

NOAA Technical Memorandum NOS OR&R 6

Leaking Tank Experiments with OrimulsionTM and Canola Oil



Seattle, Washington

United States Department of Commerce Donald E. Evans Secretary National Oceanic and Atmospheric Administration Conrad C. Lautenbacher, Jr. Under Secretary for Oceans and Atmosphere National Ocean Service Margaret A. Davidson (Acting) Assistant Administrator for Ocean Services and Coastal Zone Management

Office of Response and Restoration NOAA Ocean Service National Oceanic and Atmospheric Administration U.S. Department of Commerce

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Debra Simecek-Beatty William J. Lehr Jeffrey F. Lankford

Hazardous Materials Response Division Office of Response and Restoration NOAA Ocean Service National Oceanic and Atmospheric Administration Seattle, Washington Hazardous Materials Response Division Office of Response and Restoration NOAA Ocean Service National Oceanic and Atmospheric Administration U.S. Department of Commerce Silver Spring, Maryland

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Abstract

During oil spill incidents involving damaged tankers, the amount of product released may be uncertain. Many accidents occur under adverse conditions so that determining the volume lost by sounding the tanks may not be practical. Thus, in the first few hours, initial volume estimates are often based on visual observations of the resulting slick, a notoriously unreliable approach. This problem is further complicated by oils that have special characteristics, such as Group V oils and Orimulsion[™], which could result in a surface slick. The National Oceanic and Atmospheric Administration (NOAA) has developed a leaking-tank module for its oil weathering software, ADIOS2. Because the present version of the model is not designed for heavy oils, NOAA is undertaking a series of model-scale tests using releases of Orimulsion and canola oil. These tests are part of a joint research program by NOAA and the U.S. Coast Guard Research and Development Center on the behavior of heavy oil products. This report describes these tests and their possible application to new spill release models

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Table of Contents

1.0 Introduction		1	
2.0	Experimental Design 2.1 Scale Analysis	3 3	
	2.2 Discharge Coefficients	5	
3.0	Experiments with Punctures above the Waterline	9	
	3.2 Orimsulsion [™] Oil	9	
4.0	Experiments with Punctures below the Waterline	10	
	 4.1 Canola Oil 4.2 Orimsulsion[™] Oil 	12 13	
5.0	Conclusions	27	
Ref	erences	28	
Figu	ures		
1	Diagram of small plexiglass tank used in the experiments	7	
2	Canola oil height, Zo, versus time for two experiments with similar initial conditions		
3.	Orimulsion height, Zo, versus time for three experiments with similar initial conditions		
4	Dimensions of weir	11	
5	Diagram illustrating the flow through system	11	
6	Canola oil height and ingested water level height inside the tank versus time for two experiments with similar initial conditions12		
7	Experiments S4 and S5 sample water content taken at 1 cm from the bottom of the tank1 ϵ		
8	Experiments S4, S5 and S6 sample water content taken at 2 cm from the bottom	17	
9	Experiments S5 and S6 sample water content taken at 3 cm from the bottom	18	
10	Experiments S5 and S6 sample water content taken at 4 cm from the bottom	19	

Figures, cont.

Orimulsion and saltwater level heights inside the tank versus time	20
Experiment F7 sample water content taken at 2 cm from the bottom	21
Experiment F7, F8, and F9 sample water content taken at 8 cm from the bottom	22
Experiment F7, F8, and F9 sample water content taken at 15 cm from the bottom	23
Experiment F8 and F9 sample water content taken at 20 cm from the bottom	24
Experiment F8 and F9 sample water content taken at 25 cm from the bottom	25
Freshwater experiment water levels inside the tank at 25, 20, and 15 cm	26
Liquid (Orimulsion and water) and the freshwater level inside the tank	27
	Orimulsion and saltwater level heights inside the tank versus time Experiment F7 sample water content taken at 2 cm from the bottom Experiment F7, F8, and F9 sample water content taken at 8 cm from the bottom Experiment F7, F8, and F9 sample water content taken at 15 cm from the bottom Experiment F8 and F9 sample water content taken at 20 cm from the bottom Experiment F8 and F9 sample water content taken at 20 cm from the bottom Experiment F8 and F9 sample water content taken at 25 cm from the bottom Freshwater experiment water levels inside the tank at 25, 20, and 15 cm Liquid (Orimulsion and water) and the freshwater level inside the tank

Tables

1	Physical properties of liquids at 15 to 20°C	5
2	Summary of Orimulsion experiments with puncture below waterline	15

1.0 Introduction

During an emergency, responders often have difficulties estimating the amount of oil leaking from a punctured tanker or barge. Adverse conditions (e.g., stormy weather, vessel instability) can significantly hamper the responders' ability to make measurements. When direct oil-loss measurements, such as tank soundings, are unavailable, volume estimates are often made from visual observations of the slick, a notoriously unreliable approach. A simple computer model that calculates leak rates would help the responder estimate the volume loss from a punctured tank.

Contingency planners, as well as emergency responders, are interested in leak rates from punctured tankers. Spill scenarios used in contingency planning are typically based on historical data and the knowledge and experience of the planners. However, most planners have very little experience with vessel salvage and are not familiar with estimating leak rates from punctured tankers. As an example, the Northwest Area Contingency Plan's worse case scenario is an instantaneous release of more than 500,000 barrels of Alaska North Slope crude oil. In reality, some amount of time will pass before all of the oil drains from the tanker.

Clearly, planners and responders need a tool to help estimate realistic release scenarios. In response to this need, NOAA developed a simple model that estimates the amount of product spilled from a punctured tank and the leak rate based on easily obtainable information. The leaking tank model is included as a module within the oil weathering model, ADIOS2. Unfortunately, ADIOS2 doesn't consider releases of petroleum products with unusual characteristics like OrimulsionTM.

