

The Role of HLB in Surfactants for Drill Cuttings Cleaning

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Abstract

The increased limits of retention of oil on cuttings (ROC) imposed by regulatory agencies such as the US Environmental Protection Agency (EPA) and Norway's State Pollution Control Authority (SFT) to drilling operators pose new challenges on their side in properly addressing these new requirements. This paper describes the role played by the HLB equation in designing efficient washing solutions (WS) that utilize both non-ionic and anionic surfactants to mitigate the issue.

A range of anionic and non-ionic surfactant blends was screened for their cleaning ability on field cuttings. The main parameters considered during the selection were: chain length, branching/linearity, substitution pattern and polarity of the surfactant. For non-ionic surfactants the emphasis was placed on ethoxylated vs propoxylated molecules. Following treatment with WS the ROC was determined by using the retort distillation method (RD). The numbers obtained were graphed against HLB values for the surfactants in order to determine the best correlation between structure and cleaning ability for that particular type of cuttings.

The results show the achievement of a maximum cleaning ability of the WS for a given chain length of the surfactants used. The linearity of the molecules, although initially thought to play a significant role, proved to have a limited influence. In fact, blends containing roughly equal amounts of linear vs branched surfactants displayed the highest cleaning ability. The overall polarity of the mixture seemed to be important too, since blends containing non-ionic surfactants had almost no cleaning capacity. Of major importance in this particular study was the substitution pattern on the non-ionic surfactants. An optimum combination of propoxylated vs ethoxylated molecules was critical for the design of the most successful WS. Our results indicate that ethoxylation on the anionic component of the mixture and propoxylation on the non-ionic portion was critical since tests performed with the opposite combination showed almost no cleaning capacity. Increasing the PO content on the non-ionic molecule has a detrimental effect which is more pronounced than a similar increase in EO content on the ionic molecule.

The present study aims to help elucidate the roles played by the different surfactant molecules in designing efficient washing solutions for cleaning drill cuttings. This will

assist the oilfield service companies in addressing the continuously increasing environmental regulations for disposing of drill cuttings while reducing the present costs and carbon footprint on the environment incurred by the current methods.

Introduction

In the Oilfield industry there are three main types of wells that can be drilled. During the first phase, called the exploration phase, *exploratory wells* are drilled to determine rock mineralogy, to help map out the reservoir and to determine its physical characteristics (e.g. pressure, temperature). Then the production phase starts and *production wells* are drilled so that the accumulated hydrocarbons can be brought to the surface. Also, a third category of wells are often needed: *injector wells*. They are commonly used either during enhanced oil recovery (EOR) operations to push the oil toward the producer well or for injection of produced water or other products deep underground (waste disposal role). In the process of drilling any of these wells rock fragments of different sizes and mineralogies are created (*drill cuttings*) and they need to be removed constantly from the wellbore. This is achieved by using drilling muds (or drilling fluids), which are continuously pumped through the drill string and circulated back up to the surface through the annulus, while carrying up with them the drill cuttings. These fluids can be of two types: water-based muds (WBM) and oil-based muds (OBM). The latter ones are referred to with other names as well, based on their composition. In general, if the formulation contains a mineral oil or diesel they are termed OBM or DBM, whereas if they contain other synthetic products (such as internal olefins, esters or ester equivalents) they are commonly named synthetic-based muds (SBM). Regardless of the type, the drilling fluids play four major roles: a) cool and lubricate the drill bit; b) remove the drill cuttings from the hole; c) maintain hydrostatic pressure on the formation; d) provide stabilization of the borehole wall.

These exploration and production considerations hold true both for onshore and for offshore wells. Offshore exploration and production activities are increasingly occurring in deeper waters with formations under high temperature and high pressure (HTHP) conditions. The high costs and safety considerations associated with operating in HTHP conditions allow little room for error. In some cases, offshore reservoirs may not be very stable leading to the

concern that WBM may damage and destabilize the wellbore as it is being drilled (1, 2). In many such cases, OBM or SBM become the preferred drilling fluid systems to use. Compared to their water counterparts, OBM/SBM's have the advantage of providing better wellbore stability, especially for water-sensitive formations (3), lower mechanical friction, increased rate of penetration (ROP) and a significant reduction in fluid loss to the formation. Furthermore, by minimizing wellbore instability, the use of OBM/SBM helps reduce non-productive time. Aside from initial cost, a significant disadvantage of an OBM/SBM drilling fluid system is the perception of increased pollution/contamination risks compared to the WBM systems.

