REALISTIC STABLE WATER-IN-OIL EMULSIONS AT OHMSETT

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ABSTRACT

This paper discusses the first two phases of a multiphase study to create predictable stable water-in-oil (W/O) emulsions at Ohmsett including a lab study and a large tank-scale study. The first stage of the study refined the process of creating, characterizing, and testing small batches of W/O emulsions under controlled and reproducible conditions in the laboratory to determine if the subject crude oil was capable of emulsifying. The second phase of the study capitalized on the unique capabilities of the testing facility to "grow" mass quantities of emulsions that on a large wave tank under quasi-natural conditions with wave energy and exposure to the elements, especially UV energy from natural sunlight wave tank under similar conditions that might be present during a real spill in the marine environment. The tank-scale study supported a parallel Bureau of Safety and Environmental Enforcement (BSEE) and National Oceanic and Atmospheric Administration (NOAA) program supporting the 2010 Deepwater Horizon "lessons learned" by proving control and validation of surface oiling characterization efforts pursued under the Natural Resource Damage Assessment (NRDA) Oil on Water (OoW) workgroup. This The subject of this paper is the production of reproducible W/O emulsions at Ohmsett. This program provided a "first cut" exercise in what is intended to be an ongoing and evolving effort at Ohmsett. The lessons learned, as well as suggestions for future provisions and studies will be discussed.

INTRODUCTION

When petroleum oil is spilled on an open body of water, it is exposed to a number of natural processes that immediately set the oil on a course of transformation. Collectively, these processes are referred to as the phenomenon of weathering, which may include spreading, evaporation, dispersion in the water body, emulsification by water, dissolution, oxidation, sedimentation, and biodegradation. Crude oils are especially affected by the processes of weathering. This is of course due to the complex and varying blend of hydrocarbons of which crude oils are composed. Crude oils weather based on their composition and resultant physicochemical properties, and the extent to which they are exposed to weathering processes. The extent of weathering here refers to exposure to wind and waves, temperature and temperature excursions, exposure to sunlight, exposure to rain, physicochemical and biochemical properties of the body of water, and time. A frequent product of this complex set of processes is the development of water in crude oil (W/O) emulsions. This occurs when the mechanical action of wind and waves mixes water into the oil layer resulting in the liquid-liquid colloidal mixture of the two immiscible substances. These emulsions may be of varying stability. Emulsions are of particular importance in oil spill response and mitigation because physical properties of emulsified crude oil can differ greatly from the parent crude oil. Emulsification increases the volume of the mixture significantly over the simple additive volumes of the oil and the water. It also increases the viscosity and changes the rheological nature of the oil, often to the point of creating major operational challenges for recovery, pumping, and storage. Heavily emulsified crude oils, termed mousses in the spill industry, are usually quite stable, contain in excess of 50% water by volume, and may become semi-solid in nature.

Emulsified oil is generally recalcitrant with regard to chemical dispersant application as a response measure. Additionally, emulsion breaking to recover spilled oil requires time and energy, and the water that is recovered most often requires further treatment prior to permitted release back into the environment.

The actual process of emulsification, the colloidal suspension of liquid droplets of one liquid in a continuum of another liquid, is well defined under controlled conditions in various commercial operations. Examples of emulsions in the food industry are homogenized milk, butter, and mayonnaise; in the personal care and health care industries, cold cream and ointments; and in the chemical industry, the emulsion polymer synthesis process is well known in the production of coatings and latex. However, emulsification of water from natural water bodies into petroleum, especially crude oil, is less well defined and understood. What is known is that spreading and evaporation of more volatile components can alter the composition and internal transport characteristics of the resulting oil slick. Exposure to sunlight, which is enhanced through spreading and with time, initiates a complex array of photo oxidative reactions which can transform the oil (Shankar et al., 2015). These and other weathering processes may enhance or diminish the tendency for crude oil to emulsify with water. The energy for the shear mixing forces needed to disrupt the interfacial tension between water and oil is largely provided by the combination of wind and breaking waves. As water, the dispersed phase, becomes more and more divided into smaller droplets within the oil continuum phase, the gravitational tendency for the higher density water to drop out is counteracted by viscous and interfacial forces in the continuum (Fingas et al., 2003). This process also relies upon re-stabilization of the oil-water interface of these smaller and smaller droplets of water. Stabilization of this interface which contributes to emulsification is a function of a complex array of constituents in the crude oil, and

