Results of Laboratory Tests on the Potential for Using *In Situ* Burning on Seventeen Crude Oils

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Abstract

Over the past five years, SL Ross Environmental Research has analyzed seventeen crude oils with a suite of laboratory tests and controlled burns to determine, for each oil, the likelihood of successfully using *in situ* burning as a response tool.

The studies have provided valuable spill-response information by indicating which of the oils would respond well to *in situ* burning and which would not. As well, when the results are compared, the trends in oil properties as they relate to applicability of *in situ* burning provide direction for future research in this area.

The testing was conducted for four organizations: the US Minerals Management Service funded the testing of twelve of the oils; the Alaska Department of Environmental Conservation and Alaska Clean Seas jointly funded the testing of four; and, BP Exploration funded the testing of one. All of the oils tested are produced in the United States.

1.0 Introduction

This paper contains data taken from four separate studies, in which crude oils were tested for suitability for *in situ* burning (SL Ross, 1999, McCourt et al., 1998, Buist et al., 1996, and SL Ross, 1996). The same test procedure, with only minor differences, was used in each study. The objective of each of the studies was to determine for each crude oil such practical information as:

- The evaporation behavior under different environmental conditions
- The maximum evaporation and emulsification that would still allow ignition using gelled gasoline igniters
- The ability of commercially-available emulsion breakers and alternative fuel igniters to extend the window-of-opportunity for ignition of stable emulsions
- The effects of wave action on the combustion of emulsion slicks
- The likelihood of the residues sinking after efficient burns of thick slicks of the crude oils

2.0 Methods

The laboratory-scale test procedure used in each of the studies is described in detail in McCourt et al. (1998). It is difficult to compare lab-scale results with full-scale spill response operations; however, this procedure was shown to be a good predictor of burning success with two of the oils tested (Alaska North Slope and Milne Pt. crude oils) when compared to similar tests done on a meso-scale (2-m diameter burns, Buist et al., 1998) and with full-scale tests for one oil (Alaska North Slope, SL Ross 1995). A brief summary of the test procedure is presented here.

2.1 Evaporation and Physical Properties

The evaporative characteristics were determined by exposing small volumes (1L) of each oil to a wind tunnel at constant wind speed and temperature. The weight loss of oil over time was monitored and the rate of loss was used to develop equations to predict evaporation under varying spill conditions (Stiver and Mackay, 1983).

The evaporated samples, as well as the fresh oil, were tested for density, viscosity, and for some oils interfacial tension, pour point and flash point.

Larger quantities of evaporated oil were needed for use in the subsequent emulsification and burn tests than could be efficiently produced in the wind tunnel. These were prepared by bubbling compressed air through heated oil in 20-L buckets until the desired amounts had been evaporated.

Weathered samples at two degrees of evaporation were produced. Two degrees of evaporation provided three samples for testing (fresh and two weathered), which allows interpolation for behavior at intermediate conditions. The degrees of evaporation were chosen to correspond to what would be encountered at a real spill within achievable response times. The fraction evaporated was calculated using the evaporative exposure approach of Stiver and Mackay (1983).

2.2 Emulsification

The fresh oil and evaporated samples were analyzed for their emulsification characteristics. Specifically, the tendency of the oils to form an emulsion and the stability of the resulting emulsion were determined using the rotating flask technique (Zagorski and Mackay, 1982). The test indicates whether or not the oil will form an emulsion (low, moderate or high formation-tendency) at the degree of evaporation, as well as the stability of the emulsion (low, moderate or high).

Emulsion breakers are chemical surfactants that lower the oil-water interfacial tension and promote the coalescence of water droplets in a water-in-oil emulsion. This ideally causes the emulsion to separate. They are commonly used in the crude oil production and refining processes. Their effectiveness is oil-specific and dependent on the properties of the oil.

The effectiveness of three commercially available emulsion-breaking chemicals (also known as demulsifiers) were tested on 50 % water emulsions made with the weathered crude oil samples. The procedure described in Hokstad et al. (1993) was used. The emulsion samples for this test were made by recirculating 3.5 % salt water and oil through a small gear pump. The gear pump technique produces emulsions that are more stable than those that form naturally from wave action. The results of the emulsion breaker effectiveness test can therefore be considered as conservative.

