Decanting Tests at Ohmsett with and Without Emulsion Breakers[1]

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ABSTRACT

This paper summarizes a multi-year research program to address the decanting of water from oil spill fluids recovered by skimmers. The first series of tests, with two weir-type skimmers at Ohmsett, was conducted to study the rate and amount of free water separation that can be expected in temporary storage containers. The goal of this study was to predict the best time to decant water back into the boomed area and optimize the available onsite storage space. The results indicated that "primary break" (the initial separation of the recovered liquids) occurred within a few minutes to one hour, depending on the physical characteristics of the oil. Rapidly decanting this free water layer may offer immediate increases of 200 to 300% in available temporary storage volume. Initial oil concentrations in the decanted water also depended on the physical properties of the oil; they ranged from 100 to 3000 mg/L. These declined by a factor of approximately 3 after one hour of settling, and by a factor of approximately 5 after one day.

The second series of tests was undertaken to develop a more complete 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 from a meso-stable water-in-oil emulsion with an oil spill demulsifier. The use of a demulsifier injected into a recovery system, combined with decanting, did substantially reduce the volume of water in temporary storage tanks and the water content of emulsions for disposal/recycling.

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. 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.

In the relatively low-energy environment within a temporary storage device, the recovered fluids will begin to separate into layers of oil, emulsion and water. Periodically discharging the separated water back into the containment boom can considerably extend the available storage space and increase the effective use of available resources to remove oil from the water surface.

There is an optimum time at which the separated water should be discharged, or decanted, from the temporary storage device. This optimum time maximizes the amount of water that can be removed from the container, minimizes the oil content of the discharged water, and minimizes the time that the storage is "out of service". The decision when to decant may also depend on whether or not sensitive resources could be affected by the dispersed oil concentrations in the discharged water.

The first test series at Ohmsett in 1998 investigated the decanting of mixtures of recovered

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oil and water and gave some quantitative insight into the oil/water separation processes occurring in temporary storage devices (SL Ross 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.

That many skimmer operations are, sooner or later, faced with recovering a water-in-oil emulsion was addressed in the second test series. 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 the free water layer, with a product that contains mostly water. 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 demulsifier delivery systems, the dynamics of the separation process are not well understood. The second set of experiments was 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 and the effects of demulsifier addition of the oil content of decanted water were also assessed. Various injection locations (skimmer head, discharge hose, tank inlet, etc.) and mixing technologies (static in-line, impeller, etc.) were investigated.

1998 DECANTING TESTS AT OHMSETT

In November 1998 a series of tests was conducted at Ohmsett to investigate the decanting of oil/water mixtures recovered by weir skimmers. The following parameters were varied during the tests:

i) Two circular weir skimmers:

- Desmi Terminator - nominal Oil Recovery Rate (ORR) in waves of 20 m^3/hr (90 USgpm)
- Pharos GT-185 - nominal ORR in waves of 10 m^3/hr (45 USgpm)

ii) Two slick thicknesses:

- 20 mm and 100 mm (representing the thickness expected in a single vessel sweep system and a large, multi-vessel offshore boom system respectively)

iii) Three oil types:

- Hydrocal, Calsol and Sundex (with viscosities of 1100, 13,000 and 300,000 mPas respectively at the test temperature)

iv) Two wave conditions

- wave #1 (15 cm x 11.3 m with a period of 2.8 s) and wave #2 (15 cm x 4.6 m with a period of 1.7 s)

Methods

A 15-m (50-ft.) section of 24-in. conventional containment boom was deployed in a square at the north end of the Ohmsett basin, between the main and auxiliary bridges (Figure 1). Two recovery devices were deployed in the boomed area: a GT-185 skimmer and a Desmi Terminator skimmer (Figure 2). Only one skimmer was operated for a given test.

The skimmer discharge was directed to the eight oil recovery tank cells located on the auxiliary bridge (Figure 3). The separated water from the oil recovery tanks was either dumped

back into the Ohmsett test basin, or directed to a temporary holding tank for water sampling (Figure 4). The time when the filling of each tank cell was started and finished was recorded. The depth of fluid in each cell was measured and recorded. Simultaneously with the filling operation, two minutes after tank cell #7 was filled, the separated water was decanted until the discharge from the bottom visibly contained oil. The remaining oil recovery tank cells were decanted in sequence at 5, 10, 15, 30, 45, and 60 minutes after the time they each reached full.