to a certain extent the chemistry and physical state of the water body. It is thought that the asphaltene component of crude oil may significantly contribute to the stability of W/O emulsions (Buckley et al. 2007). Asphaltenes are an operationally defined, high molecular mass, polyaromatic, highly polar substituted spectrum of compounds found is most crude oils. Asphaltenes may aggregate at the oil-water interface where they can stabilize the interface thereby contributing to W/O emulsion formation and stability. Whether the asphaltene fraction of a crude oil may contribute to emulsification is not solely dependent upon concentration. What is important is the stability of those asphaltenes. Stability depends not only on the properties of the asphaltene fraction itself, but also on the effectiveness of the rest of the oil as solvent for asphaltenes (Long et al., 1981). It has been found that light oils with small amounts of asphaltenes may often support W/O emulsification better than heavier oils with a greater concentration of asphaltenes (de Boer et al., 1995). A light oil may consist largely of paraffinic material in which asphaltenes have limited solubility, while a heavier oil will most likely contain more intermediate components that tend to be good asphaltene solvents. Lower solubility contributes to asphaltene precipitation and aggregation which may lead to enhanced W/O emulsion formation. However, it is important to note that most crude oils probably contain some concentration of aggregated asphaltenes under almost any condition (Buckley and Wang, 2007). Resins in crude oil, another operationally defined heavy component, may also play a role in emulsification formation and stability. Resins are likely to include species that contribute to the overall solvent quality of the oil with respect to its asphaltenes.

The impetus for the test program that is the subject of this paper was provided through two related needs:

- The Department of the Interior's Bureau of Safety and Environmental Enforcement (BSEE) sought to establish the capability to provide stable, reproducible, saltwater-in-crude-oil emulsions for use at the Ohmsett Facility. The scale for producing these "standardized" emulsions needed to range from highly controlled laboratory quantities; through larger, easily produced, mid- or "drum" scale production; to large outdoor on-tank, quasi-natural production. These multi-scale, reproducible emulsions would act as standard or normalized models for comparative studies at Ohmsett or other programs.

- In addition to the program described above, BSEE and the National Oceanic and Atmospheric Administration (NOAA) partnered to directly support the 2010 Deepwater Horizon ongoing "lessons learned" by providing control and validation for surface oiling characterization efforts pursued under the Natural Resource Damage Assessment (NRDA) Oil on Water (OoW) workgroup. To advance understanding for oil spill preparedness, and in support of the needed validation, study options had been proposed for controlled as well as open water data collection experiments from multiple remote sensor technologies and platforms. The controlled portion of this effort was to be conducted in the outdoor wave tank at the Ohmsett Facility. This required production of a relatively large volume (400 to 800 gallons) of W/O emulsion "grown" under quasi-natural conditions with wave energy and exposure to the elements, especially UV energy from natural sunlight.

The two needs were operationally and functionally combined. So along with providing valuable information on their own, the laboratory and mid-scale portions provided background data for the large volume, on-tank production of emulsion for the remote sensing study. To our knowledge, this was the first time such a multifaceted effort of this type and at this scale had

been done. The subject of this paper is the production of reproducible W/O emulsions at Ohmsett. This program provided a "first cut" exercise in what is intended to be an ongoing and evolving effort at Ohmsett. The lessons learned, as well as suggestions for future provisions and studies will be discussed.

METHODS AND MATERIALS

Given the concurrent project goals of developing Ohmsett's capability to produce stable emulsions for testing and research; and, meeting the need for "naturally" produced, tank-scale emulsion for the BSEE remote sensing program, the chosen subject oil was a crude oil blend from the Hoover Offshore Oil Pipeline System (HOOPS) in the western Gulf of Mexico (GOM). This crude, which was available in sufficient volumes in the Ohmsett inventory, satisfied the need for quantity, and GOM relevance to the large remote sensing test program. HOOPS, which is considered a pipeline oil, includes oil from the constituent fields Diana, South Diana, Hoover, Marshal, and Madison. It should be noted that as a pipeline blend, HOOPS may contain additives and will probably have been pretreated with dehydrating agents.   HOOPS Blend is a medium-light crude with medium sulfur content.   Key physicochemical specifications for HOOPS Blend are given in Table 1.

