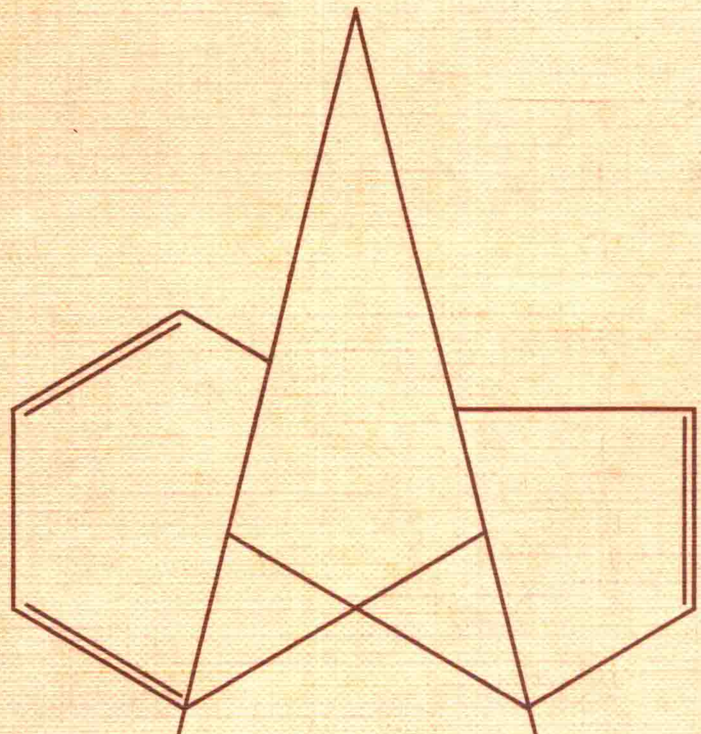
Chemicals in the Oil Industry



Edited by P.H. Ogden

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Chemicals in the Oil Industry

The Proceedings of a Symposium Organised by the North West Region of the Industrial Division of the Royal Society of Chemistry

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Introduction

The technicalities of oil production are heavily oriented towards engineering and as a result are probably fully appreciated by only a small segment of the chemical industry. Indeed the average practising chemist is likely to be uninformed concerning the industries' simplest technicalities such as the physical structure of an oil-bearing rock formation or the role of muds in the drilling operation. Nor might he appreciate the massive scale of operations which are required in order to reach, extract and transport crude oil to a point of refinery. Yet, each of the processes involved in this operation, i.e. drilling, stimulation, production and transportation is often dependent upon the use of chemical additives.

The volume of chemical additives used may be rather small when compared with the total quantity of oil produced, the proportion usually being expressed as parts per million; however, it represents a considerable quantity of chemical, frequently specialty and often expensive.

The importance of the chemical additive is particularly evident when exploration and production occur in a hostile environment such as that which confronts operators in the North Sea. In such a location, drilling costs are extremely high and the cost effectiveness of oil-based drilling muds in directional drilling is obvious. Initial crude oil treatment is limited by severe space restrictions, and the disastrous effect upon crude oil transportation caused by corrosion or wax plugging of sub-sea pipelines can readily be understood.

On the other hand, because the use of chemicals is relatively small compared with the volume of crude oil, production operatives, with a few exceptions, have been unaware of the fundamental aspects of their chemical additives. The term specialty chemical is frequently used as a misnomer for a formulated product, such as a corrosion inhibitor or scale dissolver, which might be a mixture of several active ingredients with selected solvents or surfactants in order to allow easy application and effective transportation to the site of operation.

If a technology gap exists between the oil producer and the chemical manufacturer, this has been filled by the chemical service company. Such organisations combine a knowledge of the chemistry involved with a good understanding of oil production technology. Their role has been extremely important but their interests would not be served by widespread dissemination of their knowledge and it could be argued that they sell service and expertise rather than a chemical product.

The objective of the symposium of which the proceedings follow was to draw together representatives of the oil producing industry, the chemical service companies, and the general chemical industry in order to describe some of the problems associated with oil production; to define those problems which can be solved through the use of chemical additives; the type of chemical currently favoured; the level of service required to supply such chemicals effectively to the oil industry; the volume of chemicals used; and the financial outlay required of the oil producer. As such, the symposium was to be technically informative and also to enable participants to gauge the level at which their respective organisations might reasonably participate in the future of this growth business.

