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

Regulatory and Scientific Affairs

PUBLICATION NUMBER DR145
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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 here[1]. 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

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[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		

Table 3-3. Properties of Test Oils

Oil	Initial Density [4] (g/cm^3)			Wt. Fraction 1000°F+		Wt. Fraction 1049°F+	Density [4] of 1049°F+	Asphaltenes Wt. %	
	S.L. Ross[1]	ETC[2]	HPI[3]	S.L. Ross[1]	ETC[2]	HPI[3]	HPI[3]	u8S. L. Ross	ETC[2]
ANS	0.880		0.894	0.25		0.20	1.029	3.88	
Arab Hvy	0.886	0.88	0.887	0.35	0.32	0.28	1.052	8.67	11.00
Arab Lt	0.870	0.86	0.858	0.26	0.23	0.18	1.022	4.59	3.00
ASMB	0.851			0.15		0.12		1.61	
Bonny Lt	0.852	0.84	0.848	0.08		0.06	1.007	0.24	
Diesel	0.823	0.83		0.00	0.01	0.00		0.00	
Iran Hvy	0.871	0.87	0.871	0.27	0.25	0.23	1.044	4.83	6.00
Maya	0.930	0.92	0.921	0.40	0.43	0.39	1.070	14.1	16.00

[1] Values from S.L. Ross, 1995
[2] Values obtained from Environmental Technology Centres (Environment Canada) *Catalogue of Crude Oil and Oil Product Properties* - 10/96
[3] Values obtained from HPI, 1995
[4] Densities measured at 15°C

2. The HPI Crude Oil Database which provides data on the same oils (except ASMB) with slightly different properties as exemplified in the initial densities, shown in Table 3-3. Also included are data on the 1049°F Plus cut (wt %) and the density of this same cut, which is the distillation residue density.

3. The Catalogue of Crude Oil and Oil Product Properties published by Environment Canada (1996). This document provided data for Table 3-3 on 1000°F Plus, asphaltene concentration and initial density.

Development of Correlations

In this section, an attempt is made to predict residue densities on the basis of the above-noted oil property information. The most readily available information is fresh oil density or gravity. It is clear from Figures 3-1, 3-2 and 3-3 (for the 5-cm, 10-cm and 15-cm slick thickness experiments) that there is a valid correlation between measured burn residue density and fresh oil density. (Figures 3-1 to 3-12 and Table 3-4 are located at the end of this section.) The correlation (R^2) is reasonable, especially for the 5-cm and 10-cm thickness cases, considering that there is large experimental error associated with the burn experiments and measurements of residue density (determined by adding the residue to progressively denser solutions of water until the residue became neutrally buoyant, see S.L. Ross, 1995 for details).

If one used the correlations in the Figures 3-1, 3-2, and 3-3 (or Figure 3-4 which combines all three best-fit lines without the corresponding data points) for predicting residue densities in the field, Figure 3-2, for example, would suggest that a layer of fresh oil on sea water having initial thickness of 10 cm would likely produce a non-buoyant ISB residue (i.e., > 1.025 g/cm^3) if its initial density were greater than about 0.865 g/cm^3 (or API gravity less than about 32°).

Figures 3-5 to 3-8 represent similar plots of burn residue versus percent weight distillation residue (1000°F Plus). These correlations, again for the 5-cm, 10-cm and 15-cm thickness cases, are remarkably good. They are better than the correlations done with fresh oil density (Figures 3-1 to 3-4) and much better than similar correlations done with "Wt % Asphaltenes" and "distillation residue densities (for the 1049°F Plus cut)". (The correlations for these latter two independent variables are presented in Figures A1 to A6 in Appendix A.)

As a result it seems reasonable to use "initial oil density" and "% weight distillation residue" as the key independent variables to correlate the data for use in predicting burn residue densities for various oils and thicknesses. The distillation residue information may be reported as 1000°F Plus, but more often appears as 1049°F Plus, as is the case in the HPI Crude Oil Assay Database (1995). Table 3-3 shows distillation cut data for 1000°F Plus (from S.L. Ross, 1995) versus that for 1049°F (from HPI, 1995).

Figures 3-9 to 3-12 show the results when burn residue density is plotted against the 1049°F Plus values. Note that these correlations are not as good as the ones shown in Figures 3-5 to 3-8 which use 1000°F Plus values. One possible reason for this, as shown in Table 3-3, is that the oils used in the distillations yielding the 1049°F Plus values were somewhat different than those used by S.L. Ross, 1995 in the burn experiments and in the distillations yielding the 1000°F Plus values.

The correlation equations for the set of data in Figures 3-1 to 3-4, Figures 3-5 to 3-8, or Figures 3-9 to 3-12 can be used to predict burn residue density. The equations are summarized below for the case of 10 cm initial slick thickness only:

$$\text{Burn Residue Density } (\text{g/cm}^3) = 2.47 \times [\text{Initial Density of the Oil, } (\text{g/cm}^3)] - 1.11 \qquad (1)$$

$$\text{Burn Residue Density } (\text{g/cm}^3) = 0.615 \times [\text{Wt. Fraction } 1000°\text{F} +] + 0.911 \qquad (2)$$

$$\text{Burn Residue Density } (\text{g/cm}^3) = 0.654 \times [\text{Wt. Fraction } 1049°\text{F} +] + 0.926 \qquad (3)$$

If a burn residue density equal to that of sea water (1.025 g/cm^3) is plugged into Equation 1, the cut-off value for initial density, as calculated earlier, is 0.864 g/cm^3 (or about API gravity of 32°). Similarly, for Equation 2 the cut-off value for Wt % 1000°F Plus becomes 18.6 %. That is, oils with a weight percent distillation residue (>1000°F) greater than 18.6 % are predicted to sink in sea water. Similarly, for Equation 3 the value is 15.1 % for oil distillations that use residue measurements of weight percent 1049°F Plus.

To simplify the process of predicting burn residue densities for specific oils, Table 3-4 includes 137 international crude oils. The table considers two separate prediction methods or equations that include the independent variables of initial oil density (Equation 1) and weight fraction of distillation cuts at 1049°F Plus (Equation 3). For simplicity, the table considers only initial slick thicknesses of 10 centimeters.

Of the 137 oils in the table, 57 (or 42%) would tend to float, and not sink, as predicted by both methods. About the same, 52 oils or 38%, would tend to sink in sea water once the residue cools to ambient temperatures, as predicted by both methods. The remainder, 28 oils (20%), are marginal because the methods provide different predictions. One reason there is not a perfect match between methods is that there is an imperfect correlation between initial oil density and wt% 1049°F + cut, as shown in Figure A7 in Appendix A.

Note that very light crude oils and condensates (API gravity > 45°) and very heavy crude oils (< 20°API Gravity) have been excluded from Table 3-4. This was done because these fall outside the range of initial densities of oils tested. If these had been included, residues of very light crude oils and condensates would be predicted to float, and oils with API gravity less than 20° would be predicted to sink.

Please remember that the predictions in Table 3-4 are based on the condition that the initial slick thickness is 10 cm. Please refer to the figures for predictions of thinner slicks (e.g., 5 cm) and thicker slicks (e.g., 15 cm). Of more importance, please recognize that the predictions are based on the assumption that the results of the laboratory-scale burn residue experiments are scalable to large burns in the field. Only further research with large-scale burns can determine whether this assumption is a valid one.

