

# **Extending Temporary Storage Capacity with Emulsion Breakers**

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## **Abstract**

The objective this study was to further the understanding of the use of emulsion breakers injected into an oil spill recovery system at both lab-scale (at SL Ross) and mid-scale (at Ohmsett). The experiments were designed to assess the injection/mixing/settling regimes required for optimum water-removal performance from a meso-stable water-in-oil emulsion with an oil spill demulsifier. Various injection locations (skimmer head, cargo line, tank inlet, etc.) and mixing technologies (static in-line, mechanical, etc.) were investigated.

The scaled laboratory tests involved pumping water-in-oil emulsion and free water through a piping loop consisting of ½-inch copper and plastic tubing of various lengths, an in-line mixer and eight settling tanks. Three different types of pumps were used. Demulsifier was injected at various locations, and the fluid was decanted and measured to determine the efficiency of emulsion breaking achieved.

At Ohmsett, a Desmi Terminator skimmer was used to recover the same emulsion from the water surface, using different slick thicknesses, wave heights and recovery rates. A static in-line mixer was used for some tests, and in others a bladed impeller was used to add extra mixing energy to the recovered fluids. Demulsifier was injected into the recovered fluid at various locations. The recovered fluid was allowed to separate in the recovery tanks and measured to determine the demulsifier efficiency.

The use of a demulsifier injected into a recovery system, combined with decanting, did substantially reduce the volume of water in the recovery tanks and the water content of the remaining emulsion. The efficacy of the demulsifier was a strong function of free water content: if the free water content exceeded about 60%, the effect of the surfactant was substantially reduced. If no free water was present, the level of turbulence generated by the flow was insufficient to promote emulsion breaking. A free water content of greater than about 33% was required to reduce the bulk viscosity of the fluid to the point where the flow regime was turbulent, and mixing energy was supplied to promote emulsion breaking.

The degree of emulsion breaking achieved increased with increasing mixing energy applied to the fluid. Increasing the flow rate (and hence turbulence level) and increasing the length of the flow path both resulted in enhanced emulsion breaking. The use of in-line mixers further increased the removal of emulsion water. The application of mechanical mixing energy, using a bladed impeller, after placing the recovered fluid in a recovery tank, also increased demulsification.

## **1 Introduction**

The preferred approach to cleaning up an oil spill is to contain and thicken the oil slick(s) with booms and then place skimmers in the oil or emulsion to recover it. The recovered fluids are placed in temporary storage containers for transfer to larger storage vessels or for direct input into the waste recycling and disposal system. A large amount of water, both in the form of water contained in emulsified oil and free water, is often recovered by skimmers operating in waves. In some cases, the transfer pump built into the skimming system can impart enough energy to cause additional emulsification of the recovered fluids. The problem is that the recovered water (both emulsified and free) dramatically reduces the temporary storage space available at the site of skimming operations; this can result in having to stop skimming prematurely when the storage capacity is reached and having to wait until empty temporary storage containers arrive at the response site. The treatment and separation of recovered water onsite is the largest area of neglected technology in mechanical response today (Schulze 1995).

Lab-scale and preliminary mid-scale tests were recently completed that give some quantitative insight into the oil/water separation processes occurring in temporary storage devices (SL Ross 1998 and 1999). The objective of those tests was to determine the optimum time to decant the water and maximize the available on-site storage space during a skimming operation. The results indicated that "primary break" (the initial separation of the recovered fluid into a layer containing most of the oil and a layer containing most of the free water) occurred within a few minutes to one hour, depending on the physical characteristics of the oil. Rapidly decanting this free water layer, in appropriate situations, may offer immediate increases of up to 200 to 300% in available temporary storage space.

One aspect of decanting not addressed in these earlier research studies was that many skimmer operations are, sooner or later, faced with recovering a water-in-oil emulsion. These emulsions can easily contain 70 to 80% water that is tightly held and may not separate out, even after standing for days or months. This emulsion will quickly fill the available temporary storage space, even after decanting of the free water layer, with a product that contains mostly water.

In order to facilitate and optimize open ocean containment and recovery operations, the available temporary storage space could be further extended by using chemical emulsion breakers (also called demulsifiers) to cause the water-in-oil emulsion to break into oil and water phases, followed by decanting of the water separated from the emulsion. Although some skimmer systems (notably the Framo Transrec 350) incorporate chemical emulsion breaker delivery systems, the dynamics of the separation process are not well understood.

Preliminary research into the concept performed in the early-1990s (SL Ross 1991, SL Ross et al. 1992, Lewis et al. 1995a and 1995b) gives some guidance on the concentrations of demulsifier required for rapid breaking and the importance of mixing energy to the process; however, these preliminary studies were not pursued further.

The research idea here was to conduct additional studies on the use of emulsion breakers injected into a recovery system at both lab-scale (at SL Ross) and mid-scale (at Ohmsett). Experiments were developed based on the lessons learned from the previous research and the early tasks of this project. They were designed to

assess the effectiveness of an oil spill emulsion breaker on water-in-oil emulsions and the injection/mixing/settling regimes required for optimum water-removal performance. The ability of emulsion breaker addition to reduce pumping heads was also assessed. Various injection locations (skimmer head, cargo line, tank inlet, etc.) and mixing technologies (static in-line, mechanical, etc.) were investigated.

## **2 Summary of Lab-scale Tests**

This section describes the laboratory test apparatus and results. The tests were conducted at the SL Ross Laboratory in Ottawa, ON.

### **2.1 Laboratory Test Set-up Design Basis**

The Reynolds number was used to scale the laboratory system, since the level of mixing in the system is important to the demulsification process, and much of an offshore recovery system involves flow in pumps and hoses. For the Reynolds number to be the same for different hose diameters, with the same fluid properties, it can be shown that:

$$Q_1/D_1 = Q_2/D_2 \quad (1)$$

This simply states that the ratio of the flow rate and diameter of the model system are directly proportional to the ratio of the flow rate and diameter of the full-scale system.

### **2.2 Laboratory Test Methods**

The lab-scale test system schematic is given in Figure 1. It was designed to mimic the pumping, mixing and flow processes that occur in an offshore oil recovery system. The system was based, in part, on lessons learned in the preliminary demulsifier tests carried out by SINTEF (Lewis et al. 1995b). Working from the right to left on Figure 1, pre-mixed 50% water emulsion and nominally 50% free water were pumped separately, at measured, pre-determined rates, to the suction of the test pump being used (either a gear pump, a diaphragm pump or a progressing cavity pump). The flow rate, pressure and temperature were measured at the pump outlet and just before discharge into the receiving tanks. The fluid was directed either through, or to bypass, a static in-line mixer, down different lengths of plastic tubing (nominally with total lengths - copper + plastic - of 2 m, 3 m, 5 m and 11 m of ½"-ID tubing and 11 m of ½" / ⅜"-ID tubing) and then to eight receiving tanks where samples were taken at different intervals to characterize the separation of the aqueous phase, the dehydration of the emulsion and the oil content of the decanted water. Demulsifier was injected, at a target dosage of approximately 1:500 (demulsifier:fluid), into the system, using a chemical metering pump, either before the main pump, after the main pump or just before discharge into the recovery tanks. Full details of the various components in the laboratory test loop are contained in the report (SL Ross 2002).

Considerable effort was put into finding an appropriate test oil for both scales of testing (see SL Ross 2002 for full details). The necessary characteristics of this test oil were:

1. good property stability and consistency (little variability in batches and little change in physical or chemical properties on exposure to the atmosphere) in order to minimize experimental variability;

2. high tendency to form at least meso-stable emulsions (as defined by Fingas et al. 1998) that do not lose appreciable amounts of water over time periods of a day;
3. relatively difficult to break with a resulting large range of dehydration, when treated with commercially-available oil spill demulsifier(s); and,
4. easy to procure/prepare and mix with salt water using simple large-volume emulsion-forming techniques (i.e., gear pumps).

After a series of emulsion formation and demulsifier efficiency tests (after Hokstad et al. 1993) with a variety of standard Ohmsett test oils and various additives, it was determined that Hydrocal 300 with either 2.5% or 5% Bunker C by volume was an appropriate parent oil for the test emulsions. Alcopol O 70% PG, a 70% solution of sodium diisooctyl sulfosuccinate in propylene glycol/water, was chosen as the best demulsifier during the same tests.

### **2.2.1 Test Procedures**

Full details of the test procedures are given in the report. A batch of emulsion was mixed for each test and pumped through the system along with nominally 50% free water. In some cases no free water was added. The liquid was discharged sequentially into eight settling tanks which were filled to either 2.5 or 5 L and the fill time for each was recorded. Separated water was then decanted from the recovery tanks into graduated pitchers after defined settling times (2, 5, 10, 15, 30, 45 and 60 minutes). Thirty mL samples of decanted water were taken from tanks 1, 5 and 7 for oil content analysis. The oily liquid remaining in the settling tanks was then stirred with a spatula and 20 mL was withdrawn for water content analysis.

### **2.2.2 Emulsion Sample Analysis**

The emulsion samples in 30 mL glass vials withdrawn from each tank were treated with a few drops of Alcopol O emulsion breaker, shaken vigorously, then placed in a constant temperature bath at 70°C for at least 24 hours to separate. The vials were then removed from the bath, wiped and the heights of water and oil in the vials measured with a steel rule. The water content of the emulsion remaining after decanting could then be estimated. It turned out that the demulsifier could not completely resolve the emulsion, even with heating. This was probably because the parent oil in the emulsion did not contain a significant amount of aromatics which are needed to receive the asphaltenes displaced from the oil/water interface. Without an aromatic fraction, a portion of the asphaltenes remained at the oil/water interface to stabilize some droplets. As well, the selected parent oil (Hydrocal is a de-aromatized lube stock oil) and the emulsion preparation technique (gear pump mixing) were intentionally chosen to not break too easily, in order to allow trends in the effects of test variables on emulsion breaking efficiency to be discerned from the results. Little could be learned about the effects of the test variables if the emulsion breaker perfectly resolved every emulsion.

As such, the percentage of the emulsified water removed for the lab-scale tests was calculated as the volume of water decanted from a tank less the calculated volume of free water added to that tank all divided by the volume of water in the emulsion in the tank. This method of calculating emulsion breaking efficiency gave more consistent and reasonable results than trying to use the flawed emulsion

dehydration data. The accuracy of the mass balance technique was less than a good emulsion dehydration analysis would have been. The measurement error in decanted water volumes was 50 mL, using the graduated pitchers, and the error in accurately filling the tanks during a test was on the order of 5 mm, or about 100 mL. Thus the volumes of water decanted could be in error by as much as 150 mL. Emulsified water removal efficiencies could thus be in error by up to 12% ( $150/[2500 \times 0.5]$ ). Based on the results of the BS&W analysis for the Ohmsett tests (see Section 3.1.3), the error in directly analysing emulsion water content would be on the order of 5%.