The North West Region of the Royal Society of Chemistry wishes to record its gratitude to all of the contributors to these proceedings through which we have been able to cover many of the chemical aspects of drilling, stimulation, production and transportation. Enhanced Oil Recovery, which is an extremely important aspect of future oil production and is a subject which possibly holds the highest promise for future chemical sales to the industry, will be described in a future symposium.

In addition, the R.S.C. is grateful to Britoil and the British Petroleum Company for their generous sponsorship of the event and for the valued support of my fellow members of the organising committee :

P. Brookes, Britoil; A. Gerrard, Ciba-Geigy; R. Mitchell, B.P.; J. Moorfield, Petrolite; A. Todd, Heriot-Watt University; and E. Vase, Shell EXPRO.

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Application of Chemistry to the Drilling Operation

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Before considering where chemicals are applied in the drilling operation, it will probably be profitable to outline the mechanical processes involved in drilling a bore-hole. Naturally in the context of this paper it will only be possible to develop a very simplistic outline of a very complex operation.

With the energy spotlight falling on the North Sea in recent years many people have become familiar with the massive structures that are designed to work miles offshore in hostile environments. In fact once connection to the sea-bed has been established through a 'riser' tube, drilling from an offshore platform is essentially the same as drilling from a land rig.

From the surface (or sea-bed) a hole, often 36" in diameter is drilled to a depth of 50ft and a steel casing 30" in diameter is lowered into this hole and cemented into place, filling the entire annular space with cement slurry if possible. At ground level a wellhead is fitted to the top of this casing and all subsequent operations take place through the wellhead.

If troubles develop during the drilling operation, and pressure of fluid in the formation causes the well to flow, rams in the wellhead can be closed, even with pipe in the hole, so that the well can be shut-in safely.

Working through the wellhead and the casing already in the ground, the hole will be deepened to 1000-1500ft using a 26" bit and 18⅝" or 20" casing run to bottom and hung from the wellhead. As before the annular space is filled with cement.

Drilling proceeds in stages in this manner. From inside the 18⅝" casing 17½" bits extend the well to 4-5000ft when another casing string 13⅜" diameter is run and cemented. Then with 12¼" bits to 8-10000ft when 9⅝" casing is set and so on down the hole using progressively smaller bits and casing strings. Each string of casing is hung from the wellhead, inside its predecessor and cemented into place, with the exception that often the deepest, narrowest strings are not run back to the surface but terminate just inside the previous string; these short strings are termed 'liners'.

A longitudinal section through a borehole will take the form of Fig. 1.

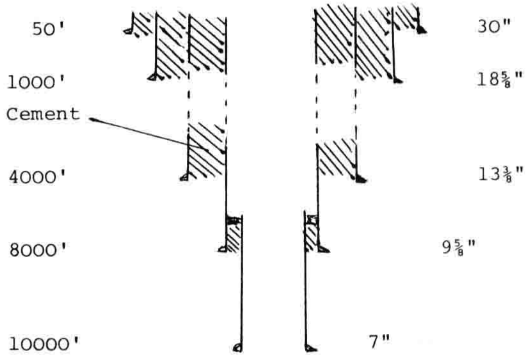

FIG. 2. SCHEMATIC SECTION THROUGH A BOREHOLE

Eventually the borehole will reach target depth - hopefully in hydrocarbon-bearing formation - and the drilling phase of the operation is completed. If hydrocarbons are encountered the well now enters a complicated testing and evaluation phase to assess commercial viability.

Bits are run on the end of a hollow drill string. This string is formed from a series of pipes 5" in diameter and about 30ft long coupled with screw connectors. As drilling proceeds and the bit penetrates a further 30ft a new joint of drill pipe has to be screwed on at the surface. The process is then resumed and new joints are constantly being added as required.

The uppermost joint of the drill string "the Kelly", differs from the others in having flat faces on its outer surface. These flats mate with bushings in a rotating table on the rig floor, so that, as power is applied to turn the rotary table, torque is transmitted to the drill string to turn the bit. At the same time the kelly is free to slide down through the bushings as the bit advances.

As each connection is made the kelly has to be removed from the string, the new joint added and the kelly screwed back into the top of this new joint.

