, drilling fluids are used to lubricate the drill bit, to control formation pressure and to remove formation cuttings. Workover and completion fluids are utilized when operating in producing formations. Chemicals are used to cement steel pipes or casing to the sides of the borehole and to encourage the flow of crude oil to the well (stimulation). Chemicals find applications at all stages from oil production at the well bore continuing on to the delivery of crude oil to the refinery. During Enhanced Oil Recovery (EOR), chemicals are used for the various techniques (ie, steam, carbon dioxide, polymer and micellar-polymer flooding) that renew the oil flow from fields that have ceased to produce by conventional methods.

Drilling fluids or muds are considered an essential component of the rotary drilling process used in drilling for oil and gas on land and in offshore environments. This fluid performs a variety of functions that influence the drilling rate, and the cost, efficiency, and safety of the operation (1–7). Some of the most important functions of drilling fluids include (*1*) the transporting of the drilling cuttings to the surface (*2*) balancing subsurface and formation pressures required for the prevention of well blowouts (*3*) cooling, lubricating and supporting part of the weight of the drill and drill pipe. During the drilling of a well, the drilling fluid mud is pumped from the mud tanks down the hollow drill pipe and through nozzles in the drill bit. Typical diameter of a drill pipe is $\sim$4 in. (10 cm). The borehole at the bottom of a deep well might be 8 in. (20 cm) in diameter. The

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flowing mud sweeps the crushed rock cuttings from under the bit and carries them back up the annular space between the drill pipe and the bore hole or casing to the surface. After reaching the surface, the drilling fluid is passed through a series of vibrating screens, settling tanks or pits, hydrocyclones and centrifuges to remove the cuttings brought to the surface. It is then treated with additives to obtain a set of desired physical and chemical properties. Once treated, the fluid is pumped back into the well and the cycle repeated.

Drilling fluids generally are composed of liquids: eg, water, petroleum oils, and other organic liquids; dissolved inorganic and organic additives; and suspended, finely divided solids of various types. The chemistry of the liquid phase and the level of suspended solids determine the treatment strategy and the efficiency of the mud-handling equipment. This chemistry also influences the type and amount of materials needed to maintain or change the density, viscosity, and other properties (8). Drilling fluids are dynamic systems. These muds constantly change in response to the changing conditions while the well is being drilled and downhole temperatures and pressures increase. Occasionally, the downhole environment requires replacement of one fluid with another of a different type.

Drilling fluid costs range from several thousand to several million dollars per well and depend on the nature of the well being drilled. The length of the drilling time may vary from a few days to more than a year. On the average, ~6–8% of the total drilling cost arises directly from the drilling fluid and additives. Additional fluid and total well costs may arise from improperly formulated or treated fluids that can prolong the drilling time. Total worldwide sales of drilling fluids in 2000 has been estimated to be ~$\$2.28 \times 10^9$ (excluding Eastern Europe and China) (9). About $\$1.1 \times 10^9$ or 40% of the total was spent in North America including the United States. It has been predicted that the worldwide sales of drilling fluids will rise to $\$2.72 \times 10^9$ in 2005.

The leading three companies in the North American market that specialize in the supply of certain aggregates of chemicals, equipment, and technology used for finding oil and drilling wells are M-I L.L.C. (owned by Schlumberger and Smith Industries), Haliburton Company (which owns Baroid), and Baker Hughes Inteq (owned by Baker Hughes). These companies are commonly referred to as drilling fluid (or drilling mud) companies.

The earliest fluid used for drilling oil wells was water. Various additives controlled the loss of water to permeable formations exposed in the borehole. As early as 1901, ground-formation material and surface clays were used to impart viscosity and density in the Spindletop well drilled near Beaumont, Texas. High density solids such as hematite and barite were applied in the early 1920s to increase the drilling fluid density, prevent influx of formation fluids, and control well blowouts. Drilling fluids were commercialized ~1926.

Drilling fluid materials are also used as completion and workover fluids. When the drilling reaches the oil producing zone, the subsequent operation is referred to as completion. These fluids are formulated to enhance production rates of crude oil and minimize permeability damage to the formation while drilling through a production zone. Workover fluids are used on existing oil and gas wells with the aim of improving or maintaining current production levels and during remedial work on older wells. Some of the workover operations in oil well drilling can include sand control measures, casing repair, reperforation, and repair or replacement of subsurface equipment. Historically, water or oil-based drilling fluids have been employed as workover and completion fluids. With the increasingly difficult conditions encountered during the drilling of very deep wells, special water- or oil-based fluids are being developed to maximize hydrocarbon recovery. Workover fluids also find use in many abandoned wells that are being reworked and converted back to producing wells.

2. Classification of Drilling Fluids

Drilling fluids are classified as to the nature of the continuous phase: gas, water, oil, or synthetic. Within each classification, there are divisions based on composition or chemistry of the fluid or the dispersed phase.

2.1. Gas-Based Muds. Gas-based drilling fluids are used mostly for hard-rock drilling. These fluids range from compressed dry air or natural gas to water-based mist and stable foams. Foam is considered gas based since the gas comprises the bulk of the fluid volume. Bottomhole pressures imposed by a gas-based fluid are low, and therefore, formation strengths must be relatively high, having little or no influx or formation fluid. Air, gas, or mist drilling requires a high annular velocity to remove drill cuttings. On the other hand, large cuttings can be removed at low annular velocities when using stable foams.

Chemical additives for gas-based drilling fluids are generally biodegradable mixtures of surfactants, certain polymers, and occasionally salts such as sodium or potassium chloride. An aqueous solution of the additives is injected into the air or gas flow to generate a mist or foam. No additives are used in dry air or gas drilling operations. Gas-based fluids are not recirculated and materials are added continuously. As the fluid exits the well, air or water vapor escapes to the atmosphere, gas and oil are burned, and water and formation solids are collected into a pit for later disposal. Stable foams must be destabilized to separate the air from the liquid phase for disposal.

2.2. Water-Based Muds. The vast majority of all drilling fluids are water-based systems. The types depend on the composition of the water phase (pH, ionic content, etc), viscosity builders (clays or polymers), and rheological control agents (deflocculants or dispersants).

Freshwater fluids can range from clear water having no additives to high density muds containing clays, barite, and various organic additives. Onshore wells typically use freshwater muds, as do some offshore wells where highly weighted muds are needed. Freshwater muds may be operated at pH levels ranging from 7 to 11. When drilling using clear water, small amounts of polymeric flocculants may be added to remove drill solids in a large settling pit in order to maintain a clean fluid for fast drilling. When a viscous fluid is required, clays or water-soluble polymers are added. Freshwater is ideal for formulating stable drilling fluids as many mud additives are most effective in a system of low ionic strength. Inorganic or organic additives control the rheological behavior of the clays, particularly at elevated temperatures. An organic polymer may be used for filtration control. Mud pH is generally alkaline and, in fact, many viscosity control agents require an environment of pH >9. Sodium hydroxide is by far the most widely used alkalinity control agent. Clay-based freshwater muds can be weighted to any desired density required to control formation pressures.

Many offshore wells are drilled using a seawater system because of ready availability. Seawater muds generally are formulated and maintained in the same way that a freshwater mud is used. However, because of the presence of dissolved salts in seawater, more additives are needed to achieve the desired flow and filtration properties.

In many drilling areas both onshore and offshore, salt beds or salt domes are penetrated. Mud saturated with the salt present in the formation is used to reduce the hole enlargement that would result from salt dissolution by contact with an undersaturated liquid. In the United States, the salt formations are primarily made up of sodium chloride. In other areas, eg, northern Europe, the salt may be composed of mixed salts, predominantly magnesium and potassium chlorides. It has become quite common to use high (20–23 wt% NaCl) salt muds in wells being drilled in deep (>500-m water depth) water regions of the Gulf of Mexico. The reasons are twofold: stabilization of water-sensitive shales (10) and inhibition of the formation of gas hydrates (11).

The high salinity of salt water muds may require different clays and organic additives than those used in fresh- or seawater muds. Salt water clays and organic polymers contribute to viscosity. Filtration properties are adjusted using starch or cellulosic polymers. Alternatively, clays used primarily in fresh and seawater muds can be prehydrated in freshwater and then added to a salt mud for viscosity and some filtration control. The pH ranges from that of the makeup brine, which may be somewhat acidic, to 9–11 through use of sodium hydroxide or lime. The presence of soluble calcium or magnesium in the mud determines whether it is feasible to maintain a high pH.

Fresh- or seawater muds may be treated with gypsum or lime to alleviate drilling problems that may arise from drilling water-sensitive shale or clay-bearing formations. Gyp muds (gypsum added) are generally maintained at a pH of 9–10, whereas lime muds (lime added) are in the 12–13 pH range. Calcium-treated muds generally require more additives to control flow and filtration properties than those without gypsum or lime.

Potassium treated systems combine one or more polymers and a potassium ion source, primarily potassium chloride, in order to prevent problems associated with drilling certain water-sensitive shales (12,13). The flow and filtration properties may be quite different from those of the other water-base fluids. Potassium muds have been applied in most active drilling regions around the world. Environmental regulations in the United States have limited the use of potassium muds in offshore drilling owing to the apparent toxicity of high potassium levels in the bioassay test required by discharge permits.

Freshwater, clay, and polymers for viscosity enhancement and filtration control make up low solid/nondispersed muds. Low solids muds are maintained using minimal amounts of clay and require removal of all but modest quantities of drill solids. These are called nondispersed systems because no additives are used to further disperse or deflocculate the viscosity building clays. Most water-based muds are considered dispersed because deflocculating additives are used to control the flow properties. Nondispersed muds can be weighted to high densities, but are used primarily in the unweighted state. The main advantage of these systems is the high drilling rate that can be achieved because of the lower colloidal solids content. These are normally applied in hard formations where increasing the penetration rate can reduce drilling costs significantly and the tendency for solids buildup is minimal.

2.3. Oil-Based Muds.

Oil-based drilling fluids have diesel or mineral oil (14) as a continuous phase with both internal water and solid phases. Fluids having no or very low water content are usually called oil-base muds or all oil muds; fluids having higher water contents are called invert oil–emulsion muds, or simply inverts. Most oil muds maintain a fixed oil–water ratio depending on the desired properties. Oil muds are employed for high angle wells where good lubricity is required, for high temperature wells where water-based systems may be thermally unstable, for drilling water-sensitive shale formations, or where corrosive gases such as hydrogen sulfide and carbon dioxide may be encountered. Environmental restrictions and cost often limit use, although higher drilling rates achievable using oil muds and polycrystalline diamond compact (PDC) bits can often offset the high fluid and disposal costs.

Oil-base muds have diesel or mineral oil as the continuous phase and either are formulated using no internal aqueous phase or have only a minimal water content (15). Organophilic clay or colloidal asphalt are used to control viscosity and filtration rates. The internal water phase, either added as part of the formulation or incorporated while drilling, is stabilized using emulsifiers. The desired density is reached by adding a powdered high specific gravity solid. A wetting agent ensures oil wetting of added or drilled formation solids.

Oil-based muds that incorporate an internal brine phase as an integral part of the formulation are called inverts or invert oil–emulsion muds. The water content can be increased up to 50 vol% of the total liquid phase using the proper emulsifiers and wetting agents. Suspension properties are achieved by the addition of organophilic clays. Colloidal solids such as oil-dispersible lignite, resins, asphalt, or gilsonite impart filtration control. Increased density is achieved using standard solid materials. The internal water phase is nearly always composed of a concentrated sodium or calcium chloride brine to provide a sufficiently reduced water activity to prevent osmotic uptake of drilling fluid water into water-sensitive formations.

Oil muds are usually characterized by very low filtration rates and at one time oil muds were not considered stable if other than minimal filtration rates were observed in standard tests. This feature contributed to the low drilling rates experienced for oil muds when using rock or natural diamond bits. Relaxing the normally tight filtration control specifications on oil muds can result in higher drilling rates without loss of emulsion or mud stability (16). These relaxed fluid-loss muds also are termed low colloid oil muds or relaxed filtration oil muds because the higher filtration rates are achieved by omitting some of the colloidal solids from the formulation and reducing the concentration of emulsifiers and surfactants in the fluid. Most relaxed fluid-loss oil muds contain 5–15 vol% brine, depending on the mud density. In most other respects these fluids are similar to a conventional invert oil–emulsion mud and can easily be converted to an invert. Use of relaxed filtration oil muds has dropped considerably owing to improvements in bit design. These improvements allow high drilling rates using the more conventional low filtration-rate oil muds.