Subsequent to the laboratory and Ohmsett tests it was determined that addition of 25% diesel fuel (an oil high in aromatics) to the Hydrocal/Bunker mix produced an emulsion that was completely resolved by the Alcopol O. It is recommended that a standard oil for emulsion testing at Ohmsett be developed.

## **2.3 Laboratory Test Results**

Table 1 summarizes the laboratory test results, grouped by the type of pump tested. The test matrix is reproduced at the left of the table for clarity. Full information on all the laboratory tests, including equipment calibrations, and data interpretation, may be found in the report .

### **2.3.1 Emulsion Breaking**

It was not possible to do the baseline tests (i.e., no demulsifier) with no free water for the test series involving the progressing cavity pump: the pump could not move the emulsion at a reasonable flow rate down even the shortest flow path. The baseline run with free water (#2) resulted in no emulsion breaking. In comparison, the results of Test 4 (done with a parent oil containing 2.5% Bunker) show the effect of injecting demulsifier into the fluid stream just before it was discharged into the tanks for settling. There was no significant difference in emulsion breaking compared to the baseline, except for an increase in the concentration of oil in the decanted water. Injecting the demulsifier just after the pump (Test 5), and allowing it to work on the emulsion while it travelled through the 2-m length of ½”-copper tubing, resulted in some breaking of the emulsion. Increasing the hose length (Tests 7 and 8) further increased the degree of emulsion breaking. Note that Test 7 contained an abnormally low amount of free water (39%). Also, Test 8 involved a 2.5% Bunker parent oil and double the normal dosage of demulsifier, seemingly without affecting the overall emulsion breaking efficiency.

For Test 9 the treated fluid was directed through the 11-m length of ½” / 3/8”-ID tubing. This resulted in a significant increase in the back pressure at the pump, and a corresponding decrease in emulsion flow rate with a commensurate increase in the free water content. The significant reduction in emulsion breaking efficiency for this test (when the increased mixing associated with the smaller-diameter hose would be expected to at least produce the same result), may be due to a critical amount of the demulsifier partitioning into the excess free water rather than mixing and reacting with the emulsion. The next few tests involved directing the flow through the in-line mixer. The emulsion breaking results of Test 10 are significantly better than Test 5; however the results of Test 12 are not as good as those of Test 7 - quite possibly because of the significantly higher free water content in Test 12 (a mixture with 55% free water contains almost twice the volume of water of a mixture that is 39% free

water). The results of Test 13 are about the same as Test 8 and also show a slight improvement with increased hose length compared to Test 12. No emulsion breaking apparently occurred in Test 14, presumably due to the very high free water content of 80%.

The final subset of tests involved injecting the demulsifier before the progressing cavity pump. Comparing the results of Test 20 to Test 10 shows no difference, as does comparing the results of Test 21 to Test 5. This is not surprising as progressing cavity pumps are specifically designed to impart little mixing energy to the fluid. Comparing the results of Test 20 to Test 21 shows that the energy imparted to the fluid by the in-line mixer improves emulsion breaking. The results of Test 22 indicate that increased hose length increases emulsion breaking too. Test 23D was included to determine the effect of reduced Bunker concentration in the parent oil (it involved 2.5% as opposed to the normal 5%); this seemed to allow the demulsifier to be more effective. Test 23C involved a 2.5% bunker parent oil with twice the normal dosage of demulsifier; this resulted in a further improvement in emulsion breaking.

The next set of tests used the gear pump, a type that adds much more mixing energy to the pumped fluid than a progressing cavity pump. Tests 24 and 25 were the baseline runs with and without free water - no emulsion breaking was observed. Tests 26 and 27 were skipped, since the type of pump used upstream would make no difference when injecting the demulsifier just before discharging it into the tanks.

The next subset of tests involved pure emulsion (no free water), injecting demulsifier into the flow stream just after the pump, with the fluid directed through the inline mixer. Note that the absence of free water decreased the overall flow rate (and thus turbulence in the inline mixer) by half and increased the relative dosage of demulsifier. In Test 15 (flow sent straight to discharge) some emulsion breaking was measured (22% of the emulsion water was removed, on average). There was no significant difference noted when the flow was directed down an additional 11 m of ½"-ID tubing. This may be due to the fact that, with no free water present, the flow is laminar, not turbulent.

The next subset involved injecting the demulsifier before the gear pump, without the inline mixer and with and without free water. The 51% emulsion water removal attained for Test 28 (no free water), compared to Test 15 indicates that the intense mixing energy supplied by the gear pump greatly assisted the emulsion-breaking process. Note also that the more effective emulsion breaking reduced the viscosity of the fluid, allowing higher flow rates. Adding free water to the system seemed to reduce the effectiveness of the demulsifier. In Test 29, the free water content was 42% and the measured emulsion water removal averaged 12% (not significantly different from the results of the similar Test 21 with the progressing cavity pump which averaged 14%). For Test 31, despite the increased flow path length, the average emulsion water removal was only 3%; the free water content was 61%. In Test 32, with a path length of 11 m, an average emulsion water removal of 22% was achieved with a free water content of 49%.

The next two tests were conducted with the flow directed through the inline mixer. Test 33 (53% free water) gave an emulsion water removal average of 56%, a significant increase over that achieved with Test 29. The best emulsion water removal for the entire laboratory program was obtained with Test 34 (81%) with the flow from the inline mixer sent through the 11 m test loop. Test 41 and 42 repeated 33 and 34,

with no free water. Increases in emulsion water removal (compared to Tests 28, 15 and 18) were measured. A trend seems to exist of increasing emulsion water removal with increasing amount of mixing energy and length of time that the energy is applied (i.e., flow path length).

The final six tests involved pumping with a double-diaphragm pump, a common type used in the inshore spill response industry. Tests 35 and 36 were the baseline runs, with no demulsifier injected, and no emulsion water removal was detected. The positive values noted for Test 36 were a result of excess free water put into the last two tanks at the end of the test run because the emulsion supply tank was nearly empty. Injection of demulsifier before the pump with no free water resulted in high emulsion water removal, as had been observed with the gear pump (Test 28). In the presence of free water, the emulsion water removal was reduced. It is not clear why, in Test 38, the addition of 41% free water caused a reduction in emulsion water removal from 58% to 46% while in Test 29 the addition of 42% free water with the gear pump caused a drop from 51% to 12%. This may relate to differences in the type of mixing energy imparted by the two pumps.

In the final two tests, the high free water contents (60% and 68%) caused significant decreases in emulsion water removal. The addition of the inline mixer and an increased flow length would otherwise be expected to increase emulsion water removal.

To summarize the emulsified water removal results with the different pumps: there was no significant effect of pump type when the demulsifier was injected after the pump; however, when the demulsifier was injected before the pump, the gear pump, which imparted the most mixing energy to the system, gave the best results, the double diaphragm pump (with a moderate level of mixing) gave the second-best results, and the progressing cavity pump (with little mixing energy imparted to the fluid) resulted in the least amount of emulsified water removal.

### **2.3.2 Oil Concentrations in Decanted Water**

Due to an inadvertent error made in extracting the water samples taken from the three settling tanks, little oil-in-water data of value was collected from the laboratory tests. The available numbers indicate that the initial concentrations of oil in water were on the order of several thousand ppm, and that these declined over a one-hour settling period to levels on the order of hundreds of ppm. Unfortunately, it was not possible to determine if demulsifier addition, mixing energy levels or mixing times had any discernable effect on the oil content of the decanted water.

### **2.3.3 Pressure Drop**

Pressure readings were collected for selected runs, which allowed the calculation of pressure drops. These are given in Table 2. The data are presented in two groups, test runs without the inline mixer, for which a pressure drop per unit length due to internal friction can be calculated, and test runs utilizing the inline mixer, for which pressure drop per unit length cannot be calculated. In the first group, all the tests involved free water, which significantly reduced pressure drop per unit length by reducing the bulk viscosity of the fluid. For the 2 m flow path (with two 90° elbows and one fully-open ball valve) the calculated pressure drop for water flowing at 32 L/min (8.5 gpm) would be 1.5 kPa/m (0.7 psi/ft), only slightly less than that

measured. For the 11 m path length the calculated pressure drop for water flowing at 21 L/min (5.5 gpm) would be 0.6 kPa/m (0.3 psi/ft) - very close to that measured.

The much higher pressures associated with the in-line mixer are apparent. Comparing the pressure data from Tests 33 and 10 to the first 4, the inline mixer adds about 140 kPa (20 psi) of back pressure to the system; for water, the theoretical back pressure would be 120 kPa (17 psi) at a flow of 23 L/min (6 gpm). The longer flow path (Tests 23, 23D and 23C) further increased the back pressure. The effect of the free water is best illustrated by the back pressure measured for Test 15 - 550 kPa (80 psi) while flowing through the 2 m path with pure emulsion, even with demulsifier addition.

### **3 Ohmsett Tests**

This section describes the procedures and results for the meso-scale tests carried out at Ohmsett. The tests were completed during two weeks in July 2001. Full details may be found in the report (SL Ross 2002).

#### **3.1 Ohmsett Test Equipment and Methods**

##### **3.1.1 Preparations**

All tests were conducted in a stationary position (i.e., no towing down the tank). A schematic layout of the test equipment is given in Figure 2.

The test area consisted of 15 m (50 feet) of 24-inch Globe boom deployed in a square between the Auxiliary Bridge and the Main Bridge (Figure 3). The boomed area was approximately 14.3 m<sup>2</sup> (156 ft<sup>2</sup>). The Desmi Terminator skimmer was placed in the test area and operated from the Auxiliary Bridge. The skimmer discharge was directed to the oil recovery tanks on the Auxiliary Bridge (Figure 4) via 3-inch flexible hose. Pressure transducers were located at either end of a 13-m (42.5-foot) section of this hose. For some tests, the skimmer discharge was directed through a Lightnin Series 45 Model 4 Type 12H in-line mixer. The separated water from the oil recovery tanks was directed to a temporary holding tank (Figure 5) for water sampling, then sent to a holding tank for eventual treatment and disposal to the sanitary sewer.

Demulsifier (Alcopol O 70% PG aka Drimax 1235B) was injected using a fixed-rate (1 L/min = 0.25 gpm) peristaltic pump into the recovered fluid in one of two locations: directly into the skimmer weir or into the discharge hose just before the wye upstream of the inline mixer. For some tests the decanted water was sent to a sampling tank (Figure 6), where it was mixed thoroughly, and sampled for oil content analysis. Oil or emulsion from the recovery tanks was pumped to the Ohmsett oily waster processing system then stored for disposal.

Two wave conditions were generated during this test series. Their nominal characteristics are defined in Table 3.

