# ON THE OIL-MINERAL AGGREGATION PROCESS: A PROMISING RESPONSE TECHNOLOGY IN ICE-INFESTED WATERS

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## ABSTRACT

*The oil-mineral aggregation (OMA) process refers to oil droplets and fine sediments interaction leading to the formation of small aggregates. Previous studies have highlighted the significance of oil-mineral aggregate formation on the persistence of oil and the feasibility of its use for the development of spill countermeasures. However, the efficiency of the OMA process in ice-infested waters is not well known. Some preliminary laboratory works have reported promising results regarding the aggregation process in the presence of ice. In the light of these results, the Canadian Coast Guard has conducted a research program that aims to elaborate clean-up measures using the OMA process in ice-infested waters. The oceanographic parameters likely to affect the efficiency of the OMA process were reviewed with respect to the oceanographic conditions prevailing in the Saint-Lawrence River during winter. These results suggested that the low turbidity values and water turbulence prevailing during icing periods are likely to be important parameters influencing oil dispersion efficiency by the OMA process. Clean-up measures which would overcome these limiting effects, based on laboratory and field tests would be developed. This paper presents a literature review on the international expertise related to oil-ice-sediment interactions. The efficiency of the OMA process and the feasibility of using OMA as an oil spill countermeasure strategy in ice-infested waters is discussed herein. The main objectives of the experimental protocol designed for the development of clean-up measures aimed at enhancing oil dispersion in ice-infested waters by the OMA process are presented.*

## DISCUSSION

### The Oil-Mineral-Aggregation process

The oil-mineral aggregation (OMA) process is defined as the oil droplets and fine sediments interaction in the water column leading to the formation of small aggregates. The most common type of aggregate is the droplet OMA which consists of an oil droplet stabilized at the surface by mineral particles (Figure 1). Other types of OMA, such the solid OMA and the flake OMA have been observed and described (Lee et al., 1999; Stoffyn-Egli and Lee, 2002). Solid OMA are elongated and curved or even branched aggregates that exhibit clay particles within the oil boundaries (Figure 2). Flake OMA are described as having a membrane-like structure (Figure 3), usually floating or low density (neutrally buoyant), which can be several mm in length (Stoffyn-Egli and Lee, 2002).

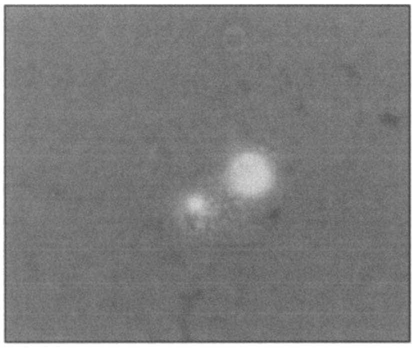

FIGURE 1. THE DROPLET OMA CONSISTS OF AN OIL DROPLET STABILIZED AT THE SURFACE BY MINERAL PARTICLES.

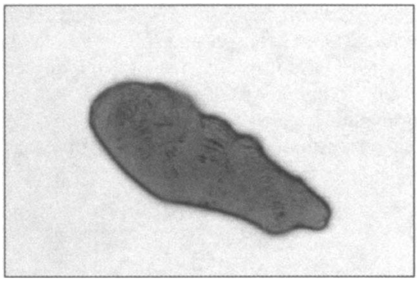

FIGURE 2. SOLID OMA ARE COMPOSED OF MINERAL PARTICLES TRAPPED WITHIN THE OIL DROPLET BOUNDARIES.

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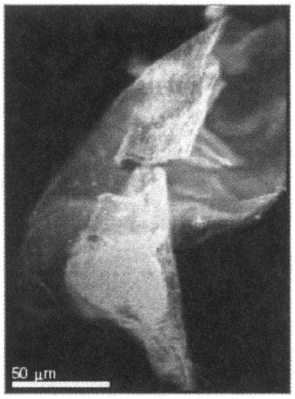

FIGURE 3. FLAKE OMA HAVE A MEMBRANE-LIKE STRUCTURE. THE FLUORESCING CHARACTER OF THE OMA SUGGESTS THE PRESENCE OF OIL.

Due to their structure, OMA have the properties to limit oil recoalescence at the water surface, oil adherence to the substrate and to enhance oil biodegradation. This type of association also provides OMA a low density which increases oil dispersion by tidal currents and a more rapid microbial degradation than free surface oil (Lee et al., 1999 ; Weise et al., 1999).

