

PRELIMINARY LABORATORY STUDY TO DETERMINE THE EFFECT OF EMULSIFICATION ON OIL SPILL EVAPORATION

by

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SUMMARY

A short laboratory study was performed to determine whether emulsification significantly affects the rate at which a marine oil spill evaporates. Four crude oils were evaporated in trays in a wind tunnel. One set of experiments considered 2-cm thick slicks having emulsion water contents of 0, 25%, 50% and 67%. The other set considered 67%-water emulsions at the three thicknesses of 0.5, 1.0 and 2 cm. The results indicate that emulsification does inhibit evaporation, that evaporation decreases with increasing emulsion water content and slick thickness, and that the process is strongly influenced by the properties of the parent oil. No attempt has been made at this point to analyze the results in depth or to model the process.

INTRODUCTION

When crude oil is spilled in the marine environment the oil gradually "weathers" and mixes with sea water to form a stable water-in-oil emulsion. The viscous emulsion is highly resistant to treatment by chemical dispersants or in-situ burning techniques. It is important to know how long it takes a specific crude oil spill to emulsify and increase in viscosity above certain critical values because it is this time that defines the "window of opportunity" for effective dispersant-use or in-situ burning.

Almost all crude oils emulsify when mixed with salt water because they contain natural, emulsion-stabilizing surfactants (asphaltenes and resins, for example). Some crude oils start emulsifying immediately when spilled at sea, and others start emulsifying only after the oil has evaporated to a point, perhaps where the natural surfactants are sufficiently concentrated in the residual oil to promote emulsification.

Much is known about the evaporation of crude oil spills, and models exist to predict crude oil slick evaporation rates. Unfortunately, little is known about how the emulsification process affects oil slick evaporation, and guesses have had to be made in existing computer models.

Until evaporation of oil in emulsions is better understood, predictions of evaporation rates from oil spills will be unreliable, as will be predictions of windows-of-opportunity for effective use of dispersants and igniter/combustion devices.

LIQUID-PHASE FACTORS CONTROLLING SLICK EVAPORATION

Mackay and colleagues at the University of Toronto have developed an analytical approach for predicting oil spill evaporation rates that is based on the so-called "evaporative exposure" concept (Mackay et al. 1980, Stiver and Mackay 1983, Stiver and Mackay 1984, Stiver et al. 1989). This approach is used in many computerized oil spill models today. It is

believed to be relatively accurate for predicting evaporation rates of most non-viscous, unemulsified oils, especially if the arbitrary constants in the model's evaporation equations are derived from the results of prescribed laboratory tests with the particular oils of interest (Bobra 1992, Belore and Buist 1994).

The evaporative exposure approach predicts the volume fraction evaporated to be:

$$F = \ln[1 + B(T_G/T) \theta \exp(A - B T_O/T)] [T/BT_G] \quad (1)$$

where F = volume fraction of oil evaporated
T = environmental temperature
A, B, T_O, T_G = various oil-dependent constants
θ = evaporative exposure or dimensionless time,

$$\theta = kAt/V \quad (2)$$

where k = air-side mass transfer coefficient
A = slick area
t = time
V = volume of oil spilled

If various thicknesses of a particular oil are evaporated in a tray at a fixed temperature and fixed air flow over the slick, the above equation indicates that plots of F versus θ should show all data falling on one curve. This has been shown to be the case in several experimental studies, for example, in Bobra (1992) from which Figure 1 is taken. The alignment of data in Figure 1 should always be the case when the evaporation is controlled by the resistance to mass transfer on the air side of the oil/air interface (as represented by k in equation 2) and when the temperature of the slick remains constant throughout the evaporation period (i.e., T remains constant in equation 1).

However, as discussed by Stiver and Mackay (1983), data will not fall on the same curve such as shown in Figure 1 for any of four reasons: (1) evaporative cooling occurs and changes T throughout the evaporation process; (2) there is a diffusivity (Schmidt Number) effect on the gas-side mass transfer coefficient; (3) a waxy crust forms on the slick surface significantly reducing evaporation rates; and (4) a significant resistance to mass transfer occurs in the liquid, oil phase. It has usually been assumed that the first two effects are relatively unimportant for most oil evaporation situations. The third effect, involving crust formation on slicks, is important for a certain class of crude oils called waxy oils (as discussed in Berger and Mackay 1994 and Buist et al. 1989), but would not apply for relatively non-waxy oils.