##### **Emulsion Preparation**

At the beginning of the tests, and subsequently as required, emulsions were prepared. A gear pump was used to prepare the emulsion, since large quantities of a consistent quality were required on a daily basis. The procedures are detailed in the report. The use of 2.5% Bunker C for the Ohmsett parent oil, as opposed to 5% used

in the laboratory tests was selected in order to ensure sufficient Bunker C was available and to make the emulsions more amenable to breaking. A sample of the first batch of emulsion prepared was allowed to sit for 24 hours, and showed no signs of breaking. The target properties of the emulsion were: 50% (vol) water content with a viscosity of approximately 1000 cP at a shear rate of  $1 \text{ s}^{-1}$  at  $21^\circ\text{C}$ . A 50% water content was chosen because it could be prepared reasonably quickly using the gear pump technique with little risk of inverting the emulsion, as can occur with higher water contents.

### **3.1.2 Test Procedures**

Before each test the Emulsion Recovery Rate (ERR) for the skimmer was estimated and the volume of emulsion removed from the boomed area during the previous test calculated. The aim was to pump emulsion into the boomed area at the same rate that it was removed by the skimmer so that a constant thickness of emulsion was being presented to the skimmer. The following procedures were then used:

1. The required volume of test emulsion was added to the boomed area to make up the desired slick thickness (20 or 100 mm).
2. The Main Bridge distribution pump speed was set to supply fresh test emulsion at the ERR estimated for the test.
3. The waves were turned on at the desired setting and allowed to come to apparent steady state (this required about two minutes). The data acquisition system was started.
4. The emulsion distribution pump was started and the skimmer turned on, with its discharge directed to recovery tank #8. The chemical injection pump was started with flow to the desired location at the desired demulsifier flow rate (nominally  $1/500^{\text{th}}$  of the Fluid Recovery Rate).
5. When the cargo line was purged, the skimmer discharge was directed to the recovery tank cells sequentially (i.e., fill cell #7, then #6, etc.). The target volume of emulsion (exclusive of free water) in each cell was 200 L.
6. The time when filling each tank cell was started and finished was recorded. The depth of fluid in each cell was measured and recorded.
7. After the last tank cell was filled, the emulsion distribution pump, demulsifier injection pump, skimmer and waves were stopped.
8. Simultaneously with the filling operation, two minutes after tank cell #7 was filled, the separated water was decanted until the discharge from the bottom was “black”. The water was sent to a temporary storage tank and not poured back into the test basin. Note that cell #8 was also decanted to the temporary storage tank for processing.
9. For selected cells in each test, the decanted water was directed to a Nalgene temporary holding tank on the deck beside the auxiliary bridge. When all water from the selected cell was transferred, the contents of the temporary holding tank were thoroughly mixed with an electric, bladed mixer and allowed to settle for five minutes to allow large droplets of emulsion to surface. The surface emulsion was removed with a sorbent pad, then the temporary holding tank was drained to the temporary storage tank. A small water sample, for oil content analysis, was taken when half the water had drained. The purpose of this was to estimate the average concentration of

“permanently dispersed” oil in the decanted water - i.e., the droplets that would not rise out and re-coalesce with the slick if the decanted water was discharged back into a boomed area.

10. The remaining emulsion recovery tank cells were decanted in sequence at 5, 10, 15, 30, 45, and 60 minutes after the time they were filled. The purpose of this was to determine the time required for “primary break” of the skimmer discharge product. “Primary break” is the point at which the bulk of the lower density phase has risen to the top and the higher density phase has settled to the bottom; both phases typically contain small droplets of the other phase at this point.
11. The depth of fluid remaining in each cell was measured (these depths, combined with the initial depths, were used to calculate the volumes of recovered product, decanted water and emulsion remaining).
12. Each recovery tank cell was mixed and sampled to determine the water content of the fluid remaining.
13. The contents of the recovery tank cells were transferred for waste processing.

### **3.1.3 Sample Analyses**

Each test involved collecting 3 oil-in-water samples and 7 water-in-oil samples, as well as selected duplicates. The oil-in-water samples were sealed in Nalgene jars and placed in a refrigerator for storage until such time as they could be analysed. The emulsion samples were analysed within 48 hours of collection. In addition, a sample of each batch of emulsion was subjected to a rheological analysis.

#### **Bottom Solids and Water**

The water content of the emulsion samples was determined using the procedures specified in ASTM D1796. The method involved splitting a well-shaken, 100-mL emulsion sample into two aliquots. Each aliquot was poured into a graduated, centrifuge tube containing 50 mL of toluene, filling the tube to the 100-mL mark. The tube was shaken vigorously, warmed and then placed in the centrifuge and spun for 10 minutes. The volume of water in the tubes was read directly from the graduations. For water volumes in the 10 to 25 mL range (20% to 50% water content emulsions) the reading error was on the order of 1 mL (2%); for higher water content emulsions the error was likely in the 3 to 5 mL range (6% to 10%). For some samples, a small amount of demulsifier was added to aid in resolving the emulsion.

#### **Total Petroleum Hydrocarbons**

The decanted water samples were extracted with carbon tetrachloride (CCl<sub>4</sub>) and then analysed with a scanning infra-red spectrometer. The techniques used generally followed those specified in EPA 413.2, except that the solvent used was not Freon. The error in this method was on the order of  $\pm 10\%$ , with the limit of detection being 10 ppm. The technique also detects the dissolved hydrocarbons in the tank water from previous testing. Generally, the “background” TPH level in the tank is 3 to 5 ppm. During the extraction process, the solvent could also remove some portion of the demulsifier that is dissolved in the water. It is not certain what this portion would be.

### **Emulsion Rheology**

A sample from each batch of emulsion was sheared in a Haake VT550 rheometer; an SV-1 sensor was used. The shearing program involved ramping the shear rate up from  $0.13 \text{ s}^{-1}$  to  $13 \text{ s}^{-1}$  in ten equal time steps over a period of 600 seconds, maintaining the shear rate at  $13 \text{ s}^{-1}$  for a period of 600 seconds, then ramping the shear rate back down to  $0.13 \text{ s}^{-1}$  over a further 600 seconds. All samples were measured at room temperature:  $25^{\circ}$  to  $27^{\circ}\text{C}$ .

### **3.2 Ohmsett Test Results**

The results from the Ohmsett tests are summarized in Table 4. Full data and equipment calibrations may be found in the report (SL Ross 2002).

#### **3.2.1 Scaling Parameter**

In terms of the scaling parameter used for the laboratory tests ( $Q/D [\text{m}^2/\text{s}]$ ) the value for the Ohmsett tests ranged from 0.08 to 0.24, with the majority at a flow rate of 530 L/min ( $32 \text{ m}^3/\text{hr} = 140 \text{ gpm}$ ) having a value of  $0.1 \text{ m}^2/\text{s}$ . The degree of turbulence in the hose would thus be higher than that achieved in the  $\frac{1}{2}$ "- or  $\frac{3}{8}$ "- ID tubing in the laboratory tests ( $Q/D = 0.04 \text{ m}^2/\text{s}$ ). It had been intended to use 6-inch hose on the skimmer (giving a  $Q/D = 0.05 \text{ m}^2/\text{s}$ ), but this was not possible.

#### **3.2.2 Test Emulsion Rheology**

A summary of the results of the rheological analyses of the various batches of emulsion mixed for the Ohmsett tests (50% seawater in 97.5% Hydrocal 300/2.5% Bunker C) are given in Table 5. Full data plots may be found in the report. The emulsion exhibited a slight, but distinct pseudo-plastic (shear-thinning) behavior (the viscosity at  $1 \text{ s}^{-1}$  was about 10% higher), with no evidence of thixotropy (time dependance). There was little difference between batches: the average viscosity was 990 mPas with a standard deviation (ignoring the slight temperature differences) of 107 mPas.

#### **3.2.3 Decanting/Emulsion Breaking Results**

The first five columns in Table 4 give the variables used for a specific test. Columns 6 and 7 give the estimated initial and final slick thicknesses in the boomed area before and after a given test. These are only rough indicators of the amount of oil in the boomed area at the beginning and end of a test because the errors in estimating slick thickness (based on emulsion added minus emulsion skimmer) accumulated in successive tests, until the boomed area was emptied at some point. The waves (both generated in the tank and reflected off the skimmer and boom) would also tend to push the oil to one side of the test area. As well, the flow of emulsion from the Main Bridge tank was spread out on a spill plate attached to the end of the distribution hose and tended to flow directly towards the skimmer weir. Significant differences in the initial and final slick thicknesses are an indication that the system was not well balanced for a specific test (i.e., significantly more or less emulsion was being added than being removed) and that conditions were not likely at steady state during the test.

Columns 8 and 9 give the measured fluid recovery rate (water + emulsion) and the percentage of the fluid made up of free water (based on comparing the total flow rate with the flow rate of 50% water content emulsion recovered - based on the

doubling the volume of oil calculated to be contained in the recovery tanks after decanting from the water content analysis). The tenth column gives the average water content of the emulsion remaining in the seven tanks after decanting, based on the BS&W analysis of a well-mixed sample from each. In general, with exceptions noted in the discussions below, the water content in each individual tank did not vary significantly beyond the error estimate range (see the report), thus the average water content adequately represented the state of the emulsion in all the tanks after decanting. Note that, as discussed in the lab results, the parent oil composition (more specifically, the lack of a significant aromatic component) prevented the demulsifier (Alcopol O 70%) from completely resolving the emulsion. Based on the lab test results, demulsification down to a water content of about 30% represented the greatest achievable with the oil/demulsifier system used. The next two columns give the water content of emulsions exposed to additional mechanical mixing energy after decanting from tanks 1 and 4. The next three columns give the oil content (TPH) of the decanted water, and the final two give the pressures recorded in the skimmer hose.

Figure 7 shows the volume of water decanted from the recovery tanks as a function of time since they were filled for the baseline (i.e., no demulsifier) tests. In all cases the majority of the separation, called primary break, was over in 15 minutes for the tests conducted in Wave #2 (the steeper of the two). Primary break seemed to occur faster with fluid recovered from tests in Wave #1 - presumably because there is less uptake of large droplets of tank water into the test slick in the lower mixing conditions. These results are entirely consistent with results from previous decanting tests (SL Ross 1999) at Ohmsett with Hydrocal oil at 9°C, at which temperature it had a viscosity of 1000 mPas.

Referring again to Table 4, the recovered emulsion water content average for the first test (#1) showed no appreciable change, as would be expected since no demulsifier was added. The slight increase in average emulsion water content for Test 2 (again, no demulsifier) may have been due to increased mixing energy from the increased wave steepness causing natural emulsification to add to the existing, 50% water content. Test 3 and 4 (demulsifier added to the skimmer hopper, but no inline mixer), showed no change in the water content of the emulsion in the recovery tanks, compared to Test 1 and 2 respectively. The free water content for these tests was 68 and 66% respectively, well above the free water contents in the lab-scale tests that significantly reduced the effectiveness of the demulsifier (ca. 60% free water).

