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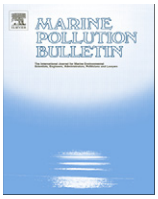

Investigation of OMA formation and the effect of minerals

Haiping Zhang[a], Mona Khatibi[a], Ying Zheng[a,*], Kenneth Lee[b], Zhengkai Li[b], Joseph V. Mullin[c]

[a] *Department of Chemical Engineering, University of New Brunswick, Fredericton, NB, Canada E3B 5A3*
[b] *Centre for Offshore Oil, Gas and Energy Research, Bedford Institute of Oceanography, Fisheries and Oceans (DFO) Canada, Dartmouth, NS, Canada B2Y 4A2*
[c] *Minerals Management Service, US Department of Interior, Herndon, VA 22070, USA*

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ABSTRACT

Oil–mineral-aggregates (OMA) have been shown to be effective in oil spills cleanup. Experimental work was carried out to study the effects of physical–chemical properties of natural minerals and chemically modified minerals on OMA formation and oil removal. The results showed that the hydrophobicity, particle sizes and specific surface of minerals played an important role in OMA formation. Appropriate hydrophobicity of minerals can enhance the formation of OMA. The surface property of minerals can also influence the shape of OMA. Spherical mineral–oil aggregates were frequently formed with hydrophilic minerals while irregular shaped OMA were observed with hydrophobic minerals. The sizes of OMA also increased when the minerals changed from hydrophilic to hydrophobic. The effects of dispersant and mixing energy were also carefully studied. The results showed that dispersant were a dominant factor. When dispersant was applied, effects of other factors became minimal.

1. Introduction

The clean-up of oil slicks on the sea surface has been studied for several decades (Conover, 1971; Jordan and Payne, 1980; Lee et al., 2003; Poirier and Thiel, 1941) and it has been widely accepted that dispersants and oil–mineral-aggregates (OMA) are effective methods for the treatment of oil in water (Kepkay et al., 2002; Lee, 2002; Stoffyn-Egli and Lee, 2002; Venosa et al., 2002). With the use of dispersants, oil droplets are easily reduced in size to micrometers which leads to quick transfer of oil slicks from the sea surface to the water column (Venosa et al., 2002). However, concerns have been raised due to the potentially toxic effects of dispersants and chemically-dispersed oil on marine biota, and application of dispersants is frequently limited by legislation, especially in coastal regions (Barry, 2007; Bayat et al., 2005). Compared to dispersants, OMA are a natural attenuation and enhanced cleanup technique for remediation of the sea surface and shorelines contaminated by oil (Kepkay et al., 2002; Lee, 2002; Stoffyn-Egli and Lee, 2002). The oil droplets that are incorporated in OMA are easily transported into the water column by wave energy. Additionally, more nutrients, dissolved oxygen, and oil-degrading microorganisms can reach the oil droplets due to the reduction of sizes of oil droplets. This can accelerate the microbial degradation process (Lee et al., 1997; Owens and Lee, 2003; Weise et al., 1999).

The first laboratory examination of the interaction of oil and minerals and the formation of OMA was conducted by Delvigne et al. (1987) and Payne et al. (1989), and since then numerous studies have been carried out. These studies have suggested that turbulent energy, dispersant and the type of mineral used could have an impact on the amount of oil incorporated in the mineral phase (Ajijolaiya et al., 2006; Khelifa et al., 2005; Stoffyn-Egli and Lee, 2002). Turbulent energy is required to disperse oil and mineral particles and Ma et al. (2008) have demonstrated that higher turbulent energy can improve the interaction between oil and minerals. Dispersant is another factor that has positive effect on the formation of OMA (Guyomarch et al., 1999, 2002; Lee et al., 2008; Li et al., 2007). Guyomarch et al. (1999, 2002) reported that dispersants significantly increased the oil amounts incorporated into OMA. The observation by Lee et al. (2008) and Li et al. (2007) indicated that, with the presence of dispersants, formed OMAs remained in suspension in the water column.

Mineral characteristics play an important role in the oil–mineral interaction. The formation of OMA is highly associated with the properties of minerals such as particle size, surface area, concentration and especially surface chemistry (Ajijolaiya et al., 2006; Guyomarch et al., 2002; Stoffyn-Egli and Lee, 2002). It has been reported that hydrophobicity is an important characteristic of minerals influencing the apparent affinity to oil in seawater (Ajijolaiya et al., 2006). Therefore, appropriate hydrophobicity of minerals would facilitate the interaction between oil and minerals. To date, however, detailed studies on the effect of hydrophobic minerals have been scarcely documented.

In the investigation of OMA, previous studies usually concentrated on those collected in the sediment phase or separated through filtration, for the purpose of focusing on the efficiency of

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* Corresponding author.
E-mail address: yzheng@unb.ca (Y. Zheng).

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total oil trapped in all OMA (Guyomarch et al., 1999; Stoffyn-Egli and Lee, 2002). For the purpose of more efficient degradation, it is preferable that OMA would suspend within the water column rather than settle to the seabed or float on the surface (Muschenheim and Lee, 2002; Quantin et al., 2005). The dilution rate of oil in the large volume of water available in the water column of the ocean environment reduces it to such low concentrations that toxicity is lower than the threshold level to most marine biota. In order to investigate OMA in the water column, Lee et al. designed a partition procedure to distribute petroleum into three different levels (top, middle and bottom) and the effects of chemical dispersants and mineral fines were investigated for each level (Lee et al., 2008). The current study adopted and modified the partition method. The relative stability of oil in the middle portion is the focus of the current research. The effects of mineral type, mixing energy level, and dispersant use were investigated and differentiated on suspended oil droplets and OMA in water. In order to assess the effect of these factors, besides the percentages of total petroleum hydrocarbon (TPH) in water phase, the size distribution of the suspended oil drops and/or OMA was also added as another criterion to determine the most significant factor. The data collected are useful in modeling the fate and transport of the dispersed oil in field application.