Main Considerations and Challenges

Regulatory Considerations

Drill cuttings are formed during drilling exploration wells, new production wells, injector wells and during work-overs on producing wells. As mentioned before, the drill cuttings are being flushed out of the wellbore by the drilling fluids and they consist of agglomerates of rock fragments of different mineralogies and sizes, mineral oils, hydrocarbons, salts, drilling muds and other chemicals, some of which are hazardous and toxic. The chemistry of modern oil-based drilling muds is designed to remain stable under the high temperature and pressure conditions present during drilling. This stability and robustness of the drilling fluid can be partially attributed to increasingly complex compositions, with each ingredient playing a role in their stability but adding, at the same time, more concern regarding their HSE profile. Once they are used downhole, even more complexity is added to these fluids as they return to the surface and carry the drill cuttings along with other chemicals from the formation (salts, extra oil or hydrocarbons from the production zone, other formation fluids). Upon returning to the surface two processes occur:

1. The drilling fluid is separated from the solids and is recirculated- also called *primary treatment*;
2. The solid waste, consisting mostly of contaminated drill cuttings, is collected and subjected to what is called *secondary treatment*, prior to disposal.

The separation of the drilling fluid from the solids it carries is done by using *primary solids-control equipment* (such as shakers, desanders, desilters, centrifuges) based on: a) type of the drilling fluid used; b) formation characteristics; c) equipment available on site; d) specific cuttings disposal requirements. Depending on the type and number of equipment pieces being used (i.e. more than one of each can be employed) a physical separation of the fluid from coarse (gravel-type) all the way down to very fine particulates (clay-like) can be achieved.

The degree to which the cuttings are cleaned is dictated by the economics of the drilling operation. If the formation is suitable, cuttings may be injected back into the formation for

disposal. If the SBM is highly expensive and difficult to replace, the cuttings may be subjected to additional separation equipment such as drying shakers and horizontal cuttings dryers. If the drill cuttings are intended for disposal, they are analyzed on site at regular intervals to determine ROC. At this stage that regulatory agencies around the world step in to provide their guidance and to set requirements regarding the maximum permissible limits (MPL) of different chemical contaminants on the solid cuttings before they can be disposed of appropriately. Before 1990, most drill cuttings generated from offshore drilling applications were simply dumped overboard into the ocean or disposed of as normal waste for onshore operations. Due to increased pollution observed around drilling sites, different environmental agencies began to take a closer look at understanding the causes of the pollution as well as the mechanisms by which oil and other chemicals were accumulating in the environment. Slowly, as data was gathered from numerous studies on this topic and as our understanding of the pollution mechanisms increased, governments started to more carefully regulate the drilling waste, be it drill cuttings, washing solutions or spent drilling muds themselves.

The tightening of the legislation in response to the environmental concerns posed by the drilling operations resulted in the standardization of procedures to establish the MPL of different contaminants such as heavy metals and polynuclear aromatic hydrocarbon (PAH). On the drill cutting, the concept of *residual oil on cuttings* or *residual oil content* (most commonly known as *retention on cuttings*), **ROC**, came into use. ROC is a unitless number and it is defined as the ratio between the mass of oil and the mass of cuttings ($M_{oil}/M_{cuttings}$) and it is reported as a percentage. In some literature publications ROC is also called SOC (synthetic on cuttings) in a more exact reference to the SBM and not to DBM, which are highly regulated.

By 1997, the North Sea countries were the first to impose a ban on the DBM and by 2001 SBM were also regulated (4-6). In general, European countries require (OSPAR regulations) ROC of the cuttings produced offshore to be no larger than 1% if they are not diesel based (those being fully banned).

For drilling offshore Gulf of Mexico, US EPA's Effluent Limitations Guidelines (7) establish the following limits for ROC:

- 0% for DBM
- 6.9% for SBM containing internal olefins 1618 (IO) as base fluid
- 9.4% for SBM containing base fluids that meet the environmental performance criteria of esters
- 1% or less for other OBM

Although other regions such as South America, Middle East, Africa or South-East Asia do not currently have such strict discharge limits it is expected that their legislation will

change in the coming years to reflect the trend towards environmentally sustainable drilling practices.

