

Laboratory Testing to Determine Operational Parameters for *In Situ* Burning of Six U.S. Outer Continental Shelf Crude Oils

J. McCourt and I. Buist
S.L. Ross Environmental Research Ltd.
Ottawa, ON, Canada
(613)232-1564
james@slross.com

J. Mullin
U.S. Minerals Management Service
Herndon, VA, United States
(703)787-1556
Joseph_Mullin@mms.gov

Abstract

A laboratory test program was conducted with six crude oils to determine the following parameters with respect to *in situ* burning:

- the limits to ignition using gelled-gasoline igniters imposed by evaporation and emulsion-formation;
- 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; and,
- the likelihood of the residues sinking after efficient burns of thick slicks of the crude oils.

As well as providing valuable spill-response oriented data, the study has shown that *in situ* burning may not be an appropriate response option for all oils. Some oils were easily ignited and burned efficiently, even when emulsified to high water contents. One oil could not be ignited even when fresh. The ability of emulsion breakers to promote emulsion ignition and burning was found to be oil-dependent.

1.0 Introduction

Before oil spill response plans are developed or approved, it is important to understand the physical characteristics of the spilled oil and how they change over time. The *Catalog of Crude Oil and Oil Products Properties*, jointly funded MMS and Environment Canada contains the physical and chemical data of over 380 different types of oils, including some information on dispersibility. This research study was intended to provide additional data on *in situ* burning that should be considered when developing oil spill response plans.

In situ burning of oil spills on water has the potential to quickly remove large quantities of oil from the water surface, and can be an effective countermeasure during a spill cleanup; however, evaporation of an oil's light ends and the formation of water-in-oil emulsions can quickly lead to an oil becoming not ignitable, thus ending the possibility of a successful *in situ* burn. Recently, research has focused on extending the window-of-opportunity for *in situ* burning by developing more powerful igniters, and investigating the use of chemical surfactants that break water-in-oil emulsions (S.L. Ross, 1995, Guénette et al., 1994). The studies concluded that the burning process for water-in-oil emulsions is much more complex than for water-free oil (Bech et al., 1992) and that success at breaking and burning depends on oil-specific factors (Strøm-Kristiansen et al., 1995).

In light of this dependency on oil properties, it is vital that specific oils be tested to determine the suitability of *in situ* burning as a response. Data for each oil must be collected on the effects of oil evaporation and emulsion formation on ignit-

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ability, burn rate and oil removal efficiency, and the potential for emulsion breakers to extend the window-of-opportunity. Burn tests should be conducted with selected oils under a range of conditions and with a variety of chemical surfactant products.

Another concern that must be addressed is the fate of the residue from a successful *in situ* burn, specifically whether it would be buoyant. Recent experiences that involved accidental burning on the sea of large volumes of heavy crude oils during actual spills (Moller, 1992, Turbini et al., 1993) and recent large-scale experiments involving thick slicks of moderately heavy oil (Buist et al., 1995) have shown that some burn residues may sink. Clearly, the propensity of the residue of an oil to sink should be determined prior to implementing an *in situ* burn.

The Minerals Management Service, in consultation with their Gulf of Mexico and Pacific regional offices, selected six U.S. crude oils produced on the Outer Continental Shelf (OCS) and subjected them to a laboratory test program. The crude oils selected by the Gulf of Mexico region were Amoco High Island, Green Canyon Block 65, and West Delta Block 30. The crude oils selected by the Pacific Region were Carpinteria, Santa Clara, and Santa Ynez.

1.1 Objective

The objective was to determine the following parameters related to *in situ* burning:

- the limits to ignition using gelled gasoline igniters imposed by evaporation and emulsification;
- the ability of commercially-available oil spill 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; and,
- the likelihood of the residues sinking after efficient burns of thick slicks of the crude oils.

2.0 Test Procedures

This section summarizes the test procedures that were used to evaluate the characteristics of the six oils related to *in situ* burning.