The whole string is supported from a travelling block suspended in the drilling mast. When for any reason a bit has to be pulled the whole string has to be hoisted from the hole. It is broken out 3 joints (90ft) at a time and racked in the derreck.

As presented above this is a very elementary outline of the drilling process; I have not attempted to discuss the problems that can arise when carrying out an operation that is taking place some two or three miles below ground with only a 5" diameter steel tube providing contact with the surface and where the total mass of the drill string can exceed a million pounds.

This session is concerned more with the chemical than with the mechanical aspects of the drilling operation.

In any drilling activity a recurring problem is the removal of debris formed by the drill. Whereas this is relatively simple to overcome in activities taking place on the surface, it is more complex when the debris are generated at the bottom of a borehole. The solution to the removal problem is the drilling fluid or mud.

Drilling fluid is held in mud pits or storage tanks on the rig. It is pumped down the hollow drill string by high-capacity positive displacement pumps which are linked to the top of the kelly by a flexible hose.

At the bottom of the string the fluid passes out through ports in the bit, and returns up to the surface in the annulus formed between the borehole wall and the drill string, carrying with it the debris created by the bit. On the surface the fluid passes over shaker screens and through hydrocyclones where the debris are extracted and the fluid returned to the pits to resume its cycle.

Large volumes of fluid are required to fill the hole and surface system - 50-60000 gallons is by no means unusual. Consequently substantial quantities of chemicals are used in preparing and maintaining this fluid.

In addition to cuttings removal a drilling fluid has to serve several other functions Fig. 2.

A drilling fluid should:

- Seal the hole to prevent fluid loss
- Provide a conductive medium for logging tools
- Lubricate the drill string and bit
- Clean the hole and bit
- Encapsulate reactive particles.
- Prevent fluids entering the hole
- Strengthen the hole to prevent collapse
- Lift cuttings and suspend solids
- Remain stable at high temperature

FIG. 2. FUNCTIONS OF A DRILLING FLUID

In order to achieve these sometimes conflicting functions a drilling mud has progressed over the years from a simple clay/water mix prepared in a convenient pond, to a sophisticated mixture using considerable quantities of expensive chemicals and forming the basis of a major service industry; extending from the prime suppliers of bulk raw materials to the service companies providing a total package of materials and engineering and design services.

Drilling fluids may be classified according to the base fluid as 'Water Based' and 'Oil Based', and both will be discussed in this session.

Water based fluids may be further classified depending upon the nature of the water used into fresh-water, sea-water or salt-saturated systems.

To enable the fluid to carry cuttings the often considerable distance up to the surface, a certain amount of viscosity has to be developed. Essentially there are two means of doing this, either by the addition of clay (bentonite or attapulgite) or by the addition of a long-chained water-soluble polymer (xanthan or polyacrylamide). In addition to viscosity however the fluid must exhibit thixotrophy to prevent cuttings en route to the surface falling back when for any reason circulation stops; this is why bentonite has proved such a useful medium in the past.

Whilst a borehole is being drilled the formation penetrated might contain fluid under pressure and it is essential that this fluid does not enter the wellbore. In many instances the normal hydrostatic head of the fluid column will suffice, but there are times when the drilling fluid weight has to be increased. This is almost invariably achieved by the addition of finely ground barytes (barium sulphate) to the fluid. Fluid density in excess of 2.2gm/ml can readily be achieved in this way, and in recent years the use of ilmenite and haematite has permitted the attainment of even higher weights in water based fluids.

Clay and barytes are the principal bulk materials, used in very substantial tonnages in drilling. Although produced to meet API (American Petroleum Institute) and OCMA (Oil Companies Materials Association - now known as Engineering Equipment & Materials Users Association) standards [2,3] these are essentially natural products and require very little processing in their production.

Many other more specific chemicals are also added to a drilling fluid to enable it to achieve its essential functions and probably these are of more interest to this Symposium.

Earlier I mentioned that viscosity could be imparted either by the use of clay, or by a long-chained polymer. In recent years considerable interest has been taken in the latter technique, with the development of the so called "no-solids" systems. This started with the introduction a few years ago of the biopolymers, xanthan gums and shortly afterwards of the polyacrylamides. In addition to imparting viscosity to the system it was claimed that these materials by "encapsulating" clay and shale particles as they were drilled inhibited the dispersion of formation in an aqueous medium. Potassium chloride was frequently added to inhibit shale hydration even further.