Technological Challenges

While there seems to be a general consensus regarding the importance of sound environmental regulations, the industry is left with finding viable solutions to address the ever increasing requirements and tighter MPL for the discharge of drilling waste and in particular for drill cuttings. The main challenge is that the current technology does not provide a quick and practical way to clean the cuttings before disposal. In fact, after the *primary treatment* of the drilling muds the collected solids are subjected to the *secondary treatment* with the aim to clean them and bring the ROC values within the accepted limits. While this is not an easy task for onshore operations, for offshore operations the challenge is far more daunting. This is due mainly to the severe space limitations on the rig platforms or on drilling boats. The space limitation is attributable to both the volumes of drilling muds that can be processed through primary and secondary treatments and also the storage capacity of the necessary equipment and chemicals to perform the separation and cleaning. For onshore drilling applications, these limitations are not generally a concern.

Charles and Sayle illustrate perfectly in their 2010 SPE paper (8) the huge and sustained efforts made by drilling operators in offshore Canada to meet the existing standards of the regulations. They report on the results of a long term study (2002-2008) on the technologies available for the offshore treatment of drill cuttings and to what extent they allowed for the tight discharge limits to be reached. The study shows that despite sustained efforts, for the IO-based SBM a 6.9% ROC is rarely achieved, the per-well average being 8.46% (only 1 in 15 wells achieved the target value in the 6 year interval). The associated mass of treated cuttings discharged (with ROC < 6.9%) was less than 10% of the total treated mass of cuttings generated from the 15 wells. Based on the type of cuttings (from production/non-production zone), on their mineralogy and on the type of drilling fluid used, meeting other ROC standards (9.4% or 1%) can be equally difficult.

The case study above demonstrates the need and the ongoing quest for better technologies capable of providing quick, practical, environmentally responsible and cost effective cleaning of the cuttings so they can be safely discharged. In this paper we will present one such approach that could contribute to the efforts made by the operators in the field to efficiently meet the regulatory requirements for ROC.

The current technology leaves the offshore drilling companies with 4 possibilities:

- a. *Offshore disposal*- for those cuttings that, after secondary treatment, are in compliance with local regulatory requirements. This is the preferred method

but seemingly only a small percentage of the total mass of cuttings being treated qualifies for it.

- b. *Cuttings re-injection (CRI)*- is one accepted measure of disposing of the cuttings that, upon secondary treatment, did not meet the regulatory requirements. Two major drawbacks to this option are: the need of an available deep injector well and the need for cuttings to be finely ground before injection, both of which increase the operation costs by the extra time required and by the special equipment necessary.
- c. *On-platform treatment systems*- in some instances repeated washing or soak-in time of the cuttings may bring down the ROC to the required level that qualifies them for offshore disposal. However, most platforms or drilling boats do not have this kind of equipment or the soak-in time adds significant operation cost that may adversely impact the economics of the process;
- d. *Ship-to-shore option (Onshore disposal)*- depending on the particular situation of the operator, the cuttings collected after the primary treatment are stored in special containers and shipped ashore for treatment and disposal. This is by far the most expensive alternative since it adds substantial cost with shipping onshore, treatment and landfill disposal.

While the last three options fully address the regulatory requirements, they do come with rather big disadvantages, some of which were mentioned above. Additionally, the onshore disposal option is encumbered by the availability of such treatment facilities and whether or not they are in close proximity. In case they are not in close proximity, supplemental (and often significant) cost increases occur due to the necessity of cuttings to be transported by truck or train to the treating facilities. Further complications arise from the paperwork needed for such ground transportation to be possible, according to local/state/federal regulations for hazardous materials. In most cases, the thermal option (high temperature furnaces, in excess of 900°F) is the preferred one since the resulting dust can be used for soil regeneration or soil restoration projects.

Drill Cuttings Cleaning Approaches

Drilling operations are essential for the oil industry. However, given that the environmental regulations are expected to get increasingly tighter in an effort to minimize the amount of oil and other chemicals released into the marine environment or underground and to encourage the use of WBM to reduce chances of accidental pollution, it is critical that continuous efforts will have to be made by the industry to develop more environmentally friendly products and to design new technologies for cleaning the drill cuttings in a fast and economically sound fashion.

