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Review on Applications of Non-ionic and Anionic Surfactants in Water Based Drilling Fluids

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Abstract: *In recent times, with the advent of exploration activities in deeper hydrocarbon reserves, drilling of wells in HPHT conditions is one of the most studied field in the upstream oil and gas industry. Water-based fluids are the most common and frequently used drilling fluids oil and gas well construction. Although, water-based drilling fluids are environment friendly and relatively in-expensive, it is often associated with many problems when used in HPHT conditions. In order to overcome these problems in such viable conditions, modified surfactants are used with the mud to counteract the problems associated with it. This paper discusses the different applications of anionic and non-ionic surfactants in water-based drilling fluids both in laboratory and field scales. The paper also discusses the mechanisms of the surfactants and the effect on various mud properties to overcome hole problems like wellbore instability, rheology and filtration loss, foaming and flocculation of mud.*

Keywords: *Surfactants, Water Based Drilling Fluids, HPHT, Anionic, Non-Ionic, Shale Inhibition, Wellbore Stability, Thermal Stability*

I. INTRODUCTION

Drilling fluid design and optimization is one of the most important part in any well planning program. The drilling fluid performs various functions: bottom hole pressure, cutting transportation to the surface, cooling and lubrication of drill-bit and maintain hole stability. During a drilling operation it continuously experiences large variations in pressure and temperature, when flowing through different sections of the circulatory system. As a result, of which the fluid often losses its rheology and/or its various constituents are degraded, and it fails to perform the necessary functions leading to hole problems. Therefore, its properties must be optimized for different shear rates, pressure and temperature conditions for different part of the circulatory system. The role of surfactant is critical in achieving the desired properties in modern drilling fluids. Surfactants and/or various surface-active agents find popular use in Enhanced Oil Recovery [1], but it has immense use as fluid additives in the drilling industry. The promising results obtained from various laboratory and field studies shows the ever-increasing importance of surfactants in optimization of water based drilling fluid. This paper provides the readers with a detailed overview of the applications of anionic and non-ionic surfactants in water-based drilling fluids and its future prospects.

A. Historical Review of Drilling Fluid Development

Before moving deeper into details of the drilling industry, allow us to recognize the sequence of issues that contribute to the varied developments during a drilling mud industry. In the past, early drilling operations are often reported using water to get rid of the cuttings from the opening. Literatures stated that Fauvelle in 1846 drilled a well in France by using flushed water as the main drilling fluid. Water alone as a drilling fluid was unable to remove cuttings completely and drilling depth became limited. Thus; the lack of water alone during this application led the researchers and oil companies to supply new fluids [2]. The basis of science driving the drilling fluids is said to have started by the Chapman's idea in which he introduced water and plastic material to be used as drilling fluid and it successfully formed a strong cake around the inner formation of the reservoir [3]. The first development well was produced in 1901, drilled by using a clay-water mixture. As a result, bentonite clay was introduced by [4] and mentioned this on his research article in 1935, and this innovation is taken as the basis of present-day drilling fluids [4].

B. Drilling fluids Types and Functions

The definition of drilling fluid varies depending on the function, formulation chemistry and its complexity. American Petroleum Institute (API) defined that, drilling fluid is a circulating fluid employed to perform the functions necessary in drilling operations [5]. Drilling fluid can be defined as a chemical composition that is circulated into the borehole to facilitate drilling operation [6]. Additionally, it can be defined as a complex fluid that consists of a large number of additives. [7]. The types of the additives and its quantity is based on the drilling operation and the formation of the target reservoir. In drilling operations, drilling fluids play a vital