2.1 Evaporation

Evaporation is one of the most significant processes that affects an oil when it is spilled. Evaporation strips the volatile, light hydrocarbons from the crude oil and leaves the heavier fractions. From the perspective of *in situ* burning, this results in the oil becoming progressively more difficult to ignite. Although high degrees of evaporation alone will not necessarily preclude the use of burning, it can when combined with other factors, such as high sea states, high wind or emulsion formation.

To assess the effect of evaporation on the ignition and burning characteristics of each oil, the oils were artificially evaporated. First, one 450-mL sample of each oil was weathered in a wind tunnel for one week, in order to quantify the rate and extent of evaporation that would occur if the oil was spilled at sea. The wind speed in the tunnel was approximately 3 m/s, measured 1 cm above the oil surface, and the air temperature averaged 24°C. The mass of oil remaining in the trays was measured periodically. The wind tunnel was calibrated during the oil evaporation so that the

duration of exposure to evaporative forces in the wind tunnel could be correlated with exposure during a spill.

Based on a hypothetical spill scenario of a 2-mm thick slick, a water temperature of 24°C and a 2.5 m/s wind, and the wind tunnel mass loss data, the degrees of evaporation corresponding to 8 and 27 hours on the ocean in the same conditions were calculated for each oil. These were chosen to represent a range of reasonable response times to a spill. While this calculation results in different degrees of evaporation for each oil, it represents the equivalent exposure to evaporative forces.

These values were used as the endpoints for the evaporation of the samples to be used in the emulsion formation-tendency and stability, emulsion breaking, and burning experiments. The evaporation of the test samples was accomplished by bubbling compressed air through two or more heated 20-L batches of each oil in buckets until the desired mass fraction was evaporated.

2.2 Emulsion Formation-Tendency and Stability

A key problem that remains with the use of *in situ* burning is the potential for the oil to form a stable water-in-oil (W/O) emulsion. The presence of as little as 25% emulsified water in a slick will usually prevent ignition and burning of the oil. Even if the W/O emulsion is less than fully stable and thus burnable, the presence of water in the oil significantly increases the heat required to ignite it.

The tendency of each of the test oils to form an emulsion and the stability of the resulting emulsion were determined using the standard rotating flask technique (Zagorski and Mackay, 1982). The test was conducted on both the fresh and weathered samples, at a temperature of 20°C. The procedure was as follows:

- 30 mL of oil was added to a 500-mL fleaker filled with 300 mL of 35-ppt salt water and sealed;
- the initial height of the oil was recorded;
- the fleaker was rotated at 60 rpm in a chamber maintained at 20°C;
- after one hour, the height of the emulsion and oil layers were measured following each of 5, 10, 20 and 30 minutes of settling; and,
- the rotation and settling was repeated for a total of four 1.5 hour cycles.

The heights of the emulsions formed were used to calculate two indicators: the emulsion formation-tendency index, and the emulsion stability index. Both indicators can have values between 0 and 1. Table 1 shows how to interpret the meaning of the indicators. Both the formation-tendency and stability indices tend to increase with increasing degree of evaporation.

Table 1 Physical Meaning of Indicators

Indicator Value	Formation-Tendency Index	Emulsion Stability Index
0 to 0.25	Unlikely to form emulsion	Emulsion very unstable
0.25 to 0.75	Moderate tendency to form emulsion	Emulsion moderately stable
0.75 to 1	High tendency to form emulsion	Emulsion very stable

2.3 Emulsion Breaker Effectiveness

Chemical surfactants are available that lower the oil-water interfacial tension

and promote the coalescence of water droplets in a W/O emulsion. This ideally causes it to separate. They are used extensively 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 emulsion breaking chemicals (also known as demulsifiers) were tested on the weathered crude oil samples. They were Alcopol 0 70% PG (Alcopol), Breaxit OEB-9 (Breaxit), and EXO-0894 (EXO).