These polymer based systems are still used extensively and on the whole perform very well. Some have limitations of temperature and lack mechanical stability and others do not perform well with electrolytes in the water, but in the right circumstances polymer fluids do an excellent job.

Cellulosic polymers (sodium carboxymethylcellulose) and starch are used in considerable quantity in the drilling fluid. These are added to control the loss of the fluid phase to the formation which tends to occur because of the pressure exerted by the hydrostatic head of the fluid column.

Many of the formations being drilled contain hydratable clays and shales, and there is always a tendency for these to develop viscosity within the drilling fluid. To some extent this can be controlled by continuous dilution but this may be expensive if other chemicals, particularly barytes, are being used. Frequently excess viscosity is better controlled chemically by the use of complex phosphates (such as sodium hydrogen pyrophosphate) or by lignites and lignosulphonates, usually with a heavy metal substitution. The first paper in this session will show that all of these chemicals have temperature limitations, and to meet the requirements of deeper, hotter holes a new series of chemical dispersants is becoming available to the drilling fluids engineer.

High downhole temperature is one of the main problems confronting a mud engineer. Bentonite in suspension flocculates and many chemicals used today degrade at the temperatures frequently encountered in a normal borehole.

Unless the well is being drilled in a specific geothermal area, temperature gradients of between 11°F (6°C) and 17°F (9°C) per thousand feet of depth are normally encountered so that at 15000 ft temperatures around 300°F (150°C) can be anticipated, and in some areas even higher temperatures are reported. New chemicals, the subject of the next paper, are enabling us to extend the economic limits of water based muds at temperature but there are obvious constraints beyond which it will always be impractical to use a water based mud.

When this situation is reached we have to resort to oil based fluids with concomitant environmental and disposal problems. Oil muds àre not a recent phenomenon: they have been is use for some twenty years but hitherto either crude oil or diesel oil has been used as a base.

Recently oils with a low aromatic content have been introduced to the industry and because of their inherently low toxicity these are gaining very wide acceptance particularly in marine locations.

The use of oil muds and the various chemicals required to produce stable emulsions, with the hole cleaning characteristics that the mud engineer demands, is discussed very fully in the second paper of this session. It is interesting to comment here however that with increasing usage of low-toxicity systems, cuttings disposal has become less rigorously controlled by the environmental agencies and in consequence there will probably be a reduction in the usage of chemicals designed for use in cuttings wash systems.

The drilling industry has a demand for large quantities of chemicals, not usually of particularly high quality but of ready availability. Almost invariably these chemicals will be obtained through one of the service company organisations who provide a total package of engineering and chemical supply.

Such companies maintain a full inventory of chemicals - mostly under their own brand name - and operating companies expect, and generally receive, an immediate response when service is required.

Certain of the commonly used chemicals, bentonite, attapulgite and barytes, are prepared to conform to the API[2] and OCMA[3] standards, and the OCMA also issue standards covering starch, CMC and thinners.

Other more specialised materials are purchased by the service companies to their own specifications so that variation in quality is sometimes apparent.

These more specialised chemicals are mostly used in systems for specific purposes such as completion brines and non-damaging fluids. In certain circumstances potential hydrocarbon reservoirs may contain clays or other minerals that would tend to hydrate if contacted by a normal drilling fluid and possibly cause blockages within the reservoir, whilst in other situations clays and weighting agent in the drilling fluid might be the cause of production impairment if they blocked reservoir pores.

Completion brines are frequently used in place of drilling fluid under these conditions. A completion brine is essentially solids free. Necessary weight is imparted by a soluble salt, usually sodium or calcium chloride, but if high weight is required zinc salts may be used although cost then becomes significant. Because carrying capacity is also required in a completion brine a suitable polymer, hydroxyethylcellulose, may have to be added and the temperature range of the polymer may be extended using a polyamine.

Flourosurfactants are sometimes recommended to reduce the surface tension of a fluid and thereby prevent water wetting of an oil reservoir.

Surface active agents are widely used in drilling fluids to influence or control viscosity, fluid loss, emulsion stability, wettability and drill string friction. These vary from simple petroleum sulphonates to the high-temperature clay stabilising agent which is a mixture of ethylene oxide adducts of phenol and nonyl phenol.