Figure 3-1. Densities: Residual vs. Initial
5 cm thickness

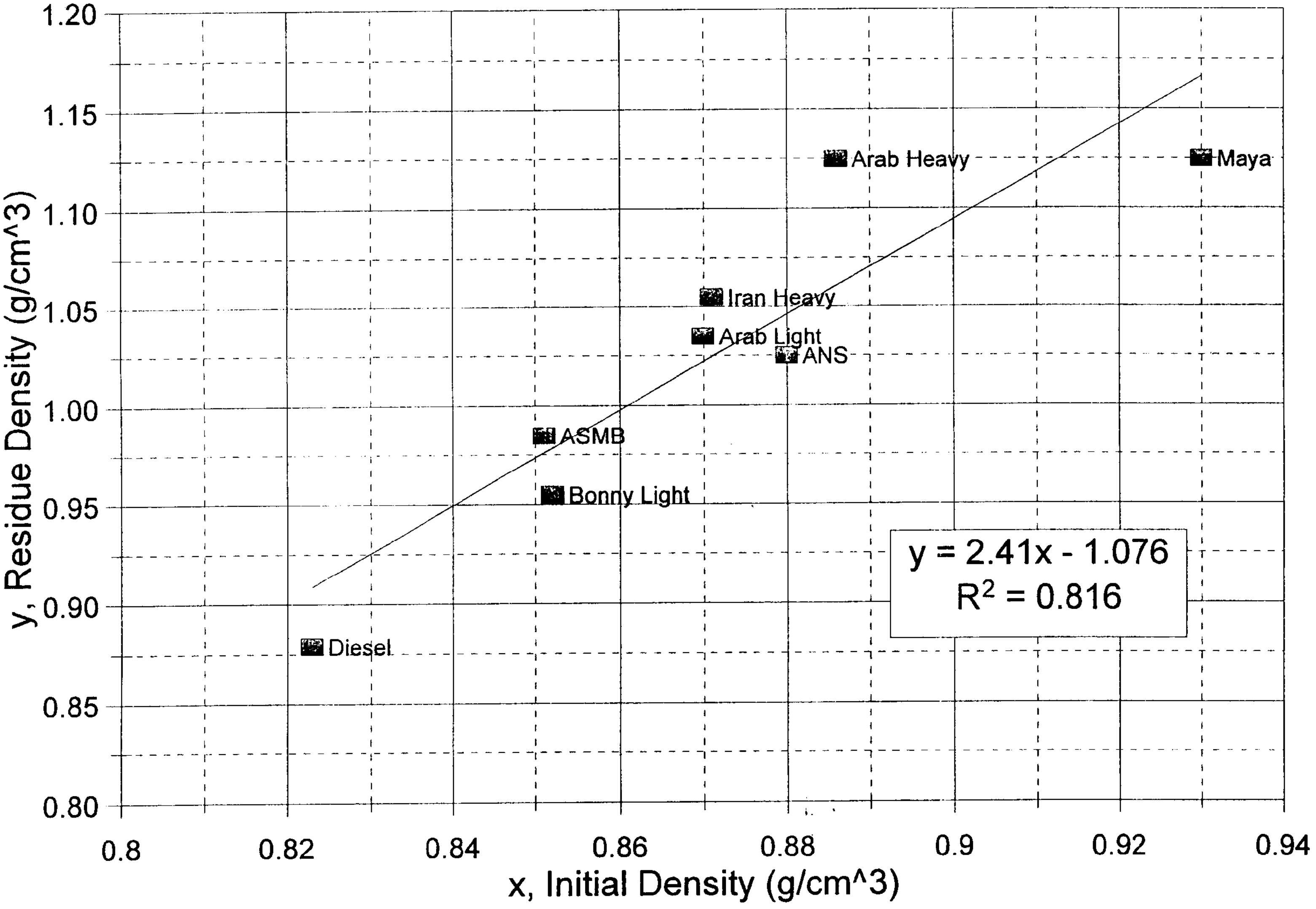


Figure 3-2. Densities: Residual vs. Initial
10 cm Thickness

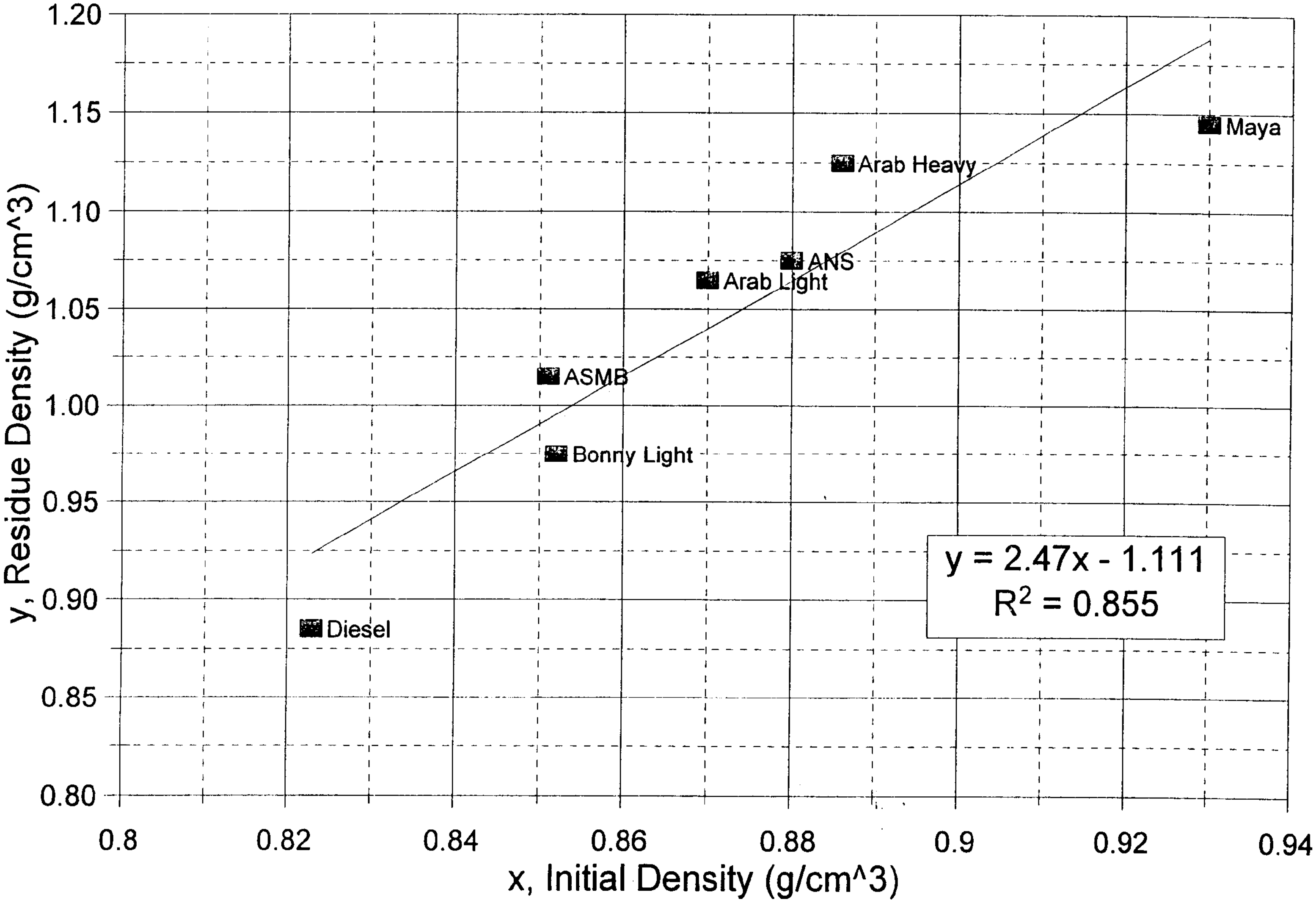


Figure 3-3. Densities: Residual vs. Initial
15 cm Thickness

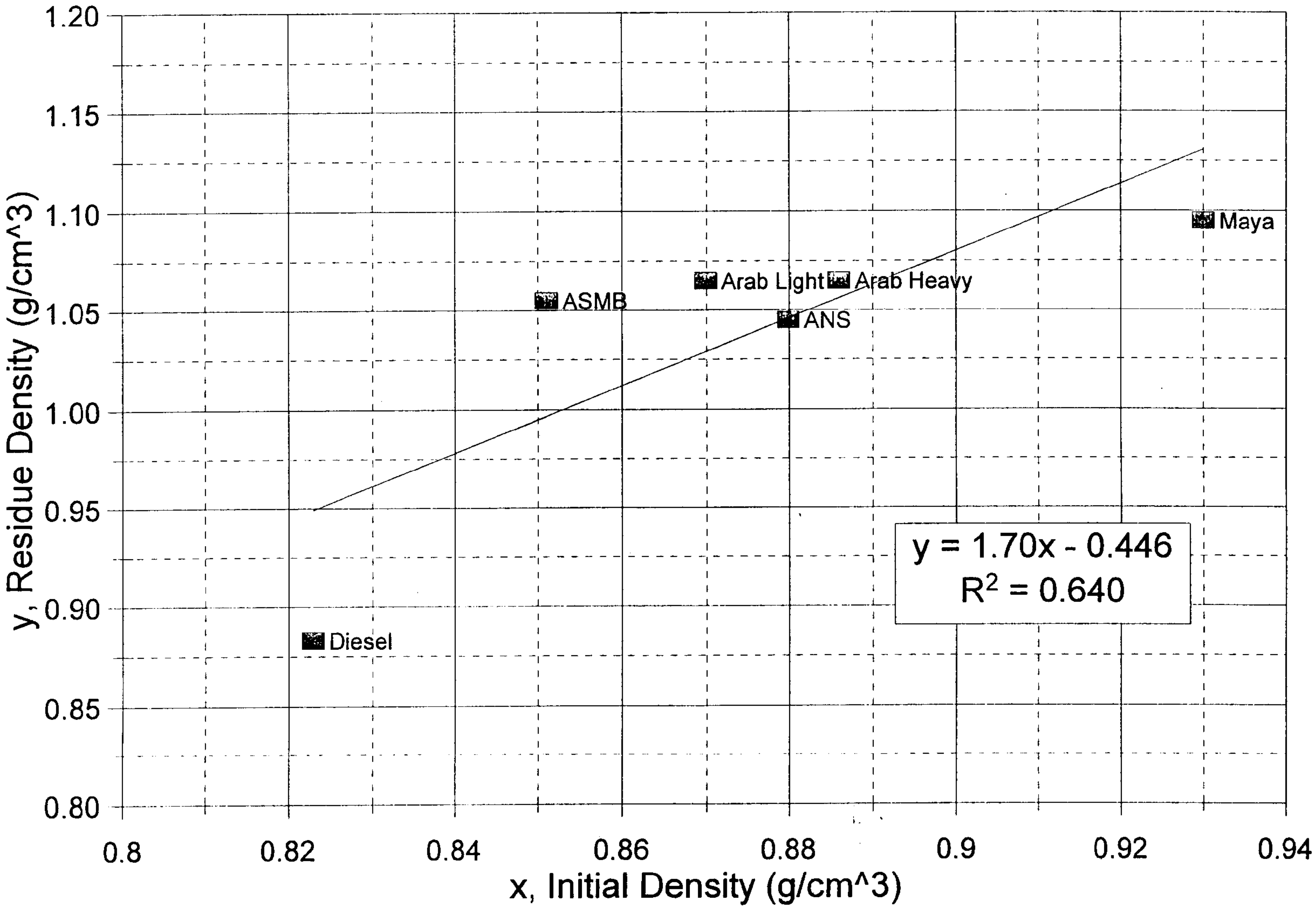
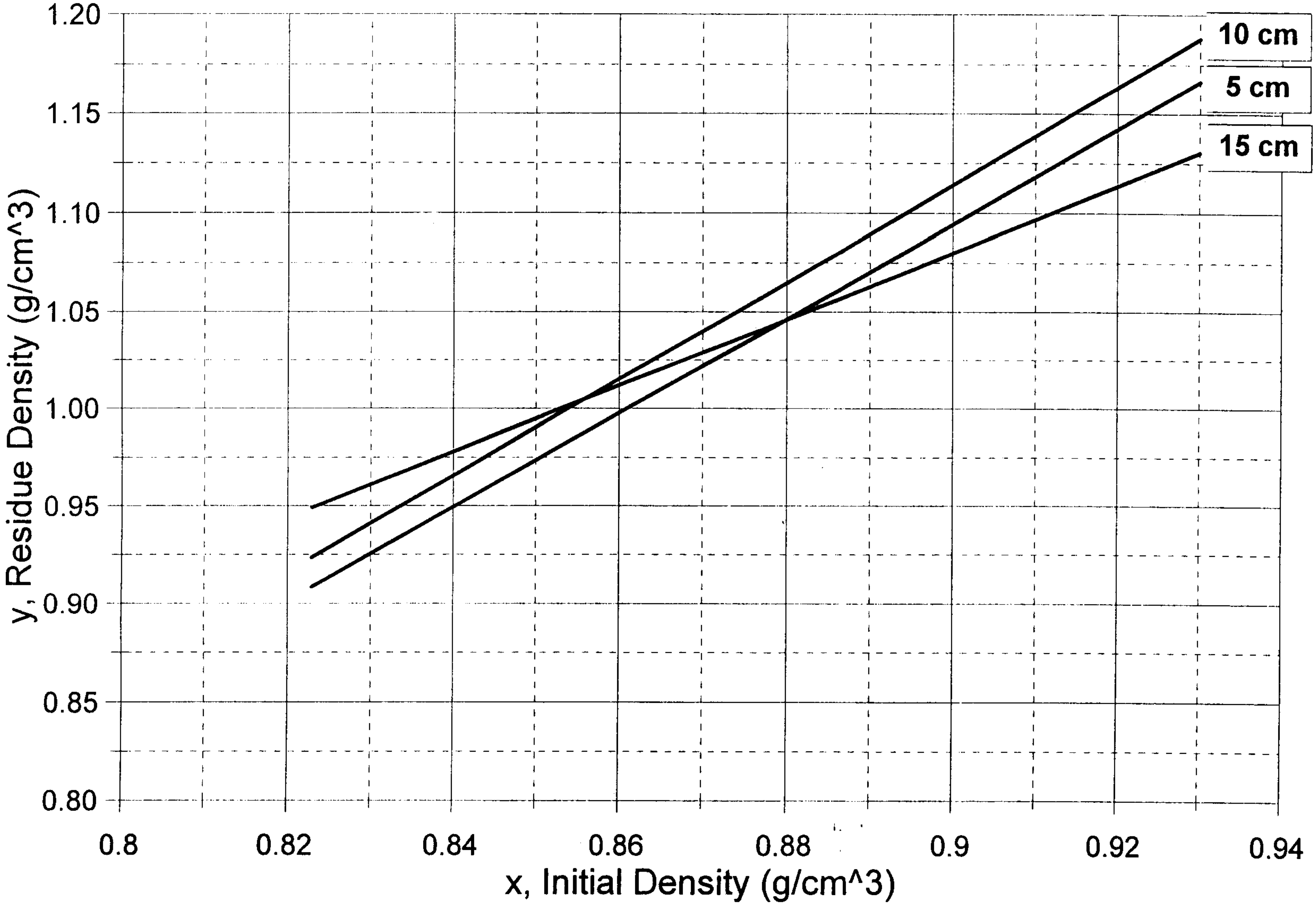


