

Surfactant-Enhanced Treatment of Oil-Contaminated Soils and Oil-Based Drill Cutting -Final Report

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Title: Surfactant-Enhanced Treatment of Oil-Contaminated Soils and Oil-Based Drill Cuttings

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Description:

Surfactant-enhanced washing of oil-based drill cuttings is an emerging technology that should benefit domestic oil producers. In this project, Alfoterra 145-4PO was shown to be a promising surfactant for liberating oils from oil-based drill cuttings. Alfoterra 145-4PO is a branched alcohol propoxylate sulfate with a high content of mono-branched isomers. Low concentrations (0.1 % by weight) of this surfactant produced ultra-low oil-water interfacial tensions (IFTs), thereby allowing the rollup mechanism to liberate drilling oil (C16, C18 alpha olefins) from oil-based drill cuttings. When comparing the surfactant-enhanced washing of oil-based drill cuttings, Canadian River Alluvium (CRA), and silica, the hydrophobic nature of the oil-based cuttings was shown to limit the amount of oil removal. It was also found that the Ca⁺⁺ content of the cuttings promotes surfactant (Alfoterra 145-4PO) abstraction by the cuttings, thereby increasing the hydrophobicity of the cuttings and increasing oil retention by the cuttings. Therefore, three necessary components of optimal formulations were found to be: 1) Alfoterra 145-4PO, 2) octyl-sulfobetaine, and 3) builder (Na₂SiO₃). Na₂SiO₃ builder was added to promote Ca⁺⁺ precipitation, thereby decreasing the Ca⁺⁺ available for precipitating surfactant. The octyl-sulfobetaine helps mitigate high hardness and high hydrophobicity by acting as a Lime Soap Dispersing Agent (LSDA). Surfactant (Alfoterra) loss was minimized and oil removal was maximized by using all three components. Oil removal was independent of operating conditions including bath-cuttings contact time and agitation energy when washing with three-component formulations. The independence of surfactant-enhanced washing from agitation energy and contact time allows for minimization of these parameters, thereby minimizing the accumulation of fines during washing operations. When washing with the three-component formulation, oil from the oil-based cuttings was liberated as a free phase layer, sans surfactant and sans solids. Greater than 85% of the initial Alfoterra 145-4PO remains in the bath after washing. The final (post-washing) oil content of oil-based cuttings was in the range of 2% to 5%.

Keywords: Drilling, Mud, Oil, Cutting, Surfactant, Interfacial, Tension, Offshore, disposal

Background

Drilling muds help lubricate and cool down the drill bit during oil well drilling. They also help carry the drill cuttings to the surface for further screening and disposal. These muds are produced by emulsifying oil and water with colloidal matter that may include organophilic clay, bentonite, barite, and other additives¹.

The continuous media in the emulsions can be water (water-based muds) or oil (oil-based muds). Oil-based muds are used in formations that can swell or react in contact with water, such as shale. When using oil-based muds, the cuttings separated after screening remain coated with up to 20% of oil (weight basis)². Traditionally, the oil of choice to formulate oil-based muds used to be diesel because its lower cost. However, diesel oils contain aromatic compounds and branched isomers that are difficult to degrade, especially in marine environments^{3,4,5}.

The disposal of oil-based drill cuttings is a major environmental and operational issue in offshore drilling. Some alternative methods include on-site disposal, ship to shore and dispose or reinjection in abandoned wells or subsurface caverns. Out of these options, the disposal on site is the more attractive (when feasible), because of the lower shipping and handling cost.

Because of the low degradability of oils in marine environments and its impact in the marine ecology, there are certain restrictions on the oil content of the cuttings before being discharged offshore. For diesel-based muds (DBM) the retention of oil on cuttings (ROC, or weight percent of oil, dry basis) has been regulated to 0%. For synthetic-based muds, such as those formulated with alpha-olefins that are used offshore in the Gulf of Mexico the ROC can be up to 6.9%².