role; fluids are employed to remove cuttings from a borehole and transport it from the sub-surface to the surface facility, to stabilize wellbore, to support the drill string, and act as coolant and lubricant for the drill bit. Addition to that, drilling fluids also help in suspending the cuttings when the well is in static condition and control formation pressure. Furthermore, drilling fluids helps in limiting damage to the environment by preventing inflow and outflow of fluids between the formation and the drilled borehole [8]. Numerous challenges are being faced during drilling operations in the petroleum industry which have led to the formulation of different types of drilling fluids. The primary ingredients of these formulated fluids are water, oil and gas in addition to chemical additives [9]. Generally, the drilling fluids are classified as water-based mud, oil-based mud and air-based mud. According to Shah et al. (2010) water-based mud (WBM) is the most popular drilling mud used in drilling, while oil-based mud (OBM) is usually used in shale swelled formation. In WBM, the fluid particles are suspended in water or brine [10]. OBM is used in shale formation because with WBM, the shale has a tendency to absorb the water inside its layers, as a result of which, it swells and this leads to pipe sticking inside the borehole and many other problems are associated with this [7]. Production from unconventional hydrocarbon resources, such as shale gas, shale oil, deep-water and arctic reservoirs require advanced drilling and production technologies. Nano surfactants have been showing promising solutions to overcome such issues in oil and gas industry. Studies are carried out to analyze the enhancement of drilling fluids through the use inexpensive and biodegradable surfactants. Literatures confirms that with addition of surfactants in water based drilling fluid the rheological, filtration, and heat transfer properties and friction reduction can be optimized.

C. Review on Chemical Additives

Chemical additives are added to drilling fluids so that they can enhance its performance by modifying the chemical properties, particularly when special mud is required to drill a particular well or well-section. Mud additive are often of several types, some performing quite one function [11]. The foremost common additives are: pH control to regulate the acidity and alkalinity of the fluids, bactericides to scale back the bacterial count and corrosion inhibitors to stop corrosion and therefore the formation of scale in drilling fluids. In addition to this, defoamers are used for reducing the foaming action, emulsifiers are also often added to help make a mixture of two liquids and a filtrate loss agent is added to help reduction of water loss to the nearby formation. Also, flocculants are used to help settle out the solids, lubricants is used in small amounts to reduce the coefficient of friction, and lost circulation materials are added, which helps to plug the target zone within the formation [12]. Surfactants and other chemical additives have an effect on the emulsion stabilization or destabilization function in the mixture of synthetic based mud and aqueous solutions. When original emulsion of the synthetic based mud is broken by mixing with aqueous fluids, phase separation occurs and solids flocculate to form solid sludge. This solid sludge becomes a drag for well cleanup operations [13].

II. REVIEW ON APPLICATION OF SURFACTANTS

Surfactants are increasingly getting used in an ever-expanding sort of applications for drilling fluids. In water-based drilling fluids, there's a continually-growing sort of applications that include: oil-in-water emulsification in base fluid formulations; shale-swelling inhibitors to stop wellbore instabilities; detergency to stop cuttings sticking to drill bit; addition of surfactants results in prevention of differential sticking; surfactants helps in promoting dispersion which inhibit flocculation of clay particles; foaming additives to get high gas-water ratio foam used as drilling fluids for low-pressure reservoirs and hard formation drilling; used as defoaming additives to eliminate unenviable foam in water-based fluids; surfactant-polymer complexes for enhanced properties in fluids for low-pressure reservoirs [14]. This review states the applications of surfactant technology in drilling fluids with time and therefore the impact of these molecules on drilling operations. Proper selection and application of surfactants in drilling fluids have a big economic impact, in terms of reducing the quantity of lost time and potential trouble, and have a direct consequence on overall drilling performance and results.

III. RESULTS AND DISCUSSION

A. Rheological Properties

Reference [14] showed the behavior of quaternary ammonium di-cationic surfactant containing phenyl linkers with Cl and Br counter-ions (PC and PB) and found addition of PC and PB surfactants reduced the rheological properties at constant temperature as shown in Table I.

Table I: Rheological parameters (AV, PV, YP) of base mud and modified drilling fluid. [14]

Additives	Apparent Viscosity (cp)	Plastic Viscosity (cp)	Yield Point (lb /100 ft2)
Base Fluid	11.1	8.2	5.7
PC (0.1%)	7.4	5.6	3.4
PB (0.1%)	8.3	6	4.7

The value of apparent viscosity provides an idea on the flowability of the drilling fluid at a particular shear rate. Plastic viscosity is a direct indication of the behaviour of solids in the drilling fluid and yield point is the ability of cutting carrying capacity to surface. High YP is generally required for proper hole cleaning but unwantedly higher YPs can lead to higher pumping power consumption. The reduction in rheological properties after addition of PC and PB surfactants is due to the agglomeration of bentonite particles, upon reduction of repulsive forces between clay platelets and electrostatic interaction with ammonium cations. [14]