Defoamers are not normally added unless foaming becomes a major problem. Various chemicals are used; tri-n-butylphosphate, aluminium stearate, higher alcohols, polyethers etc. have all been applied in the past depending upon the nature of the foam encountered.

I have not attempted to produce a comprehensive catalogue of chemicals that may be used by the mud engineer attempting to reconcile the conflicting demands made upon the drilling fluid, but I hope that I have given an indication of the range of materials, from the crude bulk minerals to the sophisticated, and expensive, co-polymers, found in a modern drilling mud.

Turning now to the cementing process. The last paper in this session will discuss in some detail the chemistry of oil-well elements and additives. As an introduction to this I would like to outline the mechanism of cementing casing in a borehole.

Cement in a borehole serves three prime functions[4]

1. To support and strengthen the casing string

2. To protect the casing string from corrosive fluids

3. To prevent fluid communication between different parts of the borehole

As illustrated at the beginning of this paper once a section of hole has been drilled, the drill string is pulled from the hole and an appropriate casing string is run. In the way that drill pipe is screwed together from 30ft joints the casing is also picked up a length at a time and screwed together. A joint of casing is usually about 40ft long and for example will probably weigh between 30lb and 50lb per foot (depending on grade and wall thickness) for a string 9⅝" in diameter.

The casing is slowly lowered into the hole, which should of course be standing full of drilling fluid, until the string almost reaches the bottom. The length of string is tailored, by using different length joints, so that the top joint of casing protrudes onto the drill floor. A cementing head is attached to this upper joint and using high pressure, quick coupling pipe, connection made to the cementing unit normally some distance from the rig floor.

After fluid circulation has been established and the hole cleaned up the cementing operation commences.

Before displacing any cement a 'pre-flush' is normally pumped into the hole to act as a spacer between the drilling fluid and the cement slurry, and to remove mud and debris ahead of the cement.

Normally 300-500 gallons of pre-flush are pumped. Often fresh water will suffice, but surfactants and/or dispersants (acid phosphates) are sometimes added to provide better hole cleaning.

Once the spacer fluid has been displaced the cement slurry is prepared and pumped downhole.

Cement from a storage silo is drawn into a mixing hopper where it is intimately mixed with water passing through a venturi jet in the base of the hopper. The slurry thus formed passes to a small holding or re-circulating tank where minor adjustments can be made to the density.

Mixing and pumping is a continuous process. As soon as the slurry is at the correct weight it is pumped to the hole. As the slurry reaches the cementing head a wiper plug is released and precedes the slurry down the inside of the casing. This plug is circular in section with vanes the same diameter as the inside of the casing, and serves to wipe the casing free of mud film and debris as it is forced downwards.

Mixing and pumping continues until a volume of slurry equal to the volume of the annular space between the casing and the borehole wall has been prepared. A second plug is then inserted into the top of the casing and the cement slurry, sandwiched between the bottom and top plugs, is now pumped down to the bottom of the casing. This is usually achieved by connecting the mud lines to the cementing head and pumping mud into the casing. Eventually the bottom plug latches into the shoe at the bottom of the casing string and there is a momentary increase in pump pressure, causing a diaphragm in the plug body to rupture. The cement slurry now floods out into the borehole and round the casing shoe to begin filling the annulus, displacing drilling fluid and preflush ahead of it.

As pumping continues the remaining slurry is forced out of the casing until eventually the top plug also reaches the shoe. This plug will not rupture and the pressure increase indicates that displacement has been completed, and given reasonable luck the annulus is now full of cement slurry. Slight pressure is maintained on the casing to prevent any leak back and after twelve hours or so sufficient strength should have developed in the cement to permit operations being resumed.

Again I have only attempted to develop a very simplified outline of a very complex operation. It is not difficult to imagine the highly specialised knowledge that is required to produce a cement slurry that is readily pumpable, remains pumpable for three or more hours whilst being forced a couple of miles down steel pipe, is subjected to very high temperatures and pressures, and returned to the surface and yet will have developed sufficient strength after

8 or 12 hours to permit drilling to resume.

The mud engineer and the cementation engineer both need a good working knowledge of the chemistry of their products, and both depend upon the chemical industry extending the range of materials available to them, as drilling operations become progressively more complex and more costly. Happily the chemical industry has never let them down; solutions have been found as rapidly as problems have arisen.

ACKNOWLEDGEMENT

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