There is less knowledge on the fourth effect related to liquid-phase resistance, although Stiver and Mackay in 1983 suggested that ignoring liquid phase resistance to mass transfer may result in errors in predicting evaporation rates for highly viscous oils. This was later confirmed by Berger and Mackay 1994. Liquid phase control of the mass transfer process will occur when the liquid phase is not well mixed during the evaporation process, and the upper surface of the slick becomes relatively depleted in the lighter components of the oil. When this happens, the rate of evaporation becomes "controlled" by the rate at which the lighter components of the oil reach the surface from below, and not by the rate at which they are removed from the surface boundary layer by the overpassing air flow. In other words, the process is controlled by the liquid phase mass transfer process and not the gas phase mass transfer process. This might be the case for slicks of highly viscous oils, as

suggested by Mackay. Perhaps it might also be the case for slicks of emulsified oil. The purpose of this experimental program was to see whether this indeed is the case.

OBJECTIVE OF STUDY

The objective of the work was to determine the extent to which water-in-oil emulsification affects oil slick evaporation. Specifically, the goal was to compare the evaporation rate of a fresh, unemulsified oil slick to the evaporation rate of the same oil when emulsified.

METHODS

The experiments involved emulsifying four fresh crude oils with various amounts of salt water, then artificially evaporating the samples in a wind tunnel.

Emulsion Formation

Each oil was emulsified using the same procedure to produce three different water contents for the wind tunnel evaporation tests. First, the oil container was heated to about 45°C in a water bath and shaken to ensure that all of the waxes and precipitates were thoroughly mixed. Next, portions of the fresh oil were measured into a plastic pail. The volumes of oil and water used were:

Water Content (% Volume)	Oil (mL)	Salt Water (mL)
67% Water-in-oil	560	1140
50% Water-in-oil	500	500
25% Water-in-oil	750	250

To mix the salt water and the oil a 13-mm gear pump driven by a 0.35 kW electric motor was used. The suction and discharge hoses were placed in the bottom of the pail containing the oil and the pump was started. The salt water (35 ppt) was poured very slowly into the oil directly above the suction hose of the pump to ensure thorough mixing. Once all of the water was added, the emulsion was recirculated an additional five minutes to guarantee complete emulsification of all the water and oil present.

Evaporation

The wind tunnel, located in the S.L. Ross Laboratory, is 0.3 m wide and 3.4 m long. For the experiments a fan located at one end was set to draw air through the tunnel at an average velocity of 4.2 m/s, measured just above the trays containing the emulsions. The entrance to the tunnel was packed with flow laminator tube bundles (3.8 cm ABS tubing cemented together) to ensure that the air entered the tunnel smoothly. The trays measured 18.5 cm wide by 24 cm long by 5 cm deep. The emulsions were poured into the trays using a graduated cylinder in order to achieve the correct thickness of slick required for the tests, as given below.

Emulsion Water Content	0%	67%	67%	67%	50%	25%
Thickness (cm)	2	2	1	0.5	2	2
Volume Emulsion in Tray (mL)	900	900	450	225	900	900

The trays were evenly spaced along the length of the tunnel. A thermocouple connected to a temperature data logger was located within the tunnel. The air temperature was recorded every hour during each 14-day evaporation run. The individual tray tare weights were measured before the emulsions were added. The trays were removed and reweighed every 24 hours during the 2-week weathering period.

The wind tunnel was calibrated for each test. A tray of reagent grade toluene was evaporated in the tunnel and its mass loss rate measured. This permitted calculation of the wind tunnel mass transfer coefficient k (after Stiver and Mackay, 1983). With this the evaporative exposure, θ , could be calculated for each tray from:

$$\theta = \frac{kt}{x} \quad (3)$$

where:

k \equiv air-side mass transfer coefficient (m/s)

= 0.0069 m/s for the S.L. Ross tunnel

t \equiv time (s)

x \equiv oil slick thickness (m) = oil volume/tray area

As discussed earlier, the above equation assumes that there is no internal resistance to mass transfer in the slick itself. All resistance is attributed to the air layer above the slick.

