
Identification of Oils that Produce non-Buoyant In Situ Burning Residues and Methods for their Recovery

Regulatory and Scientific Affairs

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EXECUTIVE SUMMARY

The study investigates the potential for residues to sink following an *in situ* burn of spilled oil. The objectives were to identify oils that may produce residues that are likely to sink, and to evaluate options for dealing with non-buoyant residues in the field.

The study was initiated in response to the concern that the residue from an *in situ* burn could sink and cause environmental damage at the sea bottom. Previous *in situ* burning experiments failed to note the possibility of residue sinking because the starting oil slick was relatively thin, usually on the order of one or two centimeters. Concerns started to develop in the early 1990s when two separate tanker spills involving heavy crude accidentally caught fire, burned, and produced large quantities of residue that did indeed sink. More recent laboratory work has indicated that there is a large range of oils that may produce non-buoyant residues after an *in situ* burn involving thick slicks.

In this study, the results of small-scale burning experiments were used to develop correlations to predict burn residue densities for specific oils. When applied to more than 100 international crude oils it was found that about half would tend to float, and the other half would tend to sink in sea water once the residue cooled to ambient temperatures. It should be noted that this finding is based on the assumption that the laboratory-scale burn experiments are scalable to large burns in the field, an assumption that should be verified through further tests with large-scale burns.

It was also concluded that no simple method exists for controlling the density of the residue. It may be possible to use skimmers or sorbents to recover the residue immediately following an *in situ* burn; however, surface countermeasures would only be applicable for a short period—a maximum of 30 minutes—before the residue cooled to ambient temperatures and began to sink. A more realistic countermeasure would be to suspend a fine-mesh net from the bottom of the fire-containment boom, such that it extends across the apex of the burn area. This might allow the capture of burn residues as they cool, become more viscous, and start to sink.

There are two recommendations from the study: 1) large-scale *in situ* burn tests should be conducted to confirm the validity of the correlations developed in this study and 2) a prototype of the netting concept should be constructed and subjected to tank testing to confirm its viability for residue containment and to document its effect on boom performance.

Section 1 INTRODUCTION

Research has established that the smoke plume from an oil spill *in situ* burning (ISB) operation will not pose a threat to persons if they are located more than about a mile or two downwind from the burn. This finding, among others, has led to advances in obtaining regulatory approval for burning. Now, another environmental concern has surfaced. This is the possible sinking of residues from *in situ* burns, leading to environmental damage at the sea bottom. Existing operational protocols do not consider this problem, and cleanup systems have not been developed and put in place to collect non-buoyant residues from ISB operations.

This “sinking” problem was not considered in the past because it had been observed in many *in situ* burn experiments that ISB residues, although dense and viscous, did not sink. Concerns started to develop in the early 1990s when two separate tanker spills involving heavy crude (the *Haven* and the *Honam Jade*) accidentally caught fire, burned, and produced large quantities of residue that did indeed sink. These observations suggested that the residues from the earlier experimental work did not sink because the starting oil involved relatively thin slicks and/or relatively light oils. Hindsight suggests that the more important factor was the relative thinness of the starting slick, which was usually on the order of one or two centimeters.

S.L. Ross examined the problem in a preliminary study completed for MSRC in 1995 entitled *Laboratory Studies of the Properties of In situ Burn Residues* (S.L. Ross, 1995). The study indicated that there is a large range of oils that may produce non-buoyant residues after an ISB operation involving thick slicks. Subsequently, in another S.L. Ross study completed for the U.S. Minerals Management Service (S.L. Ross, 1997), this was confirmed with a number of oils produced on the U.S. Outer Continental Shelf (OCS). Despite the small scale of the experiments, the results, which are discussed in detail later, suggest that non-buoyant residues may be produced more often than not in burn operations. There is thus a demand to develop a real-time capability to predict whether a particular oil and ISB operation will produce residues that sink. At the same time there is a need to develop appropriate countermeasures to deal with such residues.

Section 2

OBJECTIVE AND LIMITATIONS OF STUDY

The objective of this study was to start the process of establishing operational tools and procedures for dealing with the problem of non-buoyant residues that may result from the *in situ* burning of marine oil spills. The following are the two tasks of the study:

Task 1. Develop simple protocols, based on available information, for identifying oils that are likely to sink if set afire and burned efficiently.

Task 2. Evaluate options for dealing with non-buoyant residues in the field.

The only studies that provide quantitative burn residue information of value to Task 1 are the laboratory work completed for MSRC and the follow up work for MMS mentioned in the Introduction. These studies involved very small, efficient burns under controlled conditions. Preliminary theoretical considerations suggest that large-diameter burns in the field might produce residues that are less dense than those from small-diameter burns of the same oil and slick thickness. The results from small-scale experiments must thus be considered preliminary in terms of predicting residue densities for large burns in the field. Further research needs to be undertaken to explore the effects of scale (i.e., fire size and other burn-controlling factors) on burn residue properties.