Orimulsion 400 is the trade name for a petroleum product used as an alternative fuel for electric power plants. The product contains approximately 70% bitumen (from the Orinoco field in Venezuela), 30% water, and 0.2% surfactant (Guenette et al., 1998). It has a density of 1.0095 g/ml and a viscosity at 445 cSt at 15°C (Jokuty et al., 1999c). The surfactant is used to keep the bitumen droplets dispersed in the water to form a stable emulsion. Because of its unique characteristics, Orimulsion tends to behave differently when poured onto water. Either the Orimulsion or the resulting bitumen particles may be buoyant, neutrally buoyant, or denser than the surrounding water (Battelle, 1999; Jokuty et al., 1999a). In view of this behavior, it is likely that Orimulsion releases from punctured tankers will behave differently than releases of crude oils.

To develop a mathematical model for an Orimulsion release from a vented, leaking tanker, two types of releases were considered: those with the hole above the waterline and those from a hole below the waterline. If the release occurs under steady state conditions, the oil loss calculations are straightforward for most crude and refined products, including Orimulsion for holes above the waterline. Release estimates become more complicated for punctures below the waterline, even for typical oils. The hydrostatic pressure will determine if and when water flows into the tank and when oil flows out of the tank. When hydrostatic pressure is balanced, flow stops and, depending on the buoyancy of the oil, the tank may have a layer of water at the bottom or a water layer on top of the oil. If the spill occurs with quiescent surroundings, then a sharp oil and water interface is present inside the tank. The unique characteristics for Orimulsion suggest that releases of this product could be even more complex. Rather than observing a delineation between the oil and water as seen for a typical oil product, the bitumen particles in the Orimulsion may separate and disperse into the water flowing into the tank.

A literature review on leaking tank models revealed numerous papers describing formulas for calculating discharges of non-volatile liquids from tanks (Burgreen, 1960; Elder and Sommerfeld, 1974; Dodge and Bowles, 1982; Koehler, 1984; Shoaei and Sommerfeld, 1989; Hart and Sommerfeld, 1993; Lee and Sommerfeld, 1994; Simecek-Beatty et al, 1997; Fthenakis and Rohatgi, 1999). The search also identified software used by engineers for ship salvage operations that calculates the amount of product lost from a particular vessel (NAVSEA, 1999). In addition, hypothetical formulas can be used to determine the maximum allowable outflow for a tank breached at any location under specific conditions, as described in the International Convention for the Prevention of Pollution from Ships and its 1978 Protocol. These formulas are meant to prevent oil pollution during normal operating procedures and accidents. Further efforts have expanded formulas and tables to include other vessel designs (NRC, 1991). However, hypothetical formulas designed for limited conditions are not commonly used by area contingency planners when considering worst- case scenarios or by responders in an actual emergency. It is not known whether any of these formulas or models can accurately describe the release of petroleum products with unique characteristics like Orimulsion. Observational data would be needed to test existing models, and probably modify them in the case of Orimulsion.

The purpose of this project was to provide quantitative information on the behavior of an Orimulsion spill from a punctured tank. Ship design and movement, while important for oil release calculations, were not considered in this project. To both evaluate and improve the experiment design, tests were first undertaken with a fairly innocuous product, Canola oil. Based on these initial tests, a series of nine small-scale laboratory experiments were conducted to study Orimulsion releases from tanks with holes above and below the waterline. Spills below the waterline were conducted using fresh-and salt water. For each experiment, the oil levels and water levels within the tank were measured during the release. The levels were then plotted over time to determine the leak rate.

2.0 Experimental Design

There were two primary objectives of the laboratory experiments. The first objective was to obtain laboratory data to test existing leaking tank models, specifically one incorporated into ADIOS2. The second objective was to increase our understanding of the behavior of Orimulsion inside a tank punctured below the waterline. Very early in the project, we recognized that full-scale experiments were not feasible. If we were to use tanks much smaller than those in ships, it would be important to verify that the experimental cargo properties, in this case Orimulsion, and release conditions were similar to spills from much larger vessels.

In the event of a punctured tank, a variety of factors will determine the oil outflow. The most important factors are the oil density, initial oil level, the tank and hole dimensions, and the location of the hole relative to the waterline. However, there are other factors that can affect the discharge, some of which are subtle. Their significance depends on the specific conditions of the tank. As an example, many vessels carrying petroleum products have a fixed piping system to blow inert gas into the cargo tanks (ISGOTT, 1996)¹. Not only does this render the tank atmosphere non-flammable but it also adds a slight pressure head to the cargo that may increase oil outflow (Dodge and Bowles, 1982). Tankers typically have vacuum relief-valves on each cargo tank to admit air when the tank is gravity-draining. The valve prevents the tank from cavitating during a a very large discharge. If the valve is inoperable, the discharge can be slowed significantly as air is ingested into the tank from the discharge drain. Further, water levels outside the tank can fluctuate, increasing or decreasing the release rate.

Finally, accidents can cause other complications. Vessel instability can create freesurface waves inside the tanks, causing pressure fluctuations, particularly if the hole is exposed to the sea. The up and down movement inside the tank would result in a fluctuating gravity drain. These factors are important considerations for estimating loss. However, it is extremely difficult to scale these conditions so that smaller, experimental releases in the laboratory are applicable to much larger releases. For this reason, the experiment was simplified to consider a small, stationary, vented tank.