The most commonly used technologies currently available are:

- *Thermal desorption*- is a technique that involves the use of high temperatures to remove the oil from the cuttings. It is very energetically demanding, expensive and does not contribute to the reduction of carbon footprint on the planet, yet it is the most efficient. The oil recovered is typically used as fuel. Due to their size and safety considerations such facilities are not available offshore.
- *Solvent extraction*- uses different solvents to clean the cuttings by extracting the oils adsorbed on them. It can be further divided in two different types:
 - supercritical extraction (SCE), when supercritical fluids are used (CO₂, propane, etc).
 - counter-current extraction (CCE), a process that uses either Freon or methylene chloride, but it was never implemented on an industrial scale.
- *Surfactant-based oil removal by emulsification*- it involves the use of a mixed system, consisting of an emulsifying surfactant and an encapsulating agent to trap the cuttings followed by the addition of a silicate that gels the emulsion. In this final form the authors claim that it can be disposed of into the ocean without the risk of oil leaching out (9);
- *A biopolymer-based aqueous treatment*- developed by B.R.Reddy et al (10) that removes the oil as a flocculated mass with or without the need of a surfactant, although a beneficial, synergistic effect was observed when certain surfactants were used;
- *Thermal desorption by hammer mills*- a process reported by Williamson et al (11);
- *Surfactant Enhanced Drill Cuttings Washing*- a technique making use of different surfactant types, separate or in combination (12-13);
- *Cavitation and Electrocoagulation*- Cavitation creates very high localized pressures and release shock waves to separate oils and fine particulates from larger particles. Electrocoagulation is an electrochemical process that removes most pollutants from water (such as suspended solids, emulsified oils, etc) by applying a low-voltage/high current density between the electrode plates to destabilize the charges that normally hold particles together in emulsions (14).

Mechanistic Considerations

In an attempt to increase the efficiency of the surfactant-based washing formulations for drill cuttings, Sabatini et al (13) performed a study based on a three-component system, consisting of an anionic surfactant (four commercial surfactants were chosen), a builder molecule (sodium metasilicate, Na₂SiO₃) to trap divalent cations (such as Ca²⁺ or Mg²⁺) and a demulsifier (octyl sulfobetaine) to increase the separation kinetics. The initial concentration of olefin on the cuttings was 10% by weight. They monitored the change in interfacial tension (IFT) in the system by varying the amount

of electrolyte and noticed that one of the four surfactants, an alcohol propoxy sulfate, prompted a big drop in IFT at very low concentrations. This could be explained by understanding the three known detergency mechanisms:

- Solubilization
- Snap-off
- Roll-up

The solubilization mechanism is the most common one and it is pretty effective at removing oil from solids by dissolving it in the hydrophobic core of micelles that the surfactant forms above its critical micelle concentration (CMC). However, it may require large amounts of surfactant (depending on what the CMC is for each surfactant molecule). The snap-off mechanism comes into play when the mechanical forces (such as mechanical agitation, centrifugation, etc) are stronger than the work of cohesion of the oil droplet, leading to a break up of the droplet. However, in this case some oil residue is nonetheless left behind. The roll-up mechanism for detergency prevails when the work of adhesion of the oil droplet to the surface is zero or negative. In this case, the oil droplet detaches completely from the surface.

By monitoring the IFT variation, the right surfactant can be chosen such that the last two mechanisms can be activated with the overall effect of increased detergency and thus better oil removal from cuttings. That was the case for the example described above in reference (13).

ROC Determination Methods

With the increased regulatory standards from various environmental agencies across the globe regarding drilling operations, retention of oil on cuttings became the main concept that every regulation in the field refers to. But how can ROC be determined correctly in practice and what are the main factors influencing it? To answer these questions one needs to keep in mind some important features about drill cuttings:

1. There are no two identical cuttings samples even if they come from the same well, due to differences in:
 - size
 - density
 - shape
 - quantity
 - mineralogy
 - place of collection (shaker, desander, etc)
 - contact time with the drilling mud
 - viscosity of the drilling fluid
 - type of surfactants present in the drilling fluid
2. A big difference between cuttings is brought about by the type of drilling fluid that was used, WBM or

OBM/SBM. As expected, if a WBM was used for drilling and if the cuttings are not from a production zone, the ROC should be very low since there are almost no sources of oil contamination for the cuttings.

- Another major difference between cuttings is their origin. Do they come from a production zone, with a certain amount of hydrocarbons naturally trapped inside the pores, or are they from a different zone in the well?

