REVERSE PHASE EXTRACTION METHOD FOR DETECTING OIL CONTAMINATION IN SBM

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ABSTRACT

Waters Associates SEP PAK® reverse phase cartridges are used to separate and collect crude oil contamination from synthetic base drilling mud (SBM) in a quick and easy procedure for subsequent blacklight (ultraviolet) detection. The method is intended as a positive/negative test to determine the presence of crude oil in SBM prior to dumping drill cuttings overboard in the offshore environment. The test should be comparable to the accepted static sheen test presently used for water base muds.

INTRODUCTION

The regulatory permitting agencies that oversee the offshore oil and gas operations depend on a static sheen test (1) to determine if drill cuttings recovered from the drilling mud are contaminated with crude oil prior to dumping cuttings in the open sea environment. Crude oil contamination can result when an oil bearing geologic formation has been penetrated during the drilling operation. The static sheen test is simple and will indicate if the cuttings contain oil that could cause a sheen on the sea surface. The test is adequate when conventional water based drilling muds (WBM) are used. If the water based mud is replaced with an oil based mud (OBM), the drilling operation is greatly enhanced when drilling certain geologic structures, deviated wells and horizontal wells. Such muds have crude oil or a refined oil as the continuous phase. These OBM's and the cuttings separated from them can not be dumped in the offshore environment because of their toxicity. The industry has found certain synthetic solvents such as internal olefins (IO), esters, linear alpha-olefins (LAO) and enhanced mineral oil (EMO), to be environmentally friendly substitutes for conventional OBM's which are not environmentally acceptable. Industry studies have shown that crude oil contaminated cuttings in SBM systems do not produce a static sheen as normally seen for oil contaminated cuttings from WBM. These synthetic base mud (SBM) systems contain chemical additive packages to stabilize the drilling fluid emulsion and to maintain proper drilling mud properties such as viscosity and gel strength. The emulsifier package interferes with the static sheen test by emulsifying any oil contamination on cuttings from the SBM systems. A test that is similar to the static sheen test for WBM systems is needed by the industry to insure that oil contaminated cuttings from SBM systems are not dumped into the sea.

An industry work group (API-Synthetic Based Mud Analytical Work Group) has determined that the new test should have certain desirable characteristics. The test should work well on an offshore platform; have a detection limit comparable to the static sheen test ($\geq$ 0.5% crude oil contamination); have reasonable cost; be reproducible; use equipment that is easy to operate with a minimum of expertise; work well with a variety of crude oils and SBM's; not be prone to false positives; and have a pass/fail limit.

EXPERIMENTAL

A whole mud sample is taken at the drilling site for this test. It is necessary to have the nonaqueous phase in a polar solvent to pass through the C_{18} SEP PAK® for separation of the emulsifier from the crude oil components. After looking at several solvents, it was found that extraction of the whole mud with isopropyl alcohol (IPA) uniformly extracts the crude oil from the mud system and also has enough polarity to carry the emulsifiers through the C_{18} SEP PAK® while leaving the crude oil behind. IPA also has the added benefit of being a familiar, available and relatively safe solvent for on-site use.

The developed procedure has the following steps for extraction.

1. Transfer 0.10 ml of SBM sample to a large (16x125-mm) test tube and add 10 ml of solvent grade IPA. Stir the solvent and SBM thoroughly (10 sec. on a Vortex mixer) and let stand to allow the solids to separate.
2. Filter about 4 ml of the extract from the test tube through a syringe cartridge filter (PTFE syringe type filter, 25-mm, 0.45-µm) into a second test tube.
3. Precondition a C_{18} SEP PAK® cartridge by attaching to a five-ml syringe and pushing 3 ml of solvent grade IPA via the syringe through the SEP PAK®.
4. Transfer 0.50 ml of the extract (Step 2) to the syringe barrel and add 3 ml of IPA. Push the extract and IPA through the preconditioned C_{18} SEP PAK® cartridge to separate any crude oil contamination from the extract. Push another 2 ml of solvent grade IPA through the SEP PAK®.

5. Place the C_{18} SEP PAK® cartridge under the blacklight and observe the absence or presence of fluorescence as compared to a blank. Presence of fluorescence is a positive test for crude oil.
6. A blank is prepared by carrying out the procedure on a sample of the SBM as sent from the supplier (has not been circulated downhole).