Oil dispersion under the form of OMA was shown to be dependant on several parameters such as oil viscosity (Lee et al., 1999; Stoffyn-Egli et Lee, 2002), suspended sediment concentrations (Cloutier et al., 2002; Stoffyn-Egli et Lee, 2002), salinity (Khelifa et al., 2002), and the hydraulic energy intensity (Delvigne et al., 1987; Bragg and Owens, 1994 ; Bragg and Yang, 1995;). In particular, the water motion is critical to the process as it provides the energy necessary to break the oil film into small droplets, to induce sediment resuspension in the coastal zone, and to enhance oil and sediments interaction in the water column to form OMA.

In coastal environments where hydraulic energy is not sufficient, a new approach which consists of transferring the oiled material into the surf zone where wave action enhances oil and sediment interaction was tested (Figure 4). This procedure was used with success to enhance oil dispersion form the shorelines affected by the *Sea Empress* spill on the coasts of Wales in 1996 (Lee et al., 1999) and in Norway during *in situ* experimental work called the *Svalbard Shoreline Field Trials* (Guénette et al. 2003; Lee et al., 2003; Owens et al., 2003). The latter study was conducted using IFO30 oil in cold-water temperatures (0°C-2°C) during free ice periods. The results have shown that the amount of oil remaining on shore was dramatically reduced within five days after sediment relocation treatments due to OMA formation (Lee et al., 2003).

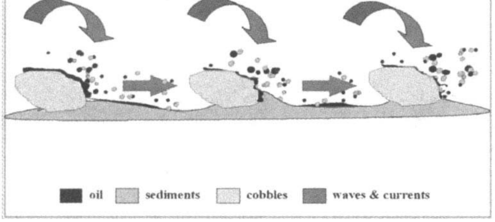

FIGURE 4. DURING SURF WASHING, THE OILED MATERIAL (COBBLES) THAT FORM THE UPPER BEACH PARTS IS TRANSFERRED INTO THE SURF ZONE WHERE WAVE ENERGY AND CURRENTS ENHANCE OIL DROPLET FORMATION, SEDIMENT RESUSPENSION AND OMA FORMATION THAT WILL BE DISPERSED BY CURRENTS AND DEGRADED *IN SITU.*

In the context of a project aimed at developing a similar procedure for mechanical dispersion of spilled oil in ice-infested waters, the Canadian Coast Guard proposes that OMA formation could be used as a response technology in ice-infested waters. The efficiency of the OMA process, that is OMA formation in an amount significant enough to enhance oil elimination and dispersion from the environment, is examined in the next section in the light of the international expertise related to this field. The most significant physico-chemical parameters likely to affect the OMA process is the eventuality of an oil spill in the Saint-Lawrence River during winter months are also presented.

### International expertise related to oil-ice-sediment interactions

To date, very few studies have been carried out to test the oil-mineral aggregation process as a potential counter measure in cold and/or in ice-infested waters. Some field work have been realized in arctic-type regions characterized by cold waters. Among these, the *Baffin Island Oil Spill (BIOS)* project and the *Svalbard Shoreline Field Trials (SSFT)*. The use of the OMA process as an oil spill countermeasure was not evaluated as a cleansing technique during *BIOS* fieldwork (Dickins, 1987). However, in terms of spill countermeasures for arctic remote beaches, the experiments indicated that in most cases, natural cleansing was as effective as other tested countermeasures. In the same manner as the *BIOS* project, the results of the *SSFT* have shown that natural oil removal, here confirmed by OMA formation, was efficient in cleaning sediments from cold regions (0°C to 2°C), free of ice, low energy shorelines (wave height ≤ 0.3 m) (Lee et al., 2003, Garrett et al. 2003).

The only experiments on OMA interaction with ice are those of Payne et al. (1989). This work was aimed at providing more information and data for future modeling purpose of the oil weathering behavior in ice-loaded sediment. Oil and sediments were mixed prior to their interaction with ice so the experiments do not characterize oil dispersion through oil-mineral aggregation process. One of the main objectives of Payne et al. (1989) experiments was to understand sediment entrainment processes responsible for generating a seasonal ice canopy with widely varying, but significant (up to 1600 mg $l^{-1}$) sediment burdens. Experiments carried out using a wave basin have shown that the presence of petroleum contaminants does not affect the incorporation of sediment into the salt-water frazil ice cover. In the light of these results, it is likely that oil contaminated sediment may be incorporated into the ice cover during storm events. Thus, this process could be a potential source of pollutant transport and dispersal. Moreover, important sediment concentrations were found after water was allowed to filter through the ice matrix, for both sediment tested (hydrocarbon contaminated and not contaminated). These results illustrate the important OMA scavenging potential of the frazil ice. It is expected that different results could be observed with different ice types.

### Evaluation of natural oil dispersion as OMA in the Saint-Lawrence River during winter

As noted above, certain parameters are known to influence the efficiency of the OMA process. The most significant parameters are related to the oil properties (polar compounds and viscosity), and the environmental characteristics (amount of suspended particles and flow turbulence characteristics).