Figure 3-4. Densities: Residual vs. Initial
5,10 and 15 cm Thicknesses



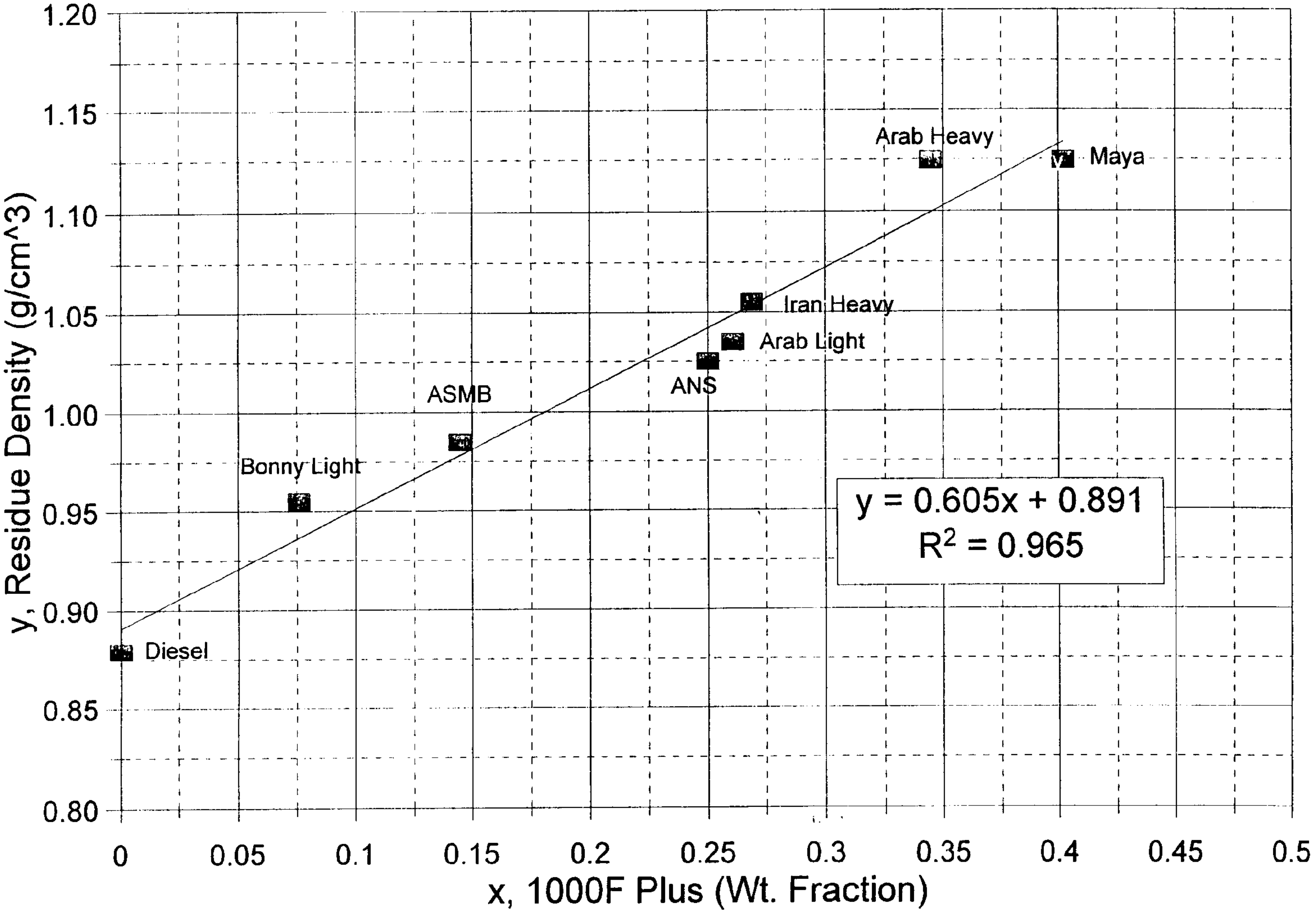


Figure 3-5. Residue Density vs. 1000F Plus
5 cm Thickness

Figure 3-6. Residue Density vs. 1000F Plus

10 cm Thickness

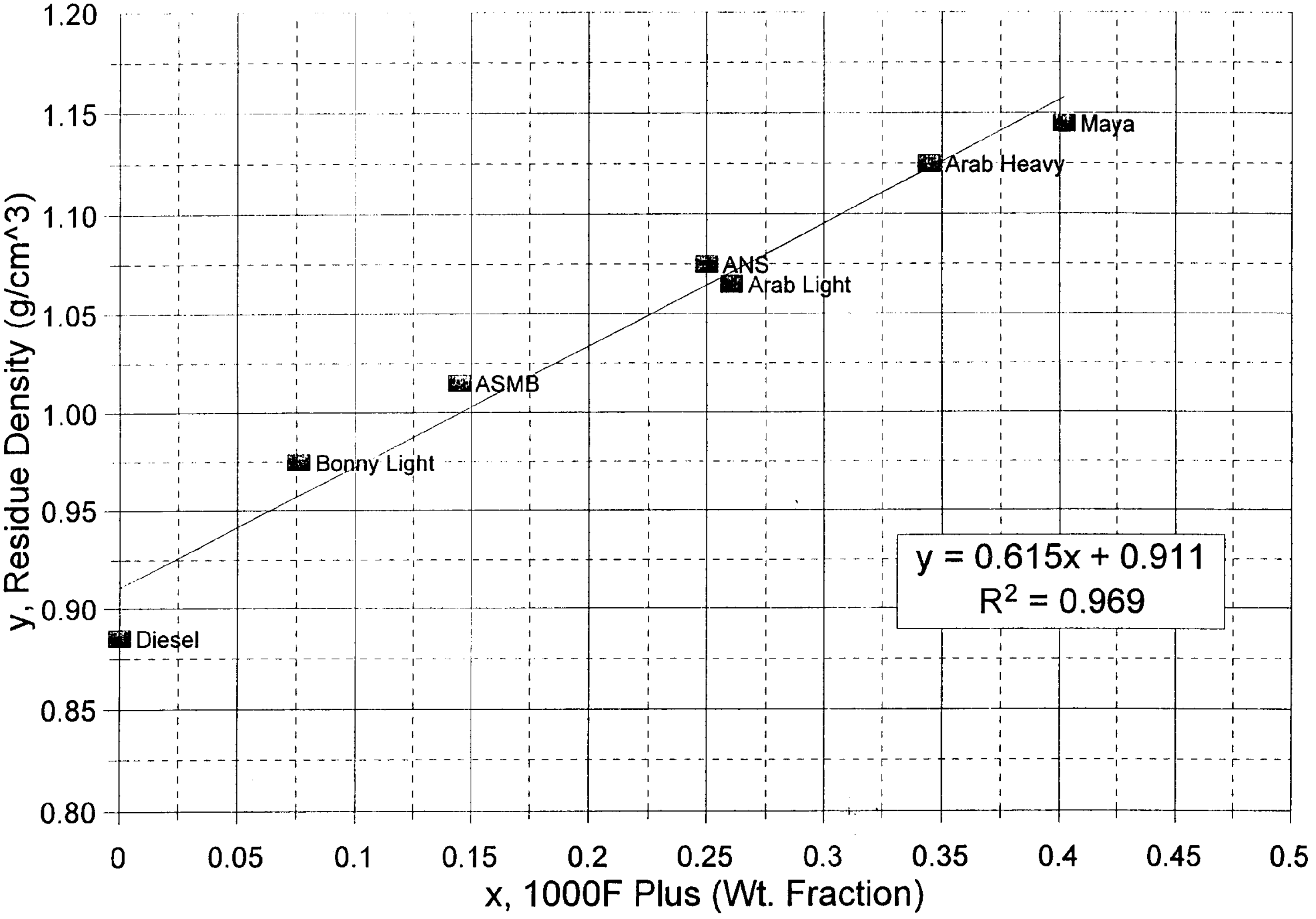


Figure 3-7. Residue Density vs. 1000F Plus
15 cm Thickness

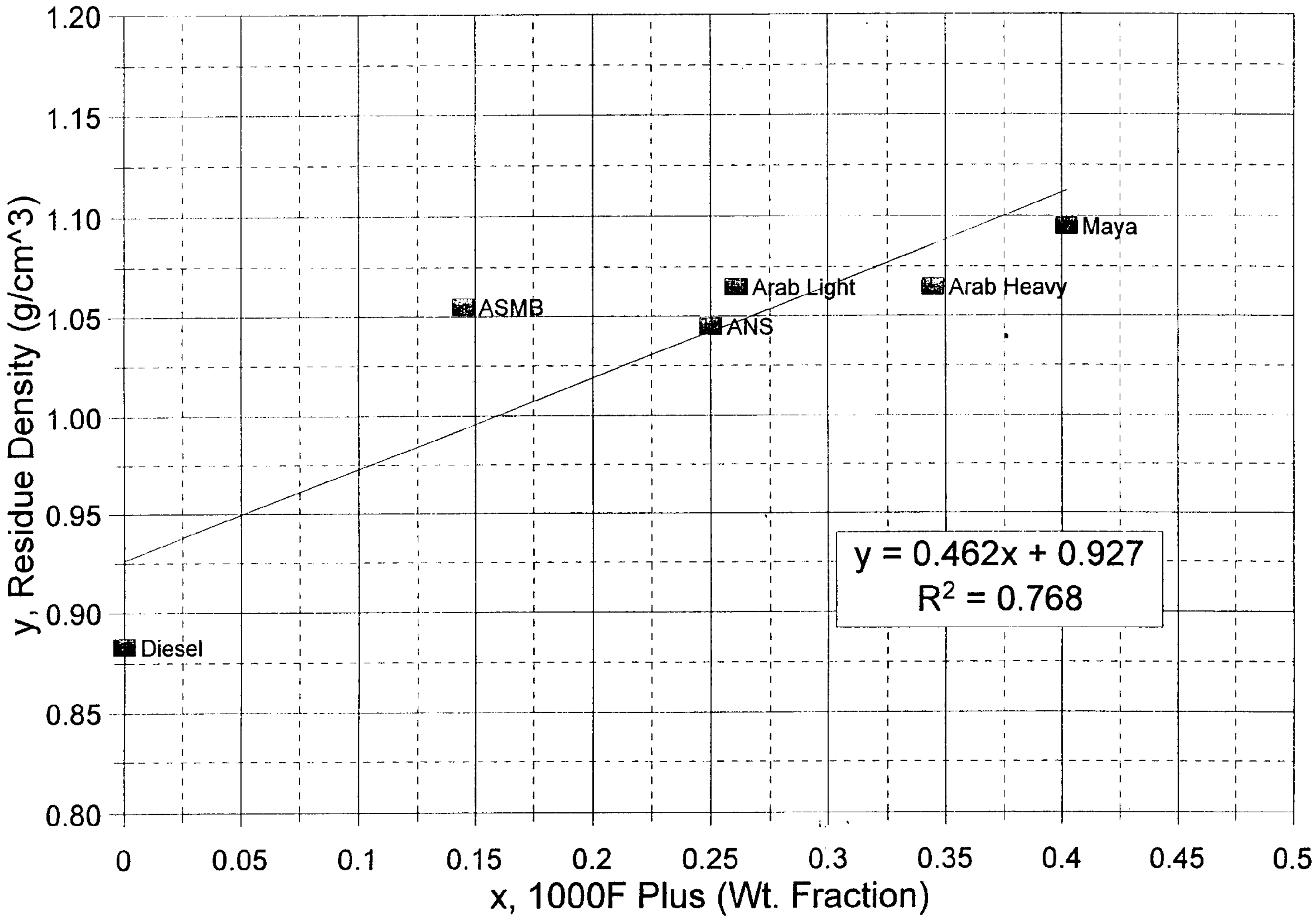


Figure 3-8. Residue Density vs. 1000F Plus
5, 10 and 15 cm Thicknesses

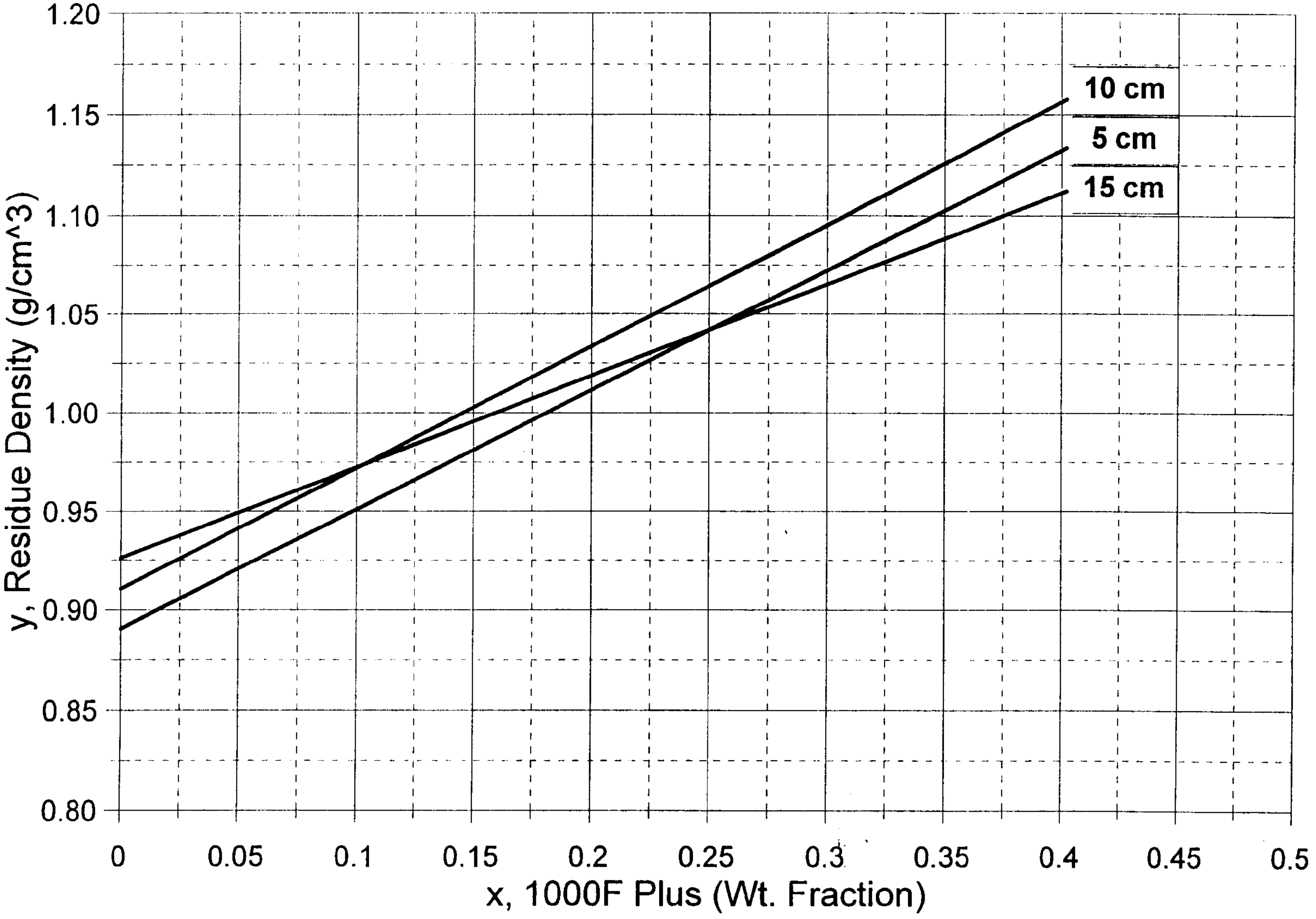


Figure 3-9. Residue Density vs. 1049F Plus
5 cm Thickness

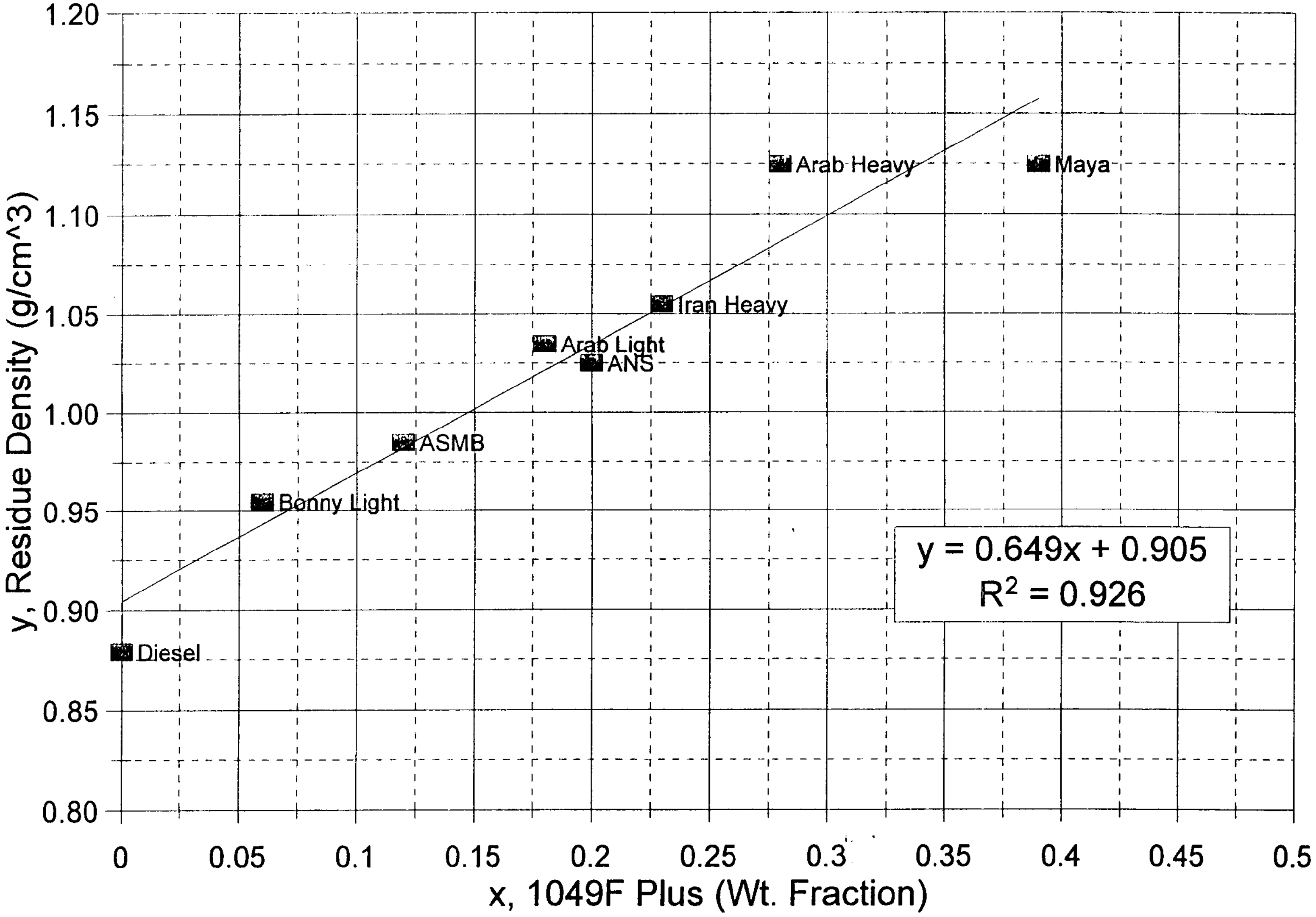


Figure 3-10. Residue Density vs. 1049F Plus

10 cm Thickness

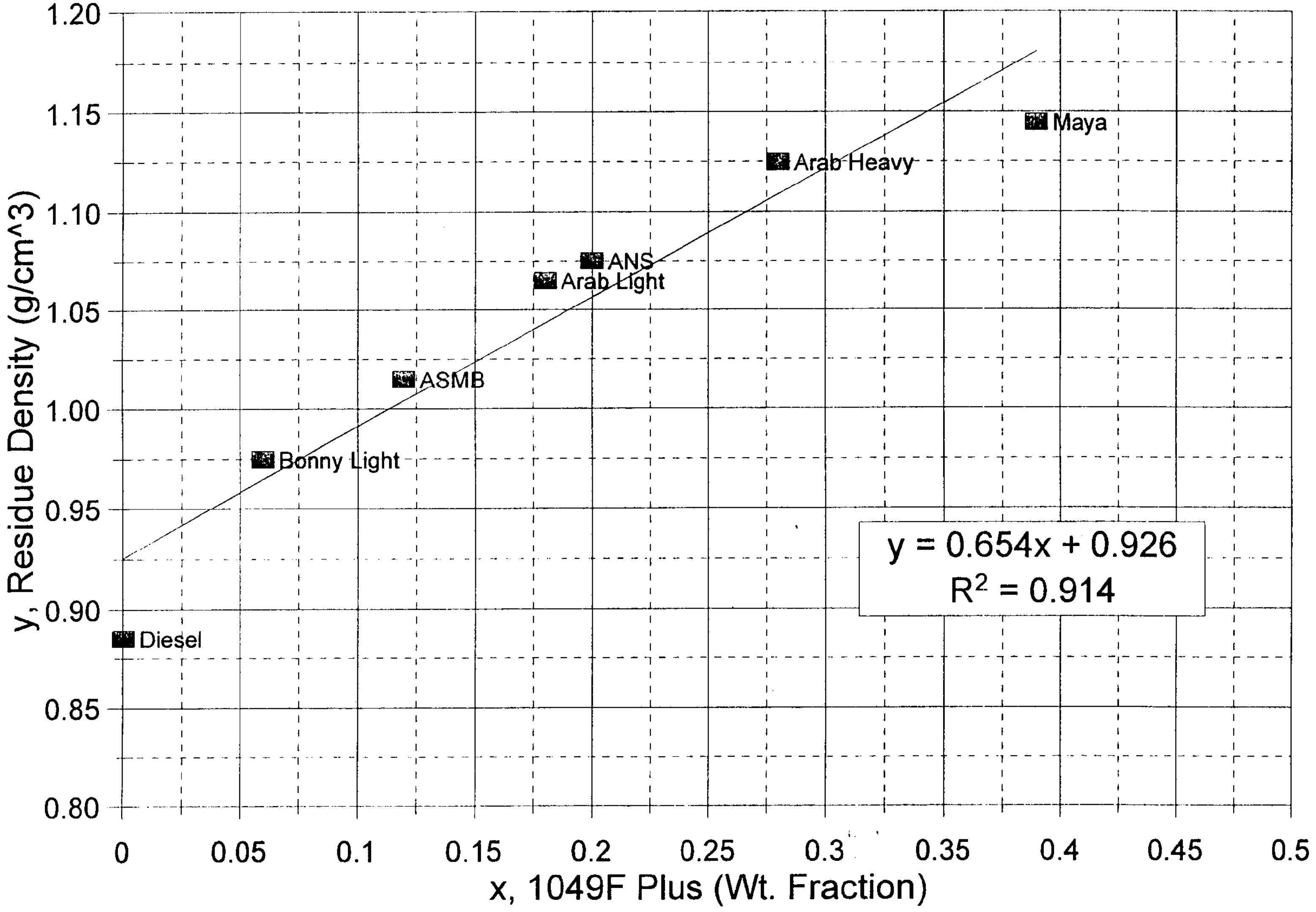


Figure 3-11. Residue Density vs. 1049F Plus
15 cm Thickness

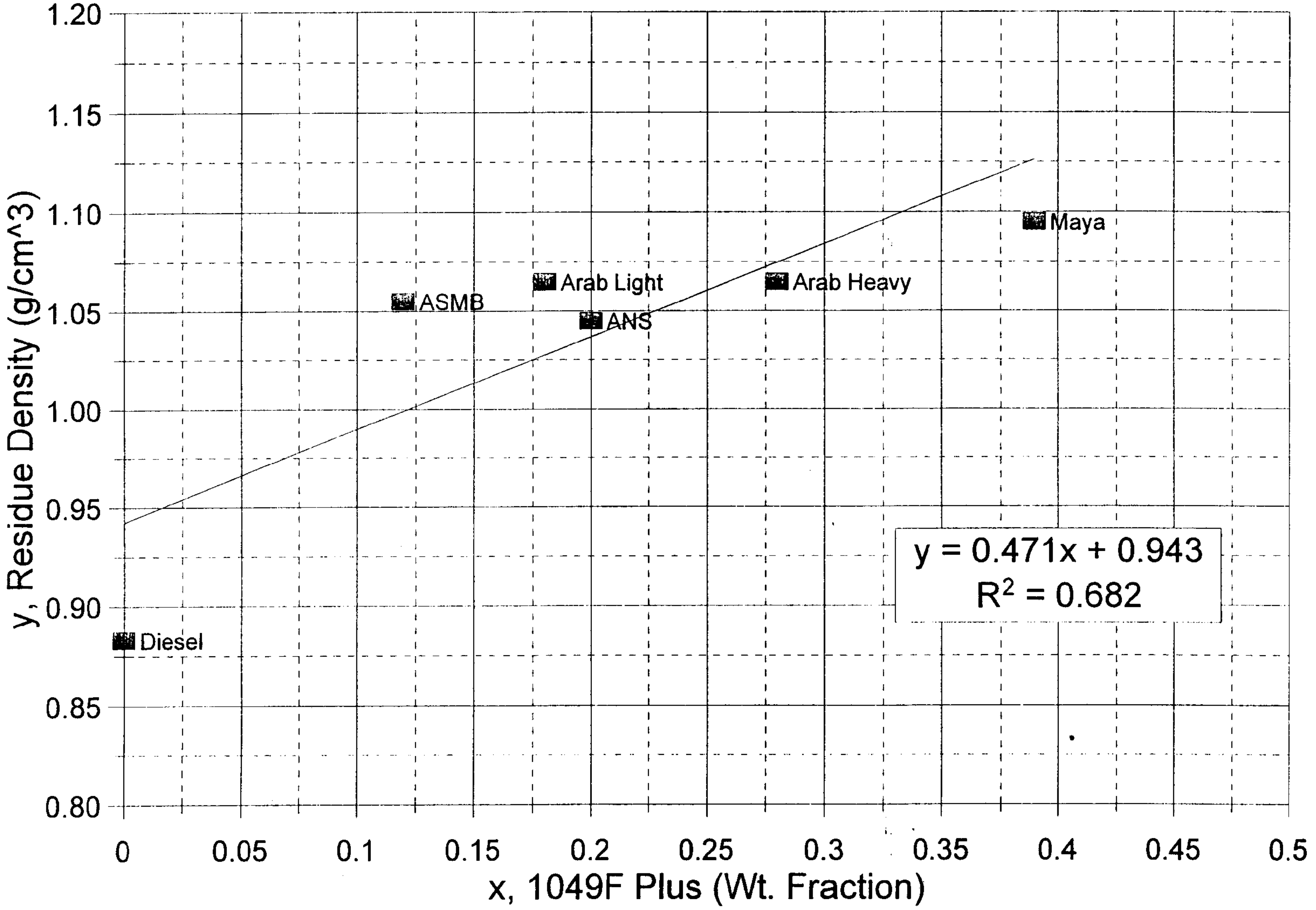


Figure 3-12. Residue Density vs. 1049F Plus
5, 10 and 15 cm Thicknesses

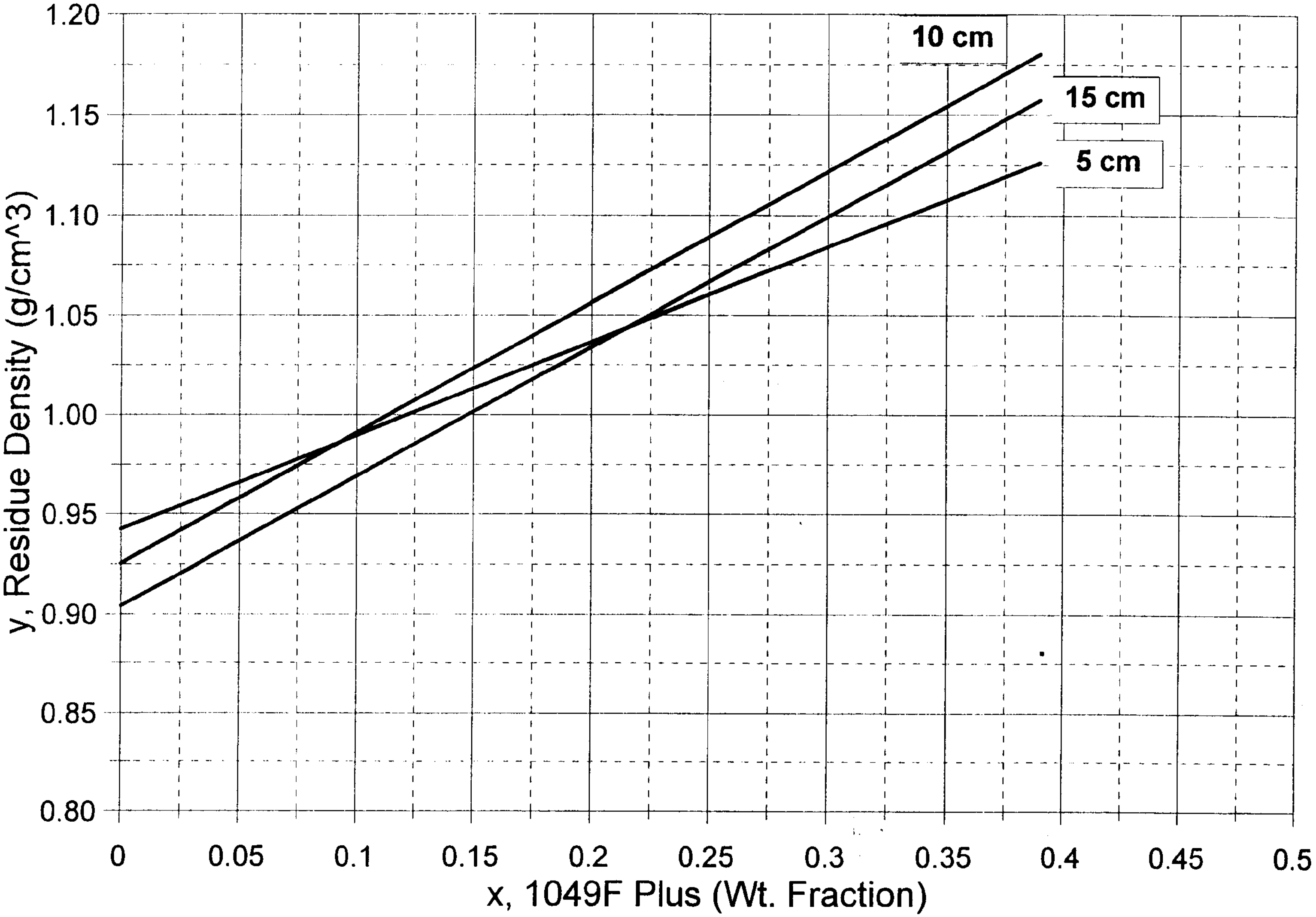


Table 3-4. Likelihood of Selected Crude Oils Producing Non-Buoyant ISB Residues[a]

Oil Type	Country of Origin	Oil Properties			Method 1			Method 2		
		API Gravity[b]	Initial Density	Weight Fraction 1049°F Plus	Calc. Residue Density[c]	Density Difference[e]	Likely to Float?	Calc. Residue Density[d]	Density Difference[e]	Likely to Float?
ABOOZAR (ARDESHIR)	IRAN	26.9	0.893	0.28	1.097	0.072	NO	1.110	0.085	NO
ABU AL BU KHOOSH	ABU DHABI, U.A.E.	31.6	0.867	0.17	1.033	0.008	NO	1.036	0.011	NO
ALASKAN NORTH SLOPE	ALASKA, USA	26.6	0.894	0.20	1.101	0.076	NO	1.057	0.032	NO
AMNA	LIBYA	36.0	0.844	0.19	0.977	-0.048	YES	1.052	0.027	NO
ARAB HEAVY (SAFANIYA)	SAUDI ARABIA	27.9	0.887	0.28	1.083	0.058	NO	1.107	0.082	NO
ARAB LIGHT	SAUDI ARABIA	33.4	0.858	0.18	1.010	-0.015	YES	1.042	0.017	NO
ARAB LIGHT (BERRI)	SAUDI ARABIA	37.8	0.835	0.11	0.954	-0.071	YES	0.996	-0.029	YES
ARAB MEDIUM (KHURSANIYAH)	SAUDI ARABIA	30.8	0.871	0.22	1.043	0.018	NO	1.071	0.046	NO
ARAB MEDIUM (ZULUF/MARJAN)	SAUDI ARABIA	31.1	0.870	0.24	1.040	0.015	NO	1.082	0.057	NO
ARDJUNA	INDONESIA	35.2	0.848	0.05	0.987	-0.038	YES	0.960	-0.065	YES
ARGYLL	NORTH SEA	38.0	0.834	0.05	0.952	-0.073	YES	0.960	-0.065	YES
ASHTART	TUNISIA	30.0	0.876	0.22	1.054	0.029	NO	1.069	0.044	NO
ATTAKA	INDONESIA	43.2	0.809	0.00	0.891	-0.134	YES	0.928	-0.097	YES
AUK	NORTH SEA	37.2	0.838	0.14	0.962	-0.063	YES	1.018	-0.007	YES
BAHRGANSAR/NOWRUZ	IRAN	27.1	0.892	0.35	1.094	0.069	NO	1.152	0.127	NO
BASRAH HEAVY	IRAQ	24.7	0.905	0.31	1.128	0.103	NO	1.130	0.105	NO
BASRAH LIGHT	IRAQ	33.7	0.856	0.17	1.006	-0.019	YES	1.037	0.012	NO
