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Evaluation of the ability of calcite, bentonite and barite to enhance oil dispersion under arctic conditions

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ABSTRACT

A test program was conducted at laboratory and pilot scale to assess the ability of clays used in drilling mud (calcite, bentonite and barite) to create oil-mineral aggregates and disperse crude oil under arctic conditions. Laboratory tests were performed in order to determine the most efficient conditions (type of clay, MOR (Mineral/Oil Ratio), mixing energy) for OMA (Oil Mineral Aggregate) formation. The dispersion rates of four crude oils were assessed at two salinities. Dispersion was characterized in terms of oil concentration in the water column and median OMA size. Calcite appeared to be the best candidate at a MOR of 2:5. High mixing energy was required to initiate OMA formation and low energy was then necessary to prevent the OMAs from resurfacing. Oil dispersion using Corexit 9500 was compared with oil dispersion using mineral fines.

1. Introduction

When spilled in the environment, especially in coastal systems, oil frequently interacts with natural fine mineral particles to form Oil Mineral Aggregates (OMAs). This process has been observed and contributes to natural shoreline restoration as the oil trapped on the fines remains mobile in the water column (Bragg and Owens, 1995; Lee et al., 1997). Laboratory experiments and field tests have established that OMA formation decreases the amount of oil at the sea surface as well as increasing the oil biodegradation rate (Lee et al., 1997; Weise et al., 1999; Jézéquel et al., 1999). Based on this knowledge, a novel oil spill response technique has been put forward. This technique is based on the application of mineral fines to oil slicks in order to enhance their dispersion in the water column through OMA formation. In addition, the oil dispersion associated with mineral fines increases the bioavailability of oil for microbial degradation (Lee et al., 2009; Lee et al., 2011).

Although a lot of studies have been conducted on the effect of mineral fines on spilled oil in open water, the amount of work that has been conducted in ice-infested waters is very limited (Arctic Response Technology, 2013a, 2013b).

In 1998, during the *Saraband* oil spill incident in the Saguenay Fjord (Canada), twenty tons of heavy fuel oil was released onto the ice. The main concern was that the oil would be trapped in the ice until it melted the following spring. Considering the local marine traffic and the availability of an ice-breaker, a recommendation was made to apply minerals to the oil during ice-breaking operations. The ice-breaker crew involved in the operation observed rapid dispersion of the oil trapped in the ice. No stranded oil was observed on the shoreline during the following weeks, suggesting successful oil dispersion with mineral fines (Canadian Coast Guard, 2002).

In the wake of this oil spill, a research program was initiated by Canadian scientists at both laboratory scale and in the field in the winter 2007–2008 (Lee et al., 2009; Lee et al., 2011). The objective of this field test was to evaluate the feasibility of the application of clay mineral particles to an oil slick in ice-packed waters. The experimentation was conducted with a Canadian Coast Guard ice-breaker in the St. Lawrence River Estuary (Quebec, Canada). For each of the three tests conducted, 200 L of a crude oil was released onto the ice surface and the twin propellers of the ice-breaker were then used alternately to break up the ice sheet. For tests 1 and 2, prior to the ice-breaker operation, a slurry containing 133 g/L of calcite was sprayed onto the oil slick using a pressurized fire-hose. The application was repeated four times. A total of 160 and 140 kg of calcite was used respectively for tests 1 and 2. During test 3 (control test), no mineral fines were applied to the oil slick before the ice-breaker operation. When mineral fines were applied, oil dispersion was immediately observed and oil recoalescence/resurfacing was insignificant. For the control test, the oil dispersion was not stable (recoalescence observed) and oil remained on the ice after mixing. Water samples collected during the field tests were used for a laboratory study in order to assess the behavior of OMAs and oil biodegradation. After 2 months of incubation, > 56% of the spilled

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oil had been degraded and alkane biodegradation appeared higher for the water samples collected during tests 1 and 2 (mineral fines).

To understand these field results, a mathematical modeling study was conducted with eight different scenarios including the 3 scenarios tested in the field. The modeling results indicate that significant proportions of the oil had been transferred from the surface to the water column and that biodegradation was enhanced for cases with mineral treatment (Niu et al., 2014).

In 2012, an Arctic Oil Spill Response Technology Joint Industry Program (JIP) was initiated by the International Association of Oil and Gas Producers (IOGP) with nine international oil and gas companies. The overall objective of this JIP was to improve the technologies and methodologies for oil spill response under arctic conditions. Numerous research projects were conducted to improve the knowledge of oil behavior and of the efficiency of oil spill response techniques: dispersants, trajectory modeling, remote sensing, mechanical recovery and in situ burning.

The present study was one part of the large research project on "dispersant testing under realistic conditions" which brought together Sintef (Norway) and SL Ross (Canada) for dispersant evaluation (Faksness et al., 2017) and Cedre (France) in charge of mineral fines testing in combination with dispersant. The goal of this study was to evaluate the potential of using clay particles commonly used in drilling muds (calcite, bentonite and barite) to form OMA. Calcite was successfully used in the St. Lawrence River field test (Lee et al., 2009; Lee et al., 2011).