There are several ways to reduce the ROC from the original oil loading (close to 20%) to the standard ROC. Ultra-centrifugation can lower the oil content to close to 8% (this is an attractive option for esters-based muds). The oil can also be removed by supercritical fluid extraction (it requires a complicated arrangement of pressurized vessels and equipment). Another alternative is to thermally treat the cuttings to evaporate the oil (a rather energetically expensive and hazardous operation). Out of these alternatives, centrifugation is attractive because is a fast and economic process, it requires less energy, and it does not produce any hazardous vapors. However, because water-based washing and centrifugation does not always reach the desired ROC level, here we propose the use of detergency mechanisms, mediated through the addition of surfactant and electrolytes, to further enhance the performance of ultra-centrifugation techniques.

The general purpose of this research is to apply the concepts of detergency to the removal of oil form drill cuttings. Figure 1 shows a schematic of an oil droplet on a solid surface, showing the interfacial tensions between the oil droplet (O), the aqueous phase (W) and the solid surface (S), and the contact angle (θ).

To remove the droplet of oil from the solid surface there are three main detergency mechanisms: solubilization, snap-off and roll-up. In the solubilization mechanism, the oil is dissolved in the hydrophobic core of micelles that are formed from the self-assembly of surfactant molecules in concentrations above the critical micelle concentration (CMC). The

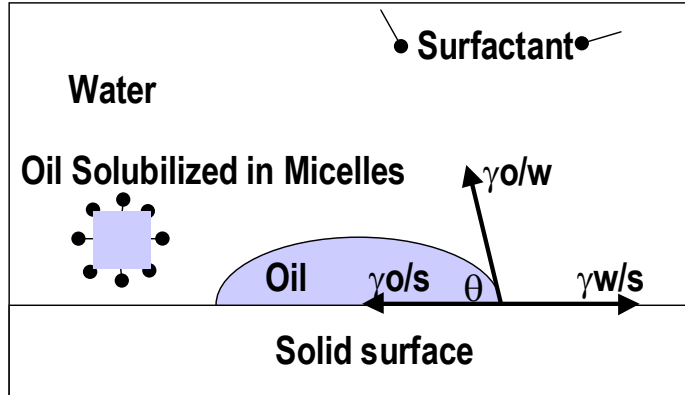


Figure 1. Oil on a solid surface

The snap-off mechanism is obtained when the mechanical agitation is stronger than the work of cohesion ($W_C=2\gamma_{O/W}$) of the droplet, which lead to a break up of the droplet, leaving behind some oil residue. In the roll-up mechanism, the work of adhesion of the droplet ($W_A=\gamma_{O/W}(\cos\theta+1)$) to the surface is zero or negative ($\theta>90^\circ$) that makes it easier for the mechanical forces to completely detach the oil droplet from the solid surface^{6,7,8}.

As we will show later, the solubilization mechanism is quite effective in removing the oil, but it also requires high concentrations of surfactant in the washing solution, and additional separation of the oil dissolved from the surfactant solution. The other two mechanisms rely on the decrease of the work of either adhesion or cohesion, which are in both cases, proportional to the interfacial tension between the oil and water ($\gamma_{O/W}$).

The interfacial tension between water and oil ($\gamma_{O/W}$) is around 50 mN/m. Adding surfactant alone at CMC levels can decrease the interfacial tension to 2 to 5 mN/m, which are typical of common laundry detergency. In our research group we have been able to formulate microemulsions at close to CMC levels of surfactants that can produce ultralow interfacial tensions (less than 0.1 mN/m), which can further enhance detergency mechanisms.

Hypothesis and Objectives

Based on this background information we hypothesized that: (1) we could formulate a microemulsion system containing low levels of surfactant concentration that could achieve ultralow interfacial tension with oils used in formulating oil-based drilling muds; (2) that by contacting this formulation with oil-based cuttings we could improve the removal of free phase oil, while keeping the surfactant in the aqueous solution for recycling without further purification.

Our first objectives included selecting a surfactant system that could produce ultralow interfacial tension with diesel and synthetic alpha olefins used in the formulation of drilling muds. The second objective was to use these formulations on cleaning oil-coated cuttings and sandy soil and evaluate the cleaning performance under different process parameters such as contact time, centrifugation power, agitation intensity and centrifugation time. Our ultimate goal was to

select a combination of operational parameters and formulation that could be used in a future pilot scale test of the technique. In the next section we report on the results of selected tests; details on experimental techniques can be found elsewhere⁹.