BASRAH MEDIUM	IRAQ	31.1	0.870	0.24	1.040	0.015	NO	1.080	0.055	NO
BCF 24	VENEZUELA	23.5	0.912	0.32	1.145	0.120	NO	1.138	0.113	NO
BEATRICE	NORTH SEA	38.7	0.831	0.16	0.944	-0.081	YES	1.033	0.008	NO
BEKAPAI	INDONESIA	40.3	0.823	0.06	0.925	-0.100	YES	0.966	-0.059	YES
BELAYIM	EGYPT	27.5	0.889	0.31	1.088	0.063	NO	1.125	0.100	NO
BERYL	NORTH SEA	37.5	0.837	0.11	0.958	-0.067	YES	1.000	-0.025	YES
BINTULU	MALAYSIA	28.1	0.886	0.03	1.080	0.055	NO	0.946	-0.079	YES
BOMBAY HIGH	INDIA	39.2	0.828	0.04	0.938	-0.087	YES	0.953	-0.072	YES
BONNY LIGHT	NIGERIA	35.3	0.848	0.06	0.985	-0.040	YES	0.964	-0.061	YES
BONNY MEDIUM	NIGERIA	25.2	0.902	0.09	1.121	0.096	NO	0.987	-0.038	YES
BOW RIVER HEAVY	CANADA (ALBERTA)	26.7	0.894	0.27	1.099	0.074	NO	1.102	0.077	NO
BRASS RIVER	NIGERIA	42.8	0.811	0.04	0.895	-0.130	YES	0.952	-0.073	YES
BREGA	LIBYA	40.4	0.823	0.11	0.923	-0.102	YES	0.998	-0.027	YES
BRENT BLEND	NORTH SEA	38.6	0.831	0.11	0.945	-0.080	YES	0.998	-0.027	YES
BUCHAN	NORTH SEA	33.7	0.856	0.14	1.006	-0.019	YES	1.019	-0.006	YES
BURGAN	NEUTRAL ZONE	23.3	0.913	0.38	1.148	0.123	NO	1.177	0.152	NO
CABINDA	ANGOLA	31.7	0.866	0.22	1.032	0.007	NO	1.068	0.043	NO
CEUTA EXPORT	VENEZUELA	27.8	0.888	0.21	1.084	0.059	NO	1.063	0.038	NO
CINTA MIX	INDONESIA	32.0	0.865	0.31	1.028	0.003	NO	1.127	0.102	NO
CORMORANT NORTH	NORTH SEA	34.9	0.850	0.13	0.991	-0.034	YES	1.009	-0.016	YES
CORMORANT SOUTH	NORTH SEA	35.7	0.846	0.08	0.980	-0.045	YES	0.975	-0.050	YES
DJENO BLEND	CONGO (BRAZZAVILLE)	27.6	0.889	0.31	1.087	0.062	NO	1.132	0.107	NO
DORROOD (DARIUS)	IRAN	33.6	0.857	0.22	1.007	-0.018	YES	1.069	0.044	NO
DUKHAN (QATAR LAND)	QATAR	40.9	0.820	0.10	0.918	-0.107	YES	0.991	-0.034	YES
DUNLIN	NORTH SEA	34.9	0.850	0.12	0.991	-0.034	YES	1.005	-0.020	YES
DURI (SUMATRAN HEAVY)	INDONESIA	21.1	0.927	0.41	1.180	0.155	NO	1.192	0.167	NO
EAST TEXAS	TEXAS, USA	37.0	0.839	0.13	0.964	-0.061	YES	1.010	-0.015	YES
EKOFISK	NORTH SEA	43.4	0.809	0.12	0.888	-0.137	YES	1.006	-0.019	YES

Notes:

a: Data based on laboratory ISB experiments with slicks of small diameter (40 mm) and thickness (5 to 15 cm). Results may not be valid for large, thick slicks.

b: Oils with API gravities less than 20° were excluded from the calculations

c: Calculated Residue Density = 2.473 x (Initial Density) - 1.111; Slick Thickness = 10 cm.

d: Calculated Residue Density = 0.6535 x (Wt. Fraction @ 1049°F) + 0.9259; Slick Thickness = 10 cm.

e: Density Difference = Calculated Density (see above) - Sea Water Density (D = 1.025 g/cm3)