Parameter - Units	Method	Results
API Gravity @ 60°	ASTM D2887	**34**
Flash Point, closed cup - °F	ASTM D93	74
Paraffin - wt. %		<0.01
Pour Point - °F	ASTM D97	-22
Sulfur - wt. %	ASTM D4294	1.360
Saturates - wt. %	ASTM D2007	29.49
Aromatics - wt. %	ASTM D2007	60.36
Asphaltenes - wt. %	ASTM D2008	0.14
Polar Compounds (Resins) - wt. %	ASTM D2009	10.00

Table 1. Specifications for HOOPS Blend crude oil. (Sampled 11/13/15; Recd. 11/25/15.)

Laboratory-Scale Study

Lab-scale samples were weathered, exposed to UV photo-oxidation, and emulsified to determine

the best candidate treatment(s) for forming a stable emulsion at the mid- and tank-scale studies.

Lab-Scale Weathering

Lab-scale weathering involved exposing the subject crude oil to controlled air sparging

(bubbling) in gas sparging tube/traps. The goal was to achieve various stages of weathering as

defined by loss of mass in the volatile fraction of the crude oil. Figure 1 shows the gas sparging

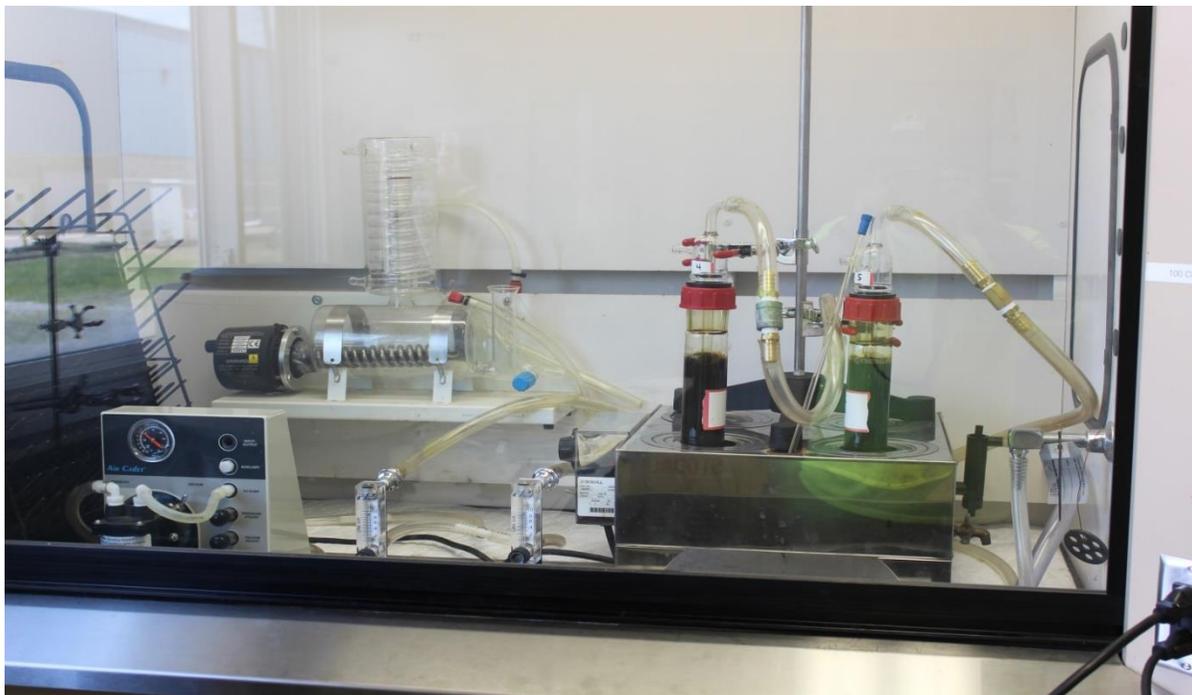traps in use for crude oil weathering.

Figure 1. Air sparging apparatus for crude oil weathering as assembled in the lab fume hood.

Provision for two concurrent samples is shown with the tubes partially lowered into a temperature controlled water bath. Air flow rotameters can be seen to the left of the water bath.