Despite the above uncertainties, and for want of better data, attempts are made in this study to use the results of the small-scale experiments to predict results in the field. It is clear, however, that the results should be used with extreme caution. It is hoped that more reliable predictions will be developed once larger-scale experiments are conducted to confirm or reject the predictions presented here.

Section 3

IDENTIFICATION OF OILS THAT YIELD NON-BUOYANT ISB RESIDUES

The three most important factors that determine whether an ISB residue will sink or not are the properties of the starting oil, its thickness and the efficiency of the burn process. Some oils that are already relatively heavy will certainly produce residues that will sink in seawater, but only if the burn process is efficient and uninterrupted. The purpose of this section of the report is to predict which oils will produce non-buoyant residues if the burn process is assumed to be “efficient.” Here “efficient” means as efficient as that experienced in controlled, small-scale burns. It is theoretically possible to control burn efficiencies operationally in the field and thereby control the density of the burn residue. These operational possibilities are dealt with in the next section.

CONFLICTING THEORIES OF *IN SITU* BURNING

(The following is a summary of the discussion in S.L. Ross, 1995.)

In situ burning of an oil slick on water proceeds because the hydrocarbon vapor above the liquid burns. The key process is radiative heat transfer from the flame back to the surface of the slick. Some of this heat transfers through the slick to the underlying water, but most vaporizes the liquid hydrocarbons, which rise to mix with air above the slick. Oxidation then occurs, releasing heat to continue the burning process. Once ignited, a burning thick oil slick reaches a quasi-steady-state in which the vaporization rate sustains the necessary heat transfer back to the slick surface.

There is uncertainty about the process by which oil vaporizes during *in situ* burning. Three possibilities exist: (1) Batch Distillation, (2) Equilibrium Flash Vaporization (EFV), or (3) a combination of the two. In Batch Distillation the lightest, most volatile components are boiled off from the entire slick first, followed by progressively heavier, less volatile components. If this happened exclusively during *in situ* burning, the temperature of the oil slick would increase over the burn period, and the residue remaining after the burn would contain no lighter hydrocarbons and would be much heavier than the original oil.

In contrast, the theory of Equilibrium Flash Vaporization (EFV) indicates that, over the entire course of the burn period, vapor of essentially constant composition is produced by a feed of oil of essentially constant composition. Researchers believe that EFV is a key vapor-producing mechanism in ISB because of the following experimental observations: (1) the surface temperatures of burning oil slicks tend to remain relatively constant during steady-state burning; (2) a steep temperature profile exists in the burning slick, indicating a poorly-mixed oil layer, as required for EFV; and, (3) the presence of lighter ends in the oil residue remaining after a burn. It is believed that EFV occurs during *in situ* burning because the hot flames and the insulating characteristics of the oil combine to create high temperatures in a thin surface layer of the slick known as the “hot zone.” This promotes near-complete vaporization of the surface of the oil slick with minimal mixing and heat transfer to the underlying oil and/or water layers.

Despite the above indications it is clear that the vaporization process that occurs during the *in situ* burning of crude oils is some combination of Batch Distillation and EFV. It is well known that the burn residue, while still containing some lighter ends, differs markedly from the original oil. The residue's high density and viscosity strongly indicate that there is a progressive concentration of the very high molecular weight compounds in the remaining slick as *in situ* burning proceeds. It is likely this concentration of heavy compounds in the residue over time that determines whether a residue will sink or not. Residues from burns of thick crude oil slicks are more likely to sink than residues from burns of thin slicks of the same crude because of the extra concentrating potential in the thick-slick case.

This possibility that the vaporization process is a combination of two very different processes greatly complicates one's ability to predict the properties of burn residues and whether they will sink or not. If the vaporization process were pure EFV, the density and other properties of the residue would simply be the same as the original oil. If the process were pure Batch Distillation, one could simply refer to standard crude oil distillation data for the oils under consideration, and use these for prediction purposes. Neither situation applies, unfortunately, and it becomes necessary to consider more complicated methods for predicting the properties of burn residues.

RESULTS OF EARLIER LABORATORY STUDY

The laboratory study for MSRC (S.L. Ross, 1995) was conducted to better understand the ISB residue problem, especially the possible tendency of residues to sink. The main results of the study are presented here¹. The intention is to use these data to help develop a simple model or equation to predict whether a particular oil will yield a non-buoyant residue following an ISB operation.

Description of Experiments

Eight oils, listed below, were selected for the project. These were representative of oils shipped by sea in North American waters, ones that have been involved in tankship fires that resulted in the residue sinking, or were used in recent *in situ* burning field research studies.