Figure A-7. Wt. Fraction 1049F+ vs. Initial Oil Density

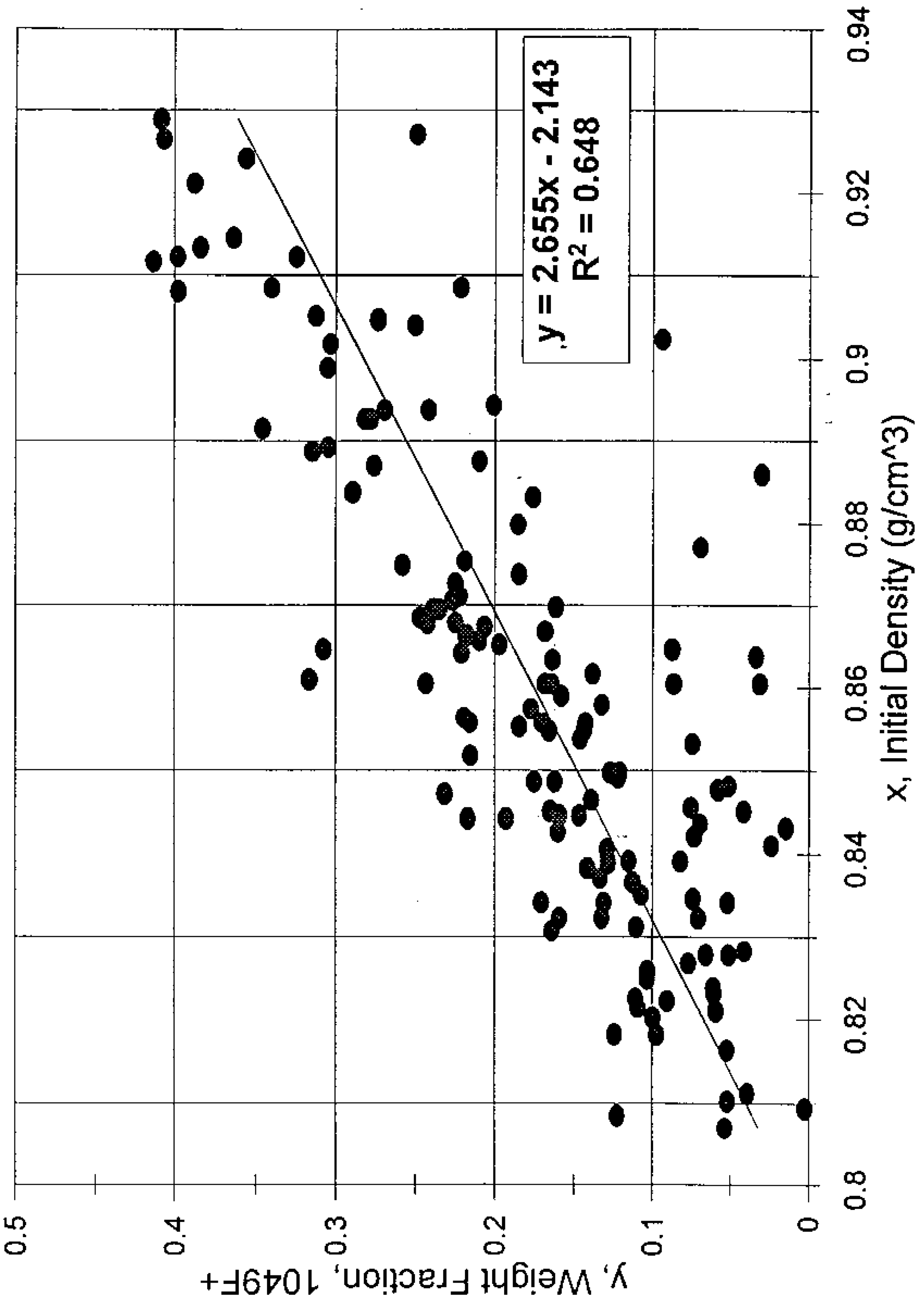


Table 3-4 (continued). Likelihood of Selected Crude Oils Producing Non-Buoyant ISB Residues[a]

Oil Type	Country of Origin	Oil Properties			Method 1			Method 2		
		API Gravity[b]	Initial Density	Weight Fraction 1049°F Plus	Calc. Residue Density[c]	Density Difference[e]	Likely to Float?	Calc. Residue Density[d]	Density Difference[e]	Likely to Float?
MURCHISON	NORTH SEA	38.0	0.834	0.13	0.952	-0.073	YES	1.011	-0.014	YES
NINIAN BLEND	NORTH SEA	35.8	0.845	0.17	0.979	-0.046	YES	1.034	0.009	NO
NORTH RUMAILA	IRAQ	33.7	0.856	0.22	1.006	-0.019	YES	1.067	0.042	NO
OFICINA	VENEZUELA	33.3	0.858	0.13	1.011	-0.014	YES	1.012	-0.013	YES
OMAN EXPORT	OMAN	36.3	0.843	0.16	0.973	-0.052	YES	1.031	0.006	NO
ORIENTE	ECUADOR	29.2	0.880	0.19	1.065	0.040	NO	1.047	0.022	NO
OSTRICA	LOUISIANA, USA	32.0	0.865	0.09	1.028	0.003	NO	0.983	-0.042	YES
PALANCA	ANGOLA	40.1	0.824	0.06	0.926	-0.099	YES	0.966	-0.059	YES
PENNINGTON	NIGERIA	36.6	0.841	0.02	0.969	-0.056	YES	0.942	-0.083	YES
PIPER	NORTH SEA	35.0	0.849	0.12	0.989	-0.036	YES	1.005	-0.020	YES
QATAR MARINE	QATAR	36.0	0.844	0.22	0.977	-0.048	YES	1.068	0.043	NO
QUA IBOE	NIGERIA	35.8	0.845	0.04	0.979	-0.046	YES	0.953	-0.072	YES
RAINBOW	CANADA (ALBERTA)	40.7	0.821	0.06	0.920	-0.105	YES	0.965	-0.060	YES
RANGELAND SOUTH	CANADA (ALBERTA)	39.5	0.827	0.08	0.934	-0.091	YES	0.976	-0.049	YES
RAS GHARIB	EGYPT	21.5	0.924	0.36	1.175	0.150	NO	1.158	0.133	NO
RATAWI	NEUTRAL ZONE	23.5	0.912	0.40	1.145	0.120	NO	1.186	0.161	NO
ROSTAM	IRAN	35.9	0.845	0.15	0.978	-0.047	YES	1.022	-0.003	YES
SAHARAN BLEND (43.7 API)	ALGERIA	43.7	0.807	0.05	0.885	-0.140	YES	0.961	-0.064	YES
SALMON (SASSAN)	IRAN	33.9	0.855	0.17	1.003	-0.022	YES	1.034	0.009	NO
SARIR	LIBYA	38.4	0.832	0.13	0.947	-0.078	YES	1.012	-0.013	YES
SEA BREEZE	TEXAS, USA	37.9	0.835	0.07	0.953	-0.072	YES	0.975	-0.050	YES
SERGIPANO PLATFORMA	BRAZIL	38.4	0.832	0.16	0.947	-0.078	YES	1.030	0.005	NO
SERGIPANO TERRA	BRAZIL	24.1	0.909	0.34	1.136	0.111	NO	1.148	0.123	NO
SERIA LIGHT	BRUNEI	36.2	0.843	0.01	0.974	-0.051	YES	0.935	-0.090	YES
SHENGLI	CHINA	24.2	0.908	0.40	1.135	0.110	NO	1.186	0.161	NO
SIRTICA	LIBYA	41.3	0.818	0.12	0.913	-0.112	YES	1.007	-0.018	YES
SOUEDIE	SYRIA	24.9	0.904	0.25	1.125	0.100	NO	1.090	0.065	NO
SOUTH LOUISIANA	LOUISIANA, USA	32.8	0.861	0.16	1.017	-0.008	YES	1.033	0.008	NO
SOVIET EXPORT BLEND	U.S.S.R.	31.8	0.866	0.21	1.030	0.005	NO	1.063	0.038	NO
STATFJORD	NORTH SEA	38.4	0.832	0.07	0.947	-0.078	YES	0.972	-0.053	YES
TACHING (DAQING)	CHINA	32.7	0.861	0.32	1.019	-0.006	YES	1.133	0.108	NO
TARTAN	NORTH SEA	41.7	0.816	0.05	0.908	-0.117	YES	0.960	-0.065	YES
TEMBLADOR	VENEZUELA	21.0	0.927	0.25	1.182	0.157	NO	1.089	0.064	NO
THISTLE	NORTH SEA	37.0	0.839	0.13	0.964	-0.061	YES	1.010	-0.015	YES
TIA JUANA 102	VENEZUELA	25.8	0.899	0.31	1.112	0.087	NO	1.126	0.101	NO
TIA JUANA LIGHT	VENEZUELA	32.1	0.864	0.22	1.026	0.001	NO	1.070	0.045	NO
TIA JUANA MEDIUM 24	VENEZUELA	24.8	0.905	0.27	1.126	0.101	NO	1.105	0.080	NO
TIA JUANA MEDIUM 26	VENEZUELA	26.9	0.893	0.28	1.097	0.072	NO	1.108	0.083	NO
UDANG	INDONESIA	38.0	0.834	0.17	0.952	-0.073	YES	1.038	0.013	NO
UMM SHAIF (ABU DHABI MARINE)	ABU DHABI, U.A.E.	37.4	0.837	0.13	0.959	-0.066	YES	1.013	-0.012	YES
WAINWRIGHT-KINSELLA	CANADA (ALBERTA)	23.1	0.915	0.36	1.151	0.126	NO	1.164	0.139	NO
WALIO EXPORT MIX	INDONESIA	35.4	0.847	0.23	0.984	-0.041	YES	1.077	0.052	NO
WEST TEXAS SOUR	TEXAS, USA	34.1	0.854	0.15	1.001	-0.024	YES	1.022	-0.003	YES
ZAIRE	ZAIRE	31.7	0.866	0.22	1.032	0.007	NO	1.069	0.044	NO
ZAKUM (LOWER)	ABU DHABI, U.A.E.	40.6	0.822	0.11	0.921	-0.104	YES	0.997	-0.028	YES
ZARZAITINE	ALGERIA	43.0	0.810	0.05	0.893	-0.132	YES	0.960	-0.065	YES
ZUEITINA	LIBYA	41.3	0.818	0.10	0.913	-0.112	YES	0.989	-0.036	YES

Notes:

a: Data based on laboratory ISB experiments with slicks of small diameter (40 mm) and thickness (5 to 15 cm). Results may not be valid for large, thick slicks.

b: Oils with API gravities less than 20° were excluded from the calculations

c: Calculated Residue Density = 2.473 x (Initial Density) - 1.111; Slick Thickness = 10 cm.

d: Calculated Residue Density = 0.6535 x (Wt. Fraction @ 1049°F) + 0.9259; Slick Thickness = 10 cm.

e: Density Difference = Calculated Density (see above) - Sea Water Density (D = 1.025 g/cm3)

Section 4
PREVENTING NON-BUOYANT RESIDUES FROM FORMING OR SINKING

It is evident that many oil types may form non-buoyant residues following an ISB operation that involves burning thick slicks of relatively heavy oil. Sinking of burn residue may be acceptable in circumstances where negligible environmental damage from the sunken residue is foreseen, such as for spills far offshore in deep waters. There are other spill situations where there may be a strong net environmental benefit to burning, but only if the residues from the burning process are not allowed to sink to the sea bed. In these cases countermeasures are needed either:

(1) to prevent the residue from forming in the first instance or from sinking once formed; or
(2) to collect non-buoyant residues at the surface or near the surface shortly after the burn.

Section 4 of the report deals with the first option; the second is dealt with in the following section (Section 5).

There are two ways of preventing ISB residues from becoming non-buoyant in the first instance. One is to manipulate the slick or the fire in such a manner that the final residue remains buoyant. The other is to add a buoyant material to the oil before burning so that the residue sticks to it after burning is finished. These two options are discussed in turn.

MANIPULATING THE FIRE OR THE SLICK TO CONTROL RESIDUE DENSITY

One obvious, but impractical, idea for ensuring that an ISB residue will not be heavy enough to sink is to extinguish the ISB fire at some point during the operation so that a sufficient percentage of lighter components remains in the residue. This idea can be dismissed because (1) large oil fires are very difficult to put out at any time, let alone at any set time, and (2) the exercise adds a complex step to the countermeasures process.

The earlier analysis of factors that influence burn residue density suggested that there is a positive relationship between initial slick thickness and burn residue density: generally, the thicker the slick the heavier the burn residue. Therefore, one way of reducing the density of the burn residue would be to increase the area of burning oil and thus reduce the effective thickness of the burning slick. This could be done in a towed-boom situation by reducing the towing velocity relative to the water current velocity. In a zero-current, full-containment situation this could be done by increasing the length of boom containing the oil. In either case, this would have the added advantage of increasing the burn rate of the oil, which is directly related to the area of the burning slick. The disadvantages of this tactic would be that (1) more fireboom would be needed; (2) the increase in burn rate would increase the rate of soot production and therefore the concentrations of soot in the smoke plume; and (3) more residue would be left to clean up.

In certain spill containment/burning situations, where there is a continuous discharge of oil into the boom or where the boom system continuously advances into a spill, the density of the burn residue may be controlled because the burning oil in the pocket of the boom will be constantly fed with relatively fresh oil and may therefore have a tendency to remain more buoyant.

Aside from the above possibilities, there seem to be few practical possibilities for controlling the density of residues from ISB operations by simple manipulation of the slick or the fire.

ADDING BUOYANT MATERIALS TO THE SLICK TO CONTROL RESIDUE DENSITY

Introduction

It is known that certain materials, called combustion promoters or wicking agents, can be added to floating oil to enhance the ISB process. These are usually granular materials that are very light and oleophilic. The particles are used to wick the oil away from the relatively cold water surface and keep it better insulated at the same time. Research (as summarized, for example, in Buist *et al.*, 1994) indicates that treated peat moss is a good combustion promoter for ISB enhancement, and there are other promising materials as well. Such products are not usually considered for *in situ* burning of marine spills because they are difficult to apply and require high application rates.

It is hypothesized that if such a combustion-promoting substance were used with oils that otherwise would tend to produce non-buoyant ISB residues, the residue would stick with the buoyant substance and not sink at the end of the operation. To test this hypothesis a small experimental program was conducted in the S.L. Ross Laboratory, as described below. Because of budget limitations, the program was very modest, involving only one oil, two substances, and a few days of effort.

Laboratory Trials of Combustion Promoters

After researching the available literature many combustion promoters were identified, but only two were selected for laboratory trials. In previous studies other products were found to be either too difficult to apply to even a small spill (*Seabeads* - as reported in Freiberger and Byers, 1971, *Cab-O-Sil, Aerosil and Tullanox* - Glaeser and Vance, 1970, *Vermiculite* - Tam and Purves, 1980) or of little or no benefit to the combustion (*Straw* - Glaeser and Vance, 1971).

The first material selected was peat moss. Peat moss has been used extensively as a combustion promoter, although usually for shoreline cleanups (Energetex, 1981) or for burning oil in ice (Coupal, 1972 and 1976). It appears to work by first burning to a web of filamentous carbon, which then assists the burning of oil through a wicking action. Peat moss was tested to see if it would affect the burn conditions and the residue properties.

The second material selected was a nylon mesh screen. This was tested to see if it would survive a burn, affect the burn conditions and effectively consolidate the residue after the extinction of the burn. The objective was to try a variation on submerged nets to catch sinking oil residue, in this case by actually embedding the netting in the burn residue. By attaching the netting to a cable or to the boom, the residue could be retrieved even if it were to sink.

Alaska North Slope crude oil (ANS) was used to test the two techniques since a small quantity was already on hand and its burn characteristics are well known. The burns were conducted in a 40-cm diameter ring suspended in the middle of an 11 x 1.1 x 1.1 m (length x width x height) tank filled with water to a depth of 85 cm. Each burn used 12.5 L of fresh oil, which corresponds to a 10-cm thick slick. A preliminary burn without promoters was conducted to determine the "normal" burn performance of ANS under these conditions. The ANS burned efficiently for 1 hour and 17 minutes and produced a residue that would sink in sea water (see Table 4-1).

