



Johannes Fink

WATER-BASED CHEMICALS AND TECHNOLOGY FOR DRILLING, COMPLETION, AND WORKOVER FLUIDS



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by

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PREFACE

This manuscript focuses on water-based fluids with respect to chemical aspects. After a short introduction in the basic issues water-based fluids, the text focuses mainly on the organic chemistry of such fluids and special additives.

The nature of the individual additives and the justification why the individual additives are acting in the desired way are explained. The material presented here is a compilation from the literature, including patents. In addition, as environmental aspects are gaining increasing importance, this issue is also dealt carefully.

HOW TO USE THIS BOOK

There are four indices: an index of tradenames, an index of acronyms, an index of chemicals, and a general index.

In a chapter, if an acronym is occurring the first time, it is expanded to long form and to short form, e.g., acrylic acid (AA) and placed in the index. If it occurs afterwards, it is given in the short form only, i.e., AA. If the term occurs only once in a specific chapter, it is given exclusively in the long form.

In the chemical index, bold face page numbers refer to the sketches of structural formulas or to reaction equations.

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CHAPTER I

General Aspects

1. HISTORY

Some aspects of the history of drilling fluids can be found in monographs and in the Internet [1–8]. Also a compact time table of the history is available [9].

The earliest known oil wells were drilled in China in 347 before Christ. These wells had depths of up to some 240 m [10]. They were drilled by bits attached to bamboo poles. In 1845, the French engineer Pierre-Pascal Fauvelle (1797–1867) introduced a new method of well drilling [11–13]. He used hollow iron tubes to direct the water into the drill hole [14]. Drilling fluids were used around 1850 in the percussion drilling technique in order to suspend the cuttings.

In the early time, water-based fluids were used. Already the old Egyptians used water to remove the cuttings from their holes. In 1846, Robert Beart proposed that cuttings from drilling holes may be removed by water. Around 1890, clay was added to drilling fluids. At the same time, it has been proposed that a mixture of water and a plastic material—to be recycled—can be used to remove the cuttings. Such a mixture also should form an impermeable layer along the wall of the borehole [15].

Historically, water-based drilling fluids have been used to drill a majority of wells [16]. Their lower cost and better environment acceptance as compared to oil-based drilling fluids continue to make them the first option in drilling operations.

In addition, emulsion muds have been the systems of choice in drilling onshore, continental shelf, and deepwater wells to minimize the risk, maximize drilling performance, and reduce the costs [17]. However, because of environmental constraints, a high frequency of lost circulation, and the high unit cost of emulsion systems sometimes their benefits can not be fully emerge. Lost circulation materials and treatments have been reviewed [18].

2. FIELDS OF APPLICATION FOR WATER-BASED COMPOSITIONS

Water-based compositions are used in the petroleum industry for several purposes:

- drilling muds,
- fracturing fluids,
- cementing,
- filter cake removal,
- waterflooding,
- enhanced oil recovery,
- squeezing,
- transporting aids, and
- pipeline pigging.

For these operations, a basic fluid is needed and also in most cases certain additives are needed that are improving the performance of the basic fluid. For different purposes, for example, bacteria control or corrosion control, the same additive compounds can be used, at least with minor variations of the chemical structure. These general purpose additives are collected in special sections.

Guidelines for the selection of materials and the mechanism of corrosion in the petroleum industries have been summarized [19].

Tradenames appearing in the references are shown in Table 1.

Table 1 Tradenames in references

Tradename Description	Supplier
Biovis® Scleroglucan viscosifier [16]	Messina Chemicals, Inc.
Duovis® Xanthan gum [16]	M-I Swaco - Schlumberger
Flotrol™ Starch derivative [16]	M-I Swaco - Schlumberger
Glydril® Poly(glycol) (cloud point additive) [16]	M-I Swaco - Schlumberger
Poly-plus® HD Acrylic copolymer (shale encapsulation) [16]	M-I SWACO - Schlumberger
Polypac® UL Polyanionic cellulose [16]	M-I SWACO - Schlumberger
Polyplus® RD Acrylic copolymer (shale stabilizator) [16]	M-I SWACO - Schlumberger

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CHAPTER II

Drilling Fluids

A drilling fluid or mud is a specially designed fluid that is circulated through a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid include removing drill cuttings or solids from the wellbore, cooling and lubricating the drill bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation [1].

For a drilling fluid to perform its functions, it must have certain desirable physical properties. The fluid must have a viscosity that is readily pumpable and easily circulated by pumping at pressures ordinarily employed in drilling operations, without undue pressure differentials.