When combined, all these factors account for a large variation between cuttings and emphasize the need for minimizing analytical errors during determination of ROC in order for the results to be consistent and to prevent large deviations from the average. Much of the heterogeneity between different types of cuttings or even between different ‘crops’ from the same well can be attributed to how strongly bonded the oil is to the cuttings. Oakley et al (15) performed a study on this topic and they showed that about 50% of the oil was bound to the cuttings by capillary and cohesive forces, 30% was weakly adsorbed and 20% was more strongly adsorbed. While these numbers should not be extrapolated directly to other types of cuttings they are important because they offer plausible mechanisms to explain the observed differences between cuttings. It is assumed that the externally bound oil is more easily removed than the capillary bound one, which in turn explains why some surfactants are better at cleaning cuttings than others. The oil trapped inside the pores by capillary forces is usually referred to as the *oil imbibition* and it seems to depend mostly on the wetting properties of the surfactants formulated in the OBM. Generally, it is expected that the adsorbed oil (*externally bound oil*) require less energy to be removed from the cuttings compared to the *internally bound oil* attached by capillary forces. Other factors that can influence the ratio between the two types of oil retained on cuttings are: viscosity of the drilling fluid, cuttings residence time in the annulus and the mud weight.

Regarding the determination of ROC values, two methods are commonly used in the industry:

- Retort Distillation (Retort Kit) Method
 - Rock Evaluation Method
- The Retort Kit Method is currently the most widely used due to its simplicity, accessibility and high reproducibility. It consists of a metal cup of various standard volumes where the cuttings are loaded, a metal condenser that fits tightly on the side arm of the cup, a graduated cylinder for collecting and measuring the distillate and a high temperature oven (typically up to 950°F).



Figure 1 Retort distillation kit

The cuttings are loaded into the bottom of the cup, closed with the top, inserted into the HT oven, the condenser is attached and the graduated cylinder is fit right under the condenser to trap the distillate. The desired heating temperature is then set on the digital thermostat and the distilled fractions are collected at set intervals of time. The volume is recorded, the density of any given fraction is calculated and then the ROC value is determined.

A limitation of this method comes from the difficulty to accurately read very small volumes of liquid collected in the graduated cylinder due to normal errors (operator, meniscus, etc).

- The Rock Evaluation Method uses small amounts of cuttings and it is amenable to determine very small volumes of liquids generated. Usually the cuttings are grinded, loaded into a HT cell, heated in a HT oven from which the distillation products are directed to a Flame Ionization Detector (FID).

Materials and Method

For our tests we used cuttings with high paraffin content from GOM. Carbon distribution for them is shown Figure 2 below:

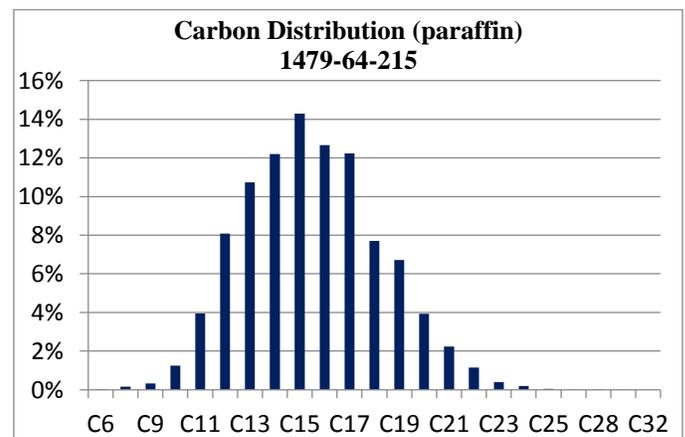


Figure 2 Carbon distribution of the oil on the drill cuttings sample

Within the sample, the ratio of branched versus linear paraffins was about 3 to 1:

Normal (Linear) Paraffin	23.08%
Branched Paraffin	75.31%
Terpene	1.61%

Figure 3 Linear vs branched ratio of oil on the drill cuttings

The method used for ROC determination in our case was the Retort Distillation kit (RD), since we found it to be the most reliable in terms of reproducibility and accuracy. By being able to measure both the volume of fluid collected and to weigh out the mass of dry cuttings generated an accurate mass balance is obtained for each sample which leaves little room for experimental errors (meniscus reading, weighing, etc).

Besides the cuttings and the RD kit, other materials necessary for the tests were: 500 mL beakers, stir bars, stir plate, graduated cylinders (10, 25 and 250 mL), lab scale, DI water, sodium metasilicate (Na_2SiO_3), n-Octyl-sulfobetaine and Sasol surfactants.