Sparging was done at room temperature (approx. 20 C) for the first series of samples. Two later samples were air sparged at an elevated temperature range (45 to 50 C) by lowering the tubes into a temperature controlled water bath (shown). Air flow to each tube was controlled and maintained at one (1) liter/minute. Three initial volatile hydrocarbon mass losses (weathering) at 20 C were targeted; 10 percent, 20 percent, and an extended weathering over approximately 6 days which yielded a mass loss of almost 24 percent. Sparging at 1 L/min at the elevated temperature range was conducted to a mass loss of approximately 14 percent for two individual samples.

Loss of mass was originally determined using the available balance that could accommodate the total mass of the apparatus and the oil sample. It should be noted that this balance provided mass measurements with a resolution of ±2.5 g. A more sensitive balance was obtained for later weights. However, even the lower resolution measurements were sufficient when the data was analyzed to determine a trend.

Lab-Scale Photo oxidation

It was decided to expose unweathered (fresh) and weathered samples to natural UV exposure on the roof of Building R24 (the tower) at the Ohmsett Facility. This decision was based on the fact that natural exposure to the full sun-based UV spectrum, plus further exposure to natural winds would be most realistic. Accordingly, 200 ml of each of these four samples were placed in each of four 182 mm Ø, Pyrex crystallization dishes. Each dish was in turn placed in a large polypropylene tray as secondary containment. The entire kit was then placed

on the roof of R24. Figure 2 shows the roof-top weathering arrangement. Over the next several days, time based sample temperatures, densities, and general weather conditions were recorded.

Figure 2. Laboratory weathered HOOPS crude oil samples spread in crystallization dishes ready for rooftop UV exposure.

Lab-Scale Emulsification

To test and choose a small scale (laboratory) simulation of water wave action on floating oil, surrogate samples of crude oil and tank water were placed in various glass vessels on mechanical mixing devices in the laboratory. The observations resulted in the choice to float 25 ml of oil on 250 ml of tank water in one quart, glass Mason jars with lids, with mixing done on the large Ohmsett laboratory platform mixing table. The mixing regime was to run the mixing table at 160 cycles per minute (cpm) for an interval of time that was to be dictated by observing the progress of any resultant water-in-oil emulsification. The tank water used had a density of 1.023 g/ml, a salinity of 27.8 parts per thousand (ppt), a surface tension of 53.8 dynes/cm, and a pH of approximately 7.2. At the start of mechanical mixing the water temperature was 23.0 C.

After five hours of mixing at 160 cpm, empirically stable emulsions developed in each of the four samples. The resulting water/oil temperature for all for samples was 27.1 C. Table 2 lists these samples and their subsequent designation:

Lab-Scale Identification Designations			
Identification Number	Weathering	Ultra Violet	Emulsification
633-FO1-UV-E1	None/Fresh	Yes	5 hours
633-W01-UV-E2	24% (extended)	Yes	5 hours
633-W02-UV-E3	10%	Yes	5 hours
633-W03-UV-E3	20%	Yes	5 hours

Table 2. Lab-scale identification designations for the four levels of weathering.

After the five hour mixing period, each of the four emulsified samples were immediately placed in individual 250 ml Pyrex separatory funnels. For each sample, free water (i.e., water not associated with emulsion or inclusion) was immediately separated, and the decanted fluids were allowed to settle/separate over time. In this way, water loss over time could be used as a measure of emulsion stability. Figure 3 shows an example of an emulsion (-E3) in a separatory funnel prior to removal (decanting) of free water.

Figure 3. Emulsified oil sample in separatory funnel prior to decanting free water.

Tank-Scale Emulsion Study

In the field, it has been observed that well developed natural emulsions are remarkably stable and display a unique color change as the emulsification process unfolds. Stable emulsions that most closely resembled open water conditions were required for the BSEE Remote Sensing project; hence, the HOOPS was naturally weathered on the Ohmsett tank for several days first, then the wave generator provided the necessary mixing and shear energy to incorporate water into the oil. The objective was to deploy HOOPS on the surface of the wave tank, while providing just enough surface control of the slick to assure the following: adequate exposure to waves and the elements; access to the slick for sampling and documentation; maintenance of an adequate slick foot print for observation, and remote sensing from various altitudes above the slick. At the same time, the surface control measures needed to minimize exposure of the slick to disturbances or energy inputs other than those of waves and natural weathering. To accomplish this task, an integrated system of booming, fixed and mobile near-surface water sprayers, hand-held fire hoses, and subsurface upwelling current devices were employed. Diagram 1 provides a simple schematic of the set-up used establish and maintain surface control of the subject crude oil slick.