The fluid must be sufficiently thixotropic to suspend the cuttings in the borehole when fluid circulation stops. The fluid must release cuttings from the suspension when agitating in the settling pits. It should preferably form a thin impervious filter cake on the borehole wall to prevent loss of liquid from the drilling fluid by filtration into the formations.

Such a filter cake effectively seals the borehole wall to inhibit any tendencies of sloughing, heaving, or cave-in of rock into the borehole. The composition of the fluid should also preferably be such that cuttings formed during drilling the borehole can be suspended, assimilated, or dissolved in the fluid without affecting physical properties of the drilling fluid.

Most drilling fluids used for drilling in the oil and gas industry are water-based muds (WBM). Such muds typically comprise an aqueous base, either of fresh water or brine, and agents or additives for suspension, weight or density, oil-wetting, fluid loss or filtration control, and rheology control.

1. CLASSIFICATION OF MUDS

The classification of drilling muds is based on their fluid phase alkalinity, dispersion, and the type of chemicals used. The classification according to Lyons [2] is reproduced in Table 2.

Table 2 Classification of drilling muds

Class	Description
Freshwater muds ^a	pH from 7 to 9.5, include spud muds, bentonite-containing muds, phosphate-containing muds, organic thinned muds (red muds, lignite muds, lignosulfonate muds), organic colloid muds
Inhibited muds ^a	WBM that repress hydration of clays (lime muds, gypsum muds, seawater muds, saturated salt water muds)
Low-solids muds ^b	Contain less than 3–6% of solids. Most contain an organic polymer
Emulsions	Oil-in-water and water in oil (reversed phase, with more than 5% water)

^aDispersed systems.
^bNondispersed systems.

2. TYPES OF WATER-BASED DRILLING FLUIDS

The growing concern among government and environmental agencies over the environmental impact of drilling fluids has led to a significant increase in the industry’s reliance on WBMs [3]. Actually, about 85% of all drilling fluid compositions used today are water-based systems. The types depend on the composition of the water phase, such as [3]:

- pH,
- ionic content,
- viscosity builders (i.e., clays, polymers, or a combination),
- filtration control agents,
- deflocculants,
- dispersants.

The mud composition selected for use often depends on the dissolved substances in the most economically available makeup water or on the soluble or dispersive materials in the formations to be drilled. Several mud types or systems are recognized and described in the literature as given in Table 3.

These types are explained below. In general, WBMs have water as the continuous phase. Water may contain several dissolved substances. These include alkalis, salts and surfactants, organic polymers in colloidal state, droplets of emulsified oil, and various insoluble substances, such as barite, clay, and cuttings in suspension.

Table 3 Mud types [3]**Mud type**

Freshwater muds
Spud muds
Dispersed/deflocculated muds
Lime muds
Gypsum muds
Seawater muds
Salt water muds
Nondispersed polymer muds
Inhibitive potassium muds
Calcium-treated muds
Potassium-treated muds
Cationic muds
Mixed metal hydroxide muds
Low-solids muds

2.1 Freshwater Types

Freshwater fluids range from clear water having no additives to high-density drilling muds containing clays, barite, and various organic additives [3]. The composition of the mud is determined by the type of formation to be drilled. When a viscous fluid is required, clays or water soluble polymers are added. Fresh water is ideal for formulating stable drilling fluid compositions, as many mud additives are most effective in a system of low ionic strength. Inorganic and/or organic additives control the rheological behavior of the clays, particularly at elevated temperatures. Water-swellable and water-soluble polymers and/or clays may be used for filtration control. The pH of the mud is generally alkaline and, in fact, viscosity control agents like montmorillonite clays are more efficient at a pH more than 9. Sodium hydroxide is by far the most widely used alkalinity control agent. Freshwater muds can be weighted with insoluble agents to the desired density required to control formation pressures.

2.2 Seawater Types

Many offshore wells are drilled using a seawater system because of ready availability [3]. Generally seawater muds are formulated and maintained in the same way as freshwater muds. However, because of the presence of dissolved salts in seawater, more electrolyte stable additives are needed to achieve the desired flow and filtration properties.

2.3 Saturated Salt Water Types

In many drilling areas both onshore and offshore, salt beds or salt domes are penetrated [3]. Saturated salt muds are used to reduce the hole enlargement that would result from formation-salt dissolution through contact with an undersaturated liquid. In the United States, salt formations are primarily made up of sodium chloride. In other areas, e.g., northern Europe, salt may be composed of mixed salts, predominantly magnesium and potassium chlorides. It has become quite common to use high (20–23% 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 and inhibition of the formation of gas hydrates. The high salinity of salt water muds may require different clays and organic additives from those used in fresh or seawater muds. Salt water clays and organic polymers contribute to viscosity. The filtration properties are adjusted using starch or cellulosic polymers. The pH ranges from that of the makeup brine, which may be somewhat acidic, to 9–11 by the use of sodium hydroxide or lime.

