Mitigation of Metallic Soap Sludges by Acid Demulsifiers

Darrell L. Gallup
Unocal Corporation
1160 N. Dutton Avenue; Ste. 200
Santa Rosa, CA 95401

Abstract

A greenish-brown sludge is formed in significant quantities during production of oil from the Serang field, offshore East Kalimantan, Indonesia. The sludge forms upon cooling of oil in sub sea pipelines and onshore terminal storage tanks. This interfacial sludge is comprised of entrained free oil, water and solids, and is stabilized by an acylic "metallic soap." In the absence of fluid treatment, removal and disposal of the sludge is tedious, expensive, and represents significant un-recovered oil.

The sludge has been characterized to understand its formation mechanism, so that remedial actions can be taken to mitigate its deposition (Gallup, et al., 2002). A variety of analytical analyses indicate that the "metallic soap" emulsion consists of about 30% water, 50% oil, and 20% of C_{14} – C_{30} carboxylate salts in sodium form. The "soap" is stabilized by fatty acid-Na-HCO_3 complexation.

Laboratory and field tests have demonstrated that the sludge can be dissolved by low dosages of commercially available sludge dissolving agents containing combinations of acids. An acid demulsifier, consisting of acetic acid and ethoxylates dissolved in an aromatic solvent mixture, has been injected full-scale into Serang produced fluid arriving at the onshore terminal since August 2002. The acid demulsifier has significantly reduced sludge deposition in oil storage tanks and water-handling facilities. In addition to "dissolving" sludge, incremental oil is recovered, which offsets chemical treatment and sludge disposal costs. Optimization of acid demulsifier application is in progress to further minimize sludge deposition and recover oil from the emulsion.

Introduction

During production of oil from the Serang field, offshore East Kalimantan, Indonesia, a greenish-brown sludge forms upon cooling. This sludge accumulates in sub sea piping tied to the Santan onshore terminal, in oil-water separation equipment and in the bottom of onshore terminal crude oil storage tanks. Initially, this waxy sludge emulsion, exhibiting the consistency of toothpaste, is observed as a thick emulsion layer between separated oil and water sampled at the inlet to the onshore oil-gas-water processing facility, and at the arrival of the production sub-sea pipeline from the Serang platform to the Melahin platform. Up to 100 barrels of the sludge may accumulate in onshore crude oil storage tanks per day, as conventional demulsification treatment with standard demulsifier chemicals does not remove this sludge layer. This sludge is difficult to remove from the tanks due to its high viscosity and pour point. The sludge is ultimately disposed at the terminal's bioremediation plant after centrifugation. The cost to remove, process and bioremediate the sludge exceeds $7/bbl.

Significant savings can be realized by inhibiting "soap" formation or breaking the emulsion. Additionally, oil held in the "soap" may be recovered. The purposes of the present study were to understand the "soap" formation mechanism, and to develop methods to inhibit or break the emulsion stabilized by "soap."

Sludge Characterization

Scales and Sludges similar to the Serang "soap" have previously been observed in Southeast Asia oil fields, as well as in fields in West Africa and the North Sea. The majority of "metallic soap" sludges appear to be emulsions consisting of oil, calcium naphthenates and water (Rousseau, et al., 2001; Goldszal, et al., 2002). The primary differences between Ca-naphthenate scales/sludges described by others and the "soap" formed from Serang fluids are: (1) the latter contains sodium and almost no calcium, (2) the fatty acids are acyclic, and (3) bicarbonate ions in water, HCO_3^-, appear to add stability to the sludge matrix.

Table 1 summarizes the results of Serang " metallic soap" characterization studies conducted by Gallup, et al., 2002.