The synthetic-based muds (drilling fluids) are a relatively new class of drilling muds that are particularly useful for deepwater and deviated hole drilling. These muds were developed to provide an environmentally superior alternative to oil-based drilling muds as well as offering an alternative to the high costs associated with the disposal of drill cuttings generated when diesel or mineral oil-based muds are used. The synthetic muds have a continuous phase that consists of synthetic organic liquid (17). The synthetic-based liquids, because of their similarity with the oil-based muds, are often called pseudo-oil muds outside the United States. While the technical and economic benefits of using such fluids in the deepwater Gulf of Mexico are recognized, the environmental impacts of the discharged drill cuttings produced are not well understood. While the drill cuttings themselves are considered toxicologically inert, there is concern that any adhering drilling fluid ingredients may be toxic, particularly if the cuttings are produced during drilling with oil-based or synthetic-based fluids. The high cost for the synthetic-based fluids can be offset by the enhanced drilling performance for fast drilling achieved when using them, and the on-site discharge of the SBFs, when this is permitted. The synthetic-based fluids (SBF) introduced at the start of the 1990s may be classified into four general categories (*1*) Synthetic hydrocarbons, eg, polymerized olefins that include poly alpha olefins (PAO), linear alpha olefins (LAO), and internal olefins (IO) (*2*) ethers (*3*) esters and (*4*) acetals. During the second half of the 1990s, the groups of synthetic drilling fluids that began to achieve enhanced popularity were the LAOs, IOs, and linear paraffins (LPs), which were often referred to as second generation SBFS (18). These second generation SBFs were found to have benefits over their predecessors in that they had lower kinematic viscosities and were less expensive. The current concerns with toxicity, biodegradation rates, environmental impacts and costs have virtually eliminated the use of synthetic-based fluids except for olefins and esters in offshore drilling. The environmental aspects of the SBFs are discussed more fully in Section 7.

3. Properties

The drilling fluids are suspensions or solutions of solids in water or oil, or of solids and one of these liquids dispersed in the other. The type of drilling fluid required for a particular well is determined by the geological formation.

The functions of the drilling fluids include:

Removal of formation cuttings from beneath the bit and transporting these cuttings to the surface.
Prevention of gases in the formation from escaping through the boreholes.
Cooling and lubrication of the bit and drill string at points of contact with the cased or uncased borehole.
Prevention of the influx of formation fluids into the wellbore.
Sealing of exposed permeable formations.
Maintainenance of the stability of exposed formations.
Helping to suspend the weight of the drill string and casing.
Control of pressure.

Furthermore, the fluid should not damage productive formations, it should not be corrosive to the equipment, and it must be cost effective. The fluid must be safe for handling and be compatible with the environment or be disposable in an environmentally sound manner.

How well the drilling fluid fulfills these functions is determined primarily by the response of the well. The whole drilling operation suffers if the fluid is not adequate. In extreme cases, drilling may be stopped or a hole may have to be redrilled. A variety of physical and chemical properties are monitored to ensure satisfactory performance and guide fluid formulation and treatment (19,20).

3.1. Density. The density of the drilling fluid is adjusted using powdered high density solids or dissolved salts to provide a hydrostatic pressure against exposed formations in excess of the pressure of the formation fluids. In addition, the hydrostatic pressure of the mud/clear brine column prevents collapse of weak formations into the borehole. Fluid densities may range from that of air to >2500 kg/m^3 (20.8 lb/gal). Most drilling fluids have densities >1000 kg/m^3 (8.33 lb/gal), the density of water. The hydrostatic pressure imposed by a column of drilling fluid is expressed as follows:

$$P = 0.098\ L\rho_{\mathrm{m}}\ (= 0.052\ L\rho_{\mathrm{m}})$$

where $P =$ the hydrostatic pressure in kPa (psi); $\rho_{\mathrm{m}} =$ the drilling fluid density, kg/m^3 (lb/gal); and $L =$ the column length or well depth, m(ft). Wells with bottomhole pressures of 100 MPa (14,500 psi) at 5000 m (16,400 ft) are not unusual. Such a well would require a mud density >2040 kg/m^3 (17 lb/gal) to prevent formation-fluid influx. At least 2 MPa (290 psi) above formation pressures normally is recommended to ensure well control. Bottomhole pressures imposed by the mud/clear brine column that are higher than necessary can reduce drilling rates and induce fractures in exposed formations, allowing loss of drilling fluid to the fractures (lost circulation). Operational safety can be adversely affected if lost circulation occurs.

3.2. Flow Properties. The fluid viscosity and annular flow velocity must be high enough to remove cuttings generated by the drill bit and other formation material that may fall into the wellbore. These solids are carried up the annulus to the surface where they are separated with varying degrees of efficiency and then disposed of. In order to accomplish this, low viscosity drilling fluids are circulated at high flow rates or high viscosity fluids at low flow rates. In addition, for maximum drilling rate, a low effective viscosity is desired at shear rates generated through the bit nozzles (10,000−100,000/s). The varying demands on the flow properties are best met by fluids exhibiting non-Newtonian rheological characteristics. Drilling fluids are normally shear thinning, having apparent viscosity decreasing with increasing shear rate.

The gel strength (thixotropy) is a measure of the capability of a drilling fluid to hold particles in suspension after the mud circulation ceases. It results from the electrical charges on the individual clay platelets. The positively charged edges of a platelet are attracted to the negatively charged flat surfaces of adjacent platelets. In a bentonite mud in which the particles are completely dispersed, the bonds between particles are broken while the mud is flowing. When the mud pump is shut off and flow ceases, the attraction between the clay particles causes the platelets to bond to each (referred to as flocculation). This edge-to-face flocculation results in an open card-house structure capable of suspending cuttings and sand and gravel particles. This property also suspends finely ground, high specific gravity material such as barite when high-density muds are required. The ability to keep cuttings in suspension prevents sandlocking (sticking) of the tools in the borehole while drill rods are added to the string and minimizes sediment collecting in the bottom of the hole after reaming and before going back in the hole with a sampler. A drawback to this property is that cuttings do not readily settle out of the drilling mud in the mud pit and may be recirculated, thus resulting in grinding of particles by the drill bit, increased mud density, increased mud pump wear, and lower penetration rate. Thixotropic properties characterized by a gel strength provide suspension of solids when mud/clear brine circulation stops. The rheological properties are adjusted using inorganic and organic additives to achieve the capacity to carry cuttings and generate adequate bit hydraulic horsepower for fast drilling at moderate flow rates. The high flow rates required to remove drill cuttings using low viscosity muds and in high angle wells can increase pump maintenance and induce fracturing and lost circulation because of excessive bottomhole pressures.

3.3. Filtration Properties. Drilling fluids have a natural tendency to flow into permeable formations because the borehole pressure is generally higher than that in the formation. To prevent excessive leak-off, a thin, low permeability filter cake is formed using additives. Filtration occurs under both dynamic (during circulation) and static (no circulation) conditions. Additives may affect each of these filtration conditions differently. The filtration rate is adjusted using colloidal solids and organic polymers to reduce loss of filtrate to the formation and prevent buildup of a thick filter cake which would restrict the wellbore. Excessive decrease of the filtration rate can be costly and may result in a viscous fluid that may affect the drilling rate adversely.

Large solid particles of various sizes and shapes may be added to control circulation loss where natural or induced fractures, highly porous formations, or vugular zones, ie, formations containing small cavities (vugs) larger than the matrix grain size, are encountered. Particle sizes from those large enough to bridge the opening down to those fine enough to seal small spaces between the larger bridging particles may be required to prevent drilling fluid losses into these zones.

3.4. Water Chemistry. Water is present in all but purely gaseous or oil drilling fluids, both of which comprise only a small percentage of drilling fluid applications. The water may be present as fine droplets in a mist, emulsified in an organic continuous phase, or as is most common, comprise the continuous phase of the drilling fluid. Water added to drilling fluids may be fresh water, seawater, or saturated salt solutions. The salt in the last is normally sodium chloride, but may be another halide or alkali or alkaline-earth salt. The nature of the dissolved salts affects colloidal clays and other additives and thus must be monitored together with properties such as salinity, total hardness (calcium plus magnesium), pH, and alkalinity. Drilling fluids are nearly always basic with a pH in the range of 6–13, depending on the type of system used. Concentrations of soluble carbonates, sulfide, sulfite, etc, may also be determined. These ions may be added intentionally or incorporated during drilling.

4. Drilling Fluid Materials

The pressure exerted by the column of drilling fluid in the well balances formation pressures to prevent uncontrolled influx of formation fluids that may result in a blowout. The mud density must be controlled accurately by suitable weighting materials that do not adversely affect the other properties. Most important is the specific gravity of the weighting agent as well as its insolubility in water and its chemical inertness. The weighting material should be ground to the preferred particle-size distribution and be relatively nonabrasive. Various finely ground, solid weighting materials that have found application in drilling are listed in Table 1. As of 1995, little weighting material other than barite was used in the United States.

Barite, which is predominately composed of $BaSO_4$, meets the overall requirements for weighting material better than other materials and is used for increasing the density of drilling fluids throughout the world. Barite in its pure form has a density of 4500 kg/m^3. Commercial barite has a lower specific gravity than pure barium sulfate owing to the presence of associated minerals, such as silica. Barite is virtually insoluble in water and does not react with other

Table 1. **Solid Materials Used to Increase Density of Drilling Muds**

Material	CAS Registry number	Formula	Specific gravity	Hardness, Mohs'	Characteristics	Advantages
barite	[13462-38-2]	$BaSO_4$	4.5[a], 4.2[b]	2.5–3.5	white gray-red	readily available; low cost
hematite	[1317-60-8]	Fe_2O_3	4.9–5.3	5.5–6.5	iron oxide, impurities; black to red depending on particle size	low attrition rate; API high density
magnetite	[1309-38-2]	Fe_3O_4	5.0–5.2	5.5–6.5	iron ore, often Ti and Mg; black ore	high density; HCl soluble; scavenges H_2S
siderite	[14476-16-5]	$FeCO_3$	3.7–3.9	3.5–4	spathic iron ore; various colors	acid soluble
dolomite	[16389-88-1]	$CaCO_3 \cdot MgCO_3$	2.8–2.9	3.5–4	carbonate of Mg, Ca	acid soluble
calcite	[13397-26-7]	$CaCO_3$	2.6–2.8	3	limestone, occurs in sedimentary rock	highly acid soluble, range of particle sizes
sodium chloride	[7647-14-5]	NaCl	2.165	2	cubic structure,	water soluble, used as bridging solids

[a] Value is for pure material.

[b] Value for API grade.

Table 2. **API Specifications for Barite and Hematite**

Assay	Barite[a]	Hematite[b]
specific gravity[c]	4.20	5.05
wet-screen analysis, % residue[d]		
>75 μm	3.0	1.5
>45 μm		15
particles, < 6μm, %[d]	30	15
soluble alkaline-earth metals as calcium, mg/kg[d]	250	100

[a] Test equipment and procedures from Ref. 21.
[b] Test equipment and procedures from Ref. 22.
[c] Value given is minimum.
[d] Values given are maximum.

mud constituents. Most operators prefer barite that meets API specifications (Table 2) (21). The barite content in mud depends on the desired density but it can be as high as 2000 kg/km^3 (700 lb/bbl).

Drilling technology favors systems having the lowest possible solids content because of the resulting higher penetration rate, easier control of mud properties, and fewer problems experienced during drilling. Alternative weighting materials having specific gravities higher than that of barite offer this advantage. The only other high specific gravity material that is used to any degree as of 1995 is hematite (iron oxide).

The specifications for drilling fluid hematite have been set by the API and are listed in Table 2 (22). Hematite is used most frequently in high density oil-based muds to minimize the total volume percent solids (23). The abrasivity of hematite limits its utility in water-based muds.