Experiments and Results

For consistency and comparison reasons our experimental procedure used throughout the experiments consisted of the following steps:

- A 40 g cuttings sample was weighed out and placed into a 500 mL beaker provided with a stir bar (if clumps were observed they were mechanically broken down with a spatula)
- 174 mL DI water was added to the beaker
- 26 g Na_2SiO_3 was weighed out and placed into the beaker (corresponding to a 13% salinity)
- Stirring was started for 10 minutes so a homogeneous mixture of finely divided particles was obtained
- Surfactants were added (to account for a total surfactant concentration of 0.5%)
- 0.1 g sulfobetaine was added
- Mixture was stirred at room temperature for 30-45 minutes on the medium setting of the stir plate
- Stirring was stopped and the contents of the beaker allowed to settle
- Supernatant liquid was decanted off
- Remaining sludge was filtered on a Buchner funnel under house vacuum
- The solids collected on the filter were removed and placed into the RD cup
- Distillation at 700°F was performed, the liquids were collected in a graduated cylinder and the solids were weighed out for final mass balance

The results are summarized in Tables 1 and 2 at the end of

the paper, where Table 1 presents the data for a two-surfactant systems while Table 2 shows the results for a three-surfactant system. The HLB values were calculated for each system and correlations were attempted to be drawn in order to determine significant patterns that would allow for successful design of washing formulations (WS) in the future. This work is shown in the Discussion section below.

Discussion

The data indicates that different surfactants or surfactant combinations produce large differences in ROC after washing the cuttings. We sought to determine a correlation between the HLB (hydrophilic lipophilic balance) values for these surfactants and the cleaning ability of the cuttings. In this regard, we chose to use Davies' HLB equation, simplified below (16):

$$\text{HLB} = 7 + \Sigma(\text{hydrophilic group numbers}) + \Sigma(\text{hydrophobic group numbers})$$

Davies' equation allows for a more comprehensive evaluation of complex molecules. Based on this model HLB values for our surfactants were calculated for each system and the results are shown in Figures 4 and 5 below:

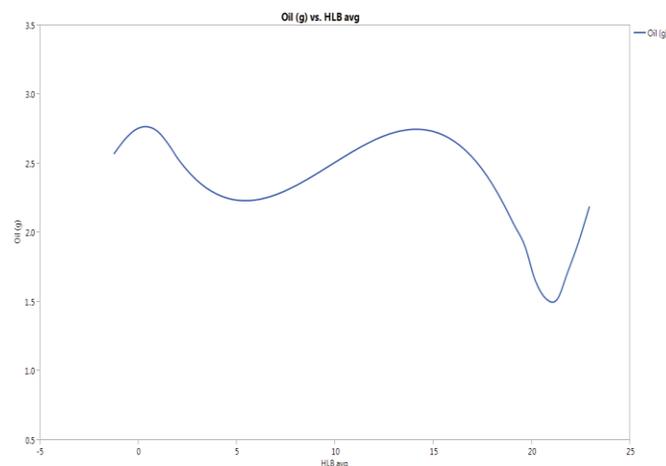


Figure 4 Schematic of ROC variation as a function of HLB values of surfactants for the 2-component systems

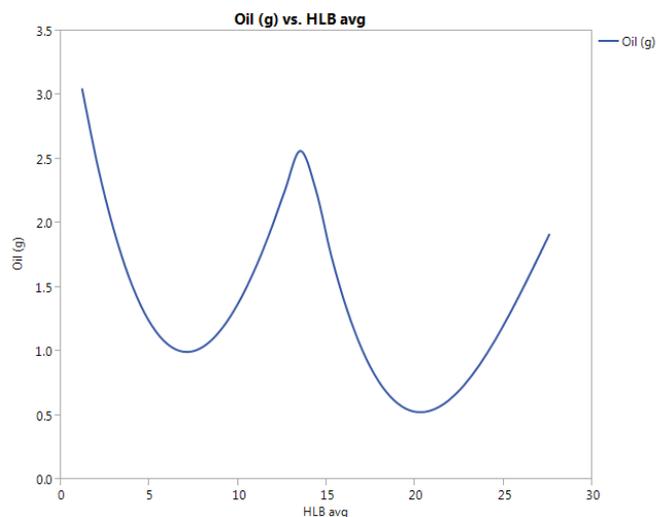


Figure 5 Schematic of ROC variation as a function of HLB values of surfactants for the 3-component systems