Analytical Technique	Results
Physical separation; high temperature centrifuge	30% H_2O; 50% oil; 20% soap (remaining emulsion)
Elemental	Organic empirical formulas: (oils) $C_{21}H_{44}$, $C_{32}H_{66}$, C_9H_{20}, $C_{24}H_{54}$, $C_{15}H_{32}$; (fatty acids) $C_{21}H_{45}O_2$, $C_{32}H_{67}O_2$, $C_9H_{24}O_2$, $C_{24}H_{47}O_2$, $C_{15}H_{30}O_2$. No S or N Inorganics: 1.3 wt% Na. Traces of Ca, K, Mg, Al, Fe, Ba
X-ray Diffraction	30% amorphous; 25% each of n-nonacosane, $C_{29}H_{60}$ and n-heneicosane-like alkanes (paraffins), $C_{21}H_{44}$; 20% triacontanoic-like acids, $C_{30}H_{60}O_2$ (fatty acids)
^1H and ^{13}C Nuclear Magnetic Resonance	Long, straight-chain and branched alkanes; carboxylate groups
Fourier Transform – Infrared Spectroscopy	H_2O, paraffins (straight chain and branched); carboxylates; clays
Gas Chromatography – Mass Spectrometry	Straight and branched chain alkanes ranging from C_9 to C_{35}; a series of n-alkanes ranging from C_{11} to C_{17}; C_{12}, C_{14}; C_{28} to C_{30} straight chain carboxylic acids
Scanning Electron Microscopy/Energy Dispersive X-ray Fluorescence	Amorphous; flecks of embedded illite and kaolinite clays, quartz, barite, feldspar, pyrite and other Fe-rich species (corrosion products?). Na >> K, Mg, Ca > Al, Si > Fe and S.
Dissolution Tests	Insoluble in most polar and non-polar organic solvents. Slightly soluble in C_2Cl_4 above 100°C. Slightly soluble in hydrochloric, acetic and formic acids at elevated temperatures.

Table 1. Serang "metallic soap" analyses

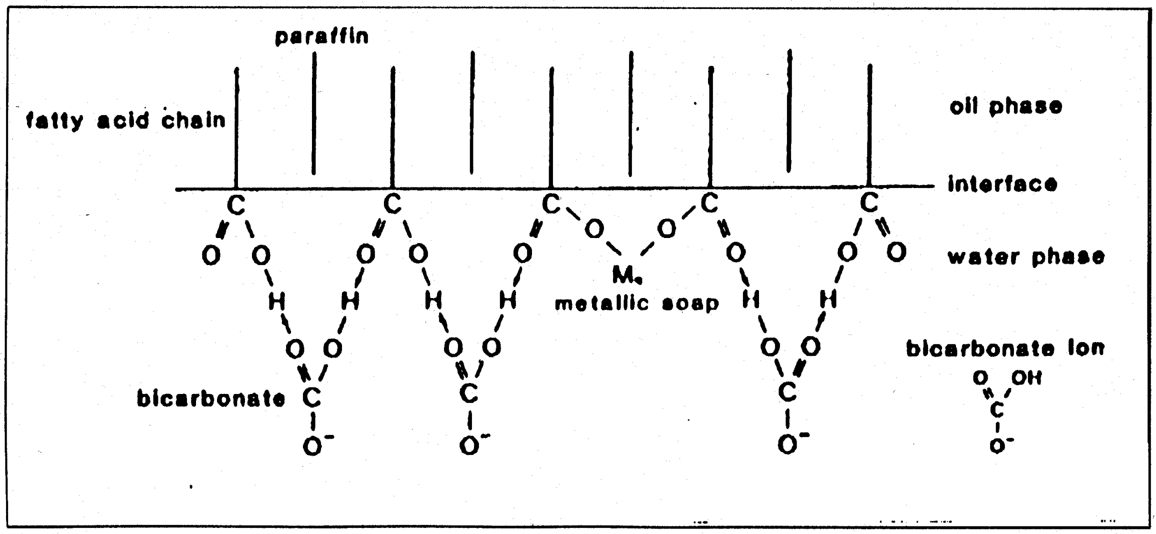

Figure 1. Theoretical Structure of "Metallic Soap"

Several investigators have proposed structures for naphthenate and fatty acid sludges (Rousseau, et al., 2001). Metallic soaps are represented by the general formula, RCOO-M, where M is a metal (alkali, alkaline earth, or transition series). Metallic soaps find use in industrial applications such as paint and ink drying (Feierstein and Morgenthaler, 1983). Berkhof (1996) states that crude oil emulsions can be stabilized by both bicarbonate ions in water and paraffins (solid-phase high-molecular-weight hydrocarbons). He concludes that water droplets held in the oil phase are protected against coalescence by films accruing through interactions between paraffins, fatty acids and bicarbonate with incorporated metallic soaps. Further, he speculates that the interactions are a consequence of hydrogen bonding or H-bridge formation (*viz.,* O $\rightarrow$ H) as shown in Figure 1 above.