On July 14 at 1130 hours, 400 gallons of fresh HOOPS crude oil were placed on the Ohmsett tank water surface. The oil was allowed to naturally weather with wind and solar radiation for almost 95 hours. The previously described surface control system was used to keep the slick spread and exposed to the elements with a minimum of disturbance. At 1000 hours on July 18, waves were introduced to the tank and the slick. The wave setting used was same 35 cpm, 6-inch stroke (1.7 sec, λ=12 ft., $H_{1/3}$=22 in.). Waves were turned off for several hours later

during the afternoon of July 18 for sampling activities. Waves remained on over the course of the week of July 18 to allow the evolution of emulsion formation. However, wave generation operations were stopped for nominal periods of time during sampling activities and when aerial remote sensing was underway by various subcontractors on the project.

Although there were a large number of sampling, monitoring, and remote sensing operations conducted by the various research and testing stakeholders during the tank-scale testing phase, this paper focuses on the analyses performed by Ohmsett in support of the emulsion production aspect of this study. Characterization of the tank-scale crude oil and W/O emulsion slick, and tracking the progress of emulsification over several days presented several challenges. Laboratory capabilities, space, and qualified personnel were limited. Sampling of a large-scale emulsion slick "on the move" is difficult and sample location choice is subjective. W/O emulsions during the early and mid-stages of emulsification are inherently unstable once removed from their energetic water environment. Often the mere act of sampling changes the nature of the emulsion itself. Finally, it was required that Ohmsett operations support the larger multifaceted goals of the program. Therefore, Ohmsett sampling and analyses needed to interfere with overall operations as little as possible. A simple program of sampling and analysis was devised to meet these challenges.

To facilitate representative sampling of the forming emulsion, a two liter separatory funnel was adapted to field (tank-side) use. Then, several visually representative samples were withdrawn from several adjacent locations at several depths using a sampling thief, and with careful ladling. These individual samples were combined on the spot in the separatory funnel where the non-emulsion associated free water was immediately decanted. Once this field

separation was affected, the sample could be transported to the lab for a toluene extracted, centrifugal determination of the water content of the collected emulsion.

The density of the composite sample as collected above was determined immediately using a hand-held, ultrasonic densitometer. In the cases where the viscosity of the emulsion did not allow the fluid to be drawn into the capillary of the densitometer, the sample was quickly transported to the laboratory for measurement using a pycnometer. Where the sample exhibited a lack of homogeneity, a "best visual judgement" determination was used to provide representative samples for the pycnometer density analysis. For all density determinations, measurements were made at prevailing ambient laboratory or air conditioned bridge-house temperatures of approximately 20 C.

Viscosity determinations were made of the composite emulsion samples using a temperature controlled, rotary viscometer with a cup and spindle rated for the anticipated viscosity range. All viscosities were determined at 20 C. Again, the "best visual judgement" technique was used to choose a representative sample for viscosity determination in the cases where there was a distinct lack of homogeneity.

Regular water sampling (at least daily during operational days) was used to provide data for density, salinity, interfacial tension, and surface tension.