2.1 Scale Analysis

Since we used tanks much smaller than those in ships, it is important to verify that the experimental cargo properties and release conditions are similar to spills from much larger vessels. This requires both geometric and dynamic similarity between the prototype (full-scale tank) and the model (small tank in laboratory). To achieve geometric similarity, a model tank was built at 1/16 scale with the dimension of 60 cm x 30 cm x 30 cm. Serendipitously, this also allowed us to compare some of the experimental data with previous work by Dodge et. al., (1980).

The primary forces that will likely influence a release from a punctured, vented tank are gravitational, inertial, and viscous forces. If the ratios of these forces are similar in both the prototype and the model, then the flow can be considered dynamically similar. The non-dimensional parameters useful for scaling these forces in fluid flows are the Froude

¹ Orimulsion is not normally shipped with the tanks inerted (Garcia Tavel, 2001).

number (inertial force/gravity force) and Reynolds number (inertial force/viscous force). The Froude number, Fr, relates the inertial term to the gravity term:

$$F_r = \frac{v}{\sqrt{gl}} \sum_p = \frac{v}{\sqrt{gl}} \sum_m$$
(1)

v is the outflow velocity, g is the acceleration due to gravity, l is the oil level, and the subscripts *p* and *m* refer respectively to the prototype and model. Because velocity in both the prototype and the model is only due to gravitational head, then equation (1) is trivially satisfied.

The Reynolds number, Re, can be related to the density of the fluid, ρ , flow velocity, v, hole diameter, *d*, and dynamic viscosity, μ , through the simple relationship

$$\operatorname{Re} = \frac{\rho v d}{\mu} = \frac{\rho v d}{\mu}$$
(2)

where the subscripts *p* and *m* refer respectively to the prototype and model. For laboratory experiments, v and d in the model would be smaller than an actual catastrophic spill release from the prototype. To achieve a similar Re for both the prototype and the model, a dramatic change in the physical properties of the oil would be required. The viscosity in the lab experiments must be less than the high viscosity expected for typical heavy oils to maintain (or at least approximate) dynamic similitude. The fluid chosen to represent heavy oil in the model releases had to meet certain criteria: it must be considerably less viscous than a low-gravity oil (< 20 API) and positively buoyant in both fresh- and salt water. An added benefit would be if the product was relatively innocuous in the laboratory environment with inexpensive purchase and waste disposal costs. Based on these criteria, canola oil was proposed for the model releases.

The viscosity of canola oil is 70 centipoise (0.07 $kg m^{-1} s^{-1}$) and the kinematic viscosity is 77 cSt, and the density is 910 $\frac{kg}{m^3}$ (Table 1). The initial outflow velocity of the fluid in the prototype, v_p , and the model, v_m were calculated from Bernoulli's equation for an inviscid fluid

$$\mathbf{v} = \sqrt{2g(Z - Z_h)} \tag{3}$$

For the model, the initial oil level, Z was at 0.5 m and the height of the hole bottom, Z_h , was set to 0.04 m. Since the model was built at 1/16 scale, Z for the prototype was assumed 8 m and Z_h was 0.64 m. The initial velocities for the model and prototype were $3.0 \frac{m}{s}$ and $12.0 \frac{m}{s}$, respectively. Using Equation (2), the kinematic viscosity can be calculated for the prototype (full-scale) oil based on a modeled canola oil release.

(4)
$$\frac{\mu_p}{\rho_p} = \frac{v_p d_p \mu_m}{\rho_m v_m d_m} = \frac{(12.0 \ m \ s^{-1})(1 \ m)(0.07 \ kg \ m^{-1} \ s^{-1})}{(910 \ kg \ m^{-3})(1/16 \ m)(3.0 \ m \ s^{-1})} = 0.005 \ m^2 \ s^{-1} = 5000 \ cSt$$

The kinematic viscosity of the oil in the prototype converted from the model oil is $0.005 \ m^2 \ s^{-1}$ (5,000 cSt at 15°C). This analysis suggests that canola releases (above the outside water level) from the model would simulate petroleum products released from the prototype with the same order of magnitude viscosities as heavy oils such as Boscan crude, Bunker C, and California heavy (NOAA, 2001). Based on this reasoning, we performed a set of leaking tank experiments using canola oil, a moderately viscous product. Unfortunately, canola oil's density is considerably different than fresh water, a situation not true for heavy crude or synthetic oils such as Orimulsion. Also, the prototype viscosity is an order of magnitude greater than fresh Orimulsion.

		Dynamic	Kinematic	
Liquid	Density $\left(\frac{kg}{m^3}\right)$	Viscosity (cP)	Viscosity (cSt)	
Water	998	1.00	1.00	
40% water-60% glycerine	1157	8.63	7.5	
Hydraulic oil	878	64.90	74	
Canola oil	910	70	77	
Orimulsion	1009	450	446	

Table 1. Physical properties of liquids at 15 to 20°C.

Source: Modified from Dodge et al. (1980), Allen and Nelson (1983), Lide (1991) and Jokuty et al. (1999c).

The unique characteristics of Orimulsion, bitumen suspended in water with a surfactant, are dramatically different when compared to canola oil. Therefore, it was also necessary to conduct a set of experiments with Orimulsion. This allowed us to study leakage and water ingestion rates when the relative density forces were small, as would be expected in the release of a heavy oil. Moreover, Orimulsion rapidly disperses into water, a phenomenon not found with traditional oil products, and we wished to examine how this factor would affect flow and water ingestion behavior. Regrettably, this property of Orimulsion greatly complicated the experimental procedures, as discussed elsewhere.