2.3 Baseline Burns

The limits to ignition imposed by evaporation and emulsion formation were determined by conducting a series of baseline burns. These tests also measured the steady-state burning characteristics of water-free and emulsified slicks of the fresh and weathered crude oils. Beginning with the fresh oil, the water content of the emulsion to be tested was increased stepwise (from 25 to 33, 50 and finally 60% water). This process was then repeated with the weathered oil samples.

The burns were conducted in a wave tank measuring 11 x 1.2 x 1.2 m (L x W x H) that was filled with water to a depth of 85 cm. The oil (or emulsion) was contained in a floating, 40-cm diameter steel ring. For each test, 2.5 L of emulsion was used, which resulted in a 2-cm thick slick.

Emulsions were prepared just prior to each test by recirculating the appropriate volumes of crude oil and water through a small gear pump. A sample of each emulsion was reserved and watched closely during the ignition attempts to confirm that the emulsion remained stable and did not break.

As was stated in section 2.2, the gear pump imparted considerable mixing energy and produced very stable emulsions; even emulsions created using weathered oils with low to moderate stability indices (as measured in the rotating flask apparatus) were observed to be very stable. Therefore, the limits to ignition reported can be considered conservative estimates.

The most common system used for igniting crude oil slicks is the Heli-torch, which uses gelled gasoline for fuel. To simulate this source of ignition, 70 to 100 g of gelled gasoline was used to ignite the baseline burns. Two ignition attempts were made before an emulsion was considered unignitable.

2.4 Emulsion-Breaker Burns

Emulsion breaker burn tests were conducted on emulsions that could not be ignited with gelled gas in the baseline burn tests. The objective was to determine if the addition of emulsion breaker would allow the ignition of the slicks, and what effect it would have on the burning characteristics of the oils. The most effective chemical, as determined from the emulsion breaker effectiveness test (see Section 2.2) was used.

The emulsion breaker was added to the slick at a dosage ratio of 1:500 and mixed into the slick with a glass stirring-rod for two minutes. After mixing, the emulsion was allowed to sit for thirty minutes. After the settling period, gelled gasoline was used to try to ignite the slick. If the gelled gasoline could not ignite the slick, another attempt was made using a 2-mm thick layer of fresh oil as a primer. The 2-mm layer of fresh oil represents the maximum strength of igniter that could reasonably be applied to large area of a real spill. If an oil could not be ignited with the fresh oil layer it was deemed unignitable.

3.0 Results and Discussion

The results of the laboratory and burning studies are summarized in Table 1. The second column in Table 1 indicates, in relative terms, the amount of weathering needed before the oil forms an emulsion. This will depend greatly on the conditions at the spill site and on the nature of the spill (e.g., blowout or batch spill). But generally speaking, *weathered* is equivalent to 4 to 8 hours of exposure, while *highly weathered* is equivalent to 12 to 36 hours of exposure.

Some commonalities were noted between oils of similar API gravity; the oils in Table 1 are arranged in order of decreasing API gravity (when fresh). Furthermore, the oils have been separated into groups of similar behavior with respect to *in situ* burning, demarcated by the heavy lines.

API gravity is calculated from the specific gravity of the oil according to:

$$\text{API gravity } (°) \equiv \frac{141.5}{\text{sp.gr.} @ 60°F} - 131.5$$

Table 1: Results of Burning Tests with Light Crude Oils.