The data from Tests 5 through 9 show an increase in the emulsion water content, despite demulsifier addition. The reason for this is not clear; however, several explanations are possible:

- The tests were completed sequentially (i.e., the emulsion remaining in the boomed area after Test 4 was used for Test 5, and so on) thus the wave action may have been continuously increasing the water content of the oil in the boomed area.
- Also the free water content of these tests was very high; meaning that the demulsifier would have been ineffective.
- The degree of turbulence in the hose was high, promoting emulsification. The Reynolds number in the hose, assuming that the high free water content fluid has a viscosity near that of water, would be about 150,000 at a flow rate of 530 L/min (140 gpm), well into the turbulent regime. The addition of the

inline mixer to the flow path did not make a significant difference to the recovered emulsion water contents.

Tests 10 and 11 were baseline tests (i.e., no demulsifier addition), with the thicker slicks (ca. 100 mm). As with Tests 1 and 2, there was no emulsion breaking observed. In fact, in Test 11, as with Test 2, the steeper waves may have been further emulsifying the oil in the boomed area.

For Test 12, the skimmer was inadvertently run at full speed, recovering fluid at 1100 L/min (287 gpm), about twice the intended rate. Test 12 was the first in which there was some evidence (albeit within the error range of the analytical technique used to determine water content) that emulsion breaking was occurring. The mean water content of the emulsion after decanting was 44%, with the samples from the first three tanks decanted (2, 5 and 10 minutes) averaging 53% and the last 4 (15, 30, 45 and 60 minutes) averaging 38% water. The free water in this run (37%) was significantly less than in the previous demulsification tests (64% to 72%). In the next test, 12A, intended to be a repeat of 12 at the correct recovery rate, almost no free water was recovered and no significant change in the emulsion water content was detected. In this situation, the recovered fluid would be much more viscous than in the case of significant amounts of free water, correspondingly reducing the turbulence level in the hose. For a viscosity of 1000 mPas, the Reynolds number would be 150, well below the 2100 cut-off point for laminar flow.

Test 13 was intended to determine the effect of steeper waves on demulsification with recovered fluid from the thicker slicks. The average water content of the recovered emulsion in the seven tanks was 55%, compared to 61% for the baseline case (Test 11) indicating no significant breaking, despite a free water content of 44%. It may be that the water content of the emulsion in the slick and recovery system had increased well above 50% (as was the case in Tests 4 and 6 and 11) and was subsequently reduced to 55% by the action of the demulsifier.

In Test 37, a slight demulsifying effect was noted, with the addition of the inline mixer to the recovery flow path; despite the relatively high free water content (58%). In the laboratory test results, there was a definite trend in increasing free water content above about 50% causing a decrease in emulsion breaking, with water contents in excess of about 60% almost completely negating the effect of the surfactant. The duplicate run of this test, Test 38, resulted in a slightly lower average emulsion water content in the recovery tanks, with a slightly lower free water content, albeit that the difference in water contents is less than the error for the water content analysis technique.

For the remaining tests, in order to see if more mixing energy could promote further emulsion breaking, an additional procedure was carried out on the recovered product in two of the tanks (#4 and #1, decanted after 15 and 60 minutes settling respectively). This involved dumping the entire contents of these two tanks into the Nalgene tank normally used to obtain a well-mixed water sample for TPH analysis. The volumes of water and emulsion added were measured by height. Then, the emulsion and water were vigorously mixed with the Lightnin mixer for 10 minutes and allowed to separate for 20 minutes. After the separation period, the Nalgene container was decanted, with the volume of water and emulsion remaining measured again. A well-mixed sample of the emulsion was obtained for water content analysis

in the lab.

Test 39 involved recovering fluid from relatively thin slicks, with the inline mixer in place in Wave #1. The free water content was estimated as 56%, and the average emulsion water content in the recovery tanks was 45%. The application of the extra mixing did result in further demulsification.

Test 40 involved a run with the skimmer operating at full speed. The free water content was about 54% and the recovered emulsion water content averaged 33%, indicating good breaking. Remember that, with the parent oil and surfactant system used, something on the order of 30% water content in the emulsion was the lowest achievable. Although the results from the additional mixing were scattered, the laboratory emulsion water content results after extra mixing also indicated good emulsion breaking. The high recovery rate (higher flow turbulence, inline mixer, and moderate free water) combined to make this the most effective test of the series. Test 41 repeated the conditions of Test 40, with the steeper waves. Good emulsion breaking was achieved again.

The results of Test 42, intended as a baseline run at the high recovery rate, are inexplicable. No demulsifier was injected, and yet the emulsion water content results from the recovery tanks indicate an average water content of only 39%. The same analyses of the samples from the tanks to which extra mixing was applied, indicate water contents in the range expected (near 50%) for both techniques (volume estimation and lab analysis). No trend in emulsion water content with time was apparent in the test data.

Tests 43, 44 and 45 were conducted to investigate the effect of recovery rate on emulsion breaking. Test 43 was carried out at a low recovery rate (300 L/min = 78 gpm), about half of the nominal rate (530 L/min = 140 gpm) with the in-line mixer. No emulsion breaking was detected in the recovery system, even with the inline mixer and an appropriate free water content. The extra mixing applied to the contents of tanks 4 and 1 did result in significant emulsion breaking. Test 44 was intended to be run with the nominal recovery rate, with no inline mixer to obtain a duplicate of Test 6, but due to a miscommunication, was actually run at the high recovery rate. Only moderate emulsion breaking was detected, probably because of the very high free water content (75%) in the recovered product. Although one volume measurement gave a water content of 27%, the rest of the extra-mix analyses indicated that the emulsion water content could not be reduced significantly with the addition of more turbulent energy, possibly because much of the demulsifier had partitioned into the water, and was no longer in the emulsion. The results of Test 45 (high recovery rate, low free water, no inline mixer) compared to Test 40 (same conditions, but with the inline mixer) illustrate the importance of mixing energy to the emulsion breaking process. Note that in Test 45 almost no free water was collected in the first three tanks (7, 6 and 5); the free water in the recovered fluid was more likely in the 50% to 60% range. In conjunction with this increase in free water, and the commensurate increase in turbulence, the emulsion water content in the tanks decreased from 53% in the first three, to 45% in the last tanks filled. The addition of extra mixing energy to the contents of tanks 4 and 1 from Test 45 did result in significantly more emulsion dehydration.

In those tests in which significant emulsion breaking occurred (38, 39, 40, 41 and 42) primary break occurred within 15 minutes, no different than in the case of the

baseline tests.

### **3.2.4 Oil Concentrations in Decanted Water**

The TPH concentrations in the decanted water for the four baseline runs (i.e., no demulsifier addition) are shown on Figure 8 (and in Table 4). The concentrations reported are oil-in-water, thus they should be doubled, at least for the baseline cases, to reflect emulsion-in-water concentrations. With this in mind, the results for the thinner slicks (Tests 1 and 2), at least for the 2- and 30-minute settling times, are entirely consistent with the results from the 1997 decanting tests (SL Ross 1999) with 1000-mPas Hydrocal in 20-mm thick slicks. It is not clear why the 60-minute sample concentrations are higher than the 30-minute ones. The 30- and 60-minute oil-in-water concentrations for the thicker baseline slicks in Test 10 are also closely in agreement with the results from 1997 for 100-mm Hydrocal slicks. The results for Test 11 are higher, for no apparent reason. Almost no water was recovered from tank 7 (decanted after 2 minutes) for Tests 10 and 11, thus no water sample could be obtained for TPH analysis.

For tests involving demulsifier addition, the oil-in-water concentrations were generally higher than those of the baseline tests, by a factor of about 2. It is not clear what portion, if any, of the TPH is attributable to the Alcopol O (i.e., how much of the response from the IR was due to Alcopol O in the water sample that was extracted by the carbon tetrachloride). A simple test is planned at the next opportunity to evaluate this. The TPH readings (which would represent about one half the dispersed emulsion concentration for those tests in which the demulsifier was not very efficient) were on the order of 1000 ppm after 2 minutes, declining to 400 ppm after 60 minutes. Neither the demulsifier injection location, the presence of the inline mixer, fluid flow rate or wave height appeared to have an appreciable effect. There does not appear to be any obvious reason why the 2-minute and 60-minute samples for Test 13 gave such high results and the 30-minute and 60-minute samples from Test 37 had such low TPH's.

### **3.2.5 Pressure Drop**

The average pressure recorded during steady-state recovery at the upstream pressure transducer, and the average pressure drop per unit length of hose (measured along a 13-m length of 3-inch hose) are given in the last two columns of Table 4. If water were being pumped down the 3-inch hose at the nominal recovery rate of 530 L/min (140 gpm), the theoretical pressure drop would be 0.05 kPa/m (0.024 psi/ft) (surface roughness of hose assumed to be 0.005 in.). The values in Table 4 are in this range, the differences probably being due to the error in subtracting low pressures measured with 0 to 200 psi-range transducers with an accuracy of 0.25% of full scale, or 7 kPa (1 psi). This is probably best illustrated by the negative pressure drop recorded for Test 43, at a low flow rate. The theoretical pressure drop for a 1000 mPas fluid (in laminar flow) would be 0.1 kPa/m (0.05 psi/ft), very close to the average value measured in Test 12A.

The tests involving higher flow rates gave higher pressure drops, as expected. Again, assuming water was the fluid being pumped, the expected pressure drops would be 0.2 and 0.3 kPa/m (0.096 and 0.15 psi/ft) at 1100 and 1300 L/min (280 and 350 gpm) respectively, very close to the values measured. Even free water contents as low as 33% are sufficient to make the emulsion/water mixture almost as pumpable as

pure water.

The average upstream pressures measured gave an indication of the extra effort required to pump fluids through the inline mixer. At 530 L/min (140 gpm) with no inline mixer, the upstream pressure was on the order of 50 kPa (7 psi). Directing the flow through the inline mixer increased this to 70 kPa (10 psi). At flow rates on the order of 1300 L/min (350 gpm) the inline mixer caused an increase in pressure from 140 kPa (20 psi) to 280 kPa (40 psi).

### **3.3 Comparison of Lab-scale and Ohmsett Results**

Since the scaling parameter ( $Q/D$ ) was different for the laboratory and Ohmsett tests, the results cannot be directly compared; however, there were several common features of the results of the two test series.

First was the importance of free water to the emulsion breaking process. At both scales, when the free water content exceeded about 60%, the efficacy of the demulsifier was noticeably reduced. This is presumed to be due to the surfactant ending up mostly in the free water, as opposed to the emulsion. This was particularly evident in the Ohmsett tests where often the decanted water drained into the steel temporary holding tank would foam. On the other hand, the presence of free water was necessary to allow efficient pumping of the emulsions and for the flow to reach turbulent levels. The free water resulted in a reduction in the apparent bulk viscosity of the fluid being pumped, which in turn increased flow rates and turbulence in the tubing and hoses. Only in the case of a system that utilized an energy-intensive transfer pump (i.e., a gear pump) with the demulsifier injected before the pump, or one that utilized additional mechanical mixing, did the demulsifier work efficiently in the absence of free water. Reviewing the tests results at both scales shows that the demulsification was most effective when the free water content was between 33% and 55%. Once the free water content exceeded about 60%, demulsification was curtailed.