Calcite and siderite (24) are used occasionally because of their solubility in hydrochloric acid, which offers a method of removing mud filter cake deposited on productive formations. The calcite (calcium carbonate) is supplied in the form of ground marble, with the particle size adjusted to the porosity of the reservoir, Calcite and siderite are used most frequently in workover or completion fluids when a nondamaging fluid is required, ie, one that can be removed by acidizing at a later time.

Solid salt, ground and packaged in several particle size grades, can be used in saturated salt brines to increase the fluid density (25). However, sized salt is also as a weighting agent, having specific use in sensitive reservoirs. In such cases, an oversaturated solution is used to form a filter cake that can easily be removed with fresh water flushing. This nondamaging has found increasing use since the early 1990s. At one time the sized salt systems were used primarily for completion or workover operations, but use has also increased as in drill-in fluids for horizontal wells (26).

The use of solids-free fluids or clear brine fluids (CBF) is occasionally resorted to for achieving high drilling rates, and also in workover and completion operations, for avoiding damage arising from particulate invasion of the productive formations. Clear brine fluids and their additives are discussed more extensively in the Section 5, Completion and Workover Fluids.

The chemical and mechanical dispersion of the drilled solids tends to increase the percentage of small-sized solids in a mud as drilling progresses.

The incorporation of a limited amount of drilled solids (several volume percent) is an economical way of increasing the density of low density muds, but it also reduces penetration rates; hence, drilled solids are usually kept to a minimum. The common clay and formation solids and their specific gravities encountered in normal drilling operations are as follows: dolomite (2.8–3.2), limestone (2.8–3.0), feldspar (2.6–2.7), sandstone (2.3–2.6), clay (2.3–2.6), bentonite (2.3–2.4), salt (2.16) cement (1.6–2.0), and coal (1.35). The cement is encountered when drilling a cement plug or out of new casing.

4.1. Viscosity Buildup. The drilling fluid removes cuttings from the wellbore as drilling progresses. This process is governed by the angle of the hole and the velocity at which fluid travels up the annulus, as well as by the fluid viscosity or flow properties, and fluid density. The cuttings removal efficiency usually increases with increasing viscosity and density, although at high wellbore angles a less viscous fluid may be desirable provided high flow rates can be achieved. Viscosity depends on the concentration, quality, and state of dispersion of suspended colloidal solids.

Although numerous mud additives aid in obtaining the desired drilling fluid properties, water-based muds have three basic components: water, reactive solids, and inert solids. The water forming the continuous phase may be freshwater, seawater, or saltwater. The reactive solids are composed of commercial clays, incorporated hydratable clays and shales from drilled formations, and polymeric materials, which may be suspended or dissolved in the water phase. Solids, such as barite and hematite, are chemically inactive in most mud systems. Oil and synthetic muds contain, in addition, an organic liquid as the continuous phase plus water as the discontinuous phase.

The most important commercial clays used for increasing the viscosity of drilling fluids are bentonite [1302-78-9], attapulgite [1337-76-4], and sepiolite [15501-74-3]. For oil-base and synthetic-base muds, organophilic clays are used. These clays produce viscosity and help suspend weighting materials. The active ingredient in bentonite is a smectite, montmorillonite [1318-93-0], an expandable 2:1 aluminosilicate mineral, having a three-layer plate-shaped crystalline structure. The three-layer sheets or platelets consist of a middle octahedral alumina layer and two outer tetrahedral silica layers. Because of lattice defects in the alumina, and less often in the silica layers, the flat planar surfaces are negatively charged and have associated cations (primarily sodium and calcium) to achieve electroneutrality. Bentonite hydrates in the presence of freshwater and disperses to varying degrees, depending on the nature of the cations that are loosely held and exchangeable. Hydration and dispersion are enhanced by the presence of sodium ions in the exchange or planar surface positions. Divalent cations such as calcium reduce the degree to which the individual platelets disperse. As hydration of bentonite proceeds in freshwater, the individual platelets separate and eventually form a stable colloidal dispersion that is stabilized by electrical interactions between clay platelets (27). This colloidal system has highly non-Newtonian rheological properties and the suspending and shear-thinning characteristics desired in a drilling fluid. The hydration and dispersion of bentonite clay, and thus the viscosity of the final system, can be altered considerably by the presence of electrolytes in the water, exchange reactions that convert the clay from a high swelling form (sodium) to a low swelling form (such as calcium), or

Table 3. **API Specifications for Bentonite Clay**[a]

Assay	Bentonite	Nontreated bentonite	OCMA bentonite
bentonite content in 350 cm^3 water, g	22.5	25.0	22.5
suspension properties			
viscometer dial reading at 600 rpm[b]	30	10[c]	30
yield point/plastic velocity ratio[d]	3	1.5	6
filtrate volume[d], cm^3	15.0	12.5	16.0
residue, % >75μm[d]	4.0		2.5
moisture, %[d]	10.0		13.0

[a] Test equipment 1 and procedures from Ref. 28.

[b] Value given is minimum.

[c] Value is dispersed plastic viscosity in mPa·s(= cP).

[d] Value given is maximum.

adsorption of polyelectrolytes which prevent separation of the clay platelets. Bentonite concentrations in drilling fluids vary widely, but may range up to 100 kg/m^3 (35 lb/bbl). Specifications for the three grades of drilling fluid bentonite recognized by the API are listed in Table 3 (28). The higher performance grades are produced mainly in the Wyoming–Montana–South Dakota area. This bentonite contains montmorillonite clay in both sodium and calcium forms. The sodium form predominates. Most such bentonites are processed using a small amount of a peptizing polymer to enhance the viscosity building properties of the clay. This is the standard API bentonite. High quality bentonite that is not treated in any way to enhance its viscosity building characteristics is sold as API nontreated bentonite.

Fast-yielding bentonite treated with high molecular weight polyacrylamide and polyacrylate polymers is also available commercially. It produces roughly the same viscosity as twice the amount of untreated bentonite. Additions of small amounts of certain polyacrylamides, called bentonite extenders, to a freshwater mud containing bentonite give the same effect. Drilling fluids formulated with bentonite and an extending polymer in this manner are called low solids, nondispersed muds (29).

Another bentonite extender, which also enhances the viscosity of attapulgite slurries, is a mixed metal (magnesium and aluminum) layered hydroxide [7732-18-5], usually called MMH (30). This material is most frequently used to increase the viscosity sufficiently so that metal cuttings can be removed from the well during milling operations. MMH-treated muds are also finding application in horizontal wells. A mixed metal (calcium, magnesium, and aluminum) silicate [1327-39-5] (MMS), is being applied in a similar way.

When the water phase of the drilling fluid contains substantial amounts of electrolyte, saltwater clays such as attapulgite and sepiolite are added to raise viscosity. Attapulgite is used solely for its suspending qualities. It has a fibrous texture and crystalline, needle-like, hydrated magnesium silicate particles. Attapulgite clays increase viscosity regardless of the composition of the makeup water. This ability does not depend on hydration, but rather on the extent to which the bundles of needles are broken up by a shearing force.

Table 4. **Properties of Attapulgite and Sepiolite**

Assay	Value
clay concentration in 350 cm^3 saturated salt water, g	20
minimum viscometer dial reading at 600 rpm	30
maximum residue, %>75 µm	8.0
maximum moisture, %	16.0

Sepiolite is a hydrated magnesium silicate that contains less substituted aluminum than attapulgite, which it closely resembles. Sepiolite occurs in fibrous and elongated lath-like particles. It is more stable at higher temperatures than attapulgite (31,32) and therefore is used in geothermal drilling fluids. The properties of attapulgite and sepiolite specified by the API for drilling fluid use are given in Table 4 (33).

Oil-dispersible or organophilic clay provides viscosity and suspending qualities in oil-based muds. It is prepared from bentonite, hectorite [12173-47-6], or attapulgite and aliphatic amine salts. The products obtained from amines having 12 or more straight-chain carbon atoms swell and form gels in hydrocarbon fluids (34–36). The amino groups replace the sodium and calcium originally present on the clay surface. Oil-dispersible clays can suspend solids in oil without requiring additional soaps and emulsifying agents. Addition levels of organophilic clays are ~3–11 kg/m^3 (1–4 lb/bbl) in diesel oil muds and ~8–23 kg/m^3 (3–8 lb/bbl) in mineral oil and synthetic-base muds.

A wide variety of organic polymers serve a number of useful purposes in drilling fluids, the most important of which are to increase viscosity and control filtration rates (Table 5). These polymers are either natural polysaccharides, eg, starch [9005-25-8], guar gum, xanthan gum [11138-66-2], and other biopolymers; or derivatives of natural polymers, eg, cellulose, lignosulfonate, and lignite and synthetic polymers, eg, polymers and copolymers of acrylic acid, acrylonitrile, acrylamide, and 2-acrylamido-2-methylpropanesulfonic acid (AMPS). The most commonly used polymeric viscosity builders are the cellulosics, xanthan gum, and polyacrylamides.

Sodium carboxymethyl cellulose [9004-32-4] (CMC) and hydroxyethyl cellulose [9004-62-0] (HEC) are the cellulosics most widely used in drilling fluids (37). CMC is manufactured by carboxymethylation of cellulose, which changes the water-insoluble cellulose into the water-soluble CMC (38). Hydroxyethyl cellulose and carboxymethyl hydroxyethyl cellulose (CMHEC) are made by a similar process. The viscosity grade of the material is determined by the degree of substitution and the molecular weight of the finished product.

The effectiveness of sodium carboxymethyl cellulose, an anionic polymer, as a viscosity builder decreases with increasing electrolyte concentration. This polymer can be coprecipitated with calcium and magnesium by raising the pH of the mud. The polyanionic cellulose (PAC), which has a higher degree of substitution than CMC, was introduced to overcome some of these limitations (37). CMC and PAC are available in several viscosity and purity grades. API specifications for high viscosity, technical-grade CMC for use as a viscosity builder are listed in Table 6 (39). The primary application of both CMC and PAC is in the control of filtration rates.

Table 5. **Polymers Used in Water-Based Drilling Fluids**

Polymer	Chemical description	Ionic state	Thermal degradation, °C	application	limitations
		Fermentable			
starch	polysaccharide: amylose, amylopectin	nonionic	110	filtration	fermentable at low pH and salinity
xanthan gum	microbial polysaccharide	anionic	140	viscosity builder	poor yield in calcium brines
hydroxypropyl guar	polysaccharide: galactose, mannose	nonionic	95	viscosity builder	low temperature stability
		Unfermentable			
CMC/PAC	sodium carboxy-methyl cellulose	anionic	140	filtration control, viscosity builder	sensitive to salinity, multivalent ions
HEC	hydroxyethyl cellulose	nonionic	110	viscosity builder, acid degradable	primarily for completion/ workover fluids
polyacrylates, polyamides	sodium polyacrylate, polyacrylamide, polyacrylic acid-*co*-acrylamide	mixed	200	dispersant, filtration control, viscosity builder, shale stabilizer	poor performance in presence of multivalent ions
lignosulfonate	sulfonated lignin, cations vary but are often Cr	anionic	175	deflocculant, filtration control	requires alkaline conditions, may contain heavy metals
tannin	quebracho sulfomethylated	anionic	200	deflocculant	wide pH range
lignite	leonardite	anionic	205+	filtration control, deflocculant	requires alkaline conditions, sensitive to salinity and alkaline conditions

Hydroxyethyl cellulose (HEC), a nonionic thickening agent, is prepared from alkali cellulose and ethylene oxide in the presence of isopropyl alcohol (40). HEC is used in drilling muds, but more commonly in completion fluids where its acid-degradable nature is advantageous. Magnesium oxide stabilizes the viscosity-building action of HEC in salt brines up to 135°C (41).

Xanthan gum is a high molecular weight microbial polysaccharide produced by the bacterium Xanthomonas campestris (42). Commercially, xanthan gum is produced by a fermentation process and precipitation of the gum in alcohol. It is

Table 6. **API Specifications for Technical-Grade High Viscosity CMC**[a]

Solvent system	CMC concentration, g/350 cm^3	Minimum viscometer dial reading at 600 rpm	Maximum filtrate volume, cm^3
distilled water	2.20	30	
40 g/L salt water	2.70	30	
saturated salt water	2.50	30	
slurry[b]	3.15		10

[a] Test equipment and procedures from Ref. 39.