Surfactant Selection and Microemulsion Formulation

Our first task was to formulate a system that could achieve ultralow interfacial tension with a mixture of C16/C18 commercial α -olefins, which are commonly used in formulation of oil-based drilling muds. We selected a series of surfactants that we had previous experience in formulating microemulsions to do an initial formulation screening: C16 diphenyloxide sulfonate (Dowfax 8390), alkyl succinic anhydride-taurine adduct (lubrizol), ethoxylated sulfate with linear C12 alkyl tail (Steol CS-330), and a propoxylated sulfate with branched C14-C15 alkyl tail (4 propoxy groups, Alfoterra 145-4PO). Our first test was to measure the interfacial tension with the α -olefins with no added electrolyte. Figure 2 shows the results obtained, noting that the interfacial tension drops to detergency levels (2-5mN/m) for the alfoterra surfactant at very low concentrations, as low as 0.001%. For this reason, alfoterra was selected for further studies to achieve ultralow interfacial tensions.

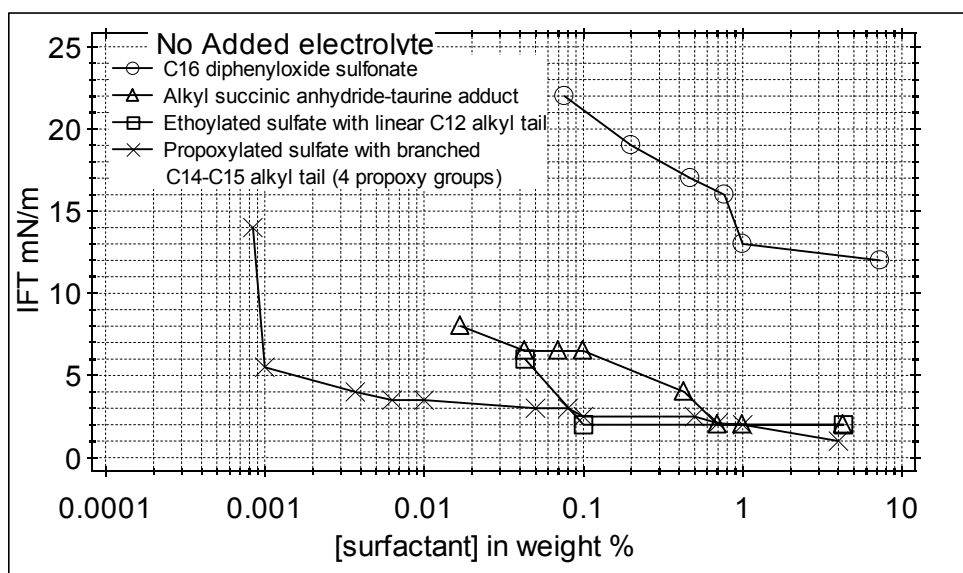


Figure 2. Interfacial tension as a function of surfactant concentration without added electrolyte

To achieve ultralow interfacial tension we selected a concentration of 0.1% of alfoterra 145-4PO (typical concentration levels in detergency) and we added increasing levels of electrolyte. At 6% of NaCl we could obtain an interfacial tension with α -olefins of 7E-3mN/m, which is almost four orders of magnitude lower than the initial oil/water interfacial tension, and almost three orders of magnitude lower than with no added electrolyte.

Washing Studies

Washing studies were performed by adding 2.0 grams of the oil-laden cuttings to 10 ml of the surfactant solution. For baseline conditions, the suspension was shaken for 30 minutes at 150 shakes per minute and then centrifuged at 1700G's for 10 minutes.

For our first set of washing tests we kept the electrolyte concentration constant at 6% NaCl, and increased the concentration of Alfoterra 145-4PO from 0.1%wt. to 6%wt. The initial content of C16/C18 α -olefin on the cuttings was 10% wt. Figure 3 shows the removal efficiency as a function of Alfoterra concentration. While at low concentrations, around 20% of oil was removed by snap-off and roll-up mechanisms, at higher concentrations, the oil is solubilized in micelles in which case we can eventually remove all of the oil.