The second common feature of the two test series was the importance of mixing energy. Given that the free water content was in the correct range, emulsion breaking improved with increased mixing energy. There are two types of mixing required for effective demulsification. The first is that which distributes the small amount of demulsifier into the continuous phase of the emulsion and allows it to come in contact with the water droplet interfaces. Second, once the demulsifier has displaced the natural interface-stabilizing compounds, mixing energy is required to cause the water droplets to collide and coalesce. Both series of tests showed conclusively that increased mixing energy, regardless of how it was added (increased flow turbulence/time, in-line mixer, or additional mechanical mixing with a bladed impeller) increased the emulsion breaking efficiency.

In the situation where the recovered fluid contains up to 50% free water, (such as would be expected in operations involving skimmers deployed in the thick oil in the apex of a long length of containment boom), the most effective location for the injection of the demulsifier appears to be at the skimmer, since this offers both the advantage of the longest possible time for the chemical to be mixed with the recovered fluid, and the possibility that, if little free water is being recovered, the surfactant will reduce the bulk viscosity of the recovered emulsion and assist in pumping. In the case where the recovered product contains more than 60% free water (as might be expected with weir skimmers deployed in small containment boom

systems, such as a VOSS) demulsifier should be added to the oily phase after separation and decanting of the free water, with mechanical agitation (recirculating with a gear pump or using a bladed impeller) added to initiate the emulsion breaking process. If pure emulsion is recovered, injection at the skimmer pump and additional mixing in the temporary storage tank would be best. In any case, the provision of some method of adding extra mixing energy to the oily phase after initial decanting would appear to be beneficial.

Once the mixing energy has been applied, it is necessary to allow the fluid to settle and the phases to separate. The results of both test series indicate that the emulsion breaking process is substantially finished in the same time frame as primary break occurs. For the small-scale lab tests this was on the order of 2 to 5 minutes, and for the Ohmsett tests this was 15 minutes, or less. The difference would likely be due to the different height scales of the settling tanks. The higher the column of fluid, the longer it takes for the two phases to separate. In the laboratory tests a volume of 5L was placed in a cylinder to a depth of approximately 200 mm, while at Ohmsett the recovered fluid volume in each tank was about 400 L (100 gallons) with a depth of 500 mm.. With all other things being equal, it should have taken about 2.5 times longer (500/200) for the Ohmsett test fluids to separate than the laboratory test fluids.

The pressure data indicated that the bulk viscosity of the emulsion/water mixture was very near that of water, as long as there was some free water present, at least 33%. The in-line mixer caused significant increases in back pressure.

Although the analysis of the oil-in-water concentrations for the lab tests was flawed, the Ohmsett results indicated that the use of a demulsifier increased TPH concentrations by approximately a factor of two in the decanted water. Even though it is not known what portion of each TPH reading was associated with dissolved demulsifier in the water, the water did contain a significant amount of surfactant, as evidenced by its foaming in the steel temporary storage tank.

## **4 Conclusions and Recommendations**

The efficiency of emulsion breaking chemicals in resolving water-in-oil emulsions is highly parent oil/surfactant specific and can be strongly affected by the dosage of the demulsifier and the weathering processes that an emulsified oil has undergone. The tests conducted for this study investigated the effects of mixing energy and other physical parameters on the efficacy of one emulsion breaker (Alcolpol O 70% PG aka Drimax 1235B, a solution of sodium diisooctyl sulfosuccinate in propylene glycol/water) on one, water-in-oil emulsion specifically “engineered” for the project by blending a Bunker C oil into Hydrocal 300 and adding 50% water via a gear pump. The conclusions drawn below are only strictly valid for the combination of demulsifier and emulsion used.

### **4.1 Conclusions**

- The use of a demulsifier injected into a recovery system, combined with decanting, can substantially reduce the volume of water in temporary storage tanks and the water content of emulsions for disposal/recycling.
- The efficacy of the demulsifier was a strong function of free water content, between an upper and a lower limit. In these tests, if the free

water content exceeded about 60%, the effect of the surfactant was substantially reduced. If no free water was present, the level of turbulence generated by the flow was insufficient to promote emulsion breaking. A free water content of greater than about 33% was required to reduce the bulk viscosity of the fluid to the point where the flow regime was turbulent, and mixing energy was supplied to promote emulsion breaking. It is possible that this phenomenon is demulsifier-specific and would not be observed with a different demulsifier. It is also possible that this phenomenon is related to the solvent used in the demulsifier, and use of a different solvent would yield different results.

- The degree of emulsion breaking achieved increased with increasing mixing energy applied to the fluid. Increasing the flow rate (and hence turbulence level) and increasing the length of the flow path both resulted in increased emulsion breaking. The use of in-line mixers further increased the removal of emulsion water. The application of mechanical mixing energy, using a bladed impeller, after placing the recovered fluid in a recovery tank, also increased demulsification.
- The best location for injection of the demulsifier was at the skimmer pump for recovered fluids containing up to 50% free water to maximize the amount and time of the mixing applied. For recovered fluids containing more than 60% free water, decanting the free water followed by the application of mechanical energy worked best.
- Primary break occurred in only a few minutes (2 to 5 in the lab tests, less than 15 for the Ohmsett tests). The application of demulsifier did not appear to affect this.
- The Ohmsett results indicated that the use of a demulsifier increased TPH concentrations by approximately a factor of two in the decanted water. Although it is not known what portion of each TPH reading was associated with dissolved demulsifier in the water, the decanted water did contain a significant amount.
- As long as the recovered fluid contained at least 33% free water, the pressure drops due to skin friction in the tubing and hoses approximated those expected for flowing water. The use of an in-line mixer significantly increased back pressures.

#### **4.2 Recommendations**

- A standard emulsion for use in testing at Ohmsett should be developed, incorporating an aromatic fraction (likely using a diesel oil) into the Hydrocal/Bunker mixture to allow better resolution of emulsions. This effort would also entail developing techniques to consistently “build” emulsions with water contents in the 70% to 80% range in order to achieve the high viscosities typical of oil spill emulsions at sea.
- A study of the partitioning of various oil spill demulsifiers between the resolved parent oil and the decanted water should be undertaken. The discharge of decanted water into the ocean environment may not be

permitted if it contains toxic levels of surfactants, eliminating any advantage to offshore recovery operations that could be gained by the use of demulsifiers.

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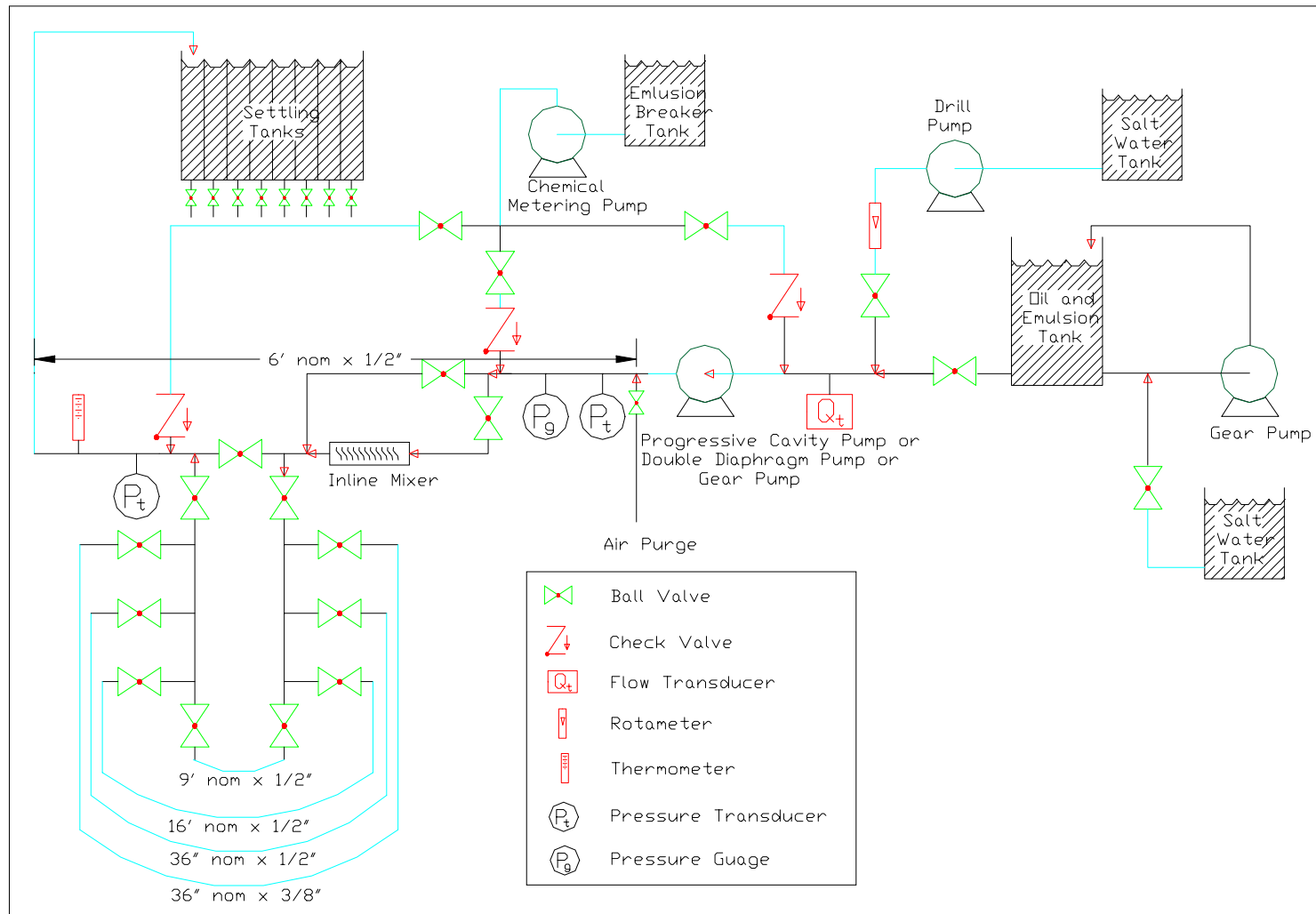
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**Figure 1** Schematic of Laboratory Test Setup