[b] Slurry contains 35 g of API Standard Evaluation Base Clay per 350-cm^3 saturated salt solution.

a viscosity builder and suspending agent and can be used in almost any type of water (43). Although xanthan gum solutions support bacterial growth, a preservative is usually not needed unless the solution is to be stored. Because of suspending ability at low concentrations and in electrolyte solutions, xanthan gum is widely used for drilling, workover, and completion fluids. Two other biopolymers, succinoglucan gum [39464-87-4] (44) and welan gum [96949-22-3] (42,45), are also finding some use in drilling fluids at concentrations similar to xanthan gum.

Guar gum is a nonionic, branched-chain polysaccharide, a galactomannan that is usually hydroxypropylated for use in drilling (46). It produces viscous solutions in fresh or saltwater at concentrations of ~3–6 kg/m^3 (1–2 lb/bbl). It is used in solids-free and low solids muds and degrades rapidly above 80°C, limiting its use to shallow wells.

High molecular weight polyacrylamides are used as viscosity builders in freshwater muds (47) or as bentonite extenders. The ionic nature of the polyacrylamide may range from nonionic to anionic (30% hydrolyzed) depending on the situation.

Occasionally polymers are used to increase the viscosity of oil-base and synthetic-base muds. The polymers for this use are typically sulfonated polystyrenes or ethylene–propylene terpolymers (EPDM) (48,49). Such polymers are usually used in conjunction with an organophilic clay.

4.2. Viscosity Reduction. Proper control of viscosity and gel strengths is essential for efficient cleaning of the borehole, suspension of weight material and cuttings when circulation is interrupted, and to minimize circulating pressure losses and swab/surge pressures owing to axial movement of the drill string. Viscosity may be increased as previously indicated, but there is often the necessity of reducing the viscosity. A reduced viscosity can be achieved by thinning or deflocculating clay–water suspensions. Thinning is measured as a reduction of plastic viscosity, yield point, or gel strength, or a combination of these properties. Viscosity is reduced by decreasing the solids content and the number of particles per unit volume, or by neutralizing the attractive forces between particles. Although mud thinners or viscosity-reducing chemicals are added to reduce flow resistance and gel development, reduction of filtration rates and filter cake thickness and stabilization of mud properties at elevated temperatures often results. Typical mud-thinning chemicals are polyanionic materials that are adsorbed on positive edge sites of the clay particles, thereby reducing the attractive forces between the particles without affecting clay hydration (27,50).

Table 7. **Phosphate Drilling Mud Thinners**

Compound	CAS Registry number	Molecular formula	pH of aqueous solution	Observations
sodium acid pyrophosphate (SAPP)	[7758-16-9]	$Na_2H_2P_2O_7$	~4.2	for cement determination
sodium tetraphosphate	[7727-67-5]	$Na_6P_4O_{13}$	~7.5	generally preferred
tetrasodium pyrophosphate (TSPP)	[7722-88-5]	$Na_4P_2O_7$	~10	
sodium hexametaphosphate	[10124-56-8]	$(NaPO_3)_6$	~7	glassy material

Thinners or deflocculants for clay–water muds include polyphosphates, tannins, lignites, lignosulfonates, and low molecular weight polyacrylates and their derivatives. These materials also can remove chemical contaminants by precipitation or chelation. Sodium polyphosphates are effective deflocculants for clays in freshwater and were among the first thinners used in drilling fluids (51). The reversion of the polyphosphates to orthophosphates occurs rapidly as the temperature approaches 95°C and may cause thickening of the mud. Table 7 gives the four most commonly used phosphates. The application of polyphosphates is limited to temperatures <80°C, and supplemental control along with organic thinners.

Tannins occur in many plants and are separated by extraction. Quebracho extract is an acidic mud thinner and performs best at high pH. It is an excellent thinner for lime-treated and cement-contaminated muds. However, it is not effective at high salt concentrations. Sulfomethylated tannin products are functional over a wide range of pH and salinity and have either been treated with chromium for good thermal stability (52) or are chrome free.

Lignite, generally leonardite, and lignite derivatives are applied in water-based muds as thinners and filtration control agents. Leonardite is an oxidized lignite having a high content of humic acids, which may be described as carboxylated phenolic polymers (53,54).

Natural lignite is not a good thinner for low pH water-based muds at moderate temperatures, but can be an excellent thinner or mud conditioner at high pH and high temperatures where the humic acids are solubilized. It has better temperature stability than most plant tannins or lignins. The performance of lignite can be greatly improved by solubilizing processes such as caustic treatment, sulfonation, sulfomethylation, or chelation with heavy metals.

Lignosulfonate thinners are among the most versatile and important chemicals used in water-based drilling fluids, and are the largest volume additives used in this category worldwide. Lignosulfonates are by-products of the sulfite process for separating cellulose pulp from wood. These can be described as polyanionic natural polymers. Their mud-thinning quality depends on the source of the lignin, degree of sulfonation, molecular weight distribution, impurities, and the amount and type of chelated heavy metals (55). Commercial chrome lignosulfonate [9066-50-6] contains up to ~3.5–4.5 weight% trivalent chromium. The chrome-free lignosulfonates may not be as effective overall as those containing trivalent chromium, but they are useful where chromium is undesrable for environmental reasons. In fact, the chrome-based lignosulfonates have been banned in many European countries due to their toxicity. Other cations associated with the lignosulfonate molecule include sodium, potassium, calcium, and titanium–zirconium (56).

Chrome and ferrochrome lignosulfonates are effective deflocculants in most water-based muds over a wide range of salinity, hardness, and pH (8.5–12.5). Lignosulfonates at high concentrations provide some filtration control and inhibit disintegration and dispersion of shale cuttings. Thinning effectiveness declines at 120–150°C, although field experience confirms that muds containing chrome lignosulfonate can be used at bottomhole temperatures of $>175°C$. The effectiveness of lignosulfonates at high temperatures depends on the solids content and the type and concentration of electrolytes. Low molecular weight (1000–5000) polyacrylates and copolymers of acrylic acid and AMPS are used as dispersants for weighted water-base muds (57). These materials, 40–50% of which is the active polymer, are usually provided in a liquid form. They are particularly useful where high temperatures are encountered or in muds, which derive most of their viscosity from fine drill solids, and polymers such as xanthan gum and polyacrylamide. Another high temperature polymer, a sulfonated styrene maleic–anhydride copolymer, is provided in powdered form (58,59). All of these materials are used in relatively low concentrations in the mud.

A hydrolyzed cereal solid, predominately a hexasaccharide, is used in high pH lime muds for reducing the yield point and gel strength (60). This additive has been used in systems treated with both sodium hydroxide and potassium hydroxide in addition to other additives common to lime muds (61). A second viscosity-reducing additive used in lime muds is a graft copolymer of acrylic acid and calcium lignosulfonate (62).

Filtration control is particularly important in permeable formations where the mud hydrostatic pressure exceeds the formation pressure. Proper filtration control reduces drill-string sticking and drag, and rotary torque, as well as minimizing damage to protective formations; in some formations it improves borehole stability. Several types of materials are available for water-based muds and application varies according to the type and the chemical environment of the mud. These include clays, organic polymers, and lignite derivatives. The bentonite present in the system often acts as the primary filtration control agent. It not only develops viscosity, but also lowers the filtration rate, particularly in freshwater muds. The ability of bentonite clay to control filtration is attributed to the flat, plate-like particle shape, the capacity to disperse and hydrate, the ability to form a compressible filter cake, and the colloidal to near-colloidal particle size.

Hydrating bentonite in freshwater before adding it to the mud greatly increases its efficiency when the makeup water is contaminated with salt and/or hardness. Prehydrated bentonite can be protected from dehydration by lignosulfonate or sulfomethylated tannin when used in saturated saltwater. Saltwater clays, such as sepiolite and attapulgite, provide no filtration control and are normally used with suitable filtration control agents.

Although a combination of bentonite clay and an organic thinner provides filtration control in many water-based muds, additional control generally is needed. Filtration additives for both fresh- and saltwater muds are usually organic polymers and lignites (see Table 5). Cost and viscosity-building characteristics should be considered, particularly in weighted high solids muds.

Starches, used first in the late 1930s for filtration control, are still in use in the 1990s. Cornstarch is most commonly used in the United States. Potato starch is also used in the United States but primarily in Europe and elsewhere. Both corn and potato starches are pregelatinized before dispersion in water (63). The API specifications for drilling fluid starch are listed in Ref. 64.

Starch is subject to fermentation by many microorganisms and, unless the mud is saturated with salt or the pH is ≥ 11.5, a preservative or biocide must be added if the mud is to be used for an extended period of time. The most common biocide until the mid-1980s was paraformaldehyde [9002-81-7]. This material has been largely replaced by isothiazolones (at 5–10 ppm conc) (65), carbamates, and glutaraldehyde [111-30-8]. Alternatively, the biocide may be incorporated during the processing of the starch and is present in the commercial product.

Starch is degraded by heat and agitation. Under continued circulation at $\geq 95°C$, starch can breakdown rapidly. Its performance also is affected by pH changes in the presence of calcium and magnesium ions. Starch coprecipitates with calcium when caustic soda is added to mud containing dissolved calcium salts. Starch molecules are hydrolyzed at very low or high pH in the presence of calcium and magnesium $>110°C$. An acidic environment also may prevent hydration and thus limit the effectiveness of starch as a filtration control agent.

Numerous modifications and derivatives of starch have been made for application in drilling and workover fluids (66). Most modified starches are cross-linked to some degree to improve thermal stability. Carboxymethyl and hydroxypropyl starches are finding increasing application in drilling fluids. There are some applications involving cationic starches as well, although toxicity must be considered for offshore use.

Carboxymethyl cellulose (CMC) and polyanionic cellulose (PAC) are available in several viscosity grades and high and low purity grades. All grades can be effective filtration control agents depending on the well conditions. The effectiveness of CMC in reducing filtration decreases with increasing salt concentration. A polyanionic cellulose (PAC) polymer is available that is designed particularly for application in muds of high salt concentration (37,67). Most CMC and PAC materials are sodium salts but there are also potassium versions to take advantage of the shale stabilizing properties of this ion (68). While not designed to control filtration, HEC may be effective as a filtration control agent in combination with other organic polymers in waters having salinities up to saturation.

Acrylate and acrylamide polymers have several uses in drilling fluids, one of which is for filtration control. Sodium polyacrylates [9003-04-7] having molecular weights near 250,000 are excellent temperature-stable filtration control agents for both fresh- and saltwater muds, provided the concentration of water-soluble calcium is <400 mg/L (69). The calcium ions are precipitated using a carbonate such as soda ash, before adding the polyacrylate.

Lignite products, mined, ground, and possibly treated with sodium or potassium hydroxide, are economical filtration control additives for some water-based muds, in addition to improving flow properties (70). A sulfonated lignite complexed with a sulfonated phenolic resin is an effective high temperature, filtration control additive, for both fresh- and seawater muds that contain high concentrations of soluble calcium, and does not affect viscosity (71,72). A high molecular weight polyanionic lignin has also found application for high temperature muds with a high electrolyte content (73). These and similar products can provide filtration control for high density, high solids muds above 120°C.

A number of synthetic polymers having the ability to control filtration rates at high temperature and in the presence of calcium and magnesium have also been developed (74). Such materials include vinyl sulfonate–vinyl amide copolymers (75,76), a copolymer of AMPS and *N*,*N*-dialkyl (meth) acrylamide (77) and a sulfonated hydroxylated polymer (78).

Filtration control in oil- and synthetic-base fluids is achieved by the emulsified aqueous phase, by the emulsifier package, and by additions of powdered solid materials. The powdered solids used for this purpose consist of asphalt [8052-42-4], gilsonite [12002-43-6], and amine-treated lignite. The choice of additive depends on the nature of the base fluid, the emulsifier package, and most importantly the downhole temperature. Styrene–butadiene copolymers in the form of aqueous dispersions have also found application as filtration control agents in oil-base muds.