To assure the quality of the IPA and filters, a reagent blank is prepared by passing 5 ml of the IPA through a PTFE cartridge filter and collected in a small test tube. Add 0.5 ml of the filtered IPA and 3 ml of IPA to a syringe and push through a preconditioned SEP PAK® cartridge (step 3 above). Add 2 ml of IPA to the syringe barrel and push it through the cartridge. Check the SEP PAK® cartridge under the black light for fluorescence. No fluorescence should be observed if the IPA and the filter are of good quality.

The procedure was carried through on laboratory prepared SBM drilling fluids that had been spiked with known amounts of crude oil. The laboratory samples were comprised of sets of three SBM types, an EMO, an IO, and a mixed Ester/LAO. Each SBM was spiked with five different crude oils at four different oil concentrations (0.5, 1.0, 2.0, 5.0 % by wt) resulting in 20 spikes and a base mud blank for each of the three SBM sample sets. The sample designations and API gravities for the crude oils are: A, 28°API; B, 31°API; C, 36°API; D, 51°API; E, 24°API. Simulated distillations of the five crude oils by gas chromatography (ASTM D2887) were performed to characterize and compare the relative boiling point and molecular size distributions.

Five observers independently determined the presence or absence of fluorescence by comparing the SEP PAK® cartridges developed for each of the prepared oil spiked SBM's to a blank in a view box with a built in UV light source. The observation was made by placing the test cartridge next to a blank cartridge corresponding to the SBM with no oil spike.

RESULTS AND DISCUSSION

Fluorescence of crude oil by ultra-violet electromagnetic energy is due to molecular excitation of multi-ring aromatic hydrocarbons and heterocyclic compounds. Non-aromatic, but highly conjugated compounds may also fluoresce (2), and such compounds and smaller heterocyclics may exist in the SBM emulsifier packages. The reverse phase extraction method passes these more polar emulsifiers through the SEP PAK® cartridge while retaining the less polar aromatics and heterocyclics found in crude oil. This test assumes that crude oil compounds are retained on the SEP PAK® cartridge, and that the concentration of fluorescent compounds in the crude oil are high enough for detection at about 0.5% or higher concentration of crude oil in the SBM.

The observation of fluorescence by comparing cartridges is somewhat subjective when there is a very low concentration of oil on the developed cartridge. Absence of fluorescence was indicated by a "0" (negative test result) and presence by a "1" (positive test result). Five observers were selected to see if a consensus result would be found in each case. The observers were to report a positive test if the sample cartridge showed "more fluorescence" than the blank. Three of the observers were experienced laboratory experimentalists while two were contract technicians with about one-year laboratory experience. Tables 1 through 3 are summaries of the results of the five observers' readings for each of the three sets of SBM samples. Each sample was given the sum of the five observers' readings. Therefore, a summary value of "0" indicates that the reading was "0" (negative) for all five observers; and a "5" indicates the reading was "1" (positive) by all five observers. Values of 1, 2, 3, and 4 show non-agreement among the observers and indicate the difficulty in determining fluorescence for these samples.

The tabulated results show the test summary by SBM. The IO based mud (Table 2) appears to be slightly more sensitive to crude oil detection than the other two systems (Tables 2 and 3), since fluorescence was more often observed at the 0.5 % concentration.

Crude oil D (51°API) was only detected once at concentrations up to and including 5% in any of the SBM systems. The API gravity and lack of fluorescence leads to the belief that the oil is paraffinic with a low concentration of multi-ring aromatic molecules present. The gas chromatogram (Figure 1) of crude oil D confirms this idea. The chromatogram shows the relative carbon numbers for the straight chain paraffins. The carbon numbers and retention times are consistent in all of the figures. Crude oil D shows very little material after C 24.

Contamination of 2% or higher is consistently detected for crude oils A, B, C, and E in all of the drilling muds. The crude oils A, B, C, and E are similar in fluorescence sensitivity as shown by the split negative and positive readings by the observers at the 0.5% and 1.0% concentrations in the various SBM's. Gas chromatograms (Figures 2-5) for these oils are similar and contain significant amounts of high molecular weight oil (>C 24) that probably contains multi-ring aromatic compounds.

IV. Conclusions

The reverse phase extraction method for determining crude oil contamination in SBM's appears to have merit as a possible field test. The inability to detect the high API gravity paraffinic oil is obvious. Aside from this, the test meets the desirable characteristics determined by the industry

study group. It is comparable to the static sheen test in detection limits, can be performed offshore with reliable equipment by field personnel, is reasonably low cost, and has a single pass/fail end point.