Field Jar and Pilot Tests

The acidic sludge dissolvers (acid demulsifying agents) appear to convert the metal carboxylate to free carboxylic acid that is less prone to emulsifying oil. Sludge may be destabilized when M is no longer complexed by the long chain fatty or naphthenic acids:

$$RCOOM + H^+ = RCOOH + M^+$$

Field trials of commercially available acid demulsifiers, and formic and acetic acids, were successfully conducted at Santan Terminal over the past year. In the jar tests, mixtures of water, oil and emulsion, and isolated "metallic soap" were treated with various non-acid formulations. Heating the mixtures and "metallic soap" to 70 - 90°C resulted in minor separation of oil and water from the emulsion, but did not appreciably "dissolve" or decrease the emulsion/sludge volume. In contrast, heating and treating with acids alone or acid demulsifier formulations broke the emulsion further into oil, water and a smaller volume of "soap." Certain formulations, usually consisting of acetic acid or exhibiting that odor, were more effective than others. Acetic acid alone was relatively effective compared to formic acid alone or in combination with acetic acid. These jar tests "screened" the formulations to be pilot tested.

Figure 2 shows a simplified diagram of the Santan Terminal process to separate gas, oil and water. Pilot tests were conducted for several days by injecting acid demulsifiers into the inlet of the low-pressure separator at full-scale, where the sludge is quite prevalent in the oil phase. The criteria for success of the acid demulsifiers are (a) a substantial reduction in the volume of sludge being sent to the oil storage tank, (b) no increase in product oil BS&W, and (c) no adverse affect on oil content of disposal water or any other operation at the Terminal.

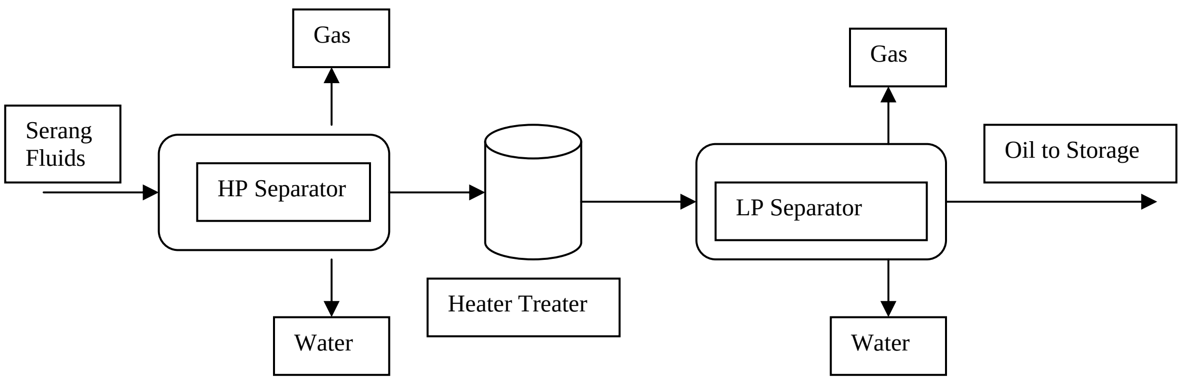

Figure 2. Schematic diagram of Santan Terminal process plant

The results of the pilot tests with the acid demulsifiers are graphically depicted in Figures 3 and 4. Figure 3 is a plot of highest sludge removal efficiencies achieved with the respective acid demulsifiers. Figure 4 is a cost-benefit plot. The demulsifier price is divided by a performance factor (efficiency quotient).