Cellulosic fibers, powdered limestone, gilsonite, and asphalt are frequently added to both water and oil muds at levels of 10–25 kg/m^3 (4–10 lb/bbl) when high differential pressures are encountered to control seepage losses to the formation. This treatment also is used to improve the quality of the mud filter cake to reduce the chance of differential pressure sticking.

4.3. Alkalinity Control. Water-base drilling fluids are generally maintained at an alkaline pH. Most mud additives require a basic environment to function properly and corrosion is reduced at elevated pH. The primary additive for pH control is sodium hydroxide [1310-73-2].

The second most common alkalinity control agent is lime [1305-78-8], normally in the form of calcium hydroxide [1305-62-0], used in both water and oil muds. In the latter, the lime reacts with added emulsifiers and fatty acids to stabilize water-in-oil emulsions. Lime is used in brine systems containing substantial quantities of soluble calcium and in high pH lime muds.

Potassium hydroxide [1310-58-3] is occasionally used for alkalinity control. This is particularly true for some polymer and lime muds where a low sodium level is desired. The potassium level of such muds is quite low but has been attributed by some to provide stability to water-sensitive shale formations (61,79).

A fourth alkalinity control additive is magnesium oxide [1309-48-4], which is used in clay-free polymer-base fluids (41). Magnesium oxide provides an alkaline environment and, as it is only slightly soluble, also has a buffering effect. It enhances the thermal stability of polymer solutions by preventing a pH decrease to neutral or slightly acidic conditions at elevated temperatures. It is mainly applied in completion or workover operations where clay-free acid-soluble fluids are desired. There are occasions where the mud pH must be lowered such as after drilling fresh cement or overtreatment by one of the alkaline materials discussed. Organic acids that have been used for this purpose include acetic acid [64-19-7], citric acid [77-92-9], and oxalic acid [144-62-7], but these materials have been employed only infrequently. Inorganic additives used to lower pH levels include sodium bicarbonate [144-55-8] and sodium acid pyrophosphate [7758-16-9] (SAPP). Of the two, sodium bicarbonate is used the most by far.

4.4. Removal of Contaminants. A drilling fluid contaminant is any material or condition encountered during drilling operations that adversely affects the performance of the fluid. Elevated temperatures and drill solids are encountered in every drilling operation. In most wells these are handled easily, but in some wells one or both can seriously reduce drilling efficiency. Temperature problems normally are treated by using viscosity or filtration control additives, materials having better thermal stability, or possibly by replacement of the mud system with an oil or synthetic mud. Drill solids are removed mechanically by various combinations of screens, hydrocyclones, and centrifuges, or chemically by flocculants. Dilution or replacement of part or all of the mud system may reduce drill solids to tolerable levels.

Various inorganic chemicals remove soluble contaminants encountered during drilling. Salt, NaCl, is a common contaminant that can be removed only by dilution. The adverse effects of salt, primarily clay flocculation, can be overcome by a deflocculant such as a lignosulfonate or sulfomethylated tannin. Soluble calcium from cement, gypsum, or anhydrite is frequently encountered and has a flocculating effect on drilling clays. Calcium is removed using a phosphate, sodium carbonate [497-19-8], sodium bicarbonate (particularly in the case of cement contamination), and occasionally oxalic acid.

If calcium problems persist, the mud may be converted to a calcium-based system by adding a calcium source, such as gypsum [13397-24-5] or lime. Gypsum and lime are also used to control bicarbonate/carbonate ions that can cause mud gelation and rheological problems, particularly in high density muds in deep, hot wells (80). Sources of carbonate include carbon dioxide bearing zones and soluble carbonate formations. Carbon dioxide is also generated by some mud additives and by excessive treatment for removal of calcium.

4.5. Stabilization of Water-Sensitive Formations. Many subsurface formations encountered during drilling are water-sensitive shales containing various amounts of clay minerals. The clay mineral components may include a highly swelling smectite or less water-sensitive illite, mixed-layer smectite–illite, kaolinite, or chlorite. All shales appear to swell to some extent when contacted by fresh water. Those containing smectite or mixed layer clays are much more sensitive than illitic shales. The uptake of water by shales has two effects: a volume change owing to swelling, and a strength reduction as the water content increases. This may result in flow of plastic shale into the wellbore, softening and erosion of the exposed shale, or spalling of hard shale, all of which can cause expensive operational problems. In the latter case, large hard pieces of formation fall around the drill string, the removal of which may become difficult.

A variety of methods have been devised to stabilize shales. The most successful method uses an oil or synthetic mud that avoids direct contact between the shale and the emulsified water. However, preventing direct contact does not prevent water uptake by the shale, because the organic phase forms a semipermeable membrane on the surface of the wellbore between the emulsified water in the mud and the water in the shale. Depending on the activity of the water, it can be drawn into the shale (activity lower in the shale) or into the mud (activity higher in the shale) (81–83). This osmotic effect is favorable when water is drawn out of the shale; thus the aqueous phase of the oil or synthetic mud is maintained at a low water activity by adding a salt, either sodium chloride or more commonly, calcium chloride. The salt concentration is carried somewhat above the concentration required to balance the water activity in the shale to ensure water movement into the mud.

High initial cost and environmental restrictions prevent use of oil and synthetic muds in many cases where shale problems are expected. It is necessary then to treat a water-base mud to minimize the destabilizing effect of the drilling fluid. Salts, polymers, and other organic materials are added to the mud to reduce the water sensitivity of the shale, shale swelling, and weakening arising from mud contact, or the rate of water uptake by the shale.

Addition of a salt can transform the shale by cation exchange to a less sensitive form of clay, or reduce the osmotic swelling effect by reducing the water activity in the mud below that which occurs in the shale. These effects depend on the salt concentration and the nature of the cation. Salts containing sodium, potassium, calcium, magnesium, and ammonium ions are used to varying degrees. Sodium chloride has long been used as a shale stabilizer because of low cost, wide availability, and its presence in many subsurface formations. The inhibitive nature of salt muds increases as the salt content increases from seawater to saturated sodium chloride. In addition to the sodium chloride consumed annually for drilling fluid, considerable quantities are incorporated while drilling salt zones. This material has been used more for minimizing washouts in salt zones than for stabilizing shales. High salt levels have found application in deep water drilling.

Calcium sources, such as gypsum and lime, promote cation exchange from sodium clay to a less-swelling calcium clay. Calcium concentrations are normally low and osmotic swelling is only reduced if other salts are present. Calcium chloride has been used infrequently for this purpose but systems are available that allow high calcium chloride levels to be carried in the mud system (84).

A variety of shale-protective muds are available that contain high levels of potassium ions (13). The reaction of potassium ions with clay, well known to soil scientists, results in potassium fixation and formation of a less water-sensitive clay. Potassium chloride, potassium hydroxide, potassium carbonate [584-08-7] (85), tetrapotassium pyrophosphate [7320-34-5] (86), have all been used as the potassium source. Potassium chloride is generally preferred because of its low cost and availability. It is generally used in combination with a polymer or other organic material as discussed below.

Ammonium chloride [12125-02-9], ammonium sulfate [7783-20-2], and diammonium phosphate [7708-28-0] have also been used for shale stabilization (87,88). Ammonium ions have essentially the same effect on shales as potassium ions but use of ammonium salts is often objectionable because of the alkaline nature of the mud. In the North Sea and northern Europe, where magnesium-bearing salt formations are encountered, magnesium chloride [7786-30-3] is used, but in the United States it is used only on a small scale.

A number of nonionic and anionic polymers are employed in water-based muds to stabilize shales. These may be added to a freshwater mud or to a system containing one of the salts mentioned. Typically, shale-stabilization polymers include modified starches (89); cellulosic polymers such as CMC and HEC; gums such as guar, xanthan (90), and flax meal (91); and high molecular weight polyacrylamides of varying degrees of hydrolysis (12,47,92). A fluid containing a combination of potassium silicate [1312-76-1] and poly(vinyl alcohol) [9002-89-5] has also been used (93).

A number of cationic muds have been developed and used. These are formulated around quaternary amines or positively charged polymers (94,95). The polymer in some instances may be a cationic polyacrylamide. Poly(dimethylamine-*co*-epichlorohydrin) is another material that has been used successfully for drilling shale formations (96,97). Some of these additives may require a salt such as sodium or potassium chloride for achieving best results.

A number of glycol and glycerol-base additives are being used to formulate shale protective muds usually in conjunction with a salt and/or a polymer (98–101). The glycols consist of a number of combinations of ethylene oxide and propylene oxide depending on the purpose of the additive, not all of which are strictly for shale stabilization, and the desired cloud point. Two polyglycerol materials have been touted as having shale-protective properties (102–104). A low molecular weight poly(amino acid) has also been touted for its shale-stabilizing properties (105,106).

Solid materials, such as gilsonite and asphalt, and partially soluble sulfonated asphalt may also be added to plug small fractures in exposed shale surfaces and thereby limit water entry into the formation (91,107). The asphalts are oxidized or treated to impart partial solubility. These materials may be softened by the downhole temperature, causing them to deform and squeeze into small openings exposed to the borehole. Laboratory tests designed to evaluate shale-stabilizing muds have confirmed the beneficial action of these materials (108).

4.6. Surfactants.

Surfactants perform a variety of functions in a drilling fluid. Depending on the type of fluid, a surfactant may be added to emulsify oil in water (o/w) or water in a nonaqueous liquid (w/o), to water-wet mud solids or to maintain the solids in a nonwater-wet state, to defoam muds, or to act as a foaming agent.

Lignites and lignosulfonates can act as o/w emulsifiers, but generally are added for other purposes. Various anionic surfactants, including alkylarylsulfonates and alkylaryl sulfates and poly(ethylene oxide) derivatives of fatty acids, esters, and others, are used. Very little oil is added to water-base muds in use offshore for environmental reasons. A nonionic poly(ethylene oxide) derivative of nonylphenol [9016-45-9] is used in calcium-treated muds (109).

Emulsifiers are incorporated in oil and synthetic mud formulations to maintain a stable emulsion of the internal brine phase. These materials include calcium and magnesium soaps of fatty acids and polyamines and amides and their mixtures (110,111). The specific chemistry of these additives depends on the nature of the continuous phase of the mud, ie, whether it is diesel oil, mineral oil, or a synthetic liquid. Lime is added along with the fatty acid to form the soap emulsifier.

Solids present in oil and synthetic muds must be kept wet with the nonaqueous phase to prevent coagulation and settling and mud instability. Oil-wetting agents are normally incorporated in the basic mud package. These materials are typically amines or quaternary ammonium salts having hydrocarbon chains of 10 or more carbon atoms. They also render clays or lignites oil-wet for use in viscosity and filtration control (112).

Defoamers are frequently needed for salty muds, although in very small quantities. A common defoamer is aluminum stearate [637-12-7]. Others include tributyl phosphate [55612-35-6], alkyl aryl sulfonates, silicones, and alcohols such as octanol [111-87-5].

Foaming agents maintain stable drilling foams in areas where minimal bottomhole pressures are required. A large number of chemicals generate drilling foams, including anionics, such as alkyl and alkylaryl sulfates and alkylarylsulfonates; nonionics, such as ethoxylated fatty alcohols and alkylaryl alcohols; and cationics, such as imidazolines and tertiary amines. The foaming agent must be chosen to handle a variety of possible contaminants (salt, crude oils, solids) and downhole temperatures (113,114).

4.7. Lost Circulation Control. To function properly, a drilling fluid must be circulated through the well and back to the surface. Occasionally, highly permeable or cavernous formations and fractured zones, both natural and induced by the mud pressure, are encountered and circulation is partially or completely lost. Loss of drilling fluid, owing to openings in the formation, can result in loss of hydrostatic pressure at the bottom of the hole and allow influx of formation fluids and possibly loss of well control. It is essential that circulation be regained for drilling to continue. A wide variety of materials can be added to the drilling fluid to seal off the lost circulation zones (115,116). The particle sizes of these materials are typically much larger than the particle sizes of solids normally suspended in the mud which are generally $<150\ \mu m$ in diameter. Some of the same materials may be used for controlling filtration rates or for stabilizing shale formations but in such cases would be much smaller in particle size than a typical lost circulation material (LCM).