2.2 Discharge Coefficients

Dodge et al. (1980) conducted a series of tests to determine discharge coefficients, C_d , for different types of punctures and fluids for a range of Reynolds numbers (1275 to 96,000). The fluids used in the Dodge tests were water, a glycerine mixture, and hydraulic oil (Table 1). The study concluded that a discharge coefficient of 0.65 should be

adequate from most punctures. Based on this work, the ADIOS2 leaking tank model defaults to a fixed value of 0.65 for the discharge coefficient of the puncture.

Tests were conducted with an open 60 cm x 30 cm x 30 cm rectangular acrylic tank. The walls of the tank were 1.27 cm (0.6 in) thick. A circular hole with a diameter of 2.2 cm was drilled into the wall of the tank approximately 4.0 cm from the tank bottom. Nicks and bumps in the hole wall were gently smoothed with a fine file. This same tank was used in subsequent experiments.

To determine whether the default value in ADIOS2 was similar to that of the experimental tank, the discharge coefficient, C_d , for the tank puncture in the laboratory experiments for Orimulsion and canola oil were calculated by using Torricelli's equation:

$$C_d = \frac{A_t}{A_h t} \frac{\sqrt{2gZ_o} - \sqrt{2gZ_f}}{g}$$
(4)

where

tank area, $0.18m^2$ A, = = hole area, 3.8 $10^{-4}m^2$ A_h Z_0 initial oil level, 0.5 m Z_{f} final oil level, 0.062 m = t total discharge time = gravity, 9.8 $\frac{m}{s^2}$ g =

The total discharge time for the canola oil was 110 s and for the Orimulsion, 90 s. The test results indicated that the discharge coefficient, C_d , for canola oil was 0.45 and Orimulsion, 0.48. These values are slightly smaller than the default C_d in ADIOS2 and those used by Dodge et al. (1980). Previous experimental work for releases from a circular orifice in the side of a large tank have shown a relationship between the C_d and the Re (Rouse, 1978). This data set indicates that a low C_d of 0.4 would be expected for a low Re (on the order of 10).

To calculate the R_e , the initial outflow velocities, v, were first calculated for both canola oil and Orimulsion. The velocity of the flow, v, out of the tank was calculated by modifying equation (2) to include the calculated drag coefficients for real fluids,

$$\mathbf{v} = C_d \sqrt{2g(Z - Z_h)} \tag{5}$$

with Z the initial oil level in the tank, 0.5 m, and, Z_h , the height of the bottom of the hole, 0.04 m. The Reynolds number, R_e was calculated

$$R_e = \frac{\rho v d}{\mu} \tag{6}$$

6

with *d*, hole diameter at 0.022 m and μ , liquid dynamic viscosity. The maximum Reynolds number for the canola oil releases was 388 and the Orimulsion, 71. These values are significantly smaller than those found in the Dodge et al. (1980) tests, 1275 to 96,000. The differences in the R_e values are likely attributed to differences in liquid viscosities. Recall that Dodge et al. (1980) calculated Re using water, a glycerine mixture, and hydraulic fluid, which are less viscous than Orimulsion and canola oil (Table 1). Finally, the relatively thick tank walls (compared to the hole diameter) might cause a small decrease in C_d .

3.0 Experiments with Puncture above the Waterline

For releases with a puncture above the waterline, the experiment setup was similar for both the canola oil and Orimulsion releases. The tank was constructed of clear acrylic to enhance visual observations of the flow. A rectangular acrylic tank with the dimensions of 60 cm x 30 cm x 30 cm was used to simulate spills. The circular hole, 2.2 cm in diameter, was drilled into the center of the 1.27 cm (0.5 in)-acrylic wall at 4.0 cm above the bottom of the tank. Time was measured with a stopwatch to within an accuracy of 1 sec. For the canola releases, a metric ruler (resolution of 1 mm) was adhered to the side of the tank and used to measure the oil level inside the tank. This worked very well due to the transparency of the tank and the canola oil.

The Orimulsion releases proved to be more difficult. As the Orimulsion drained, a thin layer of black oil coated the sides of the tank, making visual observations of the oil level through the clear acrylic impossible. As an alternative way to measure the Orimulsion height in the tank, a small foam float was attached to a 1 m x 4.7 mm acrylic rod. The acrylic rod was supported by a 1 m x 9.5 mm (inner diameter) acrylic tube. A metric ruler (resolution of 1 mm) was attached to the side of the acrylic tube.



Figure 1. Diagram of small plexiglass tank used in the experiments.

The displacement of the oil by the acrylic rod and foam float was minimal and well within the measurement error.

3.1 Canola Oil

The canola oil was purchased from a local grocery retailer in 5-gallon plastic containers. Samples of oil were taken before each experiment and the density measured. The density measurements were made using an Anton Paar DMA35 with a nominal error of $\pm 1 \times 10^{-3}$ (published in the brochure). However, actual measurement errors using 20 samples of distilled water suggest errors of ± 0.015 . The average canola oil density was 0.92 g/ml. This experiment was repeated two times under similar conditions. The initial oil level in the tank for the first experiment was 504 mm and the second, 494 mm, with the tank dimensions remaining the same for both releases. The discharge was started by releasing a plastic stop-cork from the puncture. When the cork was released, the height of the oil decreased over time (Figure 2), as expected.



Figure 2. Canola oil height, Zo, versus time for two experiments with similar initial conditions.

Near the end of the experiments, it was difficult to determine when the tank actually stopped draining. When the liquid was near the bottom of the hole, the flow was intermittent and mainly consisted of droplets. However, most of the outflow stopped at about 110 seconds.