Reference [15] showed in their experiment with 2-hexadecyloxyethanol (non-ionic surfactant) and alkyl benzene sulphonate (anionic surfactant) found significant increase in plastic viscosity, yield point and gel strengths of surfactant treated water based drilling fluids as compared to the base fluid after dynamic aging for 16 hrs at elevated temperatures. Plastic viscosity values after 16 hrs of dynamic aging at 275 F of base fluid approximately decreased by 65%, but a reduced drop of 50-55 % was recorded in the surfactant treated drilling fluid samples. Yield point values showed similar trend as of plastic viscosity. The surfactants however, showed minimal effects on gel strength optimization. A minimal increase in gel strengths was observed due to electrostatic interactions among surfactants and solid contents.

Reference [16] found that addition of polyglycol, a non-ionic surfactant, resulted in significant increase in yield point, 10 second and 10 minute gel strengths, although the plastic viscosities were similar.

Reference [17] tested alkylpolyglucosides (APG), a highly biodegradable non-ionic surfactant in different water based mud systems and it was observed that APG which interacts with other water soluble polymers to drastically reduced the fluid loss in HPHT conditions. It was suggested to use the non-ionic surfactant as a co-additive to fluid loss additives.

B. Filtration Properties

Reference [15] showed that treating water based drilling fluids with non-ionic and anionic surfactants reduces filtration loss by 12% at room temperature, 6.7% at 275 F and 41.3% better than water based drilling fluids without surfactants at 300 F. It was also observed that surfactant treated fluids produced thinner and compact mud cakes than the base fluid.

API filtrate variability is reduced upon treatment with non-ionic surfactant polyglycols in water based mud systems, consequently improving the overall quality of the drilling fluid [16].

C. Clay Adhesion

In drilling shales with high clay content with water-based mud, clays swell and results in stickiness of the shale. Bit balling is the accumulation or adhesion of drill cuttings around the cutters or teeth of the bit. Consequences of bit balling are reduced rate of penetration, ineffective hole cleaning (cuttings re crushed at bit face) and reduces mud flow decreasing cooling effect (reduces bit life) [18]. Anionic surfactants like alkyl aryl sulfonate, alcohol ethoxylates or anionic/non-ionic blends. These are popular in drilling community as 'drilling detergents' D. D's. Adsorption of surfactants onto the drill bit occurs due to the dispersion forces, dipole interactions and electrostatic effects. Example using alkyl aryl sulfonate surfactants results in 1 electrostatic interactions between the electric charges on the surfactant molecules and the metal, and 2 dipole-dipole interactions between the aryl group (which has high electron density) and the strongly polarized sites of the metal [19]. Adsorption of surfactants onto drill cuttings occurs because the clay minerals have sites with highly charged surface. Hydrophilic part adsorbed onto the clay, with hydrophobic part oriented towards aqueous phase, thus drill cuttings surrounded by hydrophobic part and less wetted by water phase [20].

D. Lubrication

Drill string upward/downward movement and rotation restricted with free flow of mud after a static period: termed as Diff Sticking. Drag exceeds the rig horsepower or excess pull may lead to drill string failure at weak points. Drag is higher in horizontal or highly inclined wells, so these are susceptible to differential sticking [10]. Permeable zones with slightly higher overbalance and thick mud cakes increases the risk of sticking. Addition of non-ionic surfactants as lubricants to increase lubricity of the water-based mud [21]. Moreover, mud cake thinning, and compacting should be achieved from surfactant addition.

E. Deflocculation

Calcium or Magnesium contamination causes the clay particles to aggregate and flocculate. The mechanism is based on divalent calcium or magnesium ions tend to replace the sodium ions from the exchange sites on the clay particles. Due to higher charge in Ca & Mg ions they are strongly attached to clay platelets and decreases the overall repulsion between negatively charged clay particles, which finally cause Ca and Mg ions enter into the mud system from either make-up water or formation solids/fluids.