From the figures above it was found that two factors were the main contributors to a reduction in ROC values: a) the number of propylene oxide (PO) units; b) the presence of sulfate groups. This suggests that the best ROC numbers (the best cleaning) were achieved for surfactant molecules that had low HLB values and a high degree of polarity. The first requirement was imparted by the presence of PO units in the molecule (water insoluble/oil soluble) while the second requirement was brought about by using polar groups (such as sulfates in the case of anionic surfactants) or by varying the number of ethylene oxide (EO) units in molecule. However, the number of PO units showed an optimum at about 4 units in our case, while adding more PO groups (increasing lipophilicity too much) had a detrimental effect for the cleaning ability and the ROC values increased. The same negative effect occurred when no PO or very few PO units were present in the molecule. Regarding the EO number, a similar tendency was observed, when the addition of too many EO residues in the molecule over a certain optimum (4 EO in our case) started to diminish the cleaning ability of the WS. The surfactant formulations containing EO and S groups did not perform well, once again confirming the need for hydrophobic (PO) groups to improve the cleaning ability.

To determine if branching of the hydrophobe has any effect on the removal of oil from the cuttings, we used statistical analysis methods (17). Each surfactant was first listed as branched or linear. A simple t-test was then used to determine if there was any significance in branching. Results indicated no effect of branching on the removal of oil (g), $t(17.8) = 0.48$, $p = 0.63$. Where $t = T$ value, $t(\text{degrees of freedom})$, and $p = \text{the } p \text{ value}$. The test has a standard $\alpha = 0.05$.

Conclusion

In summary, the paper presents the experimental

results of a surfactant screening test for establishing the best drill cuttings WS formulation for a specific type of cutting. Based on the outcomes observed we established a correlation between the HLB contribution of the structures of the surfactants used and the ROC determined experimentally. Similar approaches can be used by other research groups in designing WS formulations. In our group future work will focus on establishing new correlations between the in-house surfactants employed in this study and other types of cuttings, with a special focus on cuttings originating from drilling operations that use DBM or SBM. In addition, a review of the most recent regulations in the field, along with the most up-to-date techniques used for drill cuttings were presented.

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References

- Oort, E. V., Friedhim, J. E. and Toups, B. (1999), "Drilling Faster with Water-Based Muds" Proceedings of the AADE Annual Technical Forum, March 30-31, Houston, TX
- Schlemmer, R., Patel, A., Friedheim, J., Young, S. and Bloys, B. (2003). "Progression of Water-Based Fluids Based on Amine Chemistry-Can the Road Lead to True Oil Mud Replacements?" Proceedings of the 2003 AADE National Technology Conference, Practical Solutions for Drilling Challenges. April 1-3
- Erwin, M.D., Piersen, C., and Bennion, B. (2004), "Drilling Fluid Designed to Minimize Imbibition-Induced Water Trapping", World Oil (October), p.21
- Smith, M., Manning, A. and Lang, M. (1999), "Research on the Re-use of Drill Cuttings Onshore". Cordah Report (COR012/1999), Aberdeen
- Jones, F.V., Leuteran, A.J.J. and Still, I. (2000), "Discharge Practices and Standards for Offshore Operations Around the World", Proceedings of the International Petroleum Environmental Conference (7th IPEC), November 7-10, Albuquerque, NM
- OGP (2003), "Environmental Aspects of the Use and Disposal of Non Aqueous Drilling Fluids Associated with Offshore Oil & Gas Operations". Report no.342 prepared by the Non Aqueous Drilling Fluids Task Force for the International Association of Oil & Gas Producers
- US EPA (2000), EPA-821-B-00-013
- Charles, M., Sayle, S. (2010), "Offshore Drill Cuttings Treatment Technology Evaluation", SPE 126333, International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Rio de Janeiro, Brazil, April 12-14
- US patent 6,224,535, "Treatments for cuttings from offshore rigs"
- Reddy, B.R., Whitfill, D., Robb, I. and Dealy, T. (2003), "Chemical Method for Cleanup of Produced Oil-Coated Solids from Oil Well Operations", Proceedings of the International Petroleum Environmental Conference (10th IPEC), November 11-14, Houston, TX