Two dosage ratios of demulsifier to emulsion were used, 1 to 500 and 1 to 5000. The procedure used (based on Hokstad et al., 1993) was as follows:

- 1.5 L of 60% water emulsion was prepared by recirculating 900 mL of salt water (35 ppt) and 600 mL of oil through a gear pump;
- 150-mL samples of the emulsion were placed in each of seven 500-mL fleakers containing 200 mL of 35-ppt salt water;
- the initial heights of the emulsions were recorded (H_{REF});
- the appropriate volumes of emulsion breaker (see Table 2) were added to six of the fleakers and allowed to soak into the emulsion for 5 minutes;
- the fleakers were rotated at 30 rpm for 5 minutes; and,
- the heights of the emulsions were recorded after 2 minutes (H_{IM}) of settling and after 24 hours (H_{24}).

Table 2 Brands and Volumes of Emulsion Breaker

Fleaker	Emulsion Breaker	Volume (ml)	Ratio of Demulsifier:Emulsion
1	Alcopol	0.3	1:500
2	Alcopol	0.03	1:5000
3	Breaxit	0.3	1:500
4	Breaxit	0.03	1:5000
5	EXO	0.3	1:500
6	EXO	0.03	1:5000
7	None (control)	0	N/A

A control fleaker was included, to which no emulsion breaker was added, to test if the emulsion would break naturally. The gear pump method makes 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. Two of the oils tested were too viscous for the gear pump and the emulsions were made using an electric drill with a paint mixing attachment.

The effectiveness of the demulsifier was characterized by the percent dehydration achieved, which is the reduction in amount of water in the emulsion expressed as a percentage of the initial water. For an emulsion that originally contained 100 mL of water and 50 mL of oil (66% water), a 75% dehydration would remove 75 mL of water and leave an emulsion with 25 mL of water and 50 mL of oil (33% water).

The percent dehydration was calculated immediately (i.e., after two minutes)

and after the twenty-four hour settling period, according to equation (1).

$$\% \text{ Dehydration} = \frac{W:O_{REF} - W:O_{TEST}}{W:O_{REF}} \times 100\% \quad (1)$$

Where: $W:O_{REF}$ is the initial water to oil ratio of 1.5 parts water to 1 part oil
 $W:O_{TEST}$ is the water to oil ratio after 2 minutes or 24 hours of settling

2.4 Baseline Burns

The limits to ignition imposed by evaporation and emulsion formation were determined for each oil by conducting a series of baseline burns. These tests also measured the 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 0 to 25, 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 air and water temperatures were maintained as close to 20°C as possible. The oil or emulsion was contained in a 40-cm diameter, steel ring, supported by a steel frame that rested on the bottom of the tank. For each test, 2.5 L of emulsion was used, which resulted in a 2-cm thick slick. The smoke from the burns was removed with a 200-m³/min fan through a 60-cm diameter flexible aluminum duct that was connected to a fume hood suspended 1.5 m above the steel ring.

Emulsions were prepared just prior to each test by recirculating the appropriate volumes of crude oil and water through a small gear pump. 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 very stable. Therefore, the limits to ignition reported can be considered conservative estimates. The system of choice for igniting crude oil slicks is the Heli-torch, which uses gelled gasoline for fuel. To simulate this source of ignition, 40 to 50 g of gelled gasoline were used to start the baseline burns.

The parameters measured for the baseline burns included:

- initial mass and volume of the oil or emulsion;
- mass of the burn residue;
- air and water temperatures;
- flame and oil or emulsion slick temperatures;
- preheat time (time from ignition of gelled gasoline to initial spreading of flame);
- ignition time (time from ignition of gelled gasoline to complete ignition of slick surface);
- time to intense burn (time to the beginning of the vigorous burn phase);
- and
- time to extinction of slick.