Recommended application rates for peat moss are between 7 and 10% by weight (Glaeser and Vance, 1971). This high ratio, while perhaps achievable for a shoreline cleanup, would be impractical to apply to a marine spill. For example, a 10% by weight loading of peat moss to the experimental slick here would be 1 kg of peat moss. This is a volume of 10 L, which is almost equal to the volume of oil. Instead, a ratio of 1% was used, corresponding to a 1-cm layer of peat moss (1.25 L or 0.1 g).

Table 4-1: Results of Burn Tests

Promoter	Burn Duration, min	Burn Efficiency, %	Residue Mass, g	Residue Density, g/cm^3
None	77	95	524	1.035
Peat moss	65	?	119	1.005
Nylon screen	80	74	3012	< 0.900

When applied to the slick the moss sank into the oil layer, where it remained during the burn (i.e., no moss sank out of the bottom of the ring). The peat moss did not affect the ignition of the oil; however, it had a dramatic effect on the burn itself. At approximately 55 minutes into the burn, the oil began to burn extremely vigorously and overflowed out of the ring. Most of the oil was lost. The small amount of oil that remained in the ring burned for another 10 minutes before extinguishing. There was very little residue in the ring; what was left was solid and crumbly, and slightly buoyant.

The most probable explanation for the change in burn dynamics is that the peat moss eventually came into contact with the water under the slick and began wicking it to the hot surface of the oil. The water was quickly heated to its boiling point and vaporized violently, ejecting the oil from the ring.

It is impossible to predict how peat moss would affect a full-scale *in situ* burn, where a vigorous burn would not result in loss of oil from the boom. In such a situation, the residue would almost certainly be more dense than what was measured here, although there is no way to predict whether the peat moss would improve its buoyancy. The findings, therefore, are inconclusive, and faced with the difficulty and added complication of applying a very large volume of peat moss to a real slick, judgement is reserved on its use at this time.

The final burn used a small piece of nylon screen (clear opening of about 2 mm), cut into a circle of roughly 40-cm in diameter and set on the oil surface. The screen sank into the oil and did not affect the ignition. It was visible at the surface of the slick from time to time during the burn and appeared to be surviving the burn. The burn extinguished after 1 hour and 20 minutes even though there was a considerable amount of residue left (see Table 4-1). About 70% of the screen was still intact; only one small section had melted or been burned away.

The screen had a detrimental effect on the burn efficiency. Perhaps the small screen openings restricted the passing of the increasingly viscous oil from the body of the slick through the screen to the combustion zone, or perhaps the screen became clogged by the heavier elements of the oil and thus sealed off the surface. In any case, the screen did not have the desired effect. A coarser screen might have become less clogged or allowed viscous oil to pass through more easily, but this idea requires further testing.

SUMMARY

The results of the preliminary laboratory study and the analysis of operational considerations indicate that no simple method exists for controlling the density of the residue formed after an ISB operation. A strong incentive for considering *in situ* burning as an oil spill cleanup technique has always been the operational simplicity of the approach. Adding complexity to the response operation without considerable benefit is not an approach in the right direction. The best approach may be to develop methods for collecting non-buoyant residue. That is the subject of the next section.

Section 5

METHODS TO COLLECT RESIDUES AT OR NEAR THE WATER SURFACE

There are two possibilities for collecting non-buoyant ISB residues before they sink deeply. The first is to recover relatively hot residue with surface skimming devices just before it cools and starts to sink, and the second is to recover sinking residue with subsurface devices stationed down current of the fireboom.

During past ISB experiments where residues ultimately sank, observers have noted that there is a time delay lasting minutes, after the fire goes out but before the residue sinks, during which the hot residue remains buoyant. This time delay is likely affected by residue thickness, water temperature, wind speed, and the like.

It is possible that the time delay may be long enough to permit an efficient skimming operation before the residue cools to ambient temperature and begins to sink. To check this hypothesis and scope the issue we conducted a theoretical analysis of the situation. The modeling problem is one relating to heat transfer from one medium to another, for which there is a large body of literature and data. The main question to be answered is: How long does it take for a thickness of burn residue to cool to the ambient water temperature?

COOLING RATES FOR BURN RESIDUE

The scenario of a cooling slick of burn residue can be modeled as an infinite slab of uniform thickness, with one side exposed to a cooling medium (water) and the other perfectly insulated. The assumptions are that: (1) the residue is homogeneous; (2) the properties of the residue are constant over the temperature ranges modeled; (3) the slick has a very large ratio of surface to thickness; (4) there is negligible resistance to heat transfer between the water and residue; (5) the heat transfer to air is negligible, and only occurs downwards to water; and (6) only heat transfer by conduction occurs within the residue.

The partial differential equation for this situation is (McAdams, 1954):

$$\frac{k}{\rho c_p}\frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t} \tag{4}$$

Where: k is the thermal conductivity of the residue
ρ is the density of the residue
c_p is the specific heat of the residue
T is the temperature of the residue at position x
x is the distance from the top of the residue
t is the time from extinction of the burn

Integrating this equation for the heating or cooling of an infinite slab by a medium at constant temperature gives (McCabe *et al.*, 1985):

$$\frac{T_s - T_b}{T_s - T_a} = \frac{8}{\pi^2}\left[e^{-a_1 N_{Fo}} + \frac{1}{9}e^{-9a_1 N_{Fo}} + \frac{1}{25}e^{-25a_1 N_{Fo}} + \dots\right] \tag{5}$$

Where: T_s is the constant average temperature of the water
T_a is the initial temperature of the residue
T_b is the average temperature of the slab after cooling for time t_T
N_{FO} is the Fourier number, defined as $\alpha t_T/s^2$
α is the thermal diffusivity, defined as $\alpha = k/\rho c_p$
t_T is the time of cooling
s is the thickness of the residue
a_1 is defined as $(\pi/2)^2$

This series rapidly converges. When N_{FO} is greater than about 0.1, only the first term of the series is significant. Eliminating all but the first term and rearranging the equation to solve for time yields (McCabe *et al.*, 1985):

$$t_T = \frac{1}{\alpha}\left(\frac{2s}{\pi}\right)^2 \ln\frac{8(T_s - T_a)}{\pi^2(T_s - T_b)} \tag{6}$$

Equation 6 can be used to estimate the time required for slick of burn residue to cool to ambient conditions.

According to Buist *et al.* (1994) the surface temperature of a burning oil slick during the steady state burning phase remains almost constant in the 200 to 300°C range. At the end of a burn, the surface temperature of the slick would likely be at the high end of this range, due to the slow concentration of heavy ends in the residue increasing the boiling temperature of the oil. In some cases, the temperature could be even higher. The temperature at the water/oil interface at the end of a burn will depend on the thickness of the residue, the duration of the burn, the temperature of the water and the towing speed. Although no field data are available for a real *in situ* burn, it will likely be in the range of 30 to 60°C. Therefore, the average temperature of most burn residues will be approximately 180°C.

The thickness of the residue will depend on factors such as oil type, initial slick thickness, presence of wind and waves, and towing speed. Residue thicknesses from 1 to 6 mm have been reported (Buist *et al.*, 1994).

No. 6 fuel oil is a good analogue to a typical crude oil burn residue. Data and equations from Perry *et al.* (1997) give the following relations for the thermal properties of No. 6 fuel oil. These are sufficient to determine the thermal diffusivity ($\alpha = k/\rho c_p$) in equation 6:

$$k = 0.1168 - 5.7 \times 10^{-5} T \qquad (7)$$

Where: k is in W/m°C
T is temperature of the residue in °C

$$c_p = \frac{1.685 + 0.039T}{\sqrt{s.g.}} \qquad (8)$$

Where: c_p is in kJ/kg°C
T is temperature of the residue in °C
s.g. is specific gravity of the residue

The density of No. 6 fuel oil is given by (Bobra *et al.*, 1990):

$$\rho = 978.78 - 0.00071T \qquad (9)$$

Where: ρ is in kg/m^3
T is temperature of the residue in °C

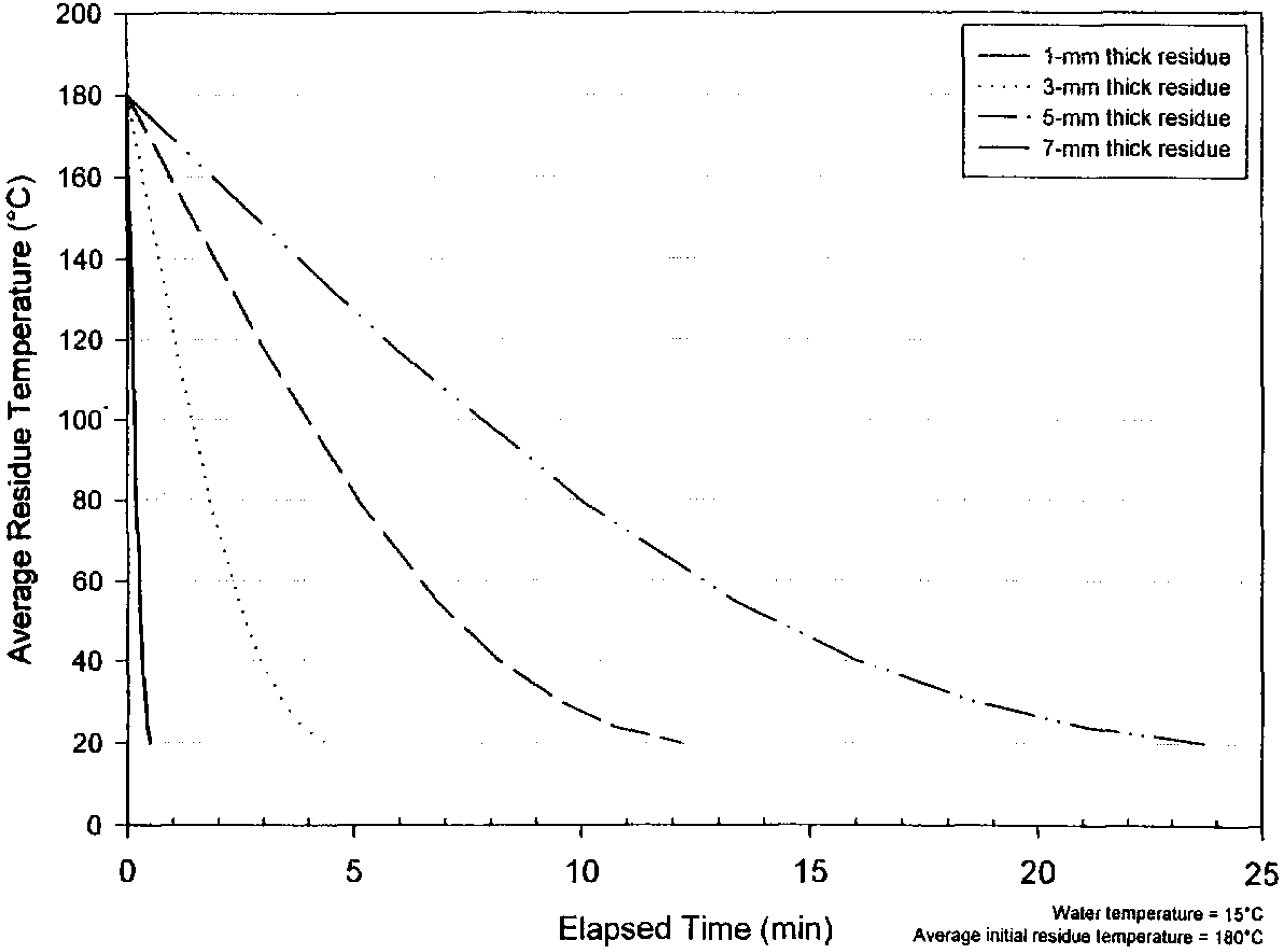
Using equations 6 through 9, an initial average residue temperature of 180°C and a water temperature of 15°C, the cooling rates were calculated for four residue thicknesses. The results are given in Figure 5-1.

POSSIBILITIES FOR COLLECTING NON-BUOYANT ISB RESIDUES

Time Available

Figure 5-1 provides indications of the time that could be available to skim residues that have densities greater than sea water at ambient temperature. Note that the time would amount to no greater than about 2 hours following the burn. These calculations were based on a uniform slick of 1 to 7 mm thickness; therefore, if the residue were in lumps or tarballs, the cooling would be more rapid and even less time would be available for surface countermeasures. Anecdotal evidence from the NOBE burn (English, pers. comm., 1998) supports the contention that this time estimate is probably a maximum. Following the NOBE burn, response crews had some success in recovering the burn residue using rakes and pitchforks. In that experiment, the residue (having a density of 0.94 g/mL) was allowed to escape the fire containment boom and was then contained within a secondary conventional boom (Fingas *et al.*, 1995). Within 30 minutes of the completion of the burn, response crews were on the scene and reported the residue to be in the form of tarry lumps that had already cooled to ambient temperature. The point made here is that surface countermeasures would have a limited time window in which to operate.

Figure 5-1: Cooling Rates of Residue Slicks of Varying Thickness



Water temperature = 15°C
Average initial residue temperature = 180°C

Conventional Skimming

It might be possible to use conventional skimming equipment during the time period that the residue is fluid and buoyant. Given that speed will be of the essence, one could consider using a high capacity weir-type skimmer. Such devices have a proven capability with highly viscous oils (S.L. Ross, 1989). The problem is that, with a highly viscous burn residue, a weir skimmer would likely be relatively inefficient; that is, a large volume of free water would be collected along with the oil. One could consider oleophilic skimmers such as brush- or drum-type devices; however, these generally do not have the recovery rate required to get the job done in the short time available. Whichever type of skimmer used, there would be difficulties with pumping the highly viscous and perhaps semi-solid fluids to storage.

Perhaps the biggest disadvantage with the concept of skimming the residue is that it calls for a substantial logistics effort in the form of a recovery skimmer, temporary storage, and a large vessel to deploy the skimmer and support the operation. This logistics requirement would seem to defeat one of the primary advantages of carrying out an *in situ* burn in the first place: that of requiring a lower level of equipment and logistical support.

Sorbent or Other Manual Recovery

A second option during the time immediately following the burn would be to use sorbents or manual equipment to recover the residue. While the residue is still fluid, it is still adhesive and could be recovered using sorbent products. A good candidate for this would be sorbent snares, a fibrous polypropylene sorbent that has a good capability for highly viscous oils. Snares could be broadcast over the area of residue and recovered manually using rakes or pitchforks. This technique would require the use of small watercraft to allow cleanup workers to reach the water surface. As with the option of skimming, this technique would only be applicable during the short post-burn period when the residue is still buoyant.

Fibrous sorbent snares could also be used to recover residue that is suspended in the water. This technique has been used for recovering viscous oils on and below the water surface as a shoreline protection technique. A series of snares are strung along a cable and anchored in the surf zone to catch tarballs suspended in the water as they approach a shoreline. A similar technique was used in the response to the *Morris J. Berman* spill in Puerto Rico. In that event, strings of snares were positioned in the vicinity of cleanup activities to catch oil that was re-suspended by dredging operations (Michel *et al.*, 1995). In the Berman cleanup, snares were also used by divers to manually clean small pockets of oil remaining after dredging operations and to remove oil from contaminated seagrasses. Although this effort was manually intensive, it was used because it was judged to cause the least physical harm to the seagrass.