11. Williamson, B., Glibertson, C., Roberts, R. and Folarncce, D. (2004), "Offshore Hammermill Process Meets OSPAR/Discharge Limit", *Oil & Gas Journal*, 102(18), 41-43
12. Gerard, C. and Antle, G. (2003), "Minimization of Residual Oil on Cuttings by Mechanical and Chemical Treatment", *Proceedings of the 2003 AADE National Technology Conference*, April 1-3, Houston, TX
13. Childs, J., Acosta, E., Scamehorn, J.F. and Sabatini, D.A. (2005), "Surfactant-Enhanced Treatment of Oil-Based Drill Cuttings", *Journal of Energy Resources Technology*, 127(2), 153-162
14. Global Advantech Limited, www.globaladvantech.com
15. Oakley, D.J., James, S.G. and Cliffe, S. (1991), *SPE Offshore Europe Conference*, September 3-6, Aberdeen, UK
16. Davies, J.T. and Rideal, E.K. (1963), "Interfacial Phenomena", 2nd Edition, Academic Press, London
17. We used JMP from SAS, version 11.0.0, 2013

Supplemental Information

Table 1 ROC values on drill cuttings using 2-component WS formulations with various HLB numbers

No	Surfactant 1	HLB1	Surfactant 2	HLB2	Oil (g)	ROC	HLB avg
0	-	-	-	-	3.36	8.4%	-
1	LCB, 4PO	-0.49	LCL, 10EO	-2.05	2.56	6.4%	-1.27
2	LCB, 8PO, S	37.61	MCB, 8PO	-0.14	1.6	4%	18.73
3	MCB, 4PO	0.46	LCB, 8PO, S	37.61	1.92	4.8%	19.04
4	MCB, 4PO	0.46	LCB, 4PO, S	38.21	1.44	3.6%	19.34
5	MCB, 4PO	0.46	MCL, 4EO, 1PO, S	40.68	1.76	4.4%	20.57
6	MCB, 4PO	0.46	MCB, 4PO, S	39.16	0.64	1.6%	19.81
7	MCB, 4PO	0.46	MCL, 4EO, 1PO, S	41.63	1.28	3.2%	21.05
8	MCB, 4PO	0.46	MCL, 4PO	2.60	1.92	4.8%	1.53
9	MCB, 4PO	0.46	MCL, 4PO, 1EO	38.83	2.24	5.6%	19.65
10	MCB, 4PO	0.46	MCB, 4PO, S	39.16	2.08	5.2%	19.81
11	MCB, 8PO	-0.14	MCB, 4PO, S	39.16	2.4	6%	19.51
12	MCB, 8PO	-0.14	MCB, 4PO, S	39.16	2.24	5.6%	19.51
13	MCB, 4EO	2.38	MCL, 4EO, 1PO, S	41.63	2.08	5.2%	22.01
14	MCL, 4EO, 1PO, S	41.63	LCL, 4EO	1.67	1.6	4%	21.65
15	MCL, 4EO, 1PO, S	41.63	MCB, 7EO	3.37	1.92	4.8%	22.50
16	MCL, 4EO, 1PO, S	41.63	MCL, 4EO, 1PO, S	4.21	2.24	5.6%	22.92
17	MCL, 4EO, 1PO, S	41.63	MCB, 3EO	2.88	1.76	4.4%	22.26

Table 2 ROC values on drill cuttings using 3-component WS formulations with various HLB numbers

No	Surfactant 1	HLB1	Surfactant 2	HLB2	Surfactant 3	HLB3	Oil (g)	ROC	HLB avg
0	-	-	-	-	-	-	3.36	8.4%	
1	LCB, 8PO, S	37.61	MCB, 8PO	-0.14	SCL, 3.5EO	4.59	3.36	8.4%	14.02
2	LCB, 4PO	-4.88	MCB, 9EO, 1PO	3.88	SCL, 3.5EO	4.59	2.72	6.8%	1.20
3	MCL, 2EO, 4PO	1.36	MCL, 4PO	1.65	MCB, 4PO	0.46	3.36	8.4%	1.16
4	MCB, 8PO	-0.14	MCB, 4PO, S	39.16	MCL, 12PO	-0.5	2.24	5.6%	12.84
5	MCB, 4PO	0.46	MCB, 4PO, S	39.16	MCL, 4EO, 1PO, S	43.07	1.92	4.8%	27.56