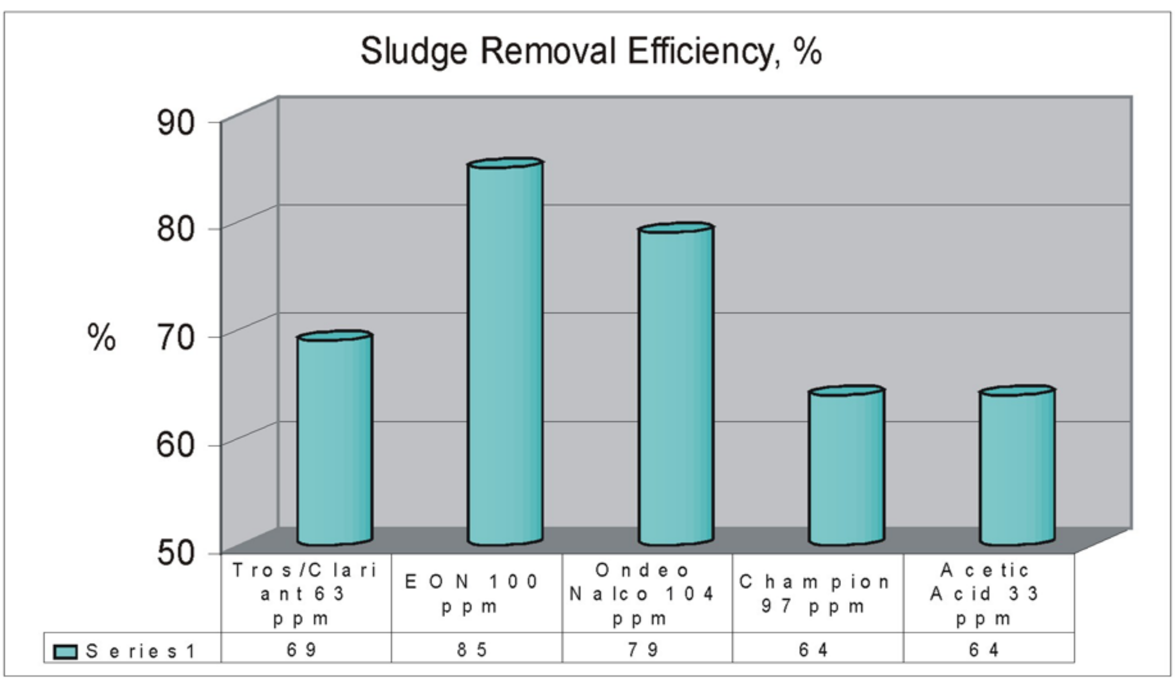

Figure 3. Performance of acid demulsifiers in pilot demonstration tests.

In the pilot demonstration testing of sludge dissolvers conducted at Santan Terminal, four vendor formulations were examined, together with the commercially available organic acids, acetic and formic. The most efficient acid demulsifier was EON Chemical's DM2230 acid demulsifier. It consists of acetic acid and ethoxylated compounds dissolved in an aromatic solvent mixture. It is also the most cost-effective acid demulsifier formulation. Ondeo Nalco's EC2068A aqueous formulation, consisting of hydrochloric and phosphoric acids also yielded good "soap" dissolution, but it is more expensive than EON's DM2230. Tros-Clariant's Dissolvan 5642A, Champion's Emulsotron SX-4086 and glacial acetic acid decreased sludge by 64 – 69%. Formic acid (90%) was not as effective alone or in combination with acetic acid as acetic acid alone. Acetic acid was the most cost-effective dissolver of the acids tested.

In addition to decreasing sludge volumes in the oil sent to storage tanks, these acid demulsifiers increased oil recovery from the emulsion. In general, the cost to treat Serang fluids to minimize "soap" production is offset by the incremental oil that is recovered during treatment. The major cost savings of treating Serang fluid to minimize sludge is sludge handling and disposal. Hot centrifuging of accrued sludge costs about $7/bbl, excluding tank cleaning and final disposition of "soap" that will not separate into oil and water. As a result of the pilot demonstration tests, EON's DM2230 was selected for full-scale treatment of Serang fluids to minimize "metallic soap" formation and deposition throughout the processing facility. As a backup, acetic acid was purchased for full-scale treatment also.