RESULTS AND DISCUSSION

Lab-Scale Weathering

As expected, loss of mass due to enhanced evaporation (sparging) proceeded with time. At approximately 20 C, reduction of the HOOPS volatile components in the realm of 10% by weight proceeded by the curve in Figure 4.
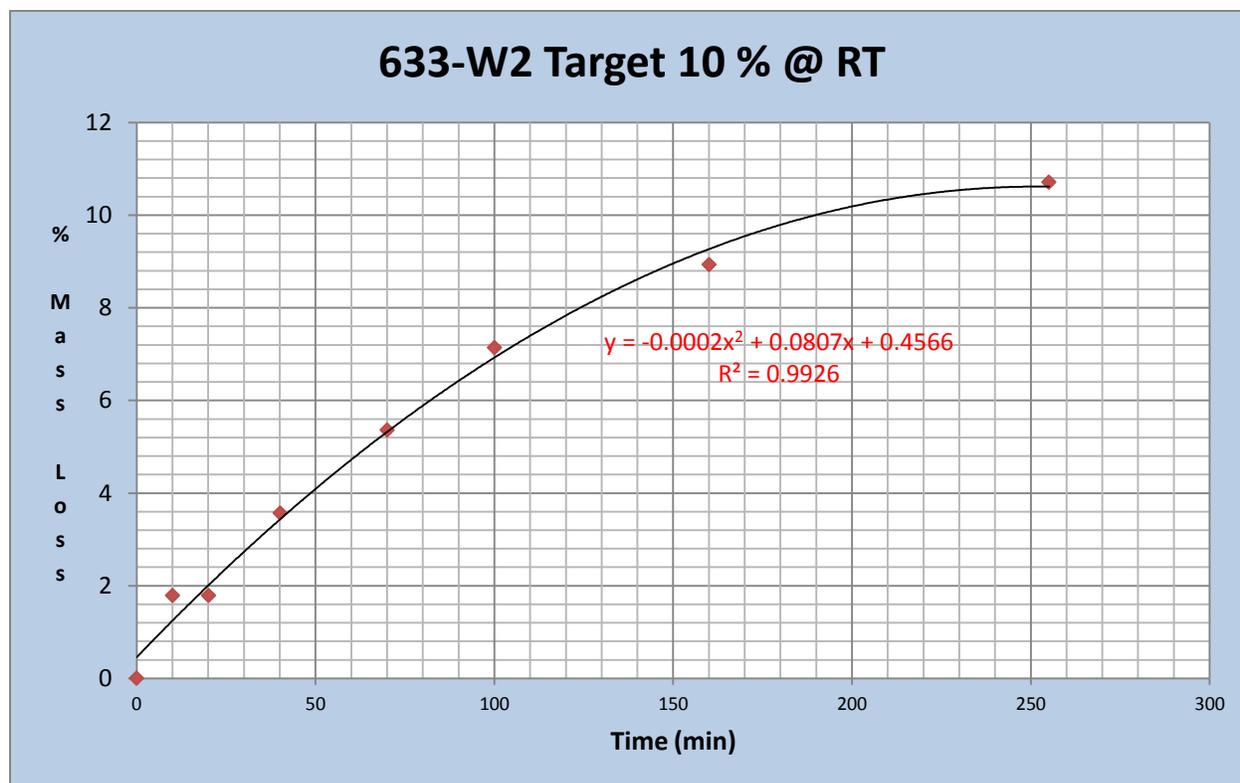
633-W2 Target 10 % @ RT

Figure 4. Mass loss to approximately 10% over time of HOOPS crude oil exposed to air sparging at 1 L/min in the lab at approximately 20 C.

At room temperature, and under the condition of air sparging at 1 L/min, mass loss weathering proceeds to approximately 10% in a little over four hours. This weathering proceeds along a curve described by a second order polynomial. This seems to typify light to medium crude oil weathering in the earlier stages of loss of volatile components.

Figure 5 shows the volatile mass loss with sparging at 1 L/min at 20 C for the extended period of approximately 148 hours. At this point in time loss of mass is leveling off at 23.6%, and the curve is well represented by an exponential relationship. Generally, this is more indicative of the overall weathering, under controlled conditions, of light to medium crude oils.