The efficiency and rate of each burn were calculated using equations (2) and (3), respectively. Burn efficiency was the ratio of the mass of oil burned to the initial

oil mass. Burn rate was defined as the rate of decrease in the equivalent oil thickness of the slick over the period of the burn. For emulsion burns, the residue was assumed to be water free for calculating burn efficiency and burn rate.

$$\text{Burn Efficiency (\%)} = \frac{M_{oil, i} - M_{res}}{M_{oil, i}} \times 100\% \quad (2)$$

$$\text{Burn Rate} = \frac{M_{oil, i} - M_{res}}{(\rho_{oil})(A_{ring})(t_{ext} - t_{ign})} \quad (3)$$

Where: $M_{oil, i}$ is the initial mass of oil (g)
 M_{res} is the mass of the residue (g)
 ρ_{oil} is the density of the oil (g/mm³)
 A_{ring} is the surface area of the ring (mm²)
 t_{ext} is the time from application of the igniter to complete extinction of flames (min)
 t_{ign} is the time from application of the igniter to complete ignition of the ring (min)

2.5 Emulsion Breaker Burns

Emulsion breaker burn tests were conducted on emulsions that were determined to be not ignitable due to their water content and/or evaporation in the baseline burn tests. The objective was to determine if the addition of emulsion breaker would promote 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 2.3) was used.

Emulsion breaker was added to the unignitable slick at a dosage ratio of 1:500 (i.e., 5 mL of emulsion breaker). The emulsion breaker was mixed into the slick with a glass stirring rod for two minutes. After mixing, the emulsion was allowed to sit for forty minutes. After the settling period, gelled gasoline was used to try to ignite the slick. In most instances, 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 not ignitable. The same parameters were measured for the emulsion breaker burns as for the baseline burns.

2.6 Burns in Waves

Burn tests in waves were conducted to determine how the waves affected the ignition and burn characteristics of each of the oils. A 40-cm diameter, floating containment ring was used for these tests. The waves were produced by a paddle-board wave generator, located at one end of the tank. Two wave settings were used for the tests: low and high (see Table 3).

Table 3 Wave Properties

Property	Low Setting	High Setting
Wave Length (m)	3.3	2.0
Wave Period (s)	2.0	1.3
Wave Height (cm)	9 to 11	14 to 15
Wave Steepness (Height/Length)	0.03	0.07
Energy (J/m ²)	123	184

If the oil was amenable to the use of emulsion breakers with burning (see section 2.5), further emulsion breaker burns were conducted in waves. These were performed with no pre-mixing of the breaker into the slick; the mixing was supplied by the wave action alone.

The same parameters were measured for the burns in waves as for the baseline burns.

2.7 Residue Burns

Burns were conducted with 5 and 10 cm thick slicks of the fresh crude oils, and the residues collected.

For those residues that were fluid at 20°C, their densities were measured with a densitometer (Anton Paar, model DMA 35). For those residue samples that were not fluid at 20°C, their densities were measured by immersing a piece of the residue in a series of aqueous solutions. Twenty-one solutions of different densities were prepared, covering a range from 0.900 to 1.100 g/cm³ in increments of 0.01 g/cm³. The solutions with densities less than water were made using methanol and water; those with densities greater than water were prepared with sodium chloride and water. Each residue sample was first placed in the lowest density solution (i.e., 0.900 g/cm³). If the residue floated in this solution, it meant that the density of the residue was less than 0.900 g/cm³, and was noted as such in the results. If the residue sank in this solution, it meant that the density of the residue was greater than 0.900 g/cm³. These samples were then placed in solutions of higher densities until one was found in which they floated.

3.0 Results

The results of the in situ burning tests for each oil are summarized in Table 4.

Amoco High Island (AHI) crude oil is produced by Amoco Corporation in the Texas sector of the Gulf of Mexico. AHI is a light crude oil (density of 0.815 g/cm³ at 20°C), resembling a condensate in many respects, with a low viscosity and density, and a high volatility. AHI was the lightest of the oils tested. Amoco High Island crude oil is an excellent candidate for *in situ* burning. The test slicks were easy to ignite, even at high degrees of evaporation and with high percentages of emulsified water. The emulsified slicks did not require emulsion breaker for ignition and the residue of the thick test burn of AHI did not sink.