For selected cells in each test, the decanted water was directed to a temporary holding tank on the deck beside the auxiliary bridge. When all water from a selected cell was transferred, the contents of the temporary holding tank were thoroughly mixed with a bladed impeller and allowed to settle for five minutes to allow large droplets of oil to surface. The surface oil was removed with a sorbent pad, then the temporary holding tank was drained. A small water sample, for oil content analysis, was taken when half the water had been 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. During three of these tests (one for each of the three test oils) duplicate samples of the decanted water were placed in vertical columns for 24 hours (Figure 5) and then drained. The water from the bottom, middle and top of the columns was sampled and was analysed for oil content.

The depth of oily 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 oil remaining). The idea 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

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risen to the top and most of the higher density phase has settled to the bottom; both phases typically contain small droplets of the other phase at this point. Each oil recovery tank cell was mixed and sampled to determine the water content of the fluid remaining. The various samples collected were analysed using standard Ohmsett procedures for water content of oil (ASTM D1796), oil concentration in water (EPA 413.1), density (ASTM D1298), interfacial tension and surface tension (ASTM D971), and kinematic viscosity (ASTM D2983).

Summary of Results

Complete details of the test results may be found in the project report (SL Ross 1999) which may be obtained using the MMS web site www.mms.gov/tarprojects/.

For the thin slicks of the less-viscous oils the separation of the water from the recovered fluid was essentially complete in 15 to 30 minutes. Up to 60 minutes was required for separation with the thicker, more-viscous slicks.

For the thin slicks, the trend appeared to be faster separation with increasing oil viscosity. This was probably because the recovered product was oil droplets entrained in a continuous water phase. The more viscous the oil the larger the oil droplets in the water; larger oil droplets rise faster than smaller ones.

For the thick slicks, the situation appeared to be different. With these slicks, much less water was recovered by the skimmers, and it is likely that the recovered fluid stream consisted of water droplets suspended in a continuous oil phase. In this case oil viscosity controlled the settling rate: higher oil viscosities meant longer settling times. With the highest viscosity oil, the water was semi-permanently emulsified in the oil and did not settle appreciably over the 60-minute test.

Doubling the volume of fluid placed in the tank cell [equivalent to doubling the height of the

fluid in the tank cell] had no discernible effect on decanting times or the final percent water decanted. Agitating the receiving tank with wave action also had no discernible effect on water separation rate or amount.

The highest concentrations of oil in the decanted water occurred when skimming Calsol slicks. Initial concentrations were in the 1400 to 3000 mg/L range. These declined to 400 to 1000 mg/L after one hour of settling. The lowest concentrations of oil in the decanted water were for the Sundex oil. In these tests, the concentrations were initially in the 100 to 450 mg/L range, declining to about 50 to 150 mg/L after 60 minutes of settling. When skimming Hydrocal the concentrations of oil in the decanted water were initially about 1000 mg/L. These declined to approximately 200 mg/L after one hour. Allowing 24 hours settling further reduced oil concentrations in the decanted water to 30 to 70 mg/L for Calsol, 2 to 20 mg/L for Sundex and 30 to 100 mg/L for the Hydrocal test series.

Doubling the volume of fluid recovered in each cell did not appreciably affect the oil-in-water concentrations.

2001 DECANTING TESTS WITH EMULSION BREAKER ADDITION

In July 2001, a second series of tests was carried out at Ohmsett to investigate 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, discharge hose, 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 scale-model 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. These tests are not discussed in this paper. They may be found in SL Ross 2002 which may be obtained using the MMS web site www.mms.gov/tarprojects/.

At Ohmsett, a Desmi Terminator skimmer was used to recover the same emulsion as used in the laboratory tests, from the water surface, using different slick thicknesses, two wave heights and different recovery rates (to vary the turbulence in the recovery system). 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.

Methods

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 (SL Ross 2002). Based on a series of emulsion formation and stability tests and experience gained from the laboratory tests 2.5% Bunker C was added to the Hydrocal oil in order to create a suitable parent oil for the preparation of a meso-stable water-in-oil emulsion. The function of the Bunker C was to provide

asphaltenes to stabilize the small water droplets in suspension in the oil. 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 s^{-1} at 21°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.

The same test setup and procedures used in the 1998 tests were employed for the 2001 tests, with some additions to accommodate the emulsion breaker. Pressure transducers were located at either end of a 13-m (42.5-foot) section of the skimmer discharge hose to measure pressure drop. 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 for water sampling, then sent to a holding tank for eventual treatment and disposal to the sanitary sewer. This was to avoid adding dissolved emulsion breaker to the 10,000 m^3 of Ohmsett tank water, that may have negatively affected subsequent test programs.