Lost circulation materials are flake, fiber, or granular-shaped particles. Each type is sold individually, often in two or more size grades, or two or more materials of different shapes may be sold as a blend (117–120). Materials of different shapes and sizes are often blended into the mud at the well site. Some common flake-shaped LCMs consist of shredded cellophane and paper, mica, rice hulls, cottonseed hulls, or laminated plastic. These materials lie flat across the opening to be sealed or are wedged into an opening such as a fracture. Some are sufficiently strong to withstand considerable differential pressure, whereas others are weak and the seal may be broken easily. Weaker flake materials typically are used near the surface or in combination with fibrous or granular additives. Fibrous additives include a variety of cellulose fibers, sawdust, sugar-cane bagasse, paper, straw, leather, and many others of similar size, shape, and availability. The larger fibers function by forming a brush-heap-type mat over the opening. The seal so formed may require smaller fibrous particles to stop seepage of mud through the mat. Fibers generally have little strength and cannot withstand high differential pressures. The brush-heap seal may extend far enough into the wellbore to be dislodged by the drill string, or be rigid enough to interfere with drill string movement.

Granular LCMs generally are much stronger than the other types and include ground rubber, nylon, plastics, limestone, gilsonite, asphalt, and ground nut shells, eg, walnut and pecan. Fine-, medium-, and coarse-size grades are available. Granular-shaped particles enter the opening, bridge it, and form a tight seal against further mud losses. Particle size and distribution are important for this mechanism to be effective. Bridging particles must generally have a diameter one-half the opening width for a fracture or one-third the diameter of a circular opening (121). An effective seal requires proper gradation of particle sizes (122). The advantage of this mechanism is that the seal is formed outside the wellbore and is not subject to drill string action.

4.8. Removal of Solids.

Solids incorporated in the mud during drilling generally are separated mechanically, reduced by dilution, or removed chemically by flocculation. It is desirable to maintain a low concentration of drill solids (4–8 vol%) and in some cases total removal is required. In the latter case, the drilling fluid is clear, consisting of freshwater or brine, and high drilling rates can be achieved. Polymeric flocculants added in small (0.03–0.06 kg/m^3 (0.01–0.02 lb/bbl)) quantities maintain a clear liquid (123).

Polymers used for flocculating drill solids generally are high molecular weight polyacrylamides of varying degrees of hydrolysis (124). The polymer may be cationic, nonionic, or anionic, depending on the chemistry of the drilling fluid and the nature of the solids. At higher concentrations, some polymers act as protective colloids and stabilize and enhance the viscosity of bentonite suspensions and protect water-sensitive shales.

4.9. Lubricants and Spotting Fluids.

The frictional resistance generated by the rotating drill string against the formation or casing may require extra torque if the hole is crooked or being drilled directionally. Considerable frictional resistance to raising and lowering the drill string may also occur; this is referred to as drag. Under certain conditions, such as in highly deviated holes, holes with frequent changes in direction, undergauge holes or poor drill string dynamics, or increased torque and drag entail a high risk of lost rig time, expensive pipe recovery operations, and limitation in well development (125). Excessive torque required to rotate the pipe generates greater strain on the drill pipe with the danger of twist-offs. Another problem occurs when the drill pipe sticks to the wall of the borehole. This may be caused by running or pulling the pipe into an undergauge section of the hole, a key seat, or a bridge of cavings. Another form of sticking, known as differential pressure sticking, occurs when the drill pipe becomes motionless against a permeable formation and a portion of the contact area of the pipe is isolated by the filter cake. The differential pressure (mud pressure-formation pressure) acts on the isolated area to press the pipe against the wall.

To overcome these difficulties, drilling fluids are treated with a variety of mud lubricants available from various suppliers. They are mostly general purpose, low toxicity, nonfluorescent types that are blends of several anionic or nonionic surfactants and products such as glycols and glycerols, fatty acid esters, synthetic hydrocarbons, and vegetable oil derivatives. Extreme pressure lubricants containing sulfurized or sulfonated derivatives of natural fatty acid products or petroleum-base hydrocarbons can be quite toxic to marine life and are rarely used for environmental reasons.

Water-dispersible and sulfonated asphalt derivatives have been used as an aid to improve mud lubricity, although these are primarily for filtration control and shale protection. Solid lubricants, including graphite, plastic beads (126), glass beads (127), and ground walnut shells, may be incorporated to impart lubricity and reduce the risk of pipe sticking. Gilsonite and air-blown asphalts blended with a glycol-carrier are used to prevent pipe sticking and to act as lubricants for water-base muds (128,129).

If the drill string becomes differentially stuck, mechanical methods or spotting fluids can be applied, or the hydrostatic pressure can be reduced (130). In general, penetration of water- or oil-based spotting fluids into the interface between the filter cake and the pipe accompanied by dehydration and cracking results in reduction of differential pressure across the drill string (130,131). Spotting fluids are usually positioned in the open hole to completely cover the problem area.

Recently, a number of water-base spotting fluids have been developed (132) and consist of a variety of surfactants, glycols (133,134), organic acids (135), glyceride esters (136), and vegetable oil derivatives. The newer water-base spotting fluids have the distinct advantage that they can be incorporated into the drilling fluid following use, without having an adverse effect on the toxicity of the system (137).

Drill string and casing corrosion can present serious problems in some drilling operations. Corrosion is generally caused by oxygen dissolved or entrained in the mud as it is circulated through the well (138). Acid gases, such as carbon dioxide and hydrogen sulfide, contribute to corrosion, particularly hydrogen sulfide which can produce catastrophic drill string failures through stress cracking. Preventing entry of these corrosive gases into the well is the most effective method of control, but is not always feasible. Therefore additives are employed to counteract corrosive attack (139,140).

Oxygen corrosion is reduced significantly at pH >11 and is generally lower at any alkaline pH than in an acidic environment. Maintaining a high pH is the most common means of corrosion control. Other methods include oxygen removal by scavengers such as sodium sulfite [7757-83-7] or ammonium bisulfite [17026-44-7] (140,141), or protecting the pipe from attack by coating with amines.

A high pH also affords protection against hydrogen sulfide and carbon dioxide. Zinc and iron compounds are used as sulfide scavengers (142). Zinc compounds include the carbonate, oxide, hydroxide, sulfate, and water-soluble organic chelates. High surface area iron oxides, particularly a synthetic magnetite, also are used (143). Scale inhibitors such as organic phosphonates and low molecular weight polyacrylates may be added to prevent buildup of carbonate scale on the pipe. Drilling rates can be severely reduced when drilling formations that tend to stick to the surface of the drill bit, a situation known as bit balling. If the bit cannot be kept clean and free of sticky material, drilling performance suffers and the operational cost can increase substantially. The new generation synthetic polycrystalline diamond compact (PDC) bits are capable of achieving high penetration rates if the cutters are kept clean and the proper hydraulics and bit rotary speeds can be maintained. Use of an oil- or a synthetic-base mud is normally preferred when drilling with a PDC bit as there is much less tendency for bit balling to occur and high drilling rates can be realized (144). Water-base muds are more prone to bit balling and PDC bit performance can be significantly poorer than when a nonaqueous continuous-phase mud is used (145). Additives being used to enhance the drilling performance of PDC bits in water-base muds include water-soluble glycols (146,147) and various terpenes (144).

5. Completion and Workover Fluids

Completion and workover fluids that are used during the completion phase of the well or when performing a workover during the life of the well. Completion fluids should (*1*) cause minimal formation damage, especially to reservoir permeability, (*2*) maintain long-term stability at downhole temperatures, (*3*) be resistant to contaminants, and (*4*) protect down-hole equipment against corrosion. These fluid types can divided into two broad classifications: solids-free and solids-laden. The solids-free completion/workover fluids are generally brines ranging in composition from potassium chloride to zinc bromide, and their densities fall into the range of 1.02 kg/L (8.5 lb/gal or ppg) to 2.46 kg/L (20.5 ppg). Weighted solids-free fluids are obtained by the use of solutions of various water-soluble or acid-soluble salts. In particular, the chlorides and bromides of sodium, potassium, calcium, and zinc, and their mixtures are used to adjust the densities of these brines. The solids-laden completion and workover fluids are generally composed of a brine as a base fluid and solids, in the form of water or acid-soluble particles, for density and fluid-loss control as well as polymers for suspension-carrying capacity and filtrate control. In general, the solids-laden fluids cover the same density range as the solids-free fluids.

Solids-free fluids are the predominant completion/workover fluids in use. Use of these fluids isdictated in many completion operations, especially in gravel pack or frac pack type completions. Use of a solids-laden fluid in such operations can lead to failure. Solids-free fluids cause a minimum amount of formation damage and allow tools to be run into and pulled out of the well with ease. Solids can penetrate into the permeable media of the formation and become lodged, thus causing reduced permeability and ultimately lower production. Solids-laden fluids also have typically increased viscosities, which can inhibit tools being run into and pulled out from the well. In order to keep solids-free fluids free of solids, filtration, either cartridge or diatomaceous earth, is generally used while these fluids are being employed.

There are a number of factors that determine the choice of fluid to be used. If there is no milling or drilling operations to be carried out, then a solids-free fluid can be used. The particular solids-free fluid/soluble salt to be employed also depends on a number of factors that include:

(1) Density required: A compilation of some of the soluble salts and their maximum brine densities that have been used as completion and workover fluids is given in Table 8. A specific density may be achieved by mixing together one or more brines listed in the table. The monovalent brines are generally mixed with monovalent brines and divalent brines mixed with divalent brines. Mixing of monovalent and divalent brines can cause the formation of precipitates and turbidity. Density adjustment can also be achieved by adding a salt to a specific brine.

(2) True crystallization temperature (TCT) required: It is important to know expected ambient temperatures and expected sea floor temperatures. The crystallization temperature can be adjusted by blending brines or water to raise or lower the crystallization temperature.

Table 8. **Soluble Salts that Increase the Density of Drilling Mud and Workover and Completion Fluids**

Salt	CAS Registry number	Formula	Specific gravity of solid	Maximum brine density, g/L (ppg)
potassium chloride	[7447-40-7]	KCl	1.984	1.14 (9.5)
sodium chloride	[7647-14-5]	NaCl	2.165	1.20 (10.0)
calcium chloride	[10043-52-4]	$CaCl_2$	2.150	1.39 (11.6)
sodium bromide	[7647-15-6]	NaBr	3.203	1.50 (12.5)
calcium bromide	[7789-41-5]	$CaBr_2$	3.353	1.70 (14.2)
zinc bromide	[7699-45-8]	$ZnBr_2$	4.201	2.46 (20.5)
potassium formate	[590-29-4]	$KCHO_2$	3.48	1.60 (13.3)
sodium formate	[141-53-7]	$NaCHO_2$	1.92	1.34 (11.2)
cesium formate	[3495-36-1]	$CsCHO_2 \cdot H_2O$	3.372	2.37 (19.7)

(3) *Compatibility with the formation:* Formation gases may not be compatible with the completion/workover fluid. For example, calcium-based brines should not be used in the presence of carbon dioxide as the formation of insoluble calcium carbonate can precipitate. Other problems can be that the formation water may be incompatible with brine, or emulsions may form with the crude oil.

(4) *Cost:* Generally speaking, the higher the density of the brine, the higher its cost. Another rule of thumb is the lower the crystallization temperature required, the higher will be its cost. Other important factors to weigh are brine corrosivity (eg, metallurgy of the casing and/or tubing in the well), brine stability, brine toxicity and brine availability (to remote and generally international locations).