633-W1 Extended Weathering @ RT

$y = 3.2851\ln(x) + 7.5596$
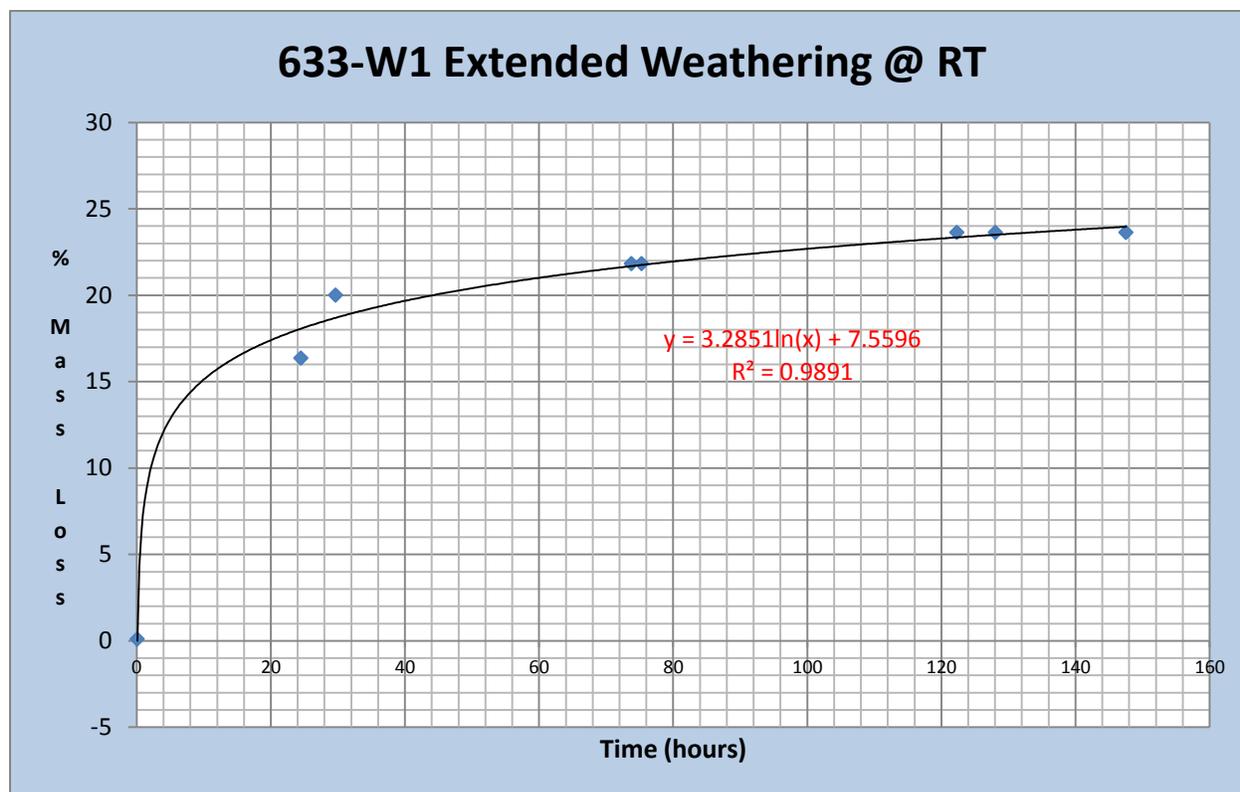$R^2 = 0.9891$

Figure 5. Mass loss of HOOPS crude oil over extended time (148 hours) with air sparging at 1 L/min in the lab at 20 C.

Air sparging at the same flow rate (1 L/min) at the elevated temperature range of 45 to 50 C produced the similar behavior albeit compressed in time. The two samples of fresh HOOPS weathered in this way produced an approximate 14% loss of mass over approximately 6 hours.

As expected, other physical characteristics changed with air sparge induced weathering. As measured in the lab, these included density (ρ), dynamic viscosity (μ), surface tension (ST) versus air, and interfacial tension (IFT) versus tank (salt) water. The data from these determinations all demonstrate increases in the measured physical characteristics, as seen in Table 3 below.

Description	Sample #	ρ (g/ml @ 20C)	Viscosity (cP @ 20C)	S.T (dynes/cm @ 20C)	I.F.T (dynes/cm @ 20C)
FRESH HOOPS	633-01	0.8519	16.17	28.9	9.2
HOOPS WEATHERED 10% BY WEIGHT	633-W02	0.8789	35.40	28.4	9.4
HOOPS WEATHERED 20% BY WEIGHT	633-W03	0.8966	60.63	30.5	13.2
HOOPS WEATHERED 24% BY WEIGHT	633-W01	0.9052	88.44	31.1	13.9

Table 3. Change in physical characteristics of HOOPS crude oil with weathering.

Lab-Scale UV PhotoOxidation

As described earlier, each of the weathered samples including fresh (unweathered) HOOPS were exposed to natural sunlight and the elements on the roof of the tower building (Bldg. R24) at the Ohmsett Facility. The samples were exposed to sunlight a total of approximately 20 hours over a five-day period. Exposure was constrained to facility hours of operation. The samples were stored indoors after-hours and during the evenings. It should be noted that this time-period included a long holiday weekend (Memorial Day) during which the samples were stored indoors. Although periodic density measurements were recorded, it became obvious that a trend analysis for these or any other physical characteristics would be uninformative. This was due to the lack of consistency and control of the time intervals of exposure, and the highly variable conditions of exposure such as and especially temperature. Operational reality sometimes overrules the need for tidy data. However