Table 4 Summary of Test Results

Crude Oil	Amenable to <i>In Situ</i> Burning?	Could Residue Sink?	Forms Emulsion?	Best Emulsion Breaker	Breaker Promotes Burning?
Amoco High Island	yes	unlikely	when highly weathered	all worked well	yes
Carpinteria	if initiated before emulsification	possible	when fresh	Alcopol	no
Green Canyon	if initiated before emulsification	possible	when fresh	Alcopol	no
Santa Clara	if initiated before emulsification	likely	when fresh	all worked poorly	no
Santa Ynez	no	unknown	when fresh	all worked poorly	no
West Delta	yes	likely	when fresh	all worked well	yes

Carpinteria is produced by Torch Operating Company in California. It is a medium crude oil (density of 0.910 g/cm^3 at 20°C). Based on the results of the test burns, *in situ* burning would only be suitable for Carpinteria crude oil if the response could be initiated before the oil emulsifies. For the test burns, evaporation did not seem to hinder ignition, but an emulsified water content greater than 25% prevented it. The Alcopol did not significantly enhance the ignition of the emulsified slicks. The residues of the thick test burns of Carpinteria would have sunk in salt water as they cooled.

Green Canyon Block 65 (Green Canyon) is produced by Shell Offshore Inc. in the Gulf of Mexico. It is a medium crude oil (density of 0.880 g/cm^3 at 20°C). Based on the results of the test burns, *in situ* burning would only be suitable for Green Canyon crude oil if the response could be initiated before the oil emulsifies. Evaporation did not seem to hinder ignition of the test burns, but an emulsified water content greater than 25% prevented it. The Alcopol did not significantly enhance the ignition of the emulsified slicks. The residues of the thick test burns of Green Canyon would have sunk in salt water as they cooled.

Santa Clara crude oil is produced by Chevron U.S.A., in California. It is a heavy, waxy crude oil (density of 0.932 g/cm^3 at 20°C), characterized by a very strong sulphur smell. Based on the test burn results, *in situ* burning would only be suitable for Santa Clara crude oil if the burn could be initiated before the oil emulsifies. Evaporation did not hinder ignition of the test slicks, but an emulsified water content greater than 25% prevented it. Alcopol did not significantly enhance ignition of the emulsified test slicks. The residues of the thick test burns of Santa Clara would have sunk in salt water as they cooled.

Santa Ynez is produced by Exxon U.S.A. in California. It is a heavy crude oil (density of 0.955 g/cm^3 at 20°C), characterized by a strong sulphur smell, and was the heaviest oil tested. Based on the results of the test burns, *in situ* burning would not be a suitable response for spills of Santa Ynez crude oil. The sample that was

received had a water content of about 30%, right out of the drum and could not be ignited even when fresh. The sample must have been taken before the de-watering stage of the refining and production process. It would be worthwhile to obtain a de-watered sample and conduct the same *in situ* burning suitability tests. It is possible that the de-watered Santa Ynez would be better suited to *in situ* burning.

West Delta Block 30 (West Delta) crude oil is produced by Exxon U.S.A. in the Louisiana sector of the Gulf of Mexico. It is a medium crude oil (density of 0.915 g/cm³ at 20°C). Based on the results of the test burns, *in situ* burning would be a suitable response option for spills of West Delta crude oil. EXO 0894 was successful in promoting the ignition of emulsified test slicks, and could potentially be used to extend the *window-of-opportunity* for burning if the oil was emulsified. The residues of the thick test burns of West Delta sank as they cooled.

4.0 Conclusions and Recommendations

The stability of a water-in-oil emulsion and its response to emulsion breakers is highly dependent on the properties of the oil. Only three of the more widely available emulsion breakers were tested on the oils in this study. It is likely that there are other emulsion breakers that would perform as well or better on some of the oils. It would be worthwhile to pursue testing with other emulsion breakers for those oils that were difficult to break (i.e., Carpinteria, Green Canyon Block 65, Santa Clara and Santa Ynez).

This study has shown that *in situ* burning is not a suitable response option for all oils. Thus, it is important that this work be continued and other oils be tested to establish a catalogue of oils and their *in situ* burning properties. This must be done before *in situ* burning can be considered for use at an actual spill.

For these six OCS crude oils, the information required now exists to make an informed decision regarding the *window-of-opportunity* for various response options.

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