While a formulation containing 4% of Alfoterra could remove all of the oil, it left the problem of separating the oil from the aqueous surfactant solution, where it was solubilized. Thus, in this project our goal was to improve the roll-up and snap-off detergency, which will produce a separate oil phase upon centrifugation.

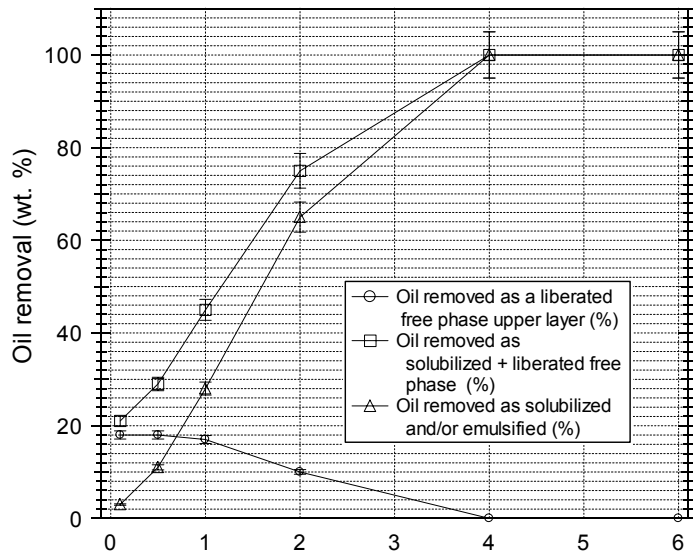


Figure 3. Washing performance with alfoterra 145-4PO

To investigate the initial poor performance of the snap-off and roll-up mechanisms (which rely on the interfacial tension) we measured the IFT between the oil liberated and the surfactant solution, finding that the initial IFT of $7E-3$ mN/m increased to 0.18 mN/m.

Additionally we measured the concentration of the surfactant in the bath solution after washing and found that we lost 90% of the Alfoterra at 0.1% wt. One reason for losing the surfactant is due to precipitation because of high hardness levels. In fact, the drilling muds can contain up to 15% wt. of $CaCl_2$. In the drill cuttings we found calcium to be present at 3% wt. (expressed as $CaCO_3$). We introduced the sodium methasilicate (Na_2SiO_3) as a builder to capture calcium ions, preventing the adsorption/precipitation of the surfactant¹⁰. After trying different combinations we found that by adding 13% of Na_2SiO_3 instead of 6% NaCl we could reduce the ROC to 4%. In this case, the interfacial tension after washing remained in the ultralow range (0.019 mN/m).

In regard to the operational variables, we found that the intensity of agitation did not play a significant role in the washing efficiency, shaking at 75 shakes had almost the same

performance as shaking at 300 shakes per minute. The difference was the production of fines, higher shaking intensity produced more fines, which are more difficult to separate by centrifugation. The centrifugation performance play some role when the cuttings were contacted with the cuttings for only 30 minutes, but if contacted overnight, the cuttings could spontaneously liberate the oil without centrifugation.

We found that the more important operational parameter is the contact time between the cuttings and the washing solution. Since the contact time of one day was simply too long to be economically feasible, we introduced octyl sulfobetaine as lime soap dispersing (LSD) to enhance the separation kinetics⁶. The octyl sulfobetaine is a zwitterionic surfactant of short hydrophobe that help prevent or dissolve any precipitation of surfactant in the system. By adding 1% of octyl sulfobetaine we could decrease the retention time from 24 hours to less than 30 minutes. The surfactant solution after contacting with the oil still had the capacity to produce ultralow interfacial tension, and therefore could be easily recycled, with additional makeup of sodium methasilicate used to precipitate the calcium ions.

Conclusion

In this research we showed that by achieving ultralow interfacial tension throughout the washing process we could enhance the cleaning performance achieved by snap-off and roll-up mechanisms. Using these mechanisms we could use low surfactant concentrations, and keep the surfactant in the washing solution. Because of the composition of the drilling muds, we needed to add sodium methasilicate to prevent losing the surfactant to precipitation, and octyl sulfobetaine to improve the kinetics of the washing process.