Brine sources may include seawater, natural brines and manufactured salt brines. Densities up to 2.3 kg/L (19.2 ppg) can be obtained using mixtures of calcium bromide and zinc bromide. Calcium bromide is commercially available as a 52 wt% solution in water, having a density of 1.704 kg/L (14.2 ppg). This brine remains clear down to a temperature of $-7°C$. Also available is a calcium bromide/zinc bromide brine having a density of 2.304 kg/L (19.2 ppg), where the brine contains approximately 52.8 wt% zinc bromide and 22.8 wt% calcium bromide. Evey manufacturer of clear brines provides detailed blending tables showing the relative amount of various brines, salts, and water in order to prepare a brine with the desired specific gravity and crystallization point. Two examples are given below. Table 9 provides the volume of water [fraction of a barrel (bbl)] and weights of 95% calcium bromide solid that are needed to prepare 1 barrel (bbl) of a calcium bromide brine having a specific brine density (ppg). The crystallization point of the brine is also included in the table. Table 10 presents the volumes of calcium bromide (1.7 kg/L /14.2 ppg) brine and zinc bromide/calcium bromide (2.3 kg/L /19.2 ppg) that are needed for preparing calcium bromide/zinc bromide brines of varying densities, together with their corresponding crystallization points.

Slightly higher densities than the above-mentioned brines can be attained using nearly saturated solutions of $ZnBr_2$ having a density of 2.46 kg/L (20.5 ppg)

Table 9. **Calcium Bromide Solution Requirements Using Calcium Bromide (95%)**[a]

Brine density, 70°F				
ppg	g/L	Water, bbl	95% $CaBr_2$, lb	Crystallization point, °F
11.6	1392	0.860	186.3	−32
11.8	1416	0.852	197.5	−40
12.0	1440	0.844	208.7	−50
12.2	1464	0.836	219.9	−61
12.4	1488	0.828	231.1	−73
12.6	1512	0.820	242.3	−88
12.8	1536	0.811	253.7	−96
13.0	1560	0.803	265.1	−78
13.2	1584	0.794	276.5	−63
13.4	1608	0.786	287.9	−43
13.6	1632	0.777	299.4	−34
13.8	1656	0.768	311.0	−20
14.0	1680	0.758	322.6	−7
14.2	1704	0.751	333.4	10
14.4	1728	0.739	346.0	23

[a] To prepare 1 barrel (bbl) or 42 gal.

or of cesium formate having a density of 2.367 kg/L (19.7 ppg) (148). The monovalent formate brines, which are highly soluble in water, were first introduced into the oil industry in the early 1990s. The formates are organic and biodegradable. Their chemistry stabilizes and protects the conventional polymers used in viscosity modifiers and other additives, allowing such additives to be used at much higher temperatures—often >350°F (176°C). Other relevant information on formate brines is included in a series of papers that are cited in Refs. 149−154.

Table 10. **Calcium Bromide/Zinc Bromide Solution Requirements Using 14.2 ppg Calcium Bromide and 19.2 ppg Zinc Bromide/Calcium Bromide**[a]

Brine density, 70°F				
ppg	g/L	14.2 ppg $CaBr_2$, bbl	19.2 ppg $CaBr_2$/ $ZnBr_2$, bbl	Crystallization point, °F
15.0	1800	0.840	0.160	−22
15.3	1836	0.780	0.220	−29
15.6	1872	0.720	0.280	−35
15.9	1908	0.660	0.340	−37
16.2	1944	0.600	0.400	−26
16.5	1980	0.540	0.460	−16
16.8	2016	0.480	0.520	−6
17.1	2052	0.420	0.580	−2
17.4	2088	0.360	0.640	4
17.7	2124	0.300	0.700	6
18.0	2160	0.240	0.760	9
18.3	2196	0.180	0.820	13
18.6	2232	0.120	0.880	19
19.0	2280	0.060	0.940	20
19.3	2316	0.000	1.000	16

[a] To prepare 1 barrel (bbl) or 42 gal.

Drilling fluids made both with $CaBr_2/ZnBr_2$ brines and with formate-based fluids generally need no solid weighting agents, since the density is an inherent property of the fluid itself.

One inherent problem with solids-free brines is that since they have no solids and in general have low viscosities, there is nothing to prevent the liquid from leaking off into the formation. Therefore, an important part of planning in the use of the solids-free completion and workover fluids is fluid loss control pills. These pills are generally a blend of the brine being used and polymers for imparting viscosity. The viscosifiers used in brine fluids should be stable at a temperature of 150°C and have good acid solubility. The polymers used are hydroxyethylcellulose, xanthan gum and other specialty polymers. Guar gums can be included in completion/workover fluids, but their use is more limited because they are not completely soluble in acid; in addition, guar gum is also only stable to ~66°C. For filtrate loss reduction, a blend of polymers and soluble solids are usually incorporated into the fluid. These polymers are used to plug the interparticle spaces within the bridging solids, thus reducing the amount of filtrate entering the formation. The selection of the solids to be used will be based on the pore throat openings in the formation in order that a bridge can be rapidly formed on the outside of the formation, preventing solids and liquids from entering the reservoir.

Some additional details about the additives used in workover/completion fluids are listed in Table 11. Some solids-laden completion and workover fluids are now being utilized as reservoir drill-in fluids. These are used once the well

Table 11. **Workover/Completion Fluid Additives**

Additive	Function	Region used	Comments
commodity salts			
calcium bromide, calcium and sodium chloride, zinc bromide, sodium bromide, monovalent formates	for density increase of brine fluids	United States	calcium chloride is a major product; blends of salts are generally used in workover fluids
viscosifiers			
hydroxyethylcellulose (HEC), xanthan gum polyacrylamides	build fluid viscosity without use of high solids system; additive must be water or acid soluble	United States	
fluid-loss additives			
(filtrate control agents) calcium carbonate, starches,	for reducing the loss of water or fluid by preventing its penetration into the reservoir formation		
other additive types			
corrosion inhibitors, biocides			

has reached the depth at which hydrocarbons are expected to be encountered. These fluids are designed especially to have the properties of a good drilling fluid, yet deposit a filter cake that is easily removed ie all the components are soluble in either water or acid, while the filtrate does not cause any damage to the reservoir.

6. Economic Aspects

Considerable changes have occurred in the makeup of drilling fluids during the the last two decades and these changes are expected to continue during the tweny first century. The price of the drilling fluid additives used in these fluids varies according to company and location so that it is almost impossible to indicate typical prices for the more common additives (used in drilling operations), which are listed in Table 12. Price information on the full line of products normally is available from drilling fluids companies. The prices for those materials listed in Table 12 would also depend on the nature of the contract between the supplier and operating companies.

It is instructive to consider the price fluctuations that have occurred for barite, a densifier that constitutes the largest of the chemical expenses incurred in

Table 12. **Summary of Drilling Fluid Additives in Use and Their Function**

Function	Additive
increase density	barite hematite
increase viscosity	bentonite attapulgite xanthan gum hydroxethylcellulose
reduce viscosity	sodium acid pyrophosphate lignite chrome lignosulfonate chrome-free lignosulfonate sodium polyacrylate (liquid)
reduce filtration rate	corn starch modified starch carboxymethyl cellulose sodium polyacrylate modified lignite
shale stability/viscosity	polyacrylamide
alkalinity control	sodium hydroxide lime potassium hydroxide
lost circulation control	walnut shells mica Cellulose fibers
miscellaneous inorganic compounds	sodium chloride potassium chloride calcium chloride sodium carbonate

drilling muds. Market competition has been significant in the barite segment, so that its prices have been historically under pressure. The oil price crash and drilling recession in 1998 resulted in the price of barites in Yarmouth (U.K.) falling from an average of \$100–120 per metric ton in 1997 to \$75–90 per metric ton in mid-1998. The price decrease continued in 1999 but started to increase in mid-2000 to ~ \$80–100 per metric ton at the end of 2000.

7. Analytical and Test Methods

Procedures for determining drilling fluid properties are available (19,20,155). Tests and test methods are constantly reviewed by API committees to ensure acceptable accuracy when performed under field conditions as well as in the laboratory. API publications are republished as new tests are added or existing tests are modified.

8. Environmental Aspects

At present, the major challenge that must be met in formulating drilling fluids is need to satisfy the increasingly demanding conditions of high temperature and pressure that are found in some deep wells and horizontal wells, while avoiding harm to the environment. Drilling fluid components should be selected in a way such that the discharge of mud or cuttings will have a minimum possible environmental impact. In addition to environmental concerns being a major driving force behind current drilling fluid R&D, the health of rig workers has become an important concern in the development and use of new products.

While drilling fluids are essential for the success of an well drill, they can also be one of messier parts of a drilling operation. Cuttings brought up from out of a borehole have to be disposed of as well as any drilling fluid attached to them. The degree of impact that drilling fluids can have on the environment depends on the type of mud used and the existing environmental conditions. Offshore, water-based muds are generally the least damaging when compared with oil-based muds. The disposal of waste drilling fluids and drill cuttings in the United States has long been regulated either by local authorities, the individual states, or by the federal government. These regulations continue to change. In many instances, it is environmental issues that have been the main driving force for product choice in the drilling fluids business. It is no secret that the mud-contaminated cuttings constitute a major portion of the waste that is generated during drilling.

The offshore disposal of both diesel and mineral oil drilling fluids and associated cuttings has always been prohibited in U.S. waters. However, offshore discharge of mineral oil mud cuttings overboard has been permitted in the North Sea and elsewhere as long as the oil content of the cuttings was below some regulatory limit. The regulatory oil-on-cuttings limit in some sectors of the North Sea has been lowered significantly over the last decade. There is a definite move toward alternative fluid systems many of which are used in U.S. offshore areas, eg, synthetic-based drilling muds. Thus, in the 1990s, due to environmental considerations, oil-based muds were partially replaced by synthetic-based muds whose synthetic-based fluids were deemed biodegradable. However, recent biodegradability tests on synthetic-based muds under real sea-bottom conditions have shown that in the absence of oxygen, biodegradability is poor. As a result, beginning in 2001, all but one type of synthetic-based muds, ie, the ester-based mud which indergoes rapid degradation, have been effectively prohibited from being used in the North Sea. At the end of 2000, it was reported that rig operators in the U.K. sector have reached zero discharge with respect to synthetic-based drilling fluid cuttings. A look at synthetic-based mud usage in the North Sea shows that from 2000 to 2001, the usage was reduced from 10–15% of all muds used to somewhere ∼5%.

As of 2001, legislation has been enacted to prohibit the discharge of environmentally unfavorable cuttings into the North Sea. When oil-based muds are employed, there also exist strict limitations on how much oil can be discharged. In the U.K. sector of the North Sea, no discharge of oil-based muds is allowed.

For water-based muds usage offshore, there are controls on the kinds of chemicals that can be used in the muds. The screening process for the water-based mud additives may include the toxicity and persistency of the chemical, its potential to bioaccumulate in marine organisms, and the toxicity of any degradation process. It is therefore not surprising that the search for environmentally friendly drilling mud additives and biodegradable alternatives to the conventional mineral oil used continues.

The most significant change in the regulations on discharges of drilling fluids and cuttings in the Gulf of Mexico occurred in July 1986 when a new toxicity-based limit was placed on disposal (156). The specific toxicity limit is based on a 96-h bioassay test in which the drilling fluid is diluted with nine parts seawater and mixed well, the suspension is allowed to settle for one hour, and the suspended particulate phase (SPP) is decanted for testing. Mysid (*mysidopsis bahia*) shrimp are exposed to a range of SPP concentrations and the lethal concentration to 50% of the shrimp (LC_{50}) is calculated from the observed shrimp mortality at the end of 96 h. (LC_{50} is the lethal concentration, where 50% of the organisms are killed.) The toxicity limit must be 30,000 ppm or higher in order to meet EPA standards and allow the overboard discharge of fluid or drill cuttings. Very few instances of water-based muds failing the mysid bioassay test existed during the 1990s.

In summary, there exist a variety of regulations that apply in different offshore drilling areas in the United States and around the world. All have had a profound effect on drilling fluid technology (157,158). Operators and service companies have eliminated use of the more toxic additives, reformulated old mud systems, while developing new ones to ensure acceptable environmental performance based on pertinent regulations.

9. New Directions in Drilling Fluids

Some recent developments and innovations in drilling fluids as proposed in recent patents are presented in the following section. These describe newly developed formulations for use in the various stages of oil and gas well drilling.