### Oil viscosity and water temperature

As soon as the oil is spilled, weathering increases the amount of polar compounds, which normally contributes to OMA formation. Weathering also contributes to an increase in oil viscosity, which in return may affect the efficiency of the OMA process. In cold environments, water temperature also contributes to an increase in oil viscosity. In the presence of ice, a greater energy level will be required for the oil droplet formation and dispersion.

### The concentrations of mineral particles

The number of particles available or the suspended sediment concentration (*SSC*) at the oil droplet surface is essential to OMA formation. It is partly determined by natural water turbidity, which is also dependant on fluid turbulence. The amount of suspended particles was shown to be critical in the rate of elimination of stranded oil on coastlines. Moderate *SSC* (≈ 250 mg/L) were shown to contribute to significant oil erosion from a surface (Cloutier et al., 2002). During icing periods, it is expected that *SSC* values would be less than during summer conditions due to reduced hydraulic conditions.

The amount of suspended sediments could also be expressed using the oil/sediment ratio. This ratio was used to investigate the parameters controlling solid aggregate formation (Stoffyn-Egli and Lee, 2002). The results have shown that this ratio could influence the type of OMA formed as the abundance of solid OMA compared to droplet OMA, was greater for oil concentrations greater than 0.2 $g\ l^{-1}$. The results have also shown that the proportion of positively buoyant aggregates have increased with the increase in O/S ratio. These results have important implications with respect to the amount of *SSC* necessary to initiate the OMA in ice filed.

### The effects of an ice field

In the same manner as the oil itself, sea ice acts as a filter for surface ocean waves. Short waves are attenuated or stretched out by the influence of the sea ice floating on the water. The end result of the damping and attenuation is that only the longer waves penetrate to the interior areas of the ice field. In these conditions, natural oil dispersion is minimal and the energy necessary to OMA formation would be available only during storm conditions. It is expected that the decrease in wave energy, along with the decrease in current velocities due to the presence of ice, would also lead to greater particle sedimentation and consequently affect the natural efficiency of the OMA process.

### The efficiency of the OMA process and the feasibility of using OMA as an oil spill countermeasure strategy in the Saint-Lawrence River during winter

The Saint-Lawrence takes its origin in the Great Lakes and extends to the Atlantic Ocean. It is subdivided in several sections, which are all characterized by different hydrodynamic, climatic, physico-chemical conditions such as water salinity, waves, currents, tides and icing process. The five main hydrographic subdivisions are the fluvial section, the fluvial estuary, the upper estuary, the maritime or lower estuary, and the Gulf of Saint-Lawrence. The dimensions of the Saint-Lawrence estuary are such that the hydrodynamic conditions prevailing in the lower part of the estuary are typically marine while those prevailing in the upper portion are typically estuarine. This section will focus on the estuarine portion of the river, the upper estuary.

The *Upper estuary* extends on 150 km from Quebec and Saguenay River. It is characterized by the widening of the river to about 17 km, a channel depth of 100 to 300 m, and semi-diurnal tides (tidal currents are of 0.3 to 0.4 m/s). Particular hydrodynamic conditions due to tidal currents and an increase in both salinity and temperature gradients in this portion of the estuary contribute to an increase in the turbidity levels and to the formation of a turbidity maximum zone (*TMZ*) which extends on the south shore. Concentrations of suspended particulate matter ranging from 50 $mg\ l^{-1}$ and 200 $mg\ l^{-1}$ are commonly observed (Ouellet and Trump, 1979; d'Anglejan, 1990). These are highly variable in space and time, and are only loosely correlated with the ebb-flood cycle because of intense turbulent mixing. There is no available data on typical *SSC* prevailing during winter months in the estuary. It is expected however that these would be lower than what is observed during summer conditions.

In the St. Lawrence estuary, the ice forms in December and persists until April (Drapeau, 1990). Observation have shown that the ice found in the estuary originated from two different sources being essentially 1) ice attached to the coast (ice foot) and 2) the ice formed upstream (Drapeau, 1990). The convergence of estuarine waters with those of Saguenay River prevents the formation of an ice cover in that area. The north shore of the Lower estuary is free of ice during most of the winter, likely due to the upwelling of warmer waters along with the presence of more salted waters.

The wave climate in the St. Lawrence estuary is controlled by winds that blow predominantly from the western quadrant and having a tendency to align parallel to the axis of the estuary and also by fetches that diminishes in size in the upper portion of the estuary. During the spring and summer seasons, winds blow more often from the eastern quadrant. In winter, the presence of ice impedes the formation of waves in the estuary. Otherwise the highest waves (≈ 2m) are found in April and December and the lowest are recorded in August (Drapeau, 1990).