We accomplished our ultimate goal of obtaining a formulation and process conditions that could be used in a future pilot scale test: 13% sodium methasilicate, 0.1% Alfoterra 145-4PO and 1% octyl sulfobetaine. The contact between the surfactant solution and the drill cuttings can be accomplished by horizontal drums or stirred tanks for 15 to 30 minutes. This solution would be separated in a continuous ultracentrifuge (standard equipment in off - shore platforms) for 5 to 10 minutes of retention time. The separated liquid will be reused, the cuttings that can be wet in the surfactant solution will contain close to 3% of oil, the cuttings can be disposed on site, and the oil could be reformulated into the mud.

Presentations and Publications

Childs J., Acosta E., Scamehorn J. F and Sabatini D. A., Surfactant-Enhanced Treatment of Oil-Based Drill Cuttings. Submitted to JERT journal, March 2003

Childs J., Sabatini D. A., Acosta E., and Scamehorn J. F *Surfactant Phase Behavior with Hydrophobic Oils: From Drill Cuttings to Detergency*. 93rd AOCS Annual Meeting & Expo. Montréal, Québec, Canada, May 7th, 2002

Childs J., Sabatini D. A., Acosta E., and Scamehorn J. F. *Surfactant Enhanced Ex-Situ Washing of Oil-Impacted Soils and Drill Cuttings*. 9th Annual International Petroleum Environmental Conference. Albuquerque, N.M. October 24th, 2002.

Childs J., Sabatini D. A., Acosta E., and Scamehorn J. F. *Surfactant Enhanced Treatment of Oil-Based Drill Cuttings and Oil-Contaminated Soils*. 8th Annual International Petroleum Environmental Conference. Houston, TX. November 7th, 2001.

Childs J., Sabatini D. A., Acosta E., and Scamehorn J. F. *Surfactant Enhanced Treatment of Oil-Based Drill Cuttings and Oil-Contaminated Soils*. 7th Annual International Petroleum Environmental Conference. Houston, TX. November 8th, 2000.

Web address of final report: <http://ipec.utulsa.edu/lpec/9.d/FinalReport.pdf>.

Literature

- ¹ Gray, G. R. *Composition and properties of drilling and completion fluids*. 5th. Edition, Gulf Publishing Co., Houston, TX. (1988)
- ² "Effluent Limitations Guidelines and New Source Performance Standards for the Oil and Gas Extraction Point Source," Federal Register, (January 22, 2001) 66, No. 14, Rules and Regulations, Environmental Protection Agency, 40 CFR Parts 9 and 435.
- ³ Chenevert, M.E.: "Shale Control with Balanced Activity Oil Continuous Muds," JPT. (Oct. 1970) 1309.
- ⁴ McIntosh, A. D. Massie, L. C., and Mackie, P. R. "A survey of hydrocarbon Levels and some biodegradation rates in water and sediments around North Sea oil platforms," paper presented by Marine Environmental Quality Committee at the 1983 ICES Committee Meeting 1983/E:42.
- ⁵ Dow, F.K., Davies, J.M., and Raffaelli, D. "The Effects of Drill Cuttings on a Model Marine Sediment System," *Marine Environmental Research* (1990) 29, 103-133.
- ⁶ Rosen, M. J.: *Surfactants and Interfacial Phenomena*, Wiley, New York (1989).
- ⁷ Kissa, E.: in *Detergency: Theory and Technology*, W. G. Cutler and E. Kissa, (eds.) Marcel Dekker, New York, Ch. 4 (1987).
- ⁸ Thompson, L., "The Role of Oil Detachment Mechanisms in Determining Optimum Detergency Conditions," *Journal of Colloid and Interface Science*, (1994) 163, 61-73.
- ⁹ Childs J., Acosta E., Scamehorn J. F and Sabatini D. A, Surfactant-Enhanced Treatment of Oil-Based Drill Cuttings. Submitted to SPE journal, November 2002
- ¹⁰ Tai, L. *Formulating Detergents and Personal Care Products*, AOCS Press, Champaign, Illinois, Ch. 2, (2001)