3.2 Orimulsion

Two steel, 55-gallon drums of Orimulsion were provided to NOAA by Bitor America Corporation. Special care was taken in handling and storing the Orimulsion so that the emulsion would be preserved (Jokuty et al., 1999b). The drums were stored in a heated room in which the temperature was maintained at 20°C. A Morse Portable Drum Rotator model 201 continuously mixed of the Orimulsion. The rotator is designed to lay the drum in a horizontal position and rotate on the longitudinal axis at 10 to 30 rpm. For this experiment a rotation speed of 10 rpm was chosen. Each drum was rotated for 2-4 hours on alternating days. Before a planned release, the drum was rotated for about 4-6 hours before the experiment. Product from the drum was discharged into 5-gallon plastic buckets and immediately used in the laboratory experiments. No visible variation in the properties of the Orimulsion extracted from the tank was observed during sequential experiments.

Samples of oil were taken before each experiment and the density was measured. The Orimulsion had a typical density of 1.005 g/ml at 18°C with an error of ± 0.015 . Jokuty et al. (1999a) indicates that Orimulsion has a density of 1.0095 g/ml, a value within the measurement error. The viscosity was not measured, however, Jokuty et al. (1999a) reports Orimulsion has a viscosity of 445 cSt at 15°C .

Experiments with the hole above the waterline were repeated three times using the same tank as the canola oil releases. The initial oil level in the tank was 580 mm for all three releases. When the stop-cork was pulled, the oil level and the float dropped. The height and time were recorded during the release. The experimental results are shown in Figure 3.



Figure 3. Orimulsion height, Zo, versus time for three experiments with similar initial conditions.

When the Orimulsion was near the bottom of the hole, the flow was intermittent and mainly consisted of droplets. However, most of the outflow stopped at about 90 seconds, which is slightly faster than the canola oil outflow. This was not unexpected as the Orimulsion is denser than canola oil and effects due to viscosity differences were minimal.

4.0 Experiments with Punctures below the Waterline

Orimulsion releases from a hole below the outside waterline present a special challenge in a closed system. The bitumen/Orimulsion released from the tank will accumulate in the outside storage tank originally holding pure water. This could affect the leak rate. The additional pressure contributed by floating bitumen could be minimized by placing the tank inside a much larger, secondary tank so that the oil layer would be very thin and the pressure contribution negligible. However, there is an additional problem with elevated oil concentrations in the secondary tank.

When spilled, the loss of the surfactant in Orimulsion depends on the salinity and temperature of the surrounding water as well as the dilution rate. Guenette and Sergy (1999) reviewed the literature for Orimulsion releases and found that, if the Orimulsion concentration in the resulting oil/water mixture is greater than 20,000 ppm, the mixture would remain as an emulsion. If the concentrations dropped below 10,000 ppm, the bitumen particles are dispersed into the water. Presumably, this reflects the fact that the surfactant and stabilizer concentrations in the Orimulsion no longer remain at effective levels. Accumulations of Orimulsion within the water column would probably increase the hole pressure outside of the tank and possibly shorten the release time.

To simulate open-water conditions and prevent Orimulsion concentrations from increasing within a secondary tank, a weir made of clear acrylic was built (Figure 4). The tank dimensions had to meet two criteria: 1) the distance between the model tank and the wall of the weir should be sufficiently large so that flow at the hole was not disturbed by turbulence generated by the wall of the weir, and 2) the amount of water and oil waste generated would be minimized. Using these criteria, acrylic was used to create a weir with a 70 cm x 70 cm base. Three of the walls were 50 cm and the fourth wall, the weir, was 30 cm. The tank used in the previous experiments was placed inside of the weir tank.



Figure 4. Dimensions of weir.

The weir made it possible to maintain a constant, relatively undisturbed, 30-cm water level through the system while allowing floating oil to slip over the top of the weir and into a waste drum (Figure 5). Oil concentrations within the weir were monitored. If elevated levels were observed, some flow would be allowed through several holes in the bottom of the weir.



Figure 5. Diagram illustrating the flow through system.

Five to seven 50-gallon drums were filled with tap water before each experiment. The water was slowly transported by electric pumps into the weir at an average rate of about 360 mL/s to maintain a constant flow through the weir system for each experiment. Additional 55-gallon drums were placed at the bottom of the weir to capture the oil/water waste. The oil/water mixture flowed over the weir and dropped into a waste drum. For the Orimulsion experiments, two small holes at the bottom of

the weir increased the amount of bitumen drained from the bottom of the weir. Over the duration of the experiment, the oil/water waste was pumped into additional steel drums. This worked very well for the canola oil experiments but, as discussed later, pumping the Orimulsion waste was not feasible.

4.1 Canola Oil

Preliminary tests conducted by Simecek-Beatty et al. (1997) showed that visual observations of the canola oil inside a clear, acrylic tank was possible due to the translucent nature of the product. Since it was possible to observe a sharp, oil-water line inside the tank as water was ingested, the oil and water levels were measured during the experiment using a metric ruler attached to the side of the tank. A similar setup was used for the release with the hole above the waterline. Because canola oil behaves in a similar manner in fresh- and saltwater, the experiments were limited to fresh water.

Releases with the hole below the waterline were repeated two times using the same tank and hole previously described. The initial oil levels in the tank were 533 mm and 534 mm, respectively. The results from experiments are combined and presented in Figure 6.



Figure 6. Canola oil height and ingested water level height inside the tank versus time for two experiments with similar initial conditions.

As expected, when the cork was pulled from the hole, the oil height quickly dropped to 310 mm in the first hundred seconds and then remained constant. Water was ingested into the tank starting at about 100 seconds and continued until approximately 1,000 seconds, finally stopping when the hole was completely covered by water on both sides.