Sorbent snares are commercially available in various forms, including an "oilsnare boom", in which snares are positioned along rope or cable, and an "oilsnare wall," in which snares are suspended from a wooden or steel frame to form a barrier to intercept suspended or submerged oil.

Netting Systems

The use of fine mesh nets has been developed as commercially available boom for the recovery of highly viscous oils (Morris *et al.*, 1985; Dowsett and Morris, 1981). With the Jackson Trawl net boom, a mesh netting material with a pore size of about 1 mm is configured as a boom of 1 m total height. Stiffeners are located along the boom to maintain it in an upright position, with foam buoyancy chambers attached to the stiffeners to position the boom at the waterline. Tests of the boom have proved its capability to contain oil with a viscosity of 10,000 mPa·s (milliPasqual seconds) or greater. The primary advantage of using a net boom in this application is that the boom is very compact and light weight relative to conventional boom, which would allow it to be easily deployed and retrieved by small watercraft. Unfortunately, the concept of using fine-mesh nets to quickly sweep residue from the water surface is fundamentally flawed in the sense that, during the period that the residue is buoyant and available for "capture" on the water surface, its viscosity would be less than the 10,000 mPa·s. This is regarded as the lower limit for effective netting.

The use of nets may be feasible if used to collect oil as it cools, becomes more viscous, and starts to sink. It may be feasible to use nets independent of the containment boom used for the burning operation, although it is likely that residue would be lost due to difficulties in locating residue once it had sunk. It would likely be more effective to use a netting system in conjunction with the fire- resistant boom used to contain the burning oil. The netting could be suspended or at least tethered from the fire-resistant boom, in a manner similar to that used by the Norwegian Oil Trawl system. With that boom, which is a conventional containment boom (i.e., non-fire resistant), a net is attached to the bottom of the boom and extends (beneath the water surface) across the apex of the contained area. (In this application, the purpose of the net is to reduce the water current at the apex of the boom and thus allow containment at greater current speeds, rather than to collect sinking oil or burn residue.) As most existing fire-resistant booms have minimal reserve buoyancy, it would be necessary to provide additional buoyancy to the netting system to counteract the added weight of the sunken residue that would be collected.

Section 6
CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. Using the results of simple, small burning experiments, correlations were developed to predict burn residue densities for specific oils. When the correlations were applied to more than 100 international crude oils, the results indicated that about half would tend to float, and the other half would tend to sink in sea water once the residue cools to ambient temperatures. The predictions were based on the assumption that the results of the laboratory-scale burn experiments are scalable to large burns in the field. Only further research with large-scale burns can determine whether this assumption is valid.

2. The results of a preliminary laboratory study and the analysis of operational considerations indicate that no simple method exists for controlling the density of the residue formed after an ISB operation.

3. Immediately following an *in situ* burn it may be possible to use skimmers or sorbents to recover the residue, but there will be only a limited time available—a maximum of 30 minutes—during which surface countermeasures would be applicable. Fine mesh nets might be used to collect residue as it cools, becomes more viscous, and starts to sink. Suspending a net to the bottom of the fire-containment boom, such that it extends across the apex of the burn area, might allow the capture of burn residues if and when they sink.

RECOMMENDATIONS

1. Large-scale *in situ* burn tests should be conducted to determine whether the correlations developed in this study to predict residue density have validity.
2. A prototype of the netting concept for capturing sinking burn residues should be constructed and subjected to tank testing to confirm its viability for residue containment and to document its effect on boom performance.