2.4 Calcium-Treated Types

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 [3]. Gypsum muds 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 do.

2.5 Potassium-Treated Types

Generally 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 [3]. 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 US 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.

2.6 Low-solids Types

Fresh water, clay, and polymers for viscosity enhancement and filtration control makeup low-solids and so called nondispersed polymer muds [3].

Low-solids muds are maintained using minimal amounts of clay and require removal of all but modest quantities of drill solids. Low-solids 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. Polymers are used in these systems to provide the desired rheology, especially xanthan has proven to be an effective solids suspending agent. These low-solids muds are normally applied in hard formations where increasing the penetration rate can reduce drilling costs significantly and the tendency for solids buildup is minimal.

2.7 Emulsified Types

Classical additives for water-based oil-in-water emulsion fluids can be [4, 5]:

- emulsifiers;
- fluid loss additives;
- structure-viscosity-building substances;
- alkali reserves;
- agents for the inhibition of undesired water-exchange between drilled formations, e.g., water-swellaable clays,
- wetting agents for better adhesion of the emulsified oil phase to solid surfaces; e.g., for improving the lubricating effect and for the improvement of the oleophilic seal of exposed rock formations;
- disinfectants for inhibiting bacterial attack on such emulsions.

WBM, in diverse known formulations, perform satisfactorily in many applications. However, a particular problem arises when drilling through oil-bearing sand formations [6].

When the oil is thick and heavy it is difficult to recover. Conventional production well technology, which relies on crude oil flowing by gravity or pressure into production wells, does not work in bituminous oil sand formations. The recovery of heavy oil can be significantly enhanced using steam-assisted gravity drainage.

Using directional drilling methods, a horizontal production well is drilled through an oil sand formation. Then, a steam injection well with a perforated liner is drilled above and substantially parallel to the production well. Superheated steam is then injected into the oil sand formation. In this way, the oil is heated. This heating effect causes the oil to become less viscous. However, an effective removal of the cuttings from the mud is difficult and the ability to clean and reuse the mud is reduced [6].

These problems can be reduced by circulating the bitumen-laden mud through a mud cooler, which is an expensive method. Another promising solution for these problems is to use a polymer drilling fluid with some 0.3% of a nonionic surface active agent.

It has been found that the emulsification of the oil and bitumen in oil sand cuttings in a WBM may be effected by the addition of surfactants with hydrophilic-lipophile balance (HLB) numbers equal to or greater than approximately 7.

The HLB of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic. This term has been created by Griffin [7].

Effective surfactants are given in Table 4. These particular surfactants are manufactured by the Stepan Company, Inc., of Burlington, Ontario, Canada.

Nonyl phenol ethoxylate is shown in Figure 1.

Ester oils in water-based drilling fluids of the oil-in-water emulsion have an improved ecological acceptability [5]. These oils may be a 2-ethylhexylester of a C₈ to C₁₄ fatty acid mixture, propylene glycol monooleate, or oleic acid isobutylester.

2.8 Inhibitive Types

The hydration of a water-sensitive formation during drilling can be prevented by using an inhibitive formulation [8]. The drilling fluid contains a high molecular weight nonionic poly(acrylamide) (PAM) with a molecular weight of 4-15 MD, a low molecular weight nonionic PAM with a molecular weight of 0.5-2 MD, long-chain alcohols, and polyanionic cellulose (PAC). An example of such a formulation is given in Table 5.

CLAY GRABBER™ is a high molecular weight PAM material, CLAY SYNC™ is a nonionic low molecular weight PAM, GEM™ is a long-chain alcohol, FILTER CHEK™ is a modified starch, and BARAZAN® is a viscosifier, all available from Halliburton, Houston, Texas.

Table 4 Nonionic surfactants [6]

Compound	HLB number	Trade name
Nonyl phenol ethoxylate	8.3	IGEPAL® CO-430
Octyl phenol ethoxylate	10	IGEPAL® CA-520

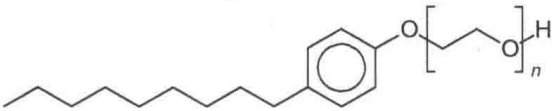


Figure 1 Nonyl phenol ethoxylate.