**Table 1                      Summary of Laboratory Test Results**

**Pump:   Progressing Cavity**

| Test Number | Demulsifier (Y/N) | Free Water (%) | Inline Mixer (Y/N) | Circuit Length (ft) | Test Description              | Free Water Removed (%) |         |         |
|-------------|-------------------|----------------|--------------------|---------------------|-------------------------------|------------------------|---------|---------|
|             |                   |                |                    |                     |                               | Average                | Minimum | Maximum |
| 1           | No                | 0              | No                 | 6                   | Baseline with and without     |                        |         |         |
| 2           |                   | 50             | No                 | 6                   | water                         | 93                     | 92      | 95      |
| 3           | Before Discharge  | 0              | No                 | 6                   | Demulsifier before tank, with |                        |         |         |
| 4           |                   | 50             | No                 | 6                   | and without water             | 90                     | 86      | 93      |
| 5           | After Pump        | 50             | No                 | 6                   | Mixing from turbulence in     | 110                    | 106     | 115     |
| 6           |                   | 50             | No                 | 9                   | piping. Check line pressure   |                        |         |         |
| 7           |                   | 50             | No                 | 16                  | before increasing circuit     | 77                     | 133     | 145     |
| 8           |                   | 50             | No                 | 36                  | length                        | 121                    | 119     | 126     |
| 9           |                   | 50             | No                 | *36                 |                               | 108                    | 104     | 114     |
| 10          | After Pump        | 50             | Yes                | 6                   | Mixing from turbulence in     | 117                    | 115     | 120     |
| 11          |                   | 50             | Yes                | 9                   | piping plus inline mixer.     |                        |         |         |
| 12          |                   | 50             | Yes                | 16                  | Check line pressure before    | 112                    | 107     | 120     |
| 13          |                   | 50             | Yes                | 36                  | increasing circuit length     | 120                    | 114     | 139     |
| 14          |                   | 50             | Yes                | *36                 |                               | 97                     | 94      | 99      |
| 20          | Before Pump       | 50             | Yes                | 6                   | Demulsifier before pump,      | 118                    | 113     | 125     |
| 21          |                   | 50             | No                 | 6                   | with and without mixer        | 109                    | 105     | 110     |
| 22          |                   | 50             | No                 | 36                  |                               | 115                    | 112     | 124     |
| 23          |                   | 50             | Yes                | 36                  |                               | 112                    | 99      | 119     |
| 23D         |                   | 50             | Yes                | 36                  |                               | 118                    | 112     | 122     |
| 23C         |                   | 50             | Yes                | 36                  |                               | 124                    | 110     | 137     |

\* 3/8" tubing

**Pump:   Gear Pump**

| Test Number | Demulsifier (Y/N) | Free Water (%) | Inline Mixer (Y/N) | Circuit Length (ft) | Test Description              | Free Water Removed (%) |         |         |
|-------------|-------------------|----------------|--------------------|---------------------|-------------------------------|------------------------|---------|---------|
|             |                   |                |                    |                     |                               | Average                | Minimum | Maximum |
| 24          | No                | 0              | No                 | 6                   | Baseline with and without     | NA                     |         |         |
| 25          |                   | 50             | No                 | 6                   | water                         | 96                     | 91      | 102     |
| 26          | Before Discharge  | 0              | No                 | 6                   | Demulsifier before tank, with |                        |         |         |
| 27          |                   | 50             | No                 | 6                   | and without water             |                        |         |         |
| 15          | After Pump        | 0              | Yes                | 6                   | Mixing from turbulence in     | NA                     |         |         |
| 16          |                   | 0              | Yes                | 9                   | piping plus inline mixer.     |                        |         |         |
| 17          |                   | 0              | Yes                | 16                  | Check line pressure before    |                        |         |         |
| 18          |                   | 0              | Yes                | 36                  | increasing circuit length     | NA                     |         |         |
| 19          |                   | 0              | Yes                | *36                 |                               |                        |         |         |
| 28          | Before Pump       | 0              | No                 | 6                   | Demulsifier before pump,      | NA                     |         |         |
| 29          |                   | 50             | No                 | 6                   | with and without water        | 108                    | 102     | 116     |
| 30          |                   | 50             | No                 | 9                   |                               |                        |         |         |
| 31          |                   | 50             | No                 | 16                  |                               | 100                    | 96      | 103     |
| 32          |                   | 50             | No                 | 36                  |                               | 119                    | 107     | 128     |
| 33          | Before Pump       | 50             | Yes                | 6                   | Demulsifier before pump,      | 125                    | 121     | 128     |
| 34          |                   | 50             | Yes                | 36                  | with water and inline mixer   | 141                    | 134     | 151     |
| 41          | Before Pump       | 0              | Yes                | 6                   | Demulsifier before pump       | NA                     |         |         |
| 42          |                   | 0              | Yes                | 36                  | with mixer but no free water  | NA                     |         |         |

**Pump:   Double-Diaphragm Pump**

| Test Number | Demulsifier (Y/N) | Free Water (%) | Inline Mixer (Y/N) | Circuit Length (ft) | Test Description            | Free Water Removed (%) |         |         |
|-------------|-------------------|----------------|--------------------|---------------------|-----------------------------|------------------------|---------|---------|
|             |                   |                |                    |                     |                             | Average                | Minimum | Maximum |
| 35          | No                | 0              | No                 | 6                   | Baseline with and without   | NA                     |         |         |
| 36          |                   | 50             | No                 | 6                   | water                       | 98                     | 86      | 113     |
| 37          | Before Pump       | 0              | No                 | 6                   | Demulsifier before pump,    | NA                     |         |         |
| 38          |                   | 50             | No                 | 6                   | with and without water      | 133                    | 119     | 142     |
| 39          | Before Pump       | 50             | Yes                | 6                   | Demulsifier before pump,    | 113                    | 104     | 119     |
| 40          |                   | 50             | Yes                | 36                  | with water and inline mixer | 105                    | 98      | 107     |

Table 1 cont'd

## Summary of Laboratory Test Results

**Pump: Progressing Cavit**

| Test Number | Demulsifier (Y/N) | Emulsified Water Removed (%) |         |         | Concentration of Oil in Water (ppm) |        |        | Free Water % | Demulsifier Dose Rate | Fluid Flow (gpm) | Upstream Pressure (psi) | Downstream Pressure (psi) |
|-------------|-------------------|------------------------------|---------|---------|-------------------------------------|--------|--------|--------------|-----------------------|------------------|-------------------------|---------------------------|
|             |                   | Average                      | Minimum | Maximum | 2 min                               | 30 min | 60 min | %            | Rate                  | (gpm)            | (psi)                   | (psi)                     |
| 1           | No                | 0                            | 0       | 0       | 3743                                | 835    | 1210   | 44%          | 0                     | 8.3              | 11.6                    | 6.1                       |
| 3           | Before Discharge  | 0                            | 0       | 0       | 4606                                | 3839   | 1429   | 45%          | 406                   | 8.5              | 10.5                    | 5.0                       |
| 4           |                   | 16                           | 10      | 24      | 2430                                | 1867   | 741    | 44%          | 925                   | 8.6              | 10.4                    | 5.2                       |
| 5           | After Pump        | 48                           | 42      | 59      | 2336                                | 554    | 460    | 39%          | 964                   | 8.9              |                         |                           |
| 6           |                   | 37                           | 33      | 47      | 12604                               | 2305   | 333    | 47%          | 346                   | 7.2              |                         |                           |
| 7           |                   | 25                           | 12      | 42      | 2618                                | 272    | 460    | 60%          | 617                   | 5.7              |                         |                           |
| 8           |                   | 33                           | 29      | 39      | 2711                                | 85     | 366    | 50%          | 761                   | 7.0              | 30.3                    | 3.8                       |
| 9           | After Pump        | 28                           | 17      | 48      | 2336                                | 85     | 178    | 55%          | 685                   | 6.3              |                         |                           |
| 10          |                   | 35                           | 32      | 40      | na                                  | na     | na     | 54%          | 685                   | 6.3              |                         |                           |
| 11          |                   | 0                            | 0       | 0       | 2149                                | 741    | 460    | 80%          | 460                   | 4.3              |                         |                           |
| 12          |                   | 34                           | 24      | 48      | 2618                                | 1210   | 1492   | 49%          | 752                   | 7.0              |                         |                           |
| 13          | Before Pump       | 14                           | 7       | 17      | 2711                                | 929    | 647    | 45%          | 913                   | 8.5              | 10.6                    | 5.3                       |
| 14          |                   | 29                           | 23      | 47      | 2336                                | 741    | 835    | 49%          | 769                   | 7.1              |                         |                           |
| 15          |                   | 24                           | 0       | 38      | 7590                                | 460    | 929    | 49%          | 699                   | 6.5              | 40.8                    | 3.1                       |
| 16          |                   | 37                           | 25      | 45      | na                                  | na     | na     | 51%          | 678                   | 6.3              | 45.8                    | 3.6                       |
| 17          | 23D               | 52                           | 21      | 79      | na                                  | na     | na     | 52%          | 296                   | 6.2              | 45.1                    | 3.6                       |
| 18          | 23C               |                              |         |         |                                     |        |        |              |                       |                  |                         |                           |