The inconsistency of this test from one crude oil to the next is not unexpected. There is no standard crude oil that can be representative of all crude oils. This field test is to be applied during exploratory drilling where the oil encountered will be unknown. It is important to note that the toxic components in petroleum hydrocarbons are generally thought to be the multi-ring aromatics or polycyclic aromatic hydrocarbons (3). These components produce fluorescence. The paraffinic components do not fluoresce under the blacklight, but the paraffinic compounds are not detrimental to the environment. Effectively, the test could be determining the presence of the components that are environmentally unfriendly. The inability to detect high API gravity oils that are primarily paraffinic may not be a draw back to using this test.

REFERENCES

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Table 1: EMO SBM					
Oil	0% Oil	0.5% Oil	1.0% Oil	2.0% Oil	5.0% Oil
A	0	0	4	4	5
B	0	0	0	4	5
C	0	0	2	3	5
D	0	0	0	0	0
E	0	1	3	5	5

Table 2: IO SBM					
Oil	0% Oil	0.5% Oil	1.0% Oil	2.0% Oil	5.0% Oil
A	0	2	1	5	5
B	0	4	2	5	5
C	0	2	5	5	5
D	0	0	0	0	0
E	0	2	5	5	5

Table 3: Ester/LAO SBM					
Oil	0% Oil	0.5% Oil	1.0% Oil	2.0% Oil	5.0% Oil
A	0	0	3	5	5
B	0	0	3	5	5
C	0	2	3	5	5
D	0	0	1	0	0
E	0	1	5	5	5

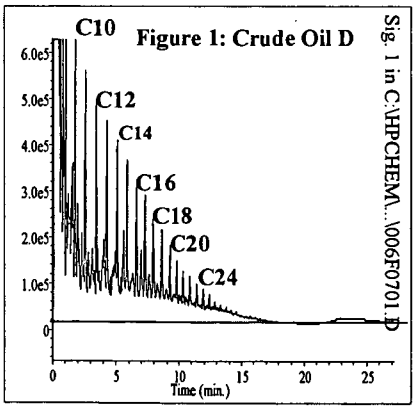

Figure 1: Crude Oil D

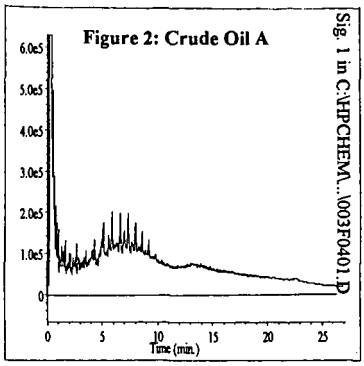

Figure 2: Crude Oil A

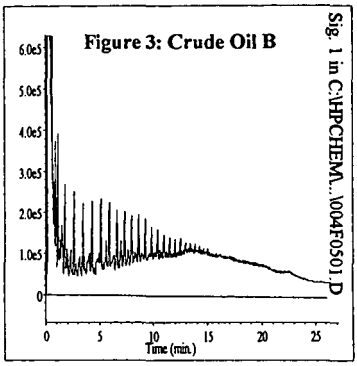

Figure 3: Crude Oil B

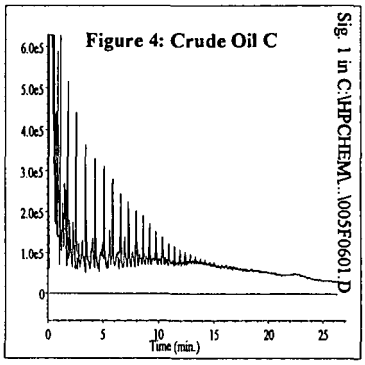

Figure 4: Crude Oil C

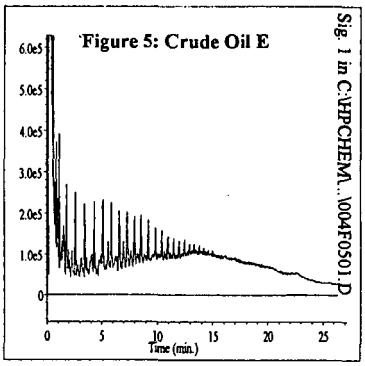

Figure 5: Crude Oil E