4.2 Orimulsion

Water ingestion experiments proved challenging when using Orimulsion. As the Orimulsion drained, a thin layer of black oil coated the sides of the tank. Unlike canola oil, Orimulsion diffuses into water, which means that it is impossible to define a sharp, oil-water line inside the tank as water is ingested. Also, a small amount of Orimulsion diluted into water can turn the water completely opaque. This meant that the visual measurement methods used in the canola oil experiments to measure the water level inside the tank as a function of time would not be possible in the Orimulsion releases. An alternative approach was applied.

For each experiment, a standard model Drummond Scientific Pipet Aid was used to extract oil/water samples at different elevations inside the tank at varying time intervals. The Pipet-Aid is an electrically powered, pipetting device capable of dispensing 1 to 150 mL volume of liquid. A two-step approach was applied to ensure the samples were consistently collected from the same location and elevation. The first step required that 6-mm, inner-diameter glass tubes were precut to a specified length. Each tube length represented the depth (measured from the bottom of the tank) at which the sample was to be taken. An additional 10 cm was added so that the pipet aid could be attached to the glass tubes.

The second step required a coarse wire mesh to be placed over the top of the tank to ensure that samples were taken from the same location. Laboratory technicians lowered the precut glass tubes, attached to a pipet aid, into a preassigned "square" in the wire mesh. The four sample locations corresponded to the four corners of the tank. To provide an additional indicator to the depth the glass rods were to be lowered into the tank, bright blue tape was wrapped around the glass tubes. The tubes were lowered into the tank until the lower edge of the tape touched the wire mesh.

The resulting samples were placed into 10 mL tubes and centrifuged at a rate of 1,800 rpm for 8 to 10 minutes, effectively separating the bitumen from the water. After the samples were centrifuged, an oil/water interface between the oil product and water was clearly visible. A micrometer was used to measure the heights of the oil and water. Samples of fresh Orimulsion centrifuged for the same time interval showed only a slight breaking of the emulsion. This consisted of a thin water layer overlaying the oil and represented less than 0.12 water fraction in the sample.

Large errors were expected from this sampling approach. Cutting glass rods to exact lengths was difficult. As the glass tube was inserted into the wire mesh, the technician attempted to hold the pipet and tube perpendicular to the tank bottom. This would ensure that the sample was drawn from the specified depth. However, it was difficult to hold the tubes steady during the experiment. The tubes were inserted into the wire mesh until the bottom edge of the blue tape touched the wire mesh. Occasionally, samples were taken with the tape slightly above and below the mesh. Measuring oil and water levels in the 10-mL tubes with a micrometer introduced additional errors. Finally, the water measured in the tubes included both water that had flowed into the tank and the water used to create the Orimulsion product. Nonetheless, this technique did provide an approximate time history of the concentration of bitumen and water inside the tank.

During the freshwater experiments, four to five 55-gallon drums were pre-filled with tap water and slowly pumped through the weir. Water temperatures ranged from 15.7 to 20.6°C. For the saltwater ingestion experiments, synthetic salt (Instant Ocean) was mixed with tap water in the same drums to obtain the desired salinity of 2.6%. These drums were continuously mixed. During these experiments, the water temperatures ranged from 19.6 to 20.2°C with density measurements ranging from 1.018 to 1.019.

Both the freshwater and saltwater experiments were similar in that the release was started by a technician reaching into the the secondary tank and removing the cork from the oil tank. Occasionally, the technician had difficulty removing the cork and additional turbulence was generated in the weir. This turbulence affected the water levels and influenced the oil outflow and water inflow. While not easily measurable, the additional turbulence is partially responsible for the "noise" apparent in the data set.

For each experiment, the tank was filled with fresh Orimulsion to a height of 530 mm. Once the cork was removed, the stopwatch was started. To monitor the fluid level inside the tank, the level of the float was noted every 10 mm and the time recorded. Samples from each of the four locations in the tank were taken every few minutes. In many instances, samples taken at the same depth for different experiments were taken by different technicians. This could also result in slight variations in the data collection.

The depths for each experiment, measured from the bottom of the tank, are shown in Table 2. As the oil and water flowed over the weir, our original intent was to use a metal hand pump to move the fluid into additional storage drums. Unfortunately, the hand pump quickly became inoperable due to bitumen clingage. To ensure that the waste drum at the base of the weir did not overflow, 2.5-gallon buckets were used to move product. This was a very time-consuming process and, in some instances, resulted in a reduction in the flow over the weir to prevent the storage drums from overflowing. Bitumen particles did not appear to aggregate inside and over the weir. However, aggregation was noted in the storage drums. After an experiment was completed, the oil in the tank was removed and the secondary tank was drained and cleaned. This was particularly important for the Orimulsion releases as clingage of the bitumen particles to the hole and the sides of the tanks could affect measurements in the subsequent experiments.

Table 2. Summary of Orimulsion experiments with puncture below waterline.

Experiment ID	Water Type	Sample Depth* (cm)
S4	salt	1, 2, 5
S5	salt	1,2,3,4
S6	salt	2,3,4,7,8
F7	fresh	2,8,15,25
F8	fresh	8,15,20,25
F9	fresh	8,15,20

*measured from the bottom of the tank.

Oil concentrations in the weir for five of the six experiments (S5 to F9) were measured by periodically siphoning samples from the center of the weir. As previously described, these samples were placed in plastic tubes and centrifuged. A micrometer was used to measure the heights of the bitumen and water in the plastic tubes. Based on these measurements, the oil-to-water concentrations in the weir ranged from 20 ppt to 60 ppt. These values are slightly above the cutoff proposed by Guenette and Sergy (1999) of 10,000 ppm for the bitumen to act as independent particles and not as an emulsion.