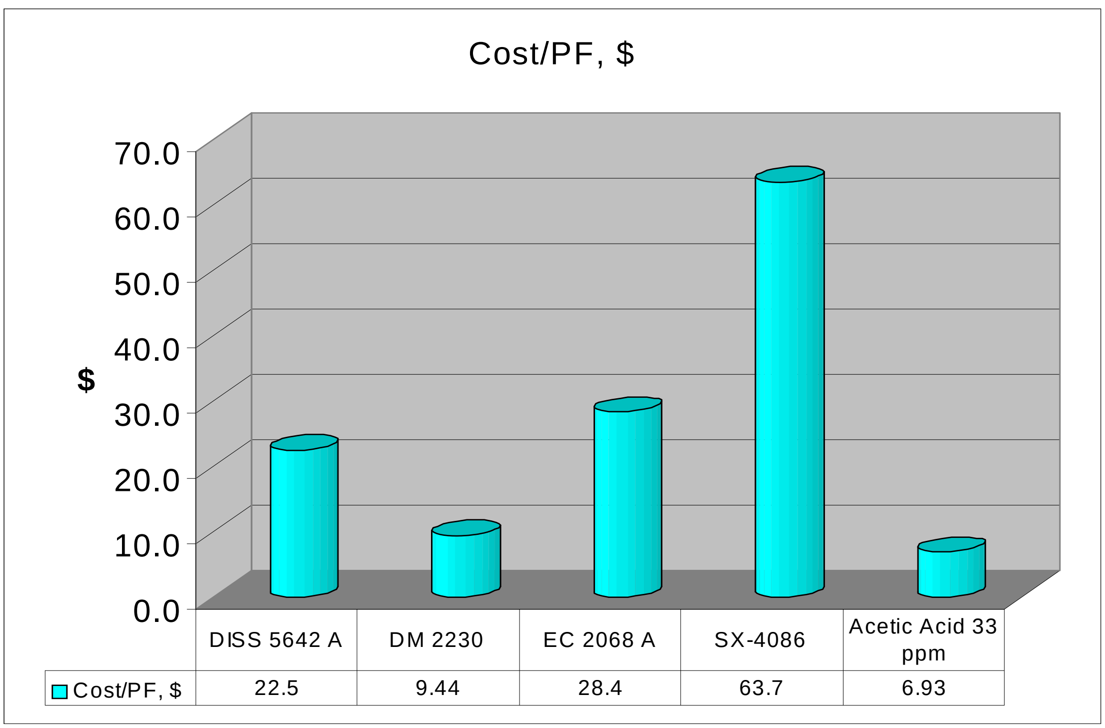

Figure 4. Cost-benefit plot of acid demulsifiers used in pilot demonstration tests.

Full-Scale Treatment

Full-scale injection of EON's DM2230 into the oil outlet leg of the high-pressure separator (upstream of the heater-treater) commenced on August 14, 2002. Figure 5 shows the average soap sludge concentration in oil sent to storage tanks. Prior to treatment, the average concentration of soap sludge in oil was ~0.5 vol%, equating to about 48 bspd. After treatment with the acid demulsifier, the sludge concentration and mass have decreased to an average of about 0.25 vol% and 29 bspd, respectively. Unfortunately, this decrease of ~50% in "metallic soap" in the oil is less than that achieved in the pilot demonstration testing (85%). It appears that after the pilot demonstration test was conducted in March 2002, the character of the sludge has changed. The oil and water chemistry between March and August 2002 changed very subtly. Some production wells that were on-line in March have been shut-in; some producers that were not on-line in March are now flowing since August.

As a result of the increased difficulty in dissolving "metallic soap," several changes in the full-scale treatment have been made. In November 2002, dual injection of EON DM2230 commenced. Three-fourths of the acid demulsifier is being injected into the inlet to the high-pressure separator, and one-fourth downstream of the heater-treater. Dosages have been varied and injection points continue to be examined in an effort to achieve >80% sludge dissolution. Acid demulsifier has been injected at the gross separator on Serang platform, and high dosages have been injected upstream and downstream of the heater-treater without much effect. A non-acid demulsifier has been injected into the high pressure separator. The highest dissolution efficiency that has been achieved in the optimization study is still only 60 – 70%.