Oil Name (°API) *Region*	Emulsifies? (Stability)*	Unaided Limit to Ignition (% H_2O)	Breaker Aids Burning?
High Island (42) *Gulf of Mexico*	When highly weathered (unstable)	All 60% water emulsions ignited.	Not needed.
Lt. Louisiana Swt. (38) *Gulf of Mexico*	When highly weathered (unstable)	All 60% water emulsions ignited.	Not needed.
Milne Point (38) *Prudhoe Bay*	When weathered (unstable)	All 60% water emulsions ignited.	Not needed.
Drift River (35) *Alaska*	When fresh (stable when weathered)	Fresh 60% Weathered 25%	Yes
Main Pass 69 (35) *Gulf of Mexico*	When weathered (stable)	Fresh 60% Weathered 25%	Yes
Pompano (33) *Gulf of Mexico*	When weathered (moderately stable)	Fresh 60% Weathered 25%	Yes
Alaska North Slope (30) *Alaska*	When weathered (stable)	Fresh 60% Weathered 25%	Yes
South Pass 49 (30) *Gulf of Mexico*	When weathered (unstable)	Fresh 33% Weathered 25%	Yes
West Delta 143 (30) *Gulf of Mexico*	When fresh (stable)	Fresh 25% Weathered 0%	No
Green Canyon (29) *Gulf of Mexico*	When fresh (stable)	Fresh 0% Weathered 0%	Slightly
Endicott (26) *Alaska*	When fresh (stable)	Fresh 25% Weathered 25%	Some
Pt. McIntyre (26) *Alaska*	When fresh (stable when weathered)	Fresh 25% Weathered 25%	Slightly
Carpinteria (24) *California*	When fresh (stable)	Fresh 0% Weathered 0%	No
West Delta 30 (23) *Gulf of Mexico*	When fresh (stable)	Fresh 0% Weathered 0%	Yes
Point Arguello (21) *California*	When fresh (stable)	Fresh 0% Weathered 0%	No
Santa Clara (20) *California*	When fresh (stable)	Fresh 0% Weathered 0%	No
Santa Ynez (17) *California*	When fresh (stable)	Unignitable	No

*based on a 24 hr settling test

The oils in the first group, with API gravities ≥ 38° are all excellent candidates for *in situ* burning (see Table 1). They only formed emulsions after extensive weathering, and the emulsions that did eventually form were unstable. Emulsion breakers were not needed; ignition was possible even at high degrees of evaporation and emulsification.

The oils in the second group, with API gravities between 33° and 35°, are slightly heavier than those in the first. These oils are also excellent candidates for *in situ* burning. After weathering for a day or two and if sufficient wave action is present, they will form stable emulsions that will hinder ignition; however, these emulsions respond well to treatment with emulsion breakers, and even high water-content emulsions could be ignited.

The third group of oils, with API gravities between 23° and 30°, contains the largest number of oils tested. These oils behave quite differently with respect to each other. Alaska North Slope, South Pass 49, Endicott and West Delta 30 are all good candidates for *in situ* burning; although they all exhibit a high tendency to form stable emulsions, they also respond well to treatment with emulsion breakers. On the other hand, West Delta 143, Green Canyon, Point McIntyre and Carpinteria are all poor candidates for *in situ* burning; the emulsions formed by these oils are very stable and resist breaking, even with chemicals.

The oils in the final group, with API gravities ≤ 21°, were the heaviest tested. These oils are all poor candidates for *in situ* burning. They all formed stable emulsions, even when fresh, and were unignitable when emulsified. Emulsion breakers worked poorly on these oils.

4.0 Conclusions and Recommendations

The results of the burn tests for the four groups of oils are summarized in Table 2. These results should allow better decisions as to when *in situ* burning will be a useful response tool, as well as to focus future research efforts.

Table 2: Summary of Burn Results by Group

Range of API Gravities	Emulsifies? (Stability)	Unaided Limit to Ignition (% H_2O)	Breaker Aids Burning?
≥ 38°	When weathered or highly weathered (unstable)	No limit	Not needed
33° to 35°	Some when fresh; all when weathered (stable when weathered)	Fresh: 60% Weathered: 25%	Yes
23° to 30°	Some when fresh; all when weathered (most are stable)	Fresh: 0 to 60% Weathered: 0 to 25%	Sometimes
≤ 21°	When fresh (stable)	Fresh: 0% Weathered: 0%	No

Based on the data, oils with API gravities higher than 35 should burn easily, while oils with API gravities less than 20 will burn only under optimum conditions. No further laboratory burn tests needs to be done on oils of these types.

On the other hand, oils with API gravities between approximately 20 and 35 have demonstrated marked differences in suitability that cannot be predicted based solely on their physical properties. Many oils in this range will be good candidates for burning, especially in the higher gravity range, but others will not. Only by doing laboratory tests will we be sure.

Also, some regional differences in suitability were noted. Oils produced off the coast of California tend to be very heavy and appear to be poor candidates for *in situ* burning. Oils produced in Alaska and the Gulf of Mexico appear to be more varied in API Gravity, but in general should be good candidates for *in situ* burning.

4.0 References

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