2. Experimental

2.1. Materials

2.1.1. Crude oils

Three different crude oils were studied: MESA, Alaska North Slope (ANS) and Heidrun. The physical properties of the crude oils are summarized in Table 1. Density was measured by portable density meter (DMA 35N, Anton Paar GmbH, Graz, Austria) at 22 °C. Viscosity was determined at 40 °C following ASTM D445-06 and the measurements were taken by X-CELL Analytical at St. Francis Xavier University in Antigonish, Nova Scotia, Canada.

2.1.2. Minerals

Different types of minerals were tested to study the effectiveness of minerals in formation of oil–mineral-aggregates. Natural minerals including kaolin (Fisher Scientific), diatomite, fly ash and graphite were studied. Two modified kaolin minerals with different hydrophobic properties were also prepared and which are referred to as modified kaolin #1 (lower hydrophobicity) and modified kaolin #2 (higher hydrophobicity). The size distribution of minerals was measured by a laser particle sizer (Analysette 22 compact, Fritsch Gmbh, Idar-Oberstein, Germany), the surface area was measured by BET nitrogen adsorption (Belsorp-max, Bel, Japan) and the hydrophobic property was measured by contact angle (JC200A, PowerEach, China).

2.1.3. Preparation of modified kaolin

Kaolin was modified using the method described by Molphy et al. (1994). The degree of hydrophobicity was monitored by varying the amount of toluene 2,4-diisocyanate (TDI) (Sigma–Aldrich). Modification was carried out in a 250 ml three-necked, round-bottom flask equipped with a condenser. 1 g of kaolin was pre-dried in an oven at 120 °C for 24 h to remove water and then transferred to the flask containing 150 ml toluene. Next, TDI was added to the mixture and stirred at 70 °C for 3 h. Thereafter, a fourfold excess butanol was introduced to the reaction while continuing to stir at 110 °C for 3 h. The resultant kaolin was then washed with hot water and ethanol.

Table 1
Physical properties of crude oils.

Crude oil	Specific gravity	Kinematic viscosity (cS)
MESA	0.8764	13.06
Alaska north slope	0.8746	10.82
Heidrun	0.9058	21.09

The reaction is shown as follows:

$$\text{Kaolin—OH}\xrightarrow[(2)\text{C}_4\text{H}_9\text{OH}]{(1)\text{TD1}}\text{Kaolin—OCONH—C}_4\text{H}_9 \quad (1)$$

The coating of alkyl groups was measured by Fourier Transform Infrared Spectrometer (Nicolet 6700, Thermo Scientific, US) and the enhancement of hydrophobicity was determined by static contact angle measurements which were conducted using a JC200A instrument (PowerEach, China) with a digital photo analyzer, imaging 3 s after water comes into contact with the sample pellets.

2.1.4. Artificial seawater

Artificial seawater with 30 ppt salinity was prepared by dissolving an appropriate amount of NaCl into deionized water.

2.2. OMA experimental procedures and conditions

2.2.1. Procedure

Experiments were conducted following a modified lab experimental procedure for partitioning of oil in three fractions (Lee et al., 2008). First, 40 mg minerals were added to a baffled flask (Fisher Scientific) containing 120 ml saline water and shaken on an orbital shaker (VWR Scientific) for 10 min. Crude oil (100 μl) was then added to the surface of the sediment/saline water suspension and 4 μl dispersant (Corexit 9500, Nalco Energy Service, L.P. Sugar Land, TX) was carefully dispensed onto the oil. The baffled flask was then shaken for another 60 min at a constant rotational speed to generate oil–mineral-aggregates, after which the entire contents in flask were transferred to a separatory funnel. The funnel was left static for 60 min to allow for three phases of oil/OMA to separate: the bottom portion – settled OMA (~5 ml); the middle portion – dispersed oil droplets and suspended OMA (~110 ml), and; the top portion – floating non-dispersed oil (~5 ml). The oil in the middle and bottom parts was extracted with dichloromethane (DCM), and oil that adhered to the walls of the flask and funnel was also rinsed with DCM and mixed with the oil that had floated in the top part of the flask. The total petroleum hydrocarbon dissolved in DCM was measured with a UV spectrophotometer (UV-1800PC, China). 5 ml of the middle and bottom portions were taken for the size analysis of oil droplet and OMA using a fluorescence microscope and a confocal laser scanning microscope. Four replicates were conducted for each condition and at least one replicate was performed separately.

2.2.2. Conditions

Each test was performed using half-fraction factorial experimental design and the treatments are summarized in Table 2. Detailed investigation was given to MESA oil using the experimental conditions shown in Table 3. One factor was changed in each set of the experiments and all the experiments were conducted following the above-mentioned procedure.

2.3. Analytical method

2.3.1. UVS analysis

Extracts of crude oils were diluted and then analyzed for absorbance at three wavelengths 340 nm, 370 nm and 400 nm (Venosa