Graphs of the samples taken at different depths provided an effective time history of the concentration of bitumen and water inside the tank. Water fraction samples for the saltwater experiments, taken at the same depths, were combined and plotted against time. When the samples containing a fraction of saltwater were centrifuged, water could be clearly seen at the bottom of the 10 mL tube with an Orimulsion/bitumen layer on top. The thin water layer observed on the surface of fresh, centrifuged Orimulsion was not observed in the saltwater experiments.

Figure 7 shows the combined data collected at 1 cm for two releases, S4 and S5. While the data set is noisy (attributed to factors discussed earlier), the trend from the two experiments are similar in that no water is observed in the samples till about 250 to 400 seconds into the release. The water fraction increases with time, becoming greater than 75% water² at approximately 600 to 800 seconds.



Figure 7. Experiments S4 and S5 sample water content taken at 1 cm from the bottom of the tank.

² Pure Orimulsion is approximately 30% water.

For three of the saltwater experiments (S4, S5, and S6), samples were taken at 2 cm. These data are plotted in Figure 8. In general, between 500 to 1000 s, water was present in the samples. After 1,000 s, a few of the samples did not contain water. This is attributed to errors in the sampling technique of the kind previously mentioned. The fraction of water in the samples continues to increase and level off at about 1200 to 1750 s.



Time (s)

Figure 8. Experiments S4, S5 and S6 sample water content taken at 2 cm from the bottom.

Samples were taken 3 cm off the bottom of the tank for two experiments, S5, and S6 (Figure 9). While the data from the two experiments do not entirely overlap, the general trend appears to be similar. The water fraction was present in the S5 samples at 1,000 s with the water fraction increasing till 2,000 s. In the S6 experiment, water first appears in the samples at about 1,800 s and increases to greater than 0.75 at about 3,000 s.



Figure 9. Experiments S5 and S6 sample water content taken at 3 cm from the bottom.

During two experiments (S5 and S6), samples were taken at a depth of 4 cm (Figure 10). This height corresponded with the height of the hole bottom. After the first experiment (S5), graphed data showed that water first appeared in the samples around 1,000 s and continued to increase till 2,500 s. At this point, no more samples were taken for this experiment. Unfortunately, the water fraction was less than 0.75, suggesting that water was still flowing into the tank at the 4-cm level. For the next experiment (S6), sampling continued over a longer period to about 4,000 s. Analysis of the samples showed that the water fraction in the samples remained greater than 0.75 after 2,000 s.



Figure 10. Experiments S5 and S6 sample water content taken at 4 cm from the bottom.

Samples taken at 5, 7 and 8 cm in experiments S4 and S6 did not contain a measurable water fraction and were therefore not graphed. Experiment S4 ran for 2,126 s and S6, 5,103 s. Based on the canola experiments, we had theorized that the Orimulsion release would continue until the water level inside the tank reached the top of the hole at 6.2 cm. The lack of water in the 5-cm samples suggests that the experiment did not continue for the appropriate duration, in this instance; it only ran for 2,126 s. There could also have been an error in the sampling procedure. For the samples taken at 7 and 8 cm, there was no measurable water fraction, which is consistent with both the results of S5 and theoretical expectations.

The data from the saltwater releases, including the oil level measurements, are summarized in Figure 11. The oil heights are the actual measurements from the salt water experiments. The water levels at a particular time were visually estimated from Figures 7 to 10. This is the time when water first appeared in the samples. The error in the measurement is also shown. For the three experiments, it took approximately 1,500 s for the water level inside the tank to reach the bottom of the hole. Recall that in the canola oil experiments, shown in Figure 6, the water levels reached the same level in about 1,000 s. Shorter releases for the canola experiments would be expected as the density difference between the product and the saltwater is greater than that between Orimulsion and saltwater.



Figure 11. Orimulsion and saltwater level heights inside the tank versus time.

For the freshwater experiments, samples taken at the same depths inside the tank were combined and plotted against time. In general, the same experimental procedure described previously was followed for all three releases, F7, F8, and F9. Unfortunately, there were some problems during F8. Several minutes into the experiment, water flow over the weir was not constant and the water level outside the tank dropped several centimeters. Eventually, the water level was increased with water flowing over the weir. This problem did affect the experiment outcome, as shown later.

Figure 12 shows a graph of the data collected during one experiment, F7, with samples taken at 2 cm above the bottom of the tank. For this type of release, water was not expected to be in the tank at levels below the bottom height of the hole, 4 cm, because the bitumen was heavier than fresh water. Although water was observed in the 2-cm samples and measurable, the water fraction remained below 0.12. This is comparable to values noted when fresh Orimulsion was centrifuged.



Figure 12. Experiment F7 sample water content taken at 2 cm from the bottom.

Figure 13 shows the graph of the data collected for three of the freshwater experiments, F7, F8, and F9 for samples taken at 8 cm. We had hypothesized that the Orimulsion above the bottom of the hole would flow out of the tank and water would fill the tank from the bottom of the hole to a height comparable to the outside water level. Therefore, we theorized the water would be inside the tank at 8 cm. For the first 4,000 s into the releases, the water fraction was expected to be not measurable but, in reality, it was about 0.12. After 4,000 s, the water fraction increased slightly but remained below 0.25. This suggests that the water did flow into the tank but at a very slow rate and, perhaps, the experiments should have been run for a longer time (greater than 7,219 s). It is also apparent that the water fraction is slightly higher for experiment F8 and could be attributed to problems discussed earlier. Finally, previous studies have indicated that the surfactant used in Orimulsion does not denature as fast in fresh water as in salt water. Because the Orimulsion concentrations inside the tank exceeded the 20,000 ppm cutoff suggested by Guenette and Sergy (1999), the fresh water ingested may have simply mixed at that level with the existing Orimulsion and remained as an emulsion.