The problems in flocculated mud are increased fluid loss, increased yield point, increased gel strengths. Anionic polymeric surfactants like lignosulphonates neutralize the positive cations on the clay platelets. However, treatment is limited to low to moderate contaminations only. Reference [22] synthesized a modified *Rhizophora* sp. tannin-lignosulfonate (RTL) and investigated its deflocculating ability in HPHT conditions as an alternative to conventional chromic-lignosulfonates which degrade readily at higher temperatures. RTL minimized the yield point and gel strengths of a high solid content water based drilling fluid sample (simulating the flocculation condition).

F. Defoaming

Any substance used to reduce or eliminate foam by reducing the surface tension is called defoamer. Foam is generated when gas is encountered occurs during drilling or air is entrapped while mixing drilling fluid at surface, as most of the additives in mud are surface active agents. Foaming needs to be controlled to maintain the required bottom hole hydrostatic pressure of the mud column. [24]. Surfactants breaks the foam by reducing the surface tension even below the foam system. Alkyl phosphate esters and siloxane surfactants are some surface active defoamers.

G. Thermal Stability

Reference [16] studied the interactions of polyglycols, a group of non-ionic surfactants, with rheological and fluid loss polymers in XC/PAC/KCl/PHPA mud systems. Polyglycols are synthesized by condensation of glycol groups through the double hydroxy groups (-OH) to form ether links (-C-O-C). Addition of 5% v/v polyglycol in XC-polymer mud system resulted in complete preservation of rheology and decreased fluid loss after hot rolling for 16 hrs at 100 C, whereas the base mud system without surfactant addition rheology was completely lost. The mechanism behind the polyglycol-polymer synergy which leads to increased HPHT stability is hydrophobic interaction and hydrogen bonding between polymer and polyglycol. The thermal stability was dependent on the type of polymer, polyglycol and brine in base fluid. A minimum of 3% v/v concentration is necessary to get desired results.

Alkylpolyglucosides (APG) were seen to increase the thermal stability of naturally occurring polymers at HPHT conditions. The mechanism involved is that clusters of rod-shaped APG micelles gets attached to the polymer long chains with APG forming hydrogen-bonds and/or hydrophobic-hydrophilic interactions with the fluid loss polymers [17].

Modified *Rhizophora* sp. tannin-lignosulfonate (RTL) a surface active deflocculant shows good thermal stability without degradation at temperatures up to 280 C [22].

H. Foaming

Foam is used as drilling fluid for drilling into hard rocks and highly depreciated reservoirs that might cause fractures and mud loss if drilled with higher density mud systems. Foam is created when the surface tension of water (attraction of surface molecules toward the center, which gives a drop of water its round shape) reduced and air is mixed in, causing bubble formulation. Water and surfactants with other polymeric additives are injected into air stream to generate drilling foams with a high gas-water ratio. Non-ionic surfactants are generally used to generate drilling foams.

I. Emulsification

Anionic, non-ionic and anionic-non-ionic surfactant blends are used to stabilize oil-in-water emulsions. Oil-in-water emulsion drilling fluids require minimum additives to attain desired rheological properties due to the intrinsic rheological properties of emulsions. The success of drilling with oil-in-water fluids depends largely on the stability of emulsions at downhole conditions, i.e., temperature and oil/rock/brine interactions.

J. Wellbore Stability

Shale swelling, as a result of physio-chemical interaction between water-based drilling fluid and shale, is directly linked to the long-term problem of borehole instability. The reason behind the instability of shale in water is due to their strong hydrating tendency, leading to swelling and dispersion. Non-ionic polymeric surfactants called 'polyols' are commonly used in the industry and are found to be effective against reactive shales. [24]

Reference [26] developed a non-ionic surfactant, *Zizyphus spina-christi* extract (ZSCE), which showed great shale hydration inhibition potential. The effectiveness of ZSCE increased with increase in its concentration up to critical micelle concentration, and SEM results confirmed its compatibility in bentonite-water based drilling fluids. Moreover, ZSCE was found to reduce the filter loss of the tested water based drilling fluid [25].

There are three popular theories on the mechanism of shale-swelling inhibition by non-ionic polymeric surfactants. First study shows that, depending on the surfactant type and salt concentration, surfactant solutions produce a cloudy fluid upon heating and reaching the surfactant cloud point. This surfactant rich phase seals the shale surface and prevent further influx of water resulting in high well bore stability [26].