9.1. Water-Based Drilling Fluids.

The most significant developments in mud materials made within the last decade have been achieved with the aim of improving the performance of the water-based muds, due to increasing limitations that have been placed on the use of oil-based muds. The main drawback of the water-based muds is their poor performance in shale stabilization, ie, the water fraction can cause swelling of the clay. Performance can be ameliorated by using inhibiting muds, ie, the addition of salt and special additives. One of the first additives used for this purpose was partially hydrolyzed polyacrylamide (PHPA), which was later followed by glycols as shale stabilizers.

A recent development has been the introduction of soluble silicate, sodium or potassium, that seal up the walls of the hole. While soluble silicates were proposed in the 1930s, they were not successful because they could not be integrated into the mud system. The new mud systems built up around the silicates have been successfully used in both the Gulf of Mexico and the North Sea. An example of such a silicate-based mud was given in a 1997 patent (159), which was proposed for use in drilling through reactive clays and shales and other soft formations. The drilling fluid contains, in addition to polymeric agents for fluid loss and rheological control, a stabilizer consisting of an alkali metal silicate (28–35% by weight potaassium silicate). This drilling fluid does not contain bentonite or barite.

Another patent (160) describes a brine for use in drilling operations that has water as the continuous phase together with at least one inorganic salt and an amount of a low molecular weight water-soluble compound that is effective in reducing the crystallization point of the brine. The low molecular weight water-soluble organic compound may be an alcohol, polyol, glycol, polyglycol, polyalkylene oxide, alkylene glycol ether, carbohydrate, amino acid, etc. Preferred compounds mentioned are ethylene glycol and tripropylene glycol bottoms. Data from the patent for two solutions are presented in Table 13 for 20% NaBr/water and 20% NaBr/20% ethylene glycol/water mixtures.

A Great Lakes Chemical patent (161) proposes a composition for either drilling and/or well bore treating operations, using a carboxylate-based brine solution to inhibit corrosion in fluid-handling equipment. In one embodiment presented, the carboxylate-based brine consists of a carboxylate salt dissolved in water for use in the preparation of halide-free drilling fluids. The drilling fluid can contain a variety of additives such as viscosifiers, weight-up agents, buffering agents and/or fluid loss control agents. In a second alternative embodiment, a mixed salt brine consisting of a carboxylate salt and a halide salt is used in drilling and/or well bore treating operations. The carboxylate salts mentioned included sodium formate, sodium acetate and sodium propionate.

Table 13. **Crystallization Point Data**[a]

	20% NaBr/Water,°F	20% NaBr/20% Ethylene glycol/water,°F
FCTA	10	−11
LCTD	18	−8

[a] Ref. 160.

A drilling, drill-in, or completion fluid described in a 1998 patent (162) had water as its continuous phase along with a nontoxic low molecular weight water-soluble organic compound, which serves as a gas hydrate inhibitor. Preferred organic compounds included ethylene glycol alone, or a blend of an ethylene glycol derivative and a propylene glycol derivative in an amount effective for inhibiting hydration of the shale by the water base.

Another patent invention (163) described clay-free well drilling, biopolymer-free well drilling, and servicing fluids that were comprised of an aqueous divalent-cation containing water-soluble salt, a bridging agent, and a pregelatinized cross-linked amylopectin starch suspending agent and a fluid-loss control additive. The water soluble divalent-cation salt is selected from the group consisting of alkaline earth metal halide salts, zinc halide salts and mixtures of these. The low shear rate viscosity was increased without increasing the high shear rate viscosity above $\sim$70 cP by adding magnesium oxide and/or dipotassium hydrogen phosphate.

A 1998 patent (164) described a potassium formate solution, used as an aqueous well servicing fluid, which also contained potassium citrate. The potassium citrate enhanced the density of the potassium formate solution and also minimized any risk of caking if potassium formate is used alone. The amount of potassium citrate used is in the range of 5–30% by weight, based on the total weight of potassium formate and potassium citrate in the liquid.

A different route used for increasing the density of fresh or depleted clear brine drilling fluids that are based on calcium bromide and calcium chloride, is achieved by the addition of solid hydrates of calcium bromide, in particular calcium bromide tri- and tetrahydrates. These hydrates, which are scarcely mentioned in the literature, are highly effective in fixing the brine concentration. The density of the solid used is about 2200 kg/m^3 and consists of 70–78% calcium bromide. This novel product, known as Calcium Bromide Forte, is currently being marketed by Dead Sea Bromine Group (DSBG).

A U.S. patent (165) described a water-based drilling fluid which is composed of 1–8% of an additive comprising a saturated terpene, a mixture of saturated terpenes, or a mixture of saturated and unsaturated terpenes. The drilling fluid is considered to be substantially nontoxic and was claimed to have an LC_{50} $>$30,000 ppm and preferably $>$100,000 ppm. The most economic additives for this fluid were a mixture of saturated and unsaturated terpenes, having at least 30% saturated terpenes. The drilling fluid also contains a weighting material, a fluid loss additive, and a viscosifier. Examples given of saturated terpenes were *p*-menthane, *m*-menthane, and pinanne.

A Perstorp AB patent (166) described the use of a saturated aqueous salt solution containing at least one alkali formate salt and at least one alkali bromide salt in a drilling fluid. The fluid was composed of 40–50% by weight water, 50–60% by weight of the salts mentioned in a weight ratio of formate to bromide of 30:70 to 60:40. The saturated aqueous salt solution had a density and a total salts content exceeding that of a saturated aqueous solution of the bromide salt. Example 1 in the patent cited a 26% sodium formate −30.4% sodium bromide aqueous mixture having a density of 1.561 g/cm^3. The individual saturated solutions at 22°C had the following densities: sodium formate 1.318 g/cm^3 and sodium bromide 1.520 g/cm^3.

In the drilling of oil wells with water-based fluids, instability problems arising in shales have to be frequently dealt with. These problems arise for two reasons: (*1*) the reactivity of the claystone to water (*2*) the transmission of pressure from the mud column to the inside of the formation, thus modifying the stress within the rock, causing it to break. Another patent (167) presents a composition for a water-based drilling fluid that is an oil-in-water emulsion. The newly proposed drilling fluid has been found particularly effective in preventing the pressure transmission. In the patent's preferred embodiment, a nonionic emulsifier was used, preferably polyoxy ethylene–sorbitan monooleate.

A nontoxic drilling fluid composition has been patented (168) and claimed to be of use as a lubricant or spotting fluid in drilling oil and gas wells. The proposed drilling fluid consists of a water-based continuous phase and a silicone fluid together with an emulsifier. The silicone fluid is comprised of dimethylsiloxane polymers and was claimed to be nontoxic to marine life.

9.2. Organic-Based Drilling Fluids. An invention described in a patent (169) is an improved glycol-based drilling fluid that is comprised of: (*1*) A predominantly glycol–continuous phase (miscible glycol at a concentration of at best 70% by volume of the continuous phase. (*2*) An antisticking drilling fluid additive present at a concentration of at least 0.5% by weight of the drilling fluid. The antisticking drilling fluid additive is selected from silicone fluids, silicone-based surfactants, hydrocarbons, glycol-ethers, carboxylic acid esters, and combinations of these.

An Exxon patent (170) presented an environmentally friendly drilling fluid or mud composition claimed to be useful in oil and gas production. The biodegradable drilling fluid was comprised of one or more weighting agents, emulsifiers, wetting agents, viscosifiers, fluid loss control agents, and other particulates such as used in a gravel pack, emulsified with a paraffin solvent composition that formed a continuous oil phase, or water-in-oil invert phase. The solvent composition (continuous oil phase) was comprised of a mixture of C_{10}–C_{24} n-paraffins and isoparaffins having an isoparaffin: n-paraffin molar ratio ranging from $\sim$0.5:1 to $\sim$9:1, and the isopaffins of the mixture contain $>$50% of mono-methyl species, based on the total weight of the isoparaffins in the mixture.

A 2003 patent (171) describes nonaqueous suspensions suitable for formulation of environmentally friendly drilling fluids that consists of a nonaqueous base fluid with a concentration of suspension aids, a dispersant, and optionally, a polymeric viscosifying agent. The base fluid was selected from glycols, polyglycols, polyoxyalkylenes, glycol ethers, glycol esters; the suspension aid was selected from hydroxypropyl cellulose, ethyl cellulose; the dispersant was selected from calcium stearate, lecithins, stearic acid, oleic acid; and the viscosifiers were selected from xanthan gum, hydroxyethyl cellulose, CM-cellulose, guar gum, polyacrylamide and starch. The compositions could be used as additives for well drilling and treatment fluids.

9.3. Viscosifiers. A 2000 patent (172) proposed the use of novel polymer compositions as viscosifiers, which can be used in well service fluids (completion fluids, work-over fluids or drilling fluids). The drilling fluid, for use at high temperatures, is composed of water-soluble copolymers having sulfonate and carboxylate groups together with alkali metal salts of carboxylic acids. The alkali metal carboxylate was selected from sodium, potassium, and cesium salts of acetic and formic acids.

A 1997 patent (173) described a composition that is useful for viscosifying aqueous drilling fluids that are utilized in subterranean drilling activities such as drilling, drill-in, completion, hydraulic fracturing, work-over, packer and well treating fluids. The composition is composed of a prehydrating alcohol having at least two hydroxyl groups (with a molecular weight of 60 to ~600), an inorganic salt, and a polymer. The prehydrating alcohol reacts physically with the polymer to cause a partial swelling effect, solvating effect or hydrating effect upon the polymer.

A Great Lakes Chemical patent (174) presented aqueous mixed salt systems that were viscosified with water-soluble or water-dispersable polymers. These systems were comprised of water, a water-soluble or water-dispersable polymers capable of viscosifying an aqueous media, and mixed salts comprised of at least two cations and two anions. The cations cited were Li, Na, K, Cs, Mg, Ca, Zn, or mixtures. The anions cited were Cl, Br, I, formate, nitrate, acetate, cyanate, thiocyanate, or a Zn-complex anion. These compositions were proposed as replacements for conventional drilling, drill-in, completion, hydraulic fracturing, work-over, packer, well-treating, testing, spacer, or hole abandonment fluids.

A patent (175) disclosed a low solid, high density fluid that was suggested as being useful in drilling, workover and completion fluids in oil and gas well operations. The fluids comprised (*1*) one or more brines having a density of 1500 kg/m^3 to ~2400 kg/m^3 (salt chosen from calcium bromide, zinc bromide or mixtures of these), (*2*) a viscosifier that is a high surface area silica, preferably a fumed silica, (*3*) a fluid loss control additive that was preferably selected from the group consisting of starch derivatives, cellulose derivatives, lignocellulose derivatives or mixtures of these; (*4*) one or more water soluble or acid soluble bridging agents, and (*5*) optionally, an alkaline buffer and a polar additive.

A 1998 patent (176) described a drilling fluid comprised of brine and additives for maintaining rheological properties in a neutral or slightly acidic brine and a method for using the drilling fluid to drill into a producing formation. The drilling fluid was comprised of a viscosifying polymer and a fluid loss polymer that function in the brine without substantially adversely affecting their properties. The brine was virtually free of insoluble solids.

A recent review (177) was published on the use of complex carbohydrates, ie, polysaccharides as additives in the petroleum and natural gas industries, especially as viscosifiers and fluid loss control additives for drilling fluids and muds. Viscosifiers are typically xanthan gum, hydroxyethyl cellulose and modified guar gum, while fluid loss control additives are typically pregelatinized starch, and polyanionic cellulose derivatives, especially CM-cellulose.

9.4. Densifiers. The invention (178) presented in another patent relates to an additive which increases the density of the well bore fluids used during the construction or repair of oil, gas, injection, water or thermal wells. The additive is comprised of solid, colloidal particles of weight average particle diameter (D_{50}) of < 2 μ. The particles have been deflocculated by the action of a dispersant, preferably incorporated during the grinding or comminution process. The colloidal particles used include barium sulfate, calcium carbonate,dolomite, illmenite, or hematite. The liquid medium can be an aqueous phase or an organic liquid of kinematic viscosity <40 cS at 40°C and of flash point >60°C.

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Shmuel D. Ukeles
Baruch Grinbaum
IMI (TAMI) Institute for Research and Development, DSBG (Israel)