**Pump: Gear Pump**

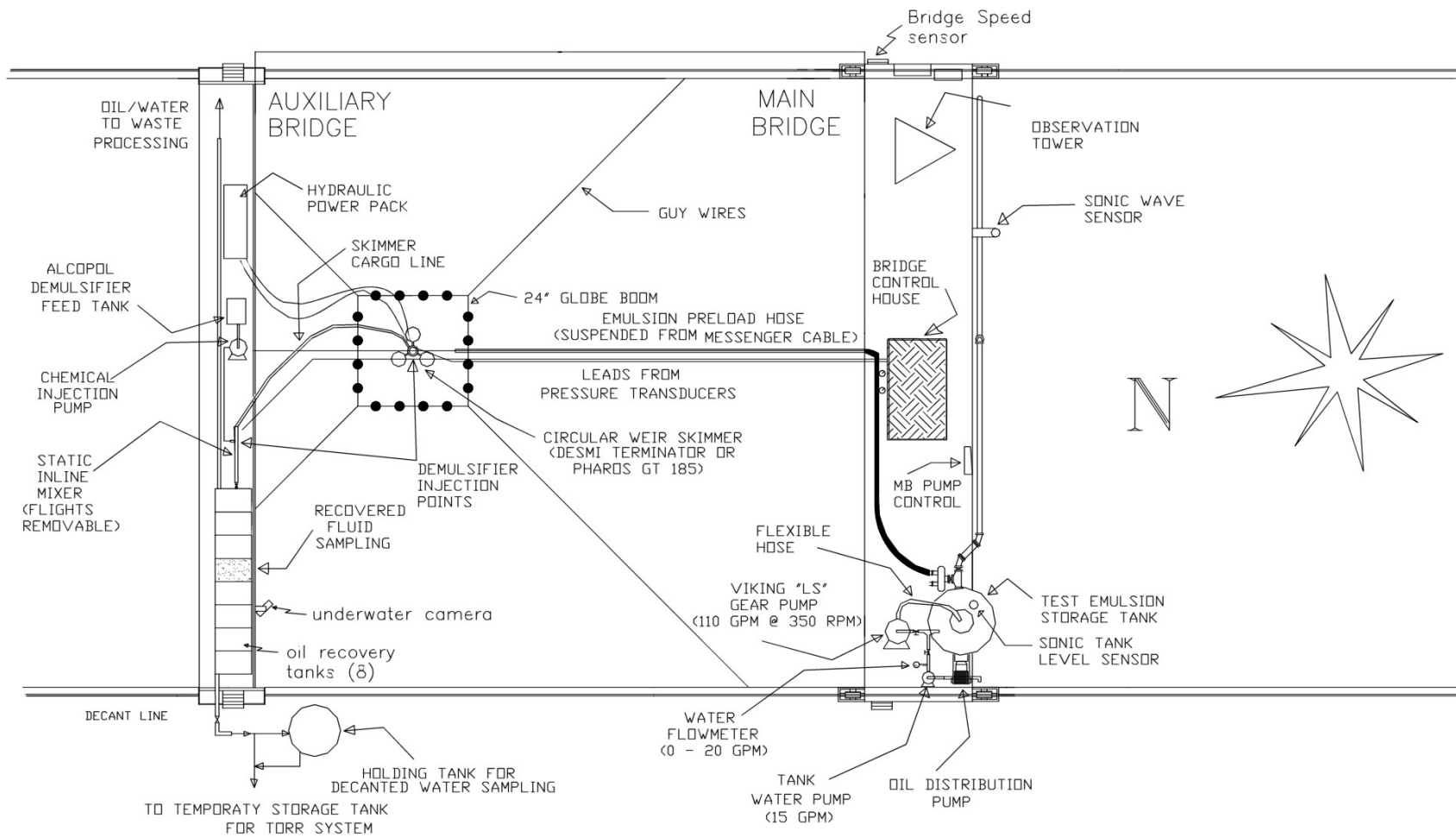
| Test Number | Demulsifier (Y/N) | Emulsified Water Removed (%) |         |         | Concentration of Oil in Water (ppm) |        |        | Free Water % | Demulsifier Dose Rate | Fluid Flow (gpm) |      |    |
|-------------|-------------------|------------------------------|---------|---------|-------------------------------------|--------|--------|--------------|-----------------------|------------------|------|----|
|             |                   | Average                      | Minimum | Maximum | 2 min                               | 30 min | 60 min | %            | Rate                  | (gpm)            |      |    |
| 24          | No                | 0                            | 0       | 0       | na                                  | na     | na     | 0%           | 0                     | 3.9              |      |    |
| 25          |                   | 1                            | 0       | 6       | 2805                                | 1117   | na     | 56%          | 0                     | 6.1              |      |    |
| 26          | Before Discharge  |                              |         |         |                                     |        |        |              |                       |                  |      |    |
| 27          |                   | 22                           | 19      | 30      | na                                  | na     | na     | 0%           | 151                   | 3.1              | 80.0 | na |
| 28          | After Pump        | 17                           | 0       | 24      | na                                  | 85     | 272    | 0%           | 181                   | 3.7              |      |    |
| 29          |                   | 51                           | 24      | 57      | 5807                                | 741    | 929    | 0%           | 628                   | 5.8              |      |    |
| 30          | Before Pump       | 12                           | 3       | 23      | 1492                                | 1304   | 1586   | 42%          | 665                   | 6.2              |      |    |
| 31          |                   | 3                            | 0       | 9       | 2242                                | 1117   | 1304   | 61%          | 634                   | 5.9              |      |    |
| 32          |                   | 33                           | 11      | 48      | 1210                                | 460    | -103   | 46%          | 611                   | 5.7              | 15.0 | na |
| 33          | Before Pump       | 56                           | 47      | 64      | 2618                                | 85     | 366    | 53%          | 571                   | 5.3              | 30.0 | na |
| 34          |                   | 81                           | 68      | 100     | 2618                                | 741    | 272    | 50%          | 585                   | 5.4              |      |    |
| 35          | Before Pump       | 59                           | 52      | 66      | 2055                                | 741    | na     | 0%           | 601                   | 5.6              |      |    |
| 36          |                   | 63                           | 46      | 72      | 5057                                | 647    | 741    | 0%           | 552                   | 5.1              |      |    |

**Pump: Double-Diaphragm**

| Test Number | Demulsifier (Y/N) | Emulsified Water Removed (%) |         |         | Concentration of Oil in Water (ppm) |        |        | Free Water % | Demulsifier Dose Rate | Fluid Flow (gpm) |  |  |
|-------------|-------------------|------------------------------|---------|---------|-------------------------------------|--------|--------|--------------|-----------------------|------------------|--|--|
|             |                   | Average                      | Minimum | Maximum | 2 min                               | 30 min | 60 min | %            | Rate                  | (gpm)            |  |  |
| 35          | No                | 0                            | 0       | 0       | na                                  | na     | na     | 0%           | 0                     | 2.0              |  |  |
| 36          |                   | 4                            | 0       | 16      | 4775                                | 835    | -9     | 37%          | 0                     | 7.5              |  |  |
| 37          | Before Pump       | 58                           | 28      | 68      | na                                  | 460    | 366    | 0%           | 543                   | 5.0              |  |  |
| 38          |                   | 46                           | 28      | 60      | 2242                                | 835    | 272    | 41%          | 938                   | 8.7              |  |  |
| 39          | Before Pump       | 38                           | 12      | 56      | 4119                                | 1210   | 929    | 60%          | 652                   | 6.0              |  |  |
| 40          |                   | 21                           | 0       | 31      | 1961                                | -103   | -197   | 68%          | 571                   | 5.3              |  |  |

**Table 2      Pressure Drops Calculated from Laboratory Test Runs**

| Test Number        | Demulsifier (Y/N) | Inline Mixer (Y/N) | Circuit Length (ft) | Emulsified Water Removed | Free Water % | Demulsifier Dose Rate | Fluid Flow (gpm) | Upstream Pressure (psi) | Downstream Pressure (psi) | Pressure Drop (psi/ft.) |
|--------------------|-------------------|--------------------|---------------------|--------------------------|--------------|-----------------------|------------------|-------------------------|---------------------------|-------------------------|
|                    |                   |                    |                     | Average                  |              |                       |                  |                         |                           |                         |
| 2 No               |                   | No                 | 6                   | 0                        | 44%          | 0                     | 8.3              | 11.6                    | 6.1                       | 0.9                     |
| 4 Before Discharge |                   | No                 | 6                   | 0                        | 45%          | 406                   | 8.5              | 10.5                    | 5.0                       | 0.9                     |
| 5 After Pump       |                   | No                 | 6                   | 16                       | 44%          | 925                   | 8.6              | 10.4                    | 5.2                       | 0.9                     |
| 21 Before Pump     |                   | No                 | 6                   | 14                       | 45%          | 913                   | 8.5              | 10.6                    | 5.3                       | 0.9                     |
| 32 Before Pump     |                   | No                 | 36                  | 33                       | 46%          | 611                   | 5.7              | 15.0                    | na                        | 0.3                     |
| 33 Before Pump     |                   | Yes                | 6                   | 56                       | 53%          | 571                   | 5.3              | 30.0                    | na                        |                         |
| 10 After Pump      |                   | Yes                | 6                   | 33                       | 50%          | 761                   | 7.0              | 30.3                    | 3.8                       |                         |
| 23 Before Pump     |                   | Yes                | 36                  | 24                       | 49%          | 699                   | 6.5              | 40.8                    | 3.1                       |                         |
| 23D Before Pump    |                   | Yes                | 36                  | 37                       | 51%          | 678                   | 6.3              | 45.8                    | 3.6                       |                         |
| 23C Before Pump    |                   | Yes                | 36                  | 52                       | 52%          | 296                   | 6.2              | 45.1                    | 3.6                       |                         |
| 15 After Pump      |                   | Yes                | 6                   | 22                       | 0%           | 151                   | 3.1              | 80.0                    | na                        |                         |



**Figure 2 Ohmsett Test Setup**



**Figure 3      Boomed Test Area**



**Figure 4      Recovery Tanks on Auxiliary Bridge**



**Figure 5**      **Steel Temporary Holding Tank for Decanted Water**



**Figure 6**      **Mixing Tank for Decanted Water Sampling**

**Table 3 Nominal Wave Characteristics**

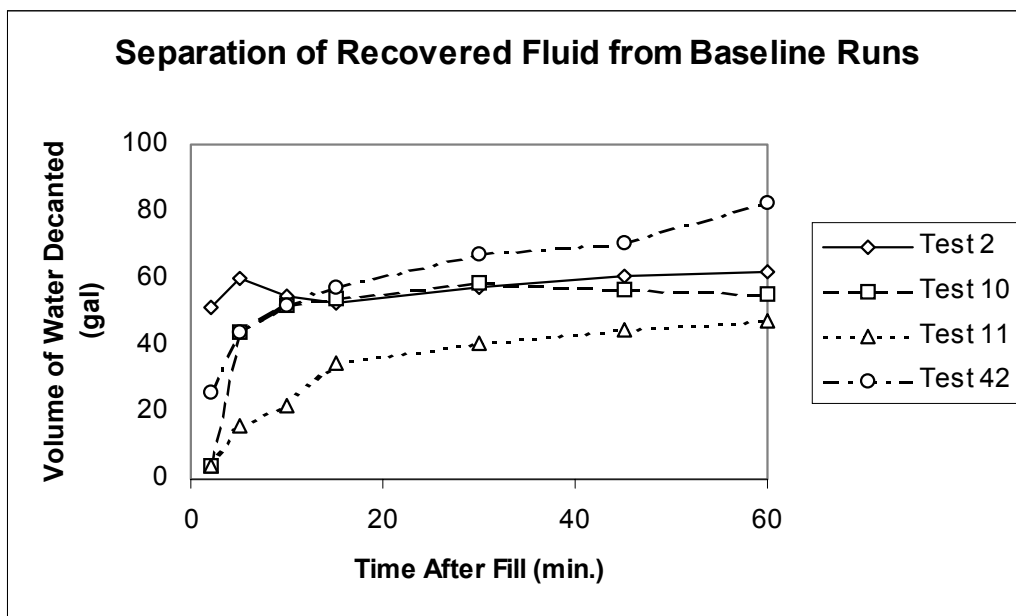
| Wave No. | Stroke (in.) | CPM | Type       | Nominal H <sup>1/3</sup> (in.) | Wave Length (ft.) | Period (sec) |
|----------|--------------|-----|------------|--------------------------------|-------------------|--------------|
| #1       | 3            | 22  | Sinusoidal | 16.5                           | 37                | 2.8          |
| #2       | 3            | 35  | Sinusoidal | 15                             | 15                | 1.7          |