Water Content

An Orion AF8 Karl Fischer Titrator was used to determine the water content of the emulsion samples. Samples of the emulsions from each tray were taken every 2 to 3 days during the test period and a minimum of 5 aliquots were gathered. The samples were taken by first stirring a section of emulsion in the tray with a spoon in an attempt to ensure homogeneity, then scooping out the required volume. The samples were placed in 20 mL glass vials and stored in a refrigerator to prevent emulsion breaking. Before the emulsion was introduced into the titrator the vials were shaken with a wrist-action shaker for a minimum of 1 hour to thoroughly mix the contents. A hand-held kitchen blender was used when the shaker method did not prove to be effective or suitable. The average sample size introduced into the titrator was between 0.10 and 0.15 g. For each individual sample a standard deviation of less than 5% H₂O was required for a minimum of 3 consecutive water content determinations for the data to be accepted. The titrator was calibrated weekly.

Crude Oils

The four oils used in this study are listed below. Definitions of the Emulsion Formation Index and Emulsion Stability Index are provided in Stiver and Mackay 1983.

Values of 1.0 for each indicate respectively that the oil has a high tendency to emulsify and the resulting emulsion is highly stable.

	<u>API Gravity (15/15°C)</u>	<u>Emulsion Formation Index*</u>	<u>Emulsion Stability Index*</u>
Kuparuk Crude	24.0°	1.00	0.92
Terra Nova DST#3	32.6°	1.00	1.00
Point McIntyre	26.6°	1.00	0.93
Iranian Heavy	30.0°	1.00	1.00

* for fresh crude

Data Analysis

The data obtained from the wind tunnel and the Karl Fischer titrator were combined to quantify the evaporation of both the emulsion and the parent oil in the slicks as a function of exposure, oil type, water content and slick thickness.

For each oil two graphs were prepared showing the mass fraction of the emulsion evaporated. The first graph compared the evaporation rate for the four different degrees of emulsification (0%, 25%, 50%, 67%) as a function of θ . Each of these four slicks was initially 2 cm thick. The second graph prepared showed the evaporation rate of the emulsions of different slick thicknesses. It showed the evaporation of a 67% water-in-oil emulsion with three different initial slick thicknesses (2 cm, 1 cm, 0.5 cm) as a function of θ .

A graph showing the water content of all six trays as function of θ was also constructed. Three data points (all within 5 wt% H₂O) calculated by the titrator were used for each aliquot from the trays. From this graph a least squares linear regression was used to determine the relationship between water content and θ for each tray. The least-square lines were then used to calculate the mass of water and oil in the trays over time. This was accomplished by multiplying the mass of emulsion in the trays measured at a given θ by the corresponding calculated water content. The corresponding mass of oil was obtained by subtraction.

RESULTS

The raw data for all tests can be found in the original report (S.L. Ross 1994) along with the results of the calculations used to produce the graphs.

Water Evaporation

Figure 2 is a typical example (involving Kuparuk crude oil) of the change in water mass in an emulsion as a function of time (or θ). The θ scale represents two weeks of evaporation. Note that the water mass essentially remains constant, indicating that the evaporation of the emulsified water is negligible for all thicknesses and %-water cases. A

similar result occurred for the tests involving the other oils. This was somewhat surprising because water surfaces are known to evaporate at relatively high rates when air is blown over them. The obvious explanation for the negligible water evaporation in this case is that the water in question is in the form of droplets surrounded by a continuous phase of oil. It is clear that the film of oil acts as an effective barrier to evaporation of the emulsified water droplets. This result simplifies the study and modeling of evaporation from spill emulsions. The following figures (3 to 18) were constructed on the basis of the assumption that water did not evaporate during the runs.