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APPENDIX A:
OTHER ATTEMPTED CORRELATIONS FOR RESIDUE DENSITY

Figure A-1. Densities: Residue vs. 1049F Plus

5 cm Thickness

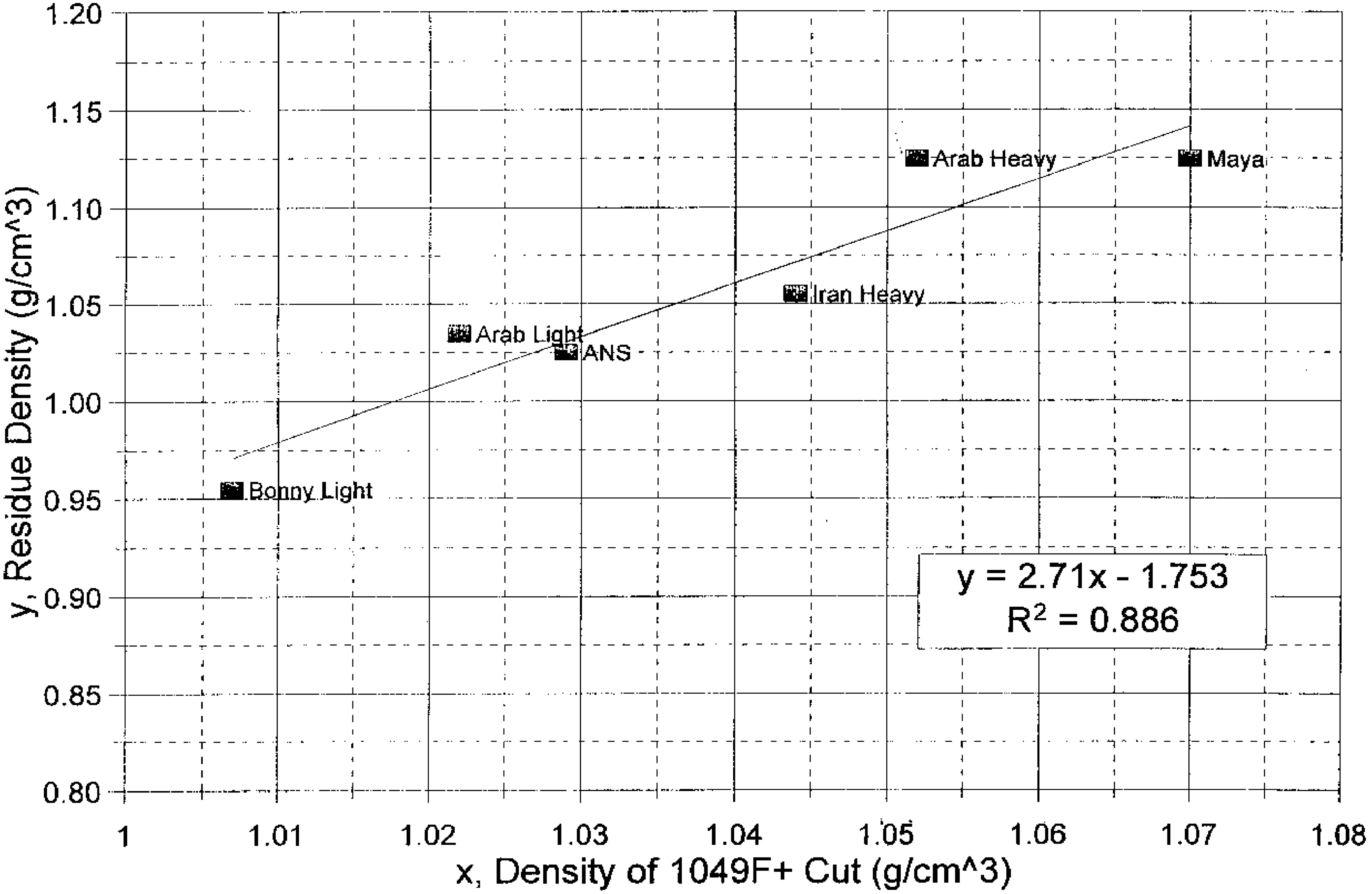


Figure A-2. Densities: Residue vs. 1049F Plus
10 cm Thickness

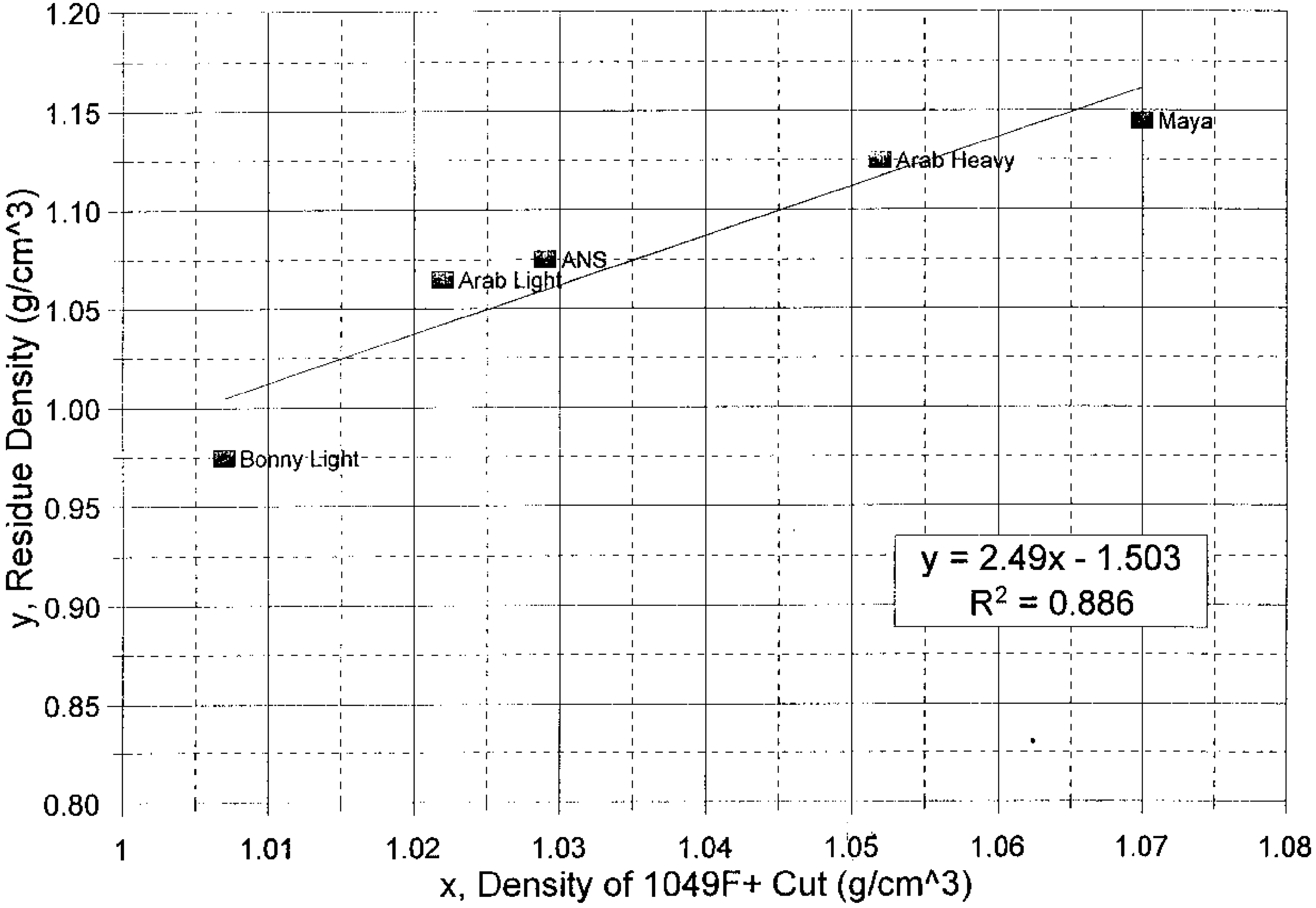


Figure A-3. Densities: Residue vs. 1049F Plus
15 cm Thickness

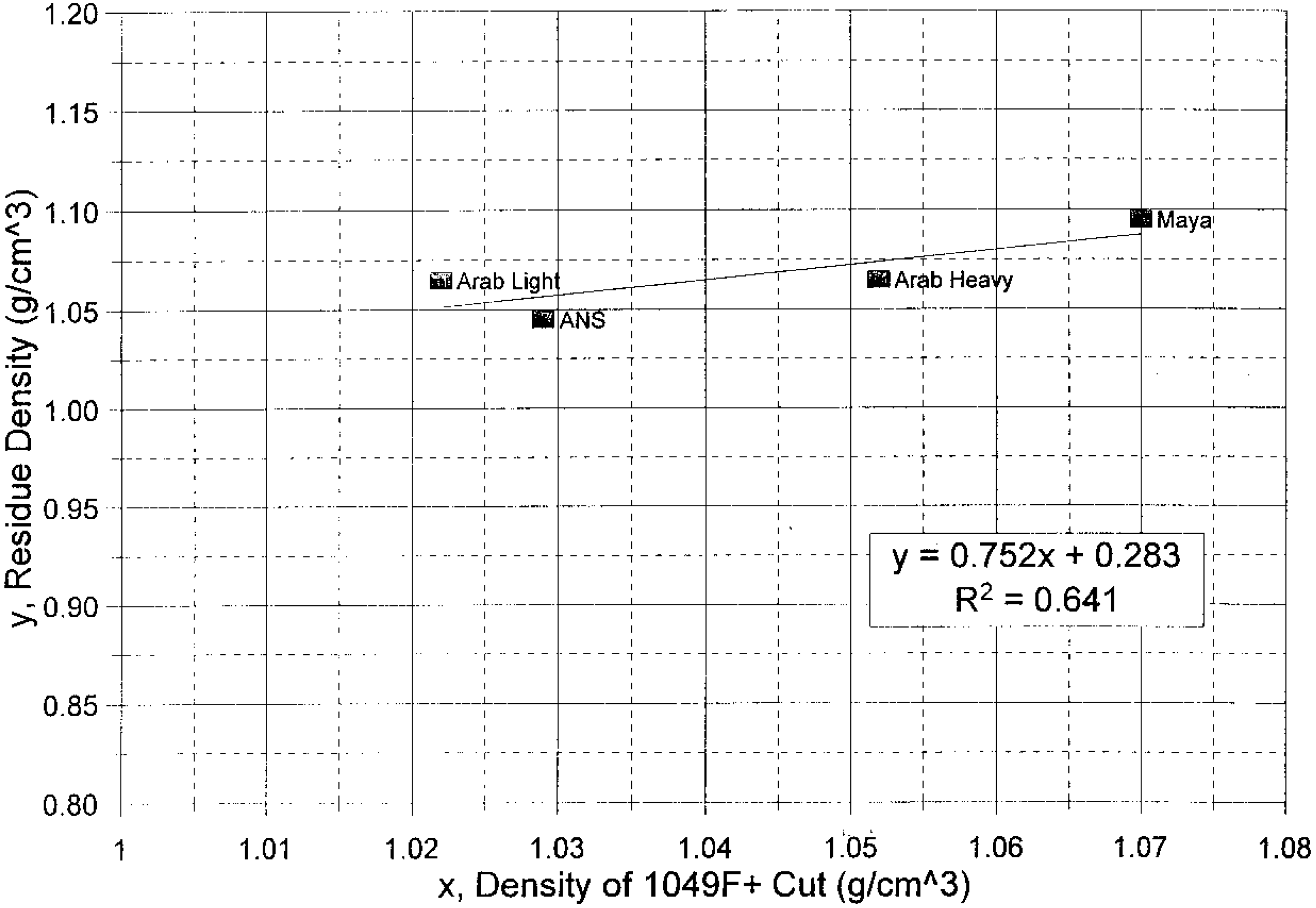


Figure A-4. Residue Density vs. Asphaltenes

5 cm Thickness

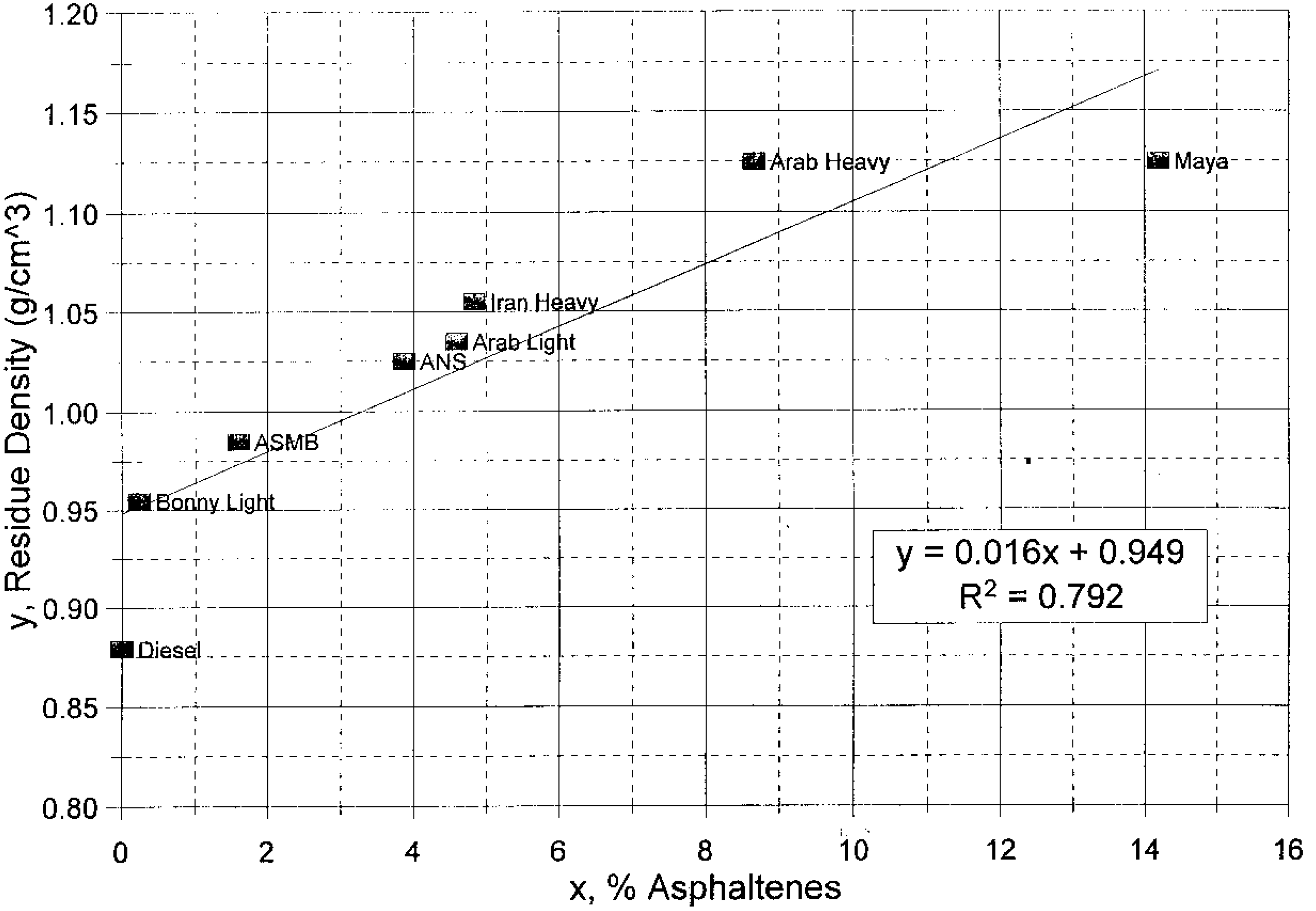


Figure A-5. Residue Density vs. Asphaltenes
10cm Thickness

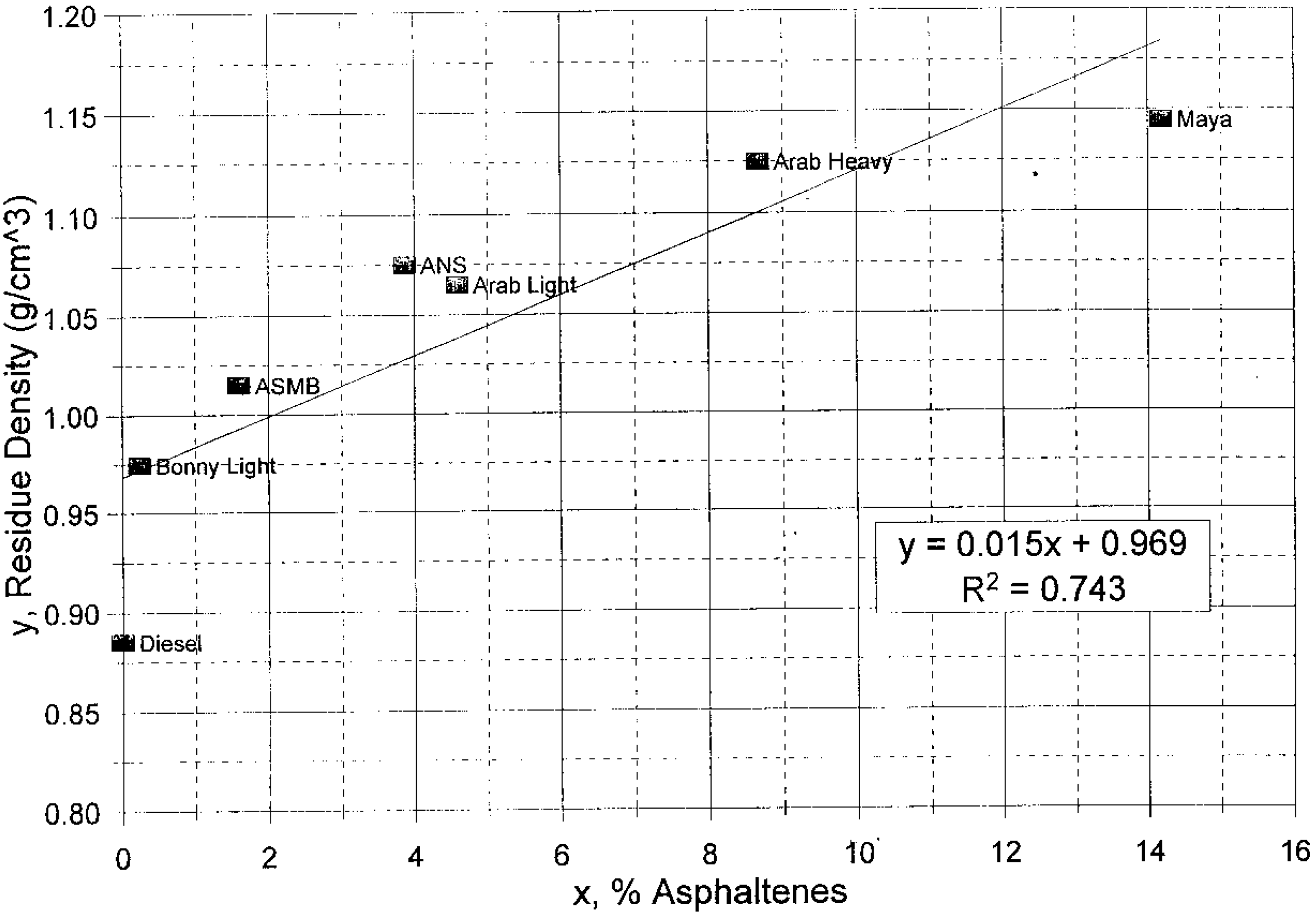


Figure A-6. Residue Density vs. Asphaltenes

15 cm Thickness

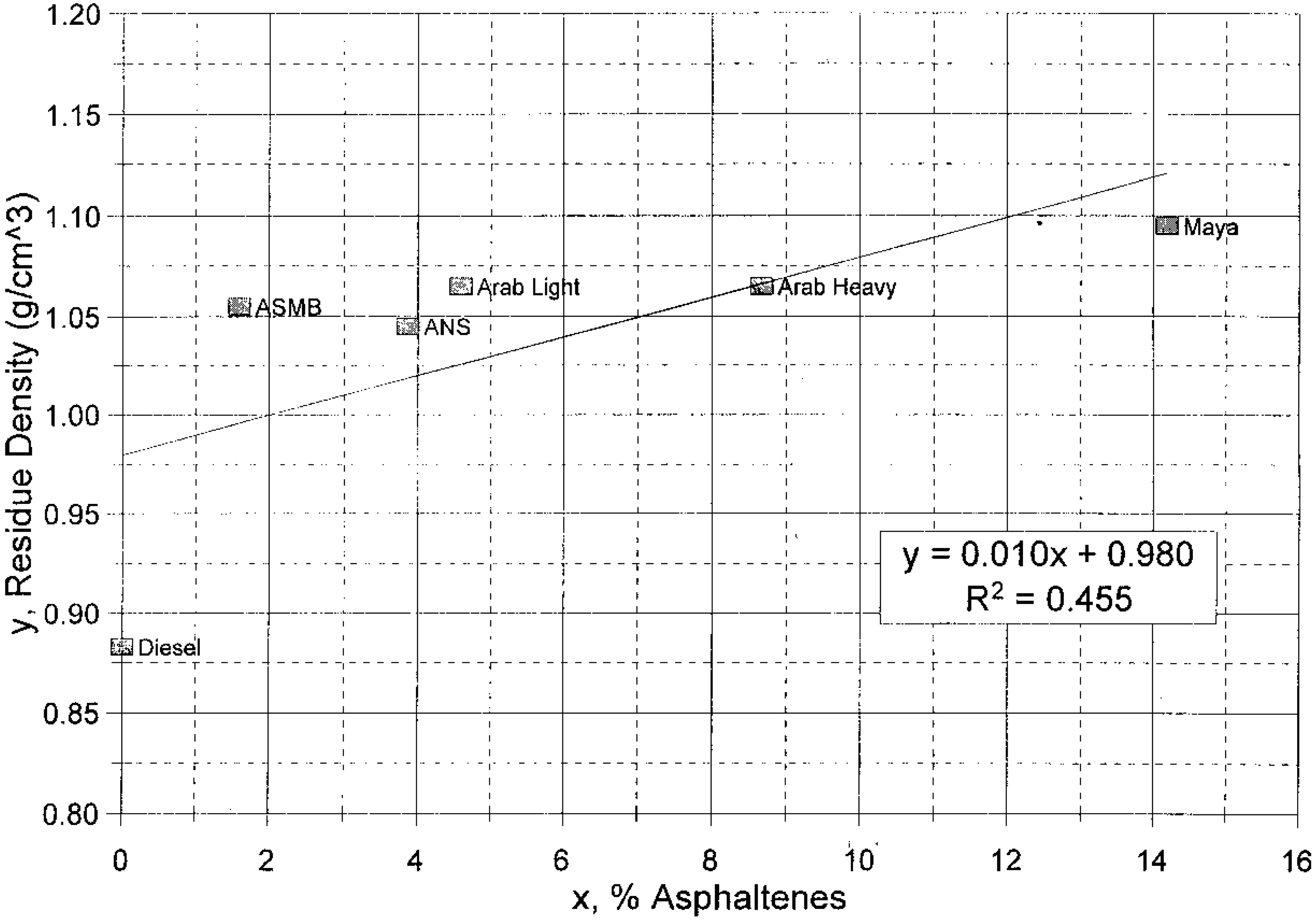
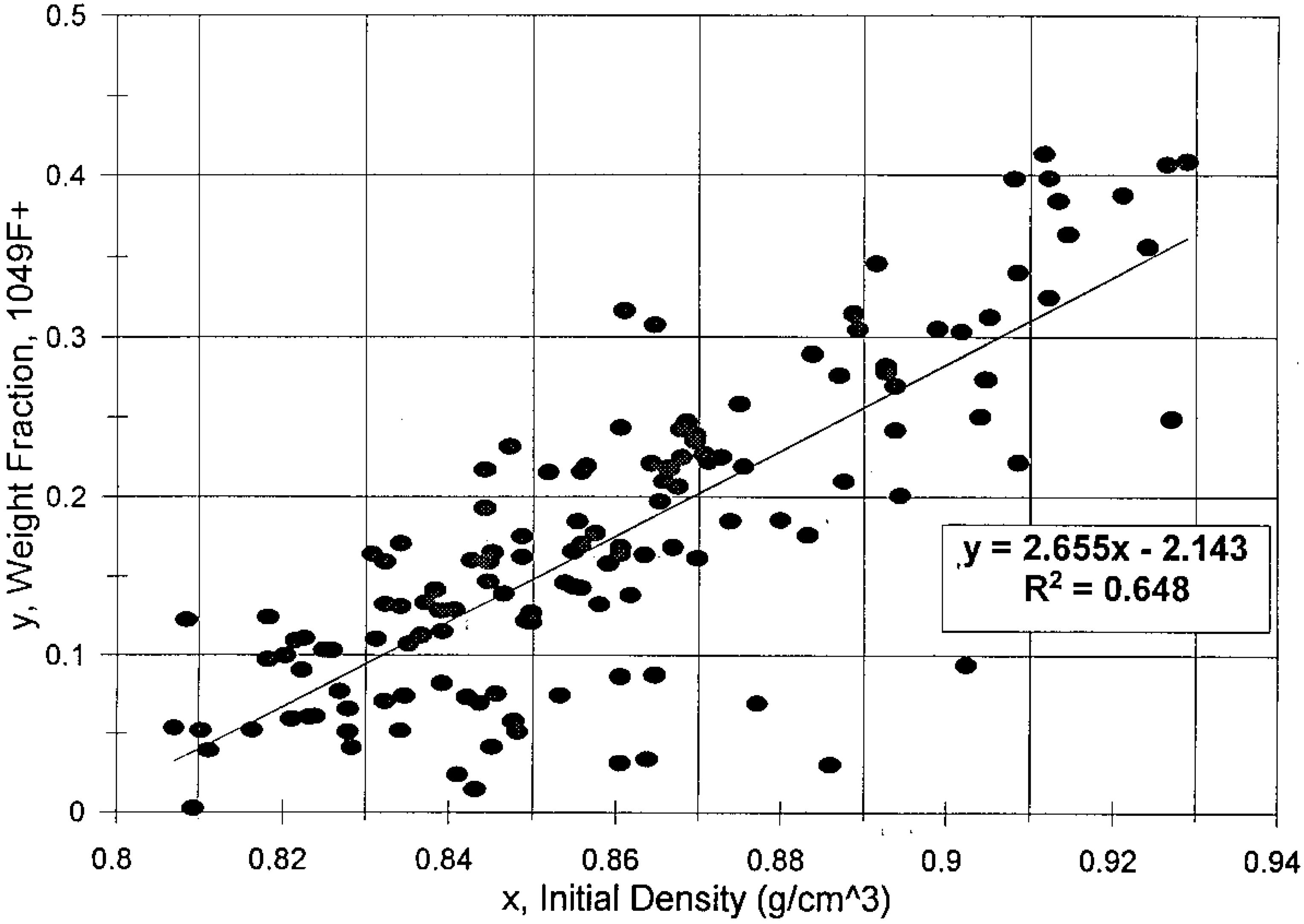


Figure A-7. Wt. Fraction 1049F+ vs. Initial Oil Density



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