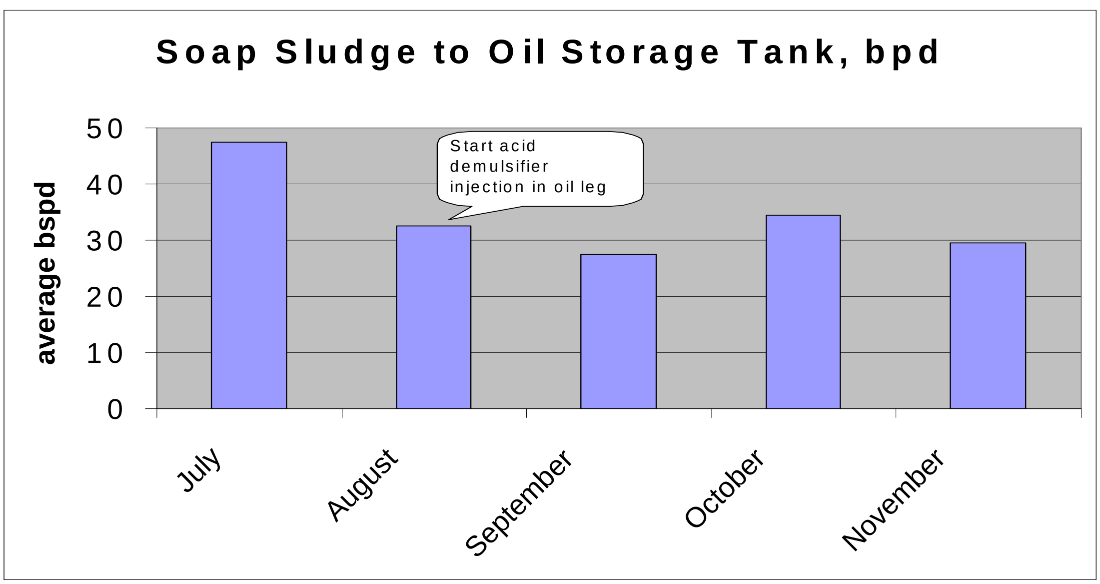

Figure 5. Soap sludge in oil sent to storage

Prior to EON DM2230 injection into the inlet of the high pressure separator in November 2002, about 140 bbl/day of sludge was being removed from the water treatment system.

This sludge is a mixture of sand, clay and fatty acid soap. After splitting injection of EON DM2230 acid demulsifier in the Process Plant, the average amount of sludge removed from the water treatment system decreased to an average of 78 bspd or a decrease of nearly 50%. Figure 6 graphically presents the results of desludging of the water treatment system.

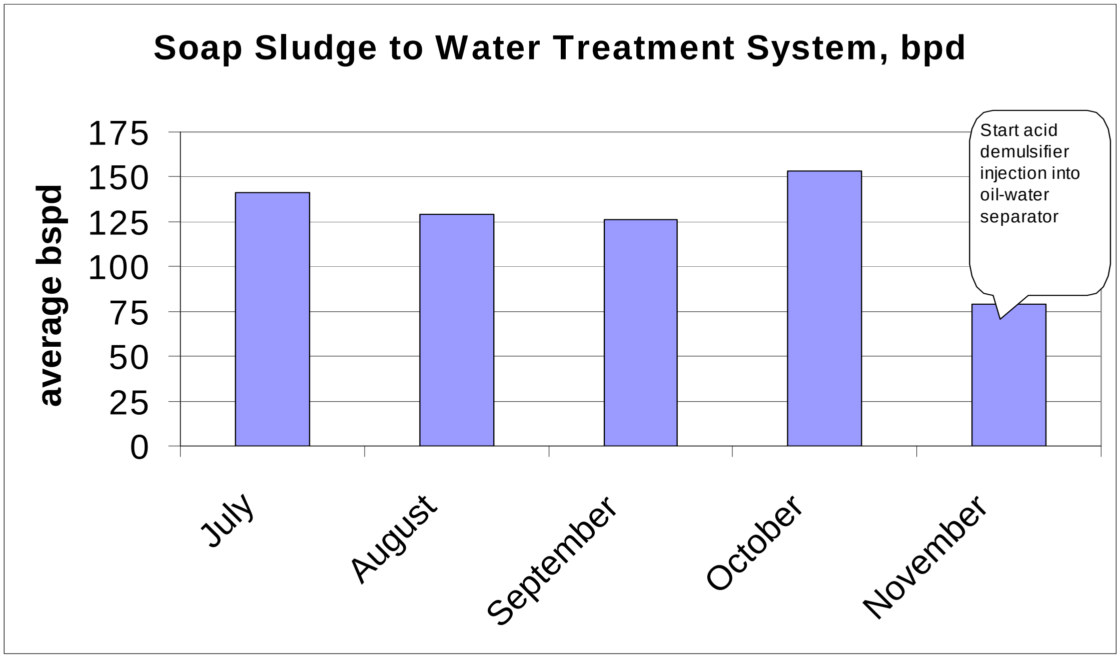

Figure 6. Sludge removal volumes from the water treatment system

Conclusions

A "metallic soap" emulsion forms from Serang, Indonesia oilfield as produced fluids cool. The emulsion consists of oil, water, long chain fatty acids and traces of formation flour. Upon arrival of Serang fluids at the Santan onshore terminal, the emulsion pad is so thick that ~25% reports to the separator oil leg and ~75% to the separator water leg. Heating the oil-rich fluid decreases BS%W from about 3.0 to 0.5 vol%. Treatment of the oil-rich fluid with EON Chemical's DM2230 acid demulsifier in pilot tests conducted in March 2002 at Santan decreased BS&W to 0.07 vol%. However, after commissioning full-scale demulsifier treatment, BS&W has only been decreased down to 0.2 to 0.25 vol%. Treatment optimization has decreased soap sludge in the water treatment system by 50%. Optimization studies are in progress to further decrease BS&W in oil to the goal of < 0.1 vol%.

Acknowledgments

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