Oil Evaporation

Kuparuk Crude

Figure 3 shows a plot of mass of Kuparuk crude oil evaporated in grams as a function of time in minutes. The four tests involved 2-cm thick slicks at various water contents ranging from zero (unemulsified oil) to 67%-water emulsified oil. The temperature ranged from 20 to 26°C over the two-week test period. The difference in evaporation rate is apparent: as the water content of the emulsion increases the amount of evaporation decreases. This is not necessarily due to a resistance to mass transfer within the emulsion, but may be due simply to the fact that there is less oil available for evaporation in the constant-thickness emulsion than in the unemulsified oil (up to 3 times less). It is best to analyze the results on a normalized basis, and this is done using Figure 4 where the mass fraction of oil evaporated (mass of oil evaporated/mass of oil in emulsion initially) is plotted against $\theta (= kt/x)$ in which x , the thickness, is expressed as the oil-equivalent thickness (or volume of initial oil divided by tray area) and not emulsion thickness. Notice in Figure 4 that the data are more bunched and even might be represented by one curve. If this were the case, the results would suggest that emulsification does not tend to affect evaporation and that there appears to be no resistance to mass transfer in the liquid phase that controls the evaporation process. However, it is noted that there is still a trend in the figure for the evaporation in the more emulsified slicks to lag slightly behind the less emulsified slicks.

Figures 5 and 6 are similar plots for the same oil, except in this case the variable is slick thickness (0.5, 1.0 and 2.0 cm) and the constant is %-water content in the emulsion (67%). In contrast to the results in Figure 4, the F versus θ plots here show a significant difference in evaporation between the three thicknesses (again, θ or θ is expressed in oil-equivalent terms). One might expect oil evaporation in the 2-cm slick to lag somewhat behind that in the 0.5-cm slick, but the difference is very large as shown in the figure (remembering that θ is log-plotted). This suggests that there is a significant liquid phase resistance to mass transfer in emulsified oil.

Pt. McIntyre Crude

Identical plots for Pt. McIntyre crude are presented in Figure 7 to 10. (Experiments with this oil were kept at a steady 23°C.) In this case the F versus θ plots in Figures 8 and 10 are less ambiguous than for the previous oil. In both cases it shows that the emulsified slicks are inhibiting the evaporation process with the evaporation rate decreasing with water content (as shown in Figure 8) and decreasing with increasing slick thickness (as shown in Figure 10).

Terra Nova Crude

Experiments with the Terra Nova crude oil were conducted within the temperature range of 17°C to 26°C over the two-week test period. Terra Nova crude is known to be highly waxy, and slicks of this oil are known to form a skin on their surface as weathering proceeds (S.L. Ross 1985 and S.L. Ross and Mackay 1988). This was observed in these experiments as well: a shiny, waxy layer formed on the slick surface soon after the oil was placed in the wind tunnel.

Evaporation results are shown in Figures 11 to 14. The results in Figure 12 and 14 are not surprising considering the barrier that the waxy crust on the slick surface must present for evaporating oil. Figure 12 shows that the 67%-water emulsion evaporates much less fractionally than the fresh and the 25%-water emulsion, and Figure 14 shows that the evaporation rate for the 67%-water emulsion is so low that the data points for all thickness cases seem to fall equally close to zero, although a close look at the curves shows that thinner slicks evaporate less than thicker slicks, an unusual phenomenon that has been observed with other waxy oils (Buist et al. 1989).

Iranian Crude

The ambient temperature during these runs was in the 23 to 25°C range. Evaporation results are presented in Figures 15 to 18. The normalized results in Figures 16 are unusual in that it shows two separate groupings between (1) the fresh oil and the 25%-water emulsion and (2) the 50%-water and 67%-water emulsions. It is possible that a large jump in viscosity occurred somewhere between the 25%-water to 50%-water emulsions, but because emulsion viscosity was not measured in the experiments, this is only speculative. Figure 18 shows that usual decrease in fraction of oil evaporated with increasing thickness.

The results for all four oils suggest that emulsification of oil slicks strongly affects the rate at which oil evaporates, but there appears to be no clear trend. The process appears to be very dependent on the nature of the parent oil. No serious attempts have been made at this stage to analyze the results further or to attempt to model the process mathematically.

CONCLUSIONS

1. The water in stable emulsified oil does not evaporate substantially relative to the oil's evaporation. This is likely due to the barrier to evaporation presented by the continuous phase of oil enveloping the water droplets in the emulsion.
2. Hydrocarbon evaporation, expressed as the fraction of oil evaporated, is reduced when the oil is mixed with water to form stable water-in-oil emulsion.
3. The degree of inhibition of evaporation appears to increase with increasing water content and increasing slick thickness, which suggests that an internal resistance to mass transfer develops in emulsified slicks.
4. Oil evaporation from emulsions is highly affected by the properties of the parent oil. At this stage the relationship between oil properties and emulsion evaporation is unclear.

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