- i) Alaska North Slope (ANS) crude
- ii) Alberta Sweet Mixed Blend (ASMB) crude
- iii) Arabian Heavy crude
- iv) Arabian Light crude
- v) Bonny Light crude
- vi) Iranian Heavy crude
- vii) Mayan crude
- viii) automotive diesel

Two of these oils, Arabian Light and Mayan, were artificially weathered to two degrees of evaporation by bubbling air through them. The burn tests were conducted in a water-filled circular steel pan measuring 1.2 m in diameter and 32 cm in height. Measured amounts of the test oils were contained in the center of the pan in a 40 cm diameter, 20 cm high metal ring supported by three legs. The initial oil height was adjusted, by altering the water level, to be 1 cm below the lip of the ring. Three slick thicknesses were burned for each fresh oil: 5 cm, 10 cm and 15 cm. These were considered to be realistic thicknesses when oil is boomed in preparation for an *in situ* burn. The burn tests were conducted at room temperature on 35 ppt salt water. A perforated ring of copper tubing connected to a constant-head supply tank was used to gently flush the bottom

¹ The subsequent study done for MMS (S.L. Ross 1997) involved an experimental procedure that differed from that used in the MSRC study (S.L. Ross 1995) and the results are not directly comparable; in the latter experiments the bottom of the slicks were flushed with a gentle flow of cool salt water to simulate slick conditions in a towed boom at sea. This was not done in the MMS study.

of the contained slick with cool salt water. This was done in order to simulate slick conditions in a towed boom at sea.

Selected results from the experiments are shown in Tables 3-1 and 3-2. Taking the density of sea water to be 1.025 g/cm^3 it is seen from Table 3-1 that all oils but the diesel and the two crude oils of Bonny Light and ASMB would sink at an ambient temperature of 15°C .

Oil Characteristics that Influence Burn Residue Density

Table 3-1 shows that there is a good correlation between fresh oil density and burn residue density, and this is shown graphically (in Figures 3-1 to 3-3). This is not surprising because oils that are relatively heavy to begin with might be expected to leave a relatively heavy residue after burning.

Properties other than fresh oil density might correlate even better with burn residue density. One property might be asphaltene content, which is usually reported in petroleum oil databases. Also readily available in existing databases (such as those produced by HPI, 1995) is information on “residues” that are produced during standard distillations. This is the material that remains after the oil (under vacuum) reaches a distillation temperature of a certain value, usually reported as 1000°F (538°C) or 1049°F (565°C) (following ASTM D1160). The density of this residue might correlate with burn residue density as might the weight percent of the above-noted distillation “cut,” which is called 1000°F Plus or 1049°F Plus.

Table 3-3 presents information on the eight oils related to the main variables discussed. The data are taken from three sources:

1. The burn residue study performed by S.L. Ross in 1995 (S.L. Ross, 1995). This study provides information on the initial density of the eight oils and their burn residue densities (as already presented in Table 3-1), and also data on mass % asphaltenes, the distillation residue and mass % of the 1000°F Plus cut.

Table 3-1. Burn Residue Densities

Oil Type (density of oil @ 15°C prior to burn)	Density at 15°C (g/cm ³)			Density at 40°C (g/cm ³)		
	5 cm ^b	10 cm	15 cm	5 cm	10 cm	15 cm
Alaska North Slope (ANS) (0.880)	1.025	1.075	1.045	1.020	1.068	1.040
Arabian Heavy (0.886)	1.125	1.125	1.065	1.11	1.084	1.020
Arabian Light (0.870)	1.035	1.065	1.065	1.020	1.030	1.069
20% Arab. Lt. ^a (0.908)	1.065			1.050		
31% Arab. Lt. (0.926)	1.075			1.07		
Alberta Sweet Mixed Blend (ASMB) (0.851)	0.985	1.015	1.055	0.97	1.011	1.040
Bonny Light (0.852)	0.955	0.975		0.97	0.981	
Diesel (0.823)	0.879	0.885	0.883	0.870	0.877	0.875
Iranian Heavy (0.871)	1.055			1.030		
Mayan (0.930)	1.125	1.145	1.095	1.08	1.084	1.059
12% Mayan (0.952)	1.135			1.11		
22% Mayan (0.975)	1.135			1.12		

- a. Some experiments were performed with samples of Arabian Light crude oil and Mayan crude oil that were evaporated before ignition and burning. "20% Arab Lt.," for example, means that 20% of the Arabian Light crude oil was evaporated before the test.
- b. The 5 cm, 10 cm and 15 cm values are the starting slick thicknesses.

Table 3-2. Test Burn Oil Removal Efficiencies

Oil Type	Burn Efficiency (Mass %)		
	5 cm Burn	10 cm Burn	15 cm Burn
ANS	84.9	91.6	90.9
Arab. Hvy.	75.2	82.3	90.9
Arab. Lt.	93.5	98.1	87.6
20% Arab. Lt.	84.0		
31% Arab. Lt.	92.2		
ASMB	88.5	97.3	96.4
Bonny Lt.	90.4	95.3	Reject
Diesel	98.6	99.3	99.7
Iranian Hvy.	93.8		
Mayan	75.1	74.3	71.1
12% Mayan	72.2		
22% Mayan	70.3		