In the light of this information, it is likely that the presence of ice during winter, would significantly affect the oil natural dispersion in that portion of the estuary. It is seems obvious that oil would preferentially follow the local circulation pattern and be deviated with the ice field on the southern shore of the river. The absence of waves along with lower turbidity levels in the presence of ice would prevent natural OMA formation. Following these observations, it is proposed that OMA formation and oil dispersion in the environment could be enhanced by the addition of mechanical energy and suspended particulate matter such as depicted on Figure 5. As the presence of ice leads to a decrease in turbidity levels and in surface waters energy level and to an increase in oil viscosity, the addition of mechanical energy and sediments is required. This could be achieved by the use of different mechanisms such as the followings :

- Use of boat propeller to produce mechanical turbulent hydraulic energy at the surface of the oil film and to enhance oil droplets formation;
- Use of hoses for energy addition (simultaneously with sediments), which would break the oil film and enhance oil droplet formation along with immediate interaction with fine sediments;
- Use of blow off system to spread sediments like a dust (dry sediments) on top of the oil film.

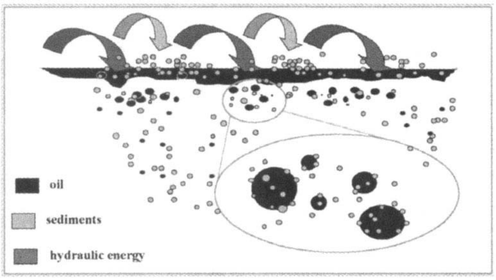

FIGURE 5. OIL-MINERAL AGGREGATE FORMATION BY THE ADDITION OF MECHANICAL ENERGY AND SEDIMENTS. THE ADDITION OF HYDRAULIC ENERGY AT THE SURFACE (BLUE ARROWS) HELPS BREAK THE OIL FILM INTO DROPLETS, WHICH WILL INTERACT WITH FINE SUSPENDED SEDIMENTS ADDED IN THE ENVIRONMENT (YELLOW ARROWS) TO FORM OIL-MINERAL AGGREGATES.

The procedure for sediment application may be dependant on the oil dispersion process. Tests to assess the spreading of minerals on the surface of the oil, either on ice or floating on water (air-oil interface), and from below the water surface (water-oil interface) were attempted (Lee, 2002). The experiments carried out in beakers (glass vessels), with sea water and sea ice have shown that when applied as a dry powder, sediments have formed floating oil cakes which can be mechanically removed. The results also have shown that clay minerals and/or natural sediment are the appropriate minerals to treat oil in water or under ice by introducing it just underneath the surface of the water. Bubbling air and delivering a concentrated suspension provided the best results. The main objectives of a laboratory protocol produced for the Canadian Coast Guard (Cloutier, 2004) aimed at evaluating the proposed method are presented here:

- To validate the aggregation potential with two different oil types:
  - The two oils tested will be IFO–180 and Heidrun.
- To validate the type of sediments to use for optimal OMA formation:
  - It is known that several types of sediments may participate to significant OMA formation (Stoffyn Egli and Lee, 2002). Artificial as well as natural sediments will be tested in laboratory. Different ranges of particle sizes will also be tested (< 15 µm).
  - It is expected that the smaller the particles the more OMA will be formed.
  - The optimal sizes and type of particles will provide significant OMA formation and avoid oil sedimentation to the seabed.
- To validate the amount of suspended sediment concentrations to use:
  - Concentrations of 200 to 500 mg/L will be tested in laboratory;
  - Although clays are not recognized to act as a "sinking" agent, it was shown that *SSC* = 600 mg/L would contribute to important settling of the oil to the bed in the absence of an applied current (Cloutier et al., 2002). This aspect will be investigated in laboratory as the use of "sinking" agents are prohibited in United States.
  - The best *SSC* is expected to provide significant OMA formation and to avoid oil sedimentation to the seabed.
- To validate the sediment introduction method in ice-infested waters (to the air-oil or to the oil-water interface);
- To validate the aggregation potential in the presence of ice:
  - This part of the study will also help determine the timeframe for removal procedure using fine sediments;
  - It is expected that oil OMA would be dispersed and degraded by microbacterial activity.

## BIOGRAPHY

Dr. Cloutier obtained a PhD in Oceanography. She has participated to several multidisciplinary research projects including bed stability in Venice lagoon, sediment dynamics in coastal subarctic regions, freshwater species Ecotoxicology and Marine Ecology. The author has developed an expertise in Environmental Sedimentology, in particular in the field of oil-sediment interaction.

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