Figure 13. Experiment F7, F8, and F9 sample water content taken at 8 cm from the bottom.

For three of the experiments, F7, F8, and F9, samples were collected at 15 cm from the bottom of the tank (Figure 14). There is an obvious difference in the F8 data set and the data from F7 and F9. Again, the discrepancy is attributed to difficulties maintaining water levels in the weir for F8. If the F8 data are ignored, then it would appear that water content in the samples were minimal (~ 0.12) and did not steadily increase until after 2,500 s. Water fractions remained below 0.25 through out the experiments. Once more, this suggests the experiments were cut too soon and should have been extended beyond 7,219 s.



Figure 14. Experiment F7, F8, and F9 sample water content taken at 15 cm from the bottom.

In two experiments, F8 and F9, samples were collected at 20 cm (Figure 15). A noticeable difference is apparent between the F8 and F9 data. If the F8 data are ignored, the water appears in the F9 samples at approximately 3,000 s. The water fraction continues to increase and level off at 6,000 s.



Figure 15. Experiment F8 and F9 sample water content taken at 20 cm from the bottom.

Water samples were taken for two experiments, F8 and F9, at 25 cm (Figure 16). The F8 data set shows a higher water fraction in the samples (~0.5) almost immediately into the release. As previously discussed this is likely a result of water flow problems in the weir. The F9 data indicate that the water fraction slowly increases almost immediately. It continues to increase to 2,000 s with a water fraction of about 0.6. We suspect that the water level had not yet passed the 25-cm level inside the tank. If the experiment had been run for a longer period (greater than 7,219 s), the water content would have leveled off at 0.75. There is also a possibility of error in the sampling procedure.



Figure 16. Experiment F8 and F9 sample water content taken at 25 cm from the bottom.

The freshwater experiments were more problematic. The surfactant was not expected to degrade as in the seawater experiments and the dilution of the Orimulsion with fresh water could be insufficient to break down the emulsion (Guenette and Sergy, 1999). There would also be a tendency of the ingested fresh water to mix with the Orimulsion inside the tank rather than form a concentrated layer at the top. This meant that the data would likely be extremely noisy, particularly for measurements that were some distance from the hole, allowing greater mixing of the ingested water and the Orimulsion. By visually observing the samples that had the best signal and selectively graphing them for three heights, 25, 20, and 15 cm, the water level inside the tank as it changed over time becomes apparent (Figure 17). In the first hundred seconds of the release, water first appears in the samples taken at 25 cm. After a much longer period (approximately 3,000 s), water is seen in the 20-cm samples. Finally, water starts to appear in the 15 cm samples at about 6,000 s into the release.



Figure 17. Freshwater experiment water levels inside the tank at 25, 20, and 15 cm.

The data from the freshwater releases, including the oil and water level measurements, are summarized in Figure 18. The liquid level heights in Figure 18 include both the Orimulsion that initially flowed out of the tank in the first 60 s of the release and the water layer that formed over time. The time when water first appeared in the samples taken at 25, 20, and 15 cm is also plotted on the graph. The error in the measurement is also shown. Liquid below these heights is assumed to be pure Orimulsion. This assumption is based on the samples collected at the 8 cm level where no water was observed for the duration of the experiments.





5.0 Conclusions

Our primary objective in this study was to collect laboratory data of Orimulsion releases. In the future, this data will be useful for evaluating and refining the leaking tank model used in ADIOS2 (NOAA, 2001). The Orimulsion study increased our understanding of the product's behavior if spilled from a punctured tanker in salt water environments. Based on scale analysis, a model tank was built at 1/16 scale. A series of tests indicated that the Reynolds numbers in the tank were small in the model and for the prototype, and indicated the flow was relatively laminar. In addition, it was determined that canola oil released from the model would represent releases from the

prototype of a much heavier oil product. Unfortunately, the unique characteristics of Orimulsion required the use of the product for the small-scale experiments.

A series of experiments was conducted for two types of oil products, canola oil and Orimulsion, for releases above and below the waterline. In the Orimulsion experiments, releases were conducted into both salt water and fresh water. In the experiments involving the tank holed above the waterline, the Orimulsion drained faster than the canola oil under the same initial conditions. This was expected as Orimulsion is denser than canola oil.

For releases below the waterline and into salt water, the drainage times were again slightly different between the Orimulsion and canola oil releases. The Orimulsion discharges took longer than the canola oil. This was due to the density differences between the product and the saltwater: the density difference was less between the Orimulsion and saltwater than between canola oil and saltwater.

For the Orimulsion releases into the fresh water, there were problems with the data collection, particularly for one experiment. In this instance, the problems were attributed to experimental procedure errors. The use of a sonic device to measure the surface and oil/water interface heights would probably have minimized these errors. In addition, the surfactant in the Orimulsion was not expected to break down as readily in fresh water as in the salt water. This is thought to contribute to the noise in the data set. Finally, the experiments were ended before the release had stopped due to waste management issues. The freshwater experiments ran considerably longer than the saltwater as the density difference between the bitumen and the fresh water was slight.

It is interesting to note that previous benchtop and flume experiments have reported heavy viscous "slicks" or patties of coalesced bitumen particles floating on the surface (Battelle, 1999; Jokuty et al., 1999a). However, we did not observe such phenomena. The particles appeared to be distributed in the water column with some of the bitumen adhering to the sides and bottom of the flow through system and weir. In neither the saltwater nor freshwater releases was there marked difference in the appearance of the Orimulsion inside the tank. Coalescence was not observed in either the fresh-or saltwater releases inside the weir system. Since the turbulence in the weir was minimal, the opportunity for collisions between the particles was significantly reduced.

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