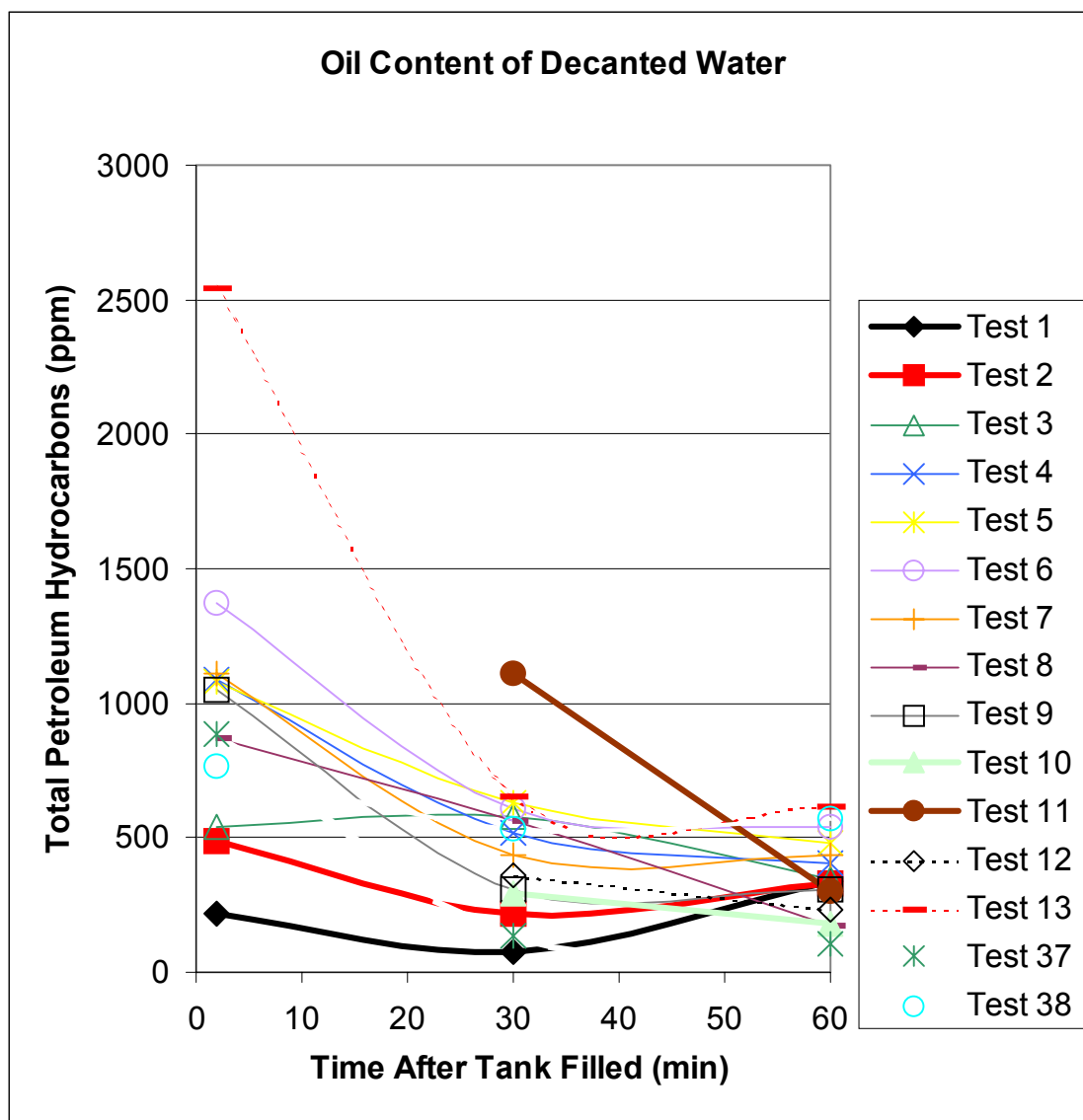
**Table 4 Summary of Ohmsett Results**

| Test Number | Demulsifier Injection Point | Demulsifier Doseage (Fluid:Demulsifier) | Wave Type | Inline Mixer | Initial Slick Thickness (mm) | Final Slick Thickness (mm) | Fluid Recovery Rate (gpm) | Estimated Free Water (%) | Recovered Emulsion Water Content (avg %) | Extra Mix Water Content (%) |                | Oil Content of Decanted Water (ppm) |        |        | Back Pressure (psig) | Pressure Drop (psi/ft) |
|-------------|-----------------------------|-----------------------------------------|-----------|--------------|------------------------------|----------------------------|---------------------------|--------------------------|------------------------------------------|-----------------------------|----------------|-------------------------------------|--------|--------|----------------------|------------------------|
|             |                             |                                         |           |              |                              |                            |                           |                          |                                          | Tank 4 Lab/Vol              | Tank 1 Lab/Vol | 2 min                               | 30 min | 60 min |                      |                        |
| 1           | No                          | none                                    | 1         | No           | 19                           | 104                        | 140                       | 48                       | 51                                       | -                           | -              | 214                                 | 72     | 337    | 6.4                  | 0.011                  |
| 2           | No                          | none                                    | 2         | No           | 21                           | 26                         | 106                       | 60                       | 57                                       | -                           | -              | 490                                 | 220    | 327    | 7.1                  | 0.020                  |
| 3           | Skimmer                     | 992                                     | 1         | No           | 62                           | 90                         | 144                       | 68                       | 52                                       | -                           | -              | 543                                 | 574    | 343    | 7.1                  | 0.025                  |
| 4           | Skimmer                     | 732                                     | 2         | No           | 90                           | 70                         | 152                       | 66                       | 57                                       | -                           | -              | 1086                                | 514    | 404    | 7.1                  | 0.020                  |
| 5           | Discharge                   | 732                                     | 1         | No           | 70                           | 57                         | 139                       | 69                       | 70                                       | -                           | -              | 1079                                | 629    | 479    | 7.0                  | 0.019                  |
| 6           | Discharge                   | 676                                     | 2         | No           | 64                           | 27                         | 137                       | 64                       | 71                                       | -                           | -              | 1376                                | 606    | 543    | 7.0                  | 0.022                  |
| 7           | Before Mixer                | 990                                     | 1         | Yes          | 27                           | 18                         | 144                       | 72                       | 71                                       | -                           | -              | 1113                                | 433    | 432    | 10.2                 | 0.031                  |
| 8           | Before Mixer                | 826                                     | 2         | Yes          | 18                           | 8                          | 142                       | 69                       | 66                                       | -                           | -              | 871                                 | 560    | 176    | 9.9                  | 0.022                  |
| 9 (DUP 8)   | Before Mixer                | 787                                     | 2         | Yes          | 20                           | 5                          | 135                       | 66                       | 67                                       | -                           | -              | 1052                                | 304    | 305    | 9.6                  | 0.020                  |
| 10          | No                          | none                                    | 1         | No           | 105                          | 62                         | 157                       | 47                       | 52                                       | -                           | -              | -                                   | 294    | 181    | 8.7                  | 0.034                  |
| 11          | No                          | none                                    | 2         | No           | 89                           | 25                         | 147                       | 45                       | 61                                       | -                           | -              | -                                   | 1110   | 301    | 8.1                  | 0.028                  |
| 12          | Skimmer                     | 1669                                    | 1         | No           | 88                           | 14                         | 287                       | 37                       | 44                                       | -                           | -              | -                                   | 357    | 233    | 18.5                 | 0.134                  |
| 12A         | Skimmer                     | 624                                     | 1         | No           | 100                          | 28                         | 135                       | 8                        | 54                                       | -                           | -              | -                                   | -      | -      | 10.4                 | 0.050                  |
| 13          | Skimmer                     | 646                                     | 2         | No           | 53                           | 18                         | 134                       | 44                       | 55                                       | -                           | -              | 2543                                | 655    | 618    | 6.9                  | 0.015                  |
| 37          | Skimmer                     | 650                                     | 2         | Yes          | 47                           | 0                          | 134                       | 58                       | 46                                       | -                           | -              | 882                                 | 136    | 104    | 9.3                  | 0.015                  |
| 38 (DUP 37) | Skimmer                     | 605                                     | 2         | Yes          | 15                           | 36                         | 125                       | 54                       | 43                                       | -                           | -              | 763                                 | 530    | 570    | 8.8                  | 0.016                  |
| 39          | Skimmer                     | 670                                     | 1         | Yes          | 36                           | 39                         | 139                       | 56                       | 45                                       | 39/36                       | 38/37          | -                                   | -      | -      | na                   | na                     |
| 40          | Skimmer                     | 2397                                    | 1         | Yes          | 87                           | 130                        | 323                       | 54                       | 33                                       | 36/23                       | 42/32          | -                                   | -      | -      | 37.6                 | 0.142                  |
| 41          | Skimmer                     | 2750                                    | 2         | Yes          | 130                          | 109                        | 371                       | 47                       | 35                                       | 45/27                       | 34/27          | -                                   | -      | -      | 37.4                 | 0.133                  |
| 42          | No                          | none                                    | 2         | Yes          | 159                          | 115                        | 377                       | 39                       | 39                                       | 45/48                       | 48/42          | -                                   | -      | -      | 38.5                 | 0.150                  |
| 43          | Skimmer                     | 582                                     | 2         | Yes          | 171                          | 85                         | 78                        | 43                       | 52                                       | 36/31                       | 33/??          | -                                   | -      | -      | 3.6                  | -0.035                 |
| 44          | Discharge                   | 2854                                    | 2         | No           | 86                           | 73                         | 385                       | 75                       | 43                                       | 57/27                       | 39/42          | -                                   | -      | -      | 20.8                 | 0.159                  |
| 45          | Discharge                   | 2800                                    | 1         | No           | 172                          | 68                         | 377                       | 32                       | 50                                       | 45/41                       | 40/37          | -                                   | -      | -      | 23.2                 | 0.192                  |

**Table 5 Emulsion Batch Viscosity**

| Emulsion Batch | Date Produced | Test Temperature [°C] | Viscosity at 10.7 s <sup>-1</sup> [cP] |
|----------------|---------------|-----------------------|----------------------------------------|
| 1              | July 11, 2001 | 25.8                  | 800                                    |
| 2              | July 12, 2001 | 27                    | 990                                    |
| 2 (duplicate)  | July 12, 2001 | 27.8                  | 990                                    |
| 3              | July 13, 2001 | 25.7                  | 1020                                   |
| 4              | July 16, 2001 | 26.3                  | 950                                    |
| 5              | July 17, 2001 | 27.5                  | 880                                    |
| 6              | July 17, 2001 | 28                    | 920                                    |
| 7              | July 18, 2001 | 26.2                  | 1040                                   |
| 8              | July 19, 2001 | 25                    | 1140                                   |
| 8 (duplicate)  | July 19, 2001 | 25.7                  | 1140                                   |

**Figure 7 Separation of Water from Recovered Liquid for Baseline Runs (No Demulsifier)**



**Figure 8**      **TPH Concentrations in Decanted Water**