The second theory suggests that, the non-ionic surfactants (glycols) compete with the hydrogen-bonding between water and shale surfaces. Glycols can hydrogen bond with the silica and alumina sites in the clay particles. It has also been found that glycols harden the shale sealing it against further water interaction [27].

The third study shows that, these surfactants work simultaneously with salts, such as KCl, causing soft shale to harden. The cloud point of the surfactant solution can be manipulated by changing the concentration of the salt (KCl) and the potassium ions replace the exchangeable ions on clay platelets through cation exchange process, thereafter the glycol is adsorbed. Each glycol molecule being larger than the complex formed in case of hydration by water are glued onto the clay surface by hydrogen bonds, making it less mobile and hardening the shale [27]. Shale inhibition does not directly correlate to the amount of glycol adsorbed but the nature of the salt cation is more important, KCl being the most preferred one. Refer to Figure. 1.

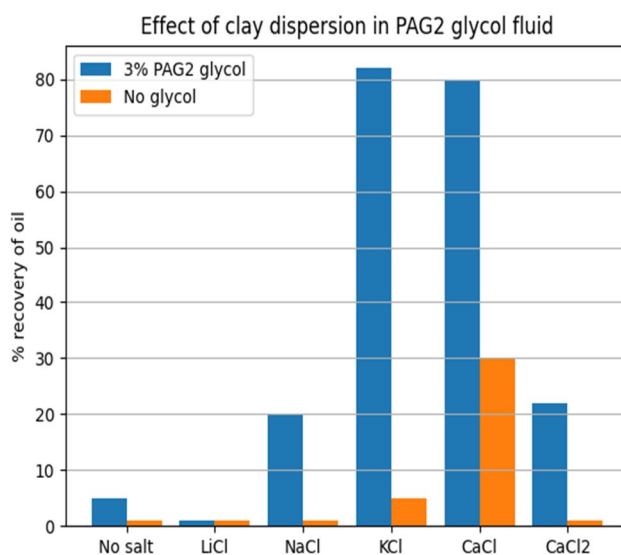


Fig.1 : Effect of salt type on clay dispersion in glycol fluid [27]

IV. CONCLUSION

From this study it can be concluded that these surfactants affect predominantly on the water-based drilling fluids. They help to decrease various non-suitable conditions in HPHT wells. It has been found that the anionic surfactants can certainly decrease the degree of flocculation to some greater extent in water-based fluids. Bit balling is considered as one of the most major problems while drilling but after the significant use of anionic surfactants it has reduced to a considerable amount. It has been found that surfactants have the potential to maintain wellbore stability in shale to a very large extent. Surfactants basically caused water-based drilling fluids to become more resistant at the higher temperature and pressure condition as shown by their improved and stabilized rheological properties. Other than that, problems like foaming, clay adhesion, emulsification which are often encountered in the HPHT wells are also thoroughly studied after addition of our desired surfactants.

Moreover, how surfactants change the physico-chemical properties of drilling fluids were further studied. Properties like plastic viscosity, yield point, gel strength act as an indicator to gain an overall knowledge of the behavior of drilling fluid in the subsurface. In this paper it has been included how these properties change drastically after addition of surfactant in a good manner which helps us to understand a brief idea of anionic and non-ionic surfactant. Utilizing all these data will help the oil industry professional to gather a greater depth of knowledge on the surfactants. In addition to this as the literature available on this particular topic is limited but looking at the continuous emerging uses of surfactant in drilling industry this work will definitely help the people who are more interested in gaining a on depth overview of surfactants.

V. FUTURE PROSPECTS

Although surfactants are being used to a large extent in drilling fluid, there remain many challenges need to be addressed, and this opens the following future prospects in this field of study.

- A. An effective surfactant is yet to be formulated to sustain a temperature higher than 150⁰C.
- B. Development of surfactant-polymer mixtures.
- C. Incorporating nanoparticles and/or synthesize nanohybrid polymer-surfactant complexes that can improve the efficiency of surfactant in WBM.
- D. Development of surfactant encapsulation techniques to control surfactant release during
- E. A better study on the complex interaction between surfactants and other additives will lead to better drilling fluid formulation.
- F. Development of natural surfactants/biosurfactants to reduce the environmental costs associated.

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