During the first stage, a total of 150 laboratory tests were conducted in order to assess the efficiency of different clays (bentonite, barite and calcite) and to define the best MOR and mixing energy to promote OMA formation. Four crude oils (Grane, Alaska North Slope, Troll and Oseberg) were tested at two salinities (5 and 35 ppt). Dispersion was characterized in terms of oil concentration in the water column and median OMA size (d_{50}) after one hour of resting time. Additional tests were performed in order to assess the combination of mineral fines with dispersant at 2 dispersant-to-oil ratios (DORs). During the second stage, two tests were performed at pilot scale, in Cedre's flume tank. Oil dispersion using Corexit 9500 was compared with oil dispersion using bentonite at a MOR of 1:10. The oil was weathered in the flume for 18 h before dispersant or mineral application.

2. Materials and methods

2.1. Properties of fine minerals

The three types of fine minerals used were Bentonite (from Total), Barite and Calcite (from Sigma Aldrich). Their main properties are summarized in Table 1. The size distribution was obtained using a laser diffraction analyzer (Malvern Instruments, Mastersizer 2000). Calcite was selected as it was the mineral fine used during field tests conducted by Lee et al. (2009). These mineral fines were selected as they are common minerals used in the oil industry for drilling mud.

A slurry of each type of mineral fines was prepared in distilled water at different concentrations according to the MOR tested.

2.2. Properties of oils

Four crude oils were used: Grane, Alaska North Slope, Troll blend and Oseberg blend. Table 2 and Fig. 1 present the physico-chemical properties and SARA (Saturates, Aromatics, Resins, Asphaltenes) fractionation of each oil. The oil viscosity was determined using a Haake VT550 viscosimeter. The oil density was measured according to ASTM D5002 using an Anton Paar DMA 5000 densimeter (American Society for Testing and Materials, 2016). Troll Blend is a mixture of the naphthenic Troll C and the more paraffinic Fram oil, which are transported in the same pipeline to the Mongstad terminal (Norway). Oseberg Blend is a paraffinic crude, Grane is an asphaltenic crude. All the tests were performed on the four oils topped at 150 °C.

Table 1
Main properties of the selected mineral fines.

Mineral name	Color	Density (g/ml)	Particle size range (μm)
Bentonite	Green	1.02	60–180
Calcite	White	2.93	5–50
Barite	White	4.48	50–170

Table 2
Physico-chemical properties of the four crude oils tested.

Oil	Density at 5 °C (g/ml)	Viscosity at 5 °C (mPa.s) (10 s^{-1})	Evaporative losses (%wt) at 150/200/250 °C
Alaska North Slope (ANS)	0.874	23	18.5/28.4/39.5
Troll blend	0.852	10	16.8/26.5/36.8
Oseberg blend	0.825	13	26.3/35.2/49.1
Grane	0.930	635	1.7/4.8/11.3

2.3. Test matrix and laboratory test protocol

The objective of this lab test was to compare and contrast the dispersion results according to the different parameters studied (mineral nature and oil type, MOR, salinity). The experimental matrix is presented in Table 3. At least duplicate runs were conducted for each condition performed at 2 ± 1 °C. The 35 ppt experiments were performed using filtered and sterilized (UV) natural sea water (Oceanopolis public ocean park - Brest - France). A water salinity of 5 ppt was reached by dilution of the natural sea water with distilled water. For tests involving dispersant application, Corexit 9500 was used as it is one of the most-used dispersants in the case of oil spills. Dispersant was sprayed onto the oil at two DORs reflecting insufficient and recommended dosage (DOR 1:50 and DOR 1:25).

In a beaker containing 300 mL of water, 500 mg of oil was added at the water surface with a syringe. After addition of a slurry of mineral fines, the mixture was subjected to 1 min of high energy mixing (2000 rpm) using a high shear rate mixer - Ultraturrax® (IKA, Germany). The aim of this very high level of energy was to recreate the energy level generated by the ice-breaker during the field experiment (Lee et al., 2009). The whole solution was transferred into a graduated separatory funnel. After an hour of resting time, the fraction below the water surface (250 mL) - considered as the water column - and the fraction corresponding to the water surface (50 mL) were collected in two separate flasks. The resting time duration (one hour) was determined following preliminary testing in which a difference in the OMA distribution in the water column was observed only after > 30 min. Between 0 and 30 min after a very high level of agitation, all the OMAs were uniformly distributed in the beaker whatever the testing conditions, meaning that no discrimination could be made between the dispersion results.

The water samples were sonicated, extracted with methylene chloride and dried on sodium sulfate. The oil concentration was measured with a previously calibrated UV–visible spectrometer (Evolution 600 UV-VIS, Thermo Fisher Scientific). The absorbance of the solvent extracts was compared to standard solutions of each crude oil. The particle size distributions in both fractions were analyzed with a laser diffraction analyzer (Malvern Instruments, Mastersizer 2000). Water samples were taken using a peristaltic pump placed after the measuring cell to avoid droplet coalescence.

2.4. Flume testing protocol

Two tests were conducted at pilot scale in order to compare