Demulsifier (Alcopol O 70% PG aka Drimax 1235B a solution of sodium diisooctyl sulfosuccinate in propylene glycol/water) 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 (Figure 6) . As with the 1998 tests, for some runs the decanted water was sent to a sampling tank, where it was mixed thoroughly, and sampled for oil content analysis. As well, this tank and mixer was used to thoroughly mix the entire contents of some recovery tank cells, to assess the effects of additional mixing energy on emulsion breaking.

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Summary of Results

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 with one water-in-oil emulsion specifically "engineered" for the project. The conclusions drawn below are only strictly valid for this combination of demulsifier and emulsion.   The tests showed that 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

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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 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 oil-in-water concentrations by approximately a factor of two in the decanted water. Although it is not known what portion of each oil-in-water reading was associated with dissolved demulsifier in the water, the decanted water did contain a significant amount, as evidenced by its tendency to foam.

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.

ACKNOWLEDGEMENTS

REFERENCES

SL Ross Environmental Research Ltd. *Testing at Ohmsett to determine optimum times to decant simple temporary storage devices*. Final report to MM S. Herndon, VA. 1999.

SL Ross Environmental Research Ltd. *Extending Temporary Storage Capacity Offshore with Emulsion Breakers*. Final report to MMS. Herndon, VA. 2002.

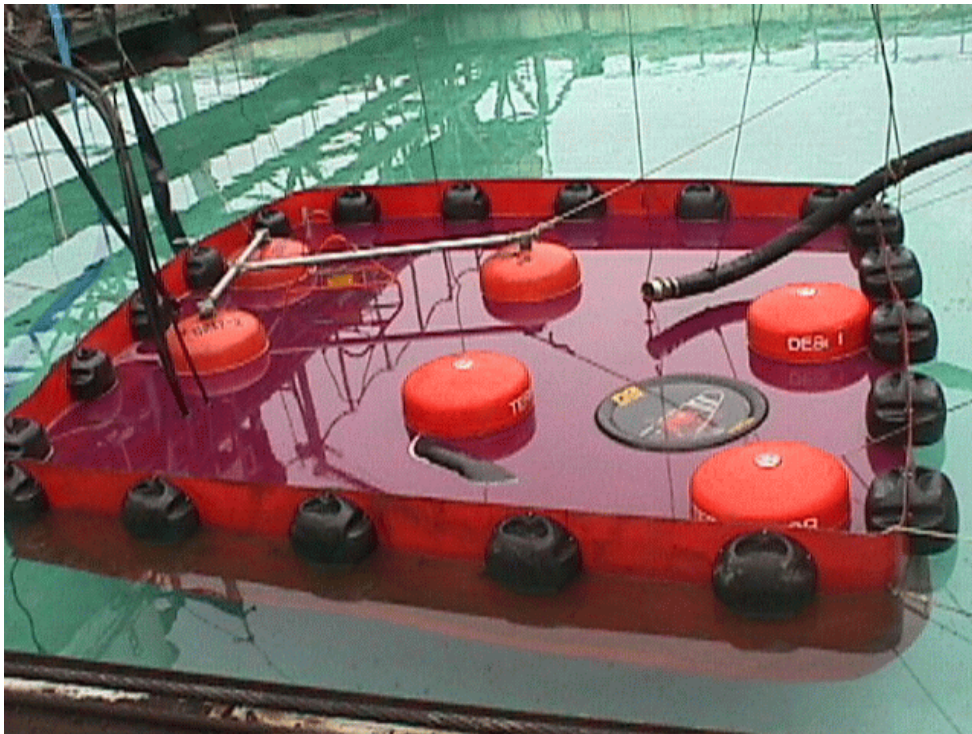Figure 1. Boomed test area between main and auxiliary bridges.

Figure 2. Skimmers in boomed test area with Calsol oil. Desmi Terminator at front right, Pharos GT-185 at back left.

Figure 3. Recovery tank on auxiliary bridge.

Figure 4. Mixing tank for decanted water sampling.

Figure 5. Steel columns used to hold 24-hour water samples (plastic buckets are to prevent rain entering tops)

Figure 6. In-line mixer on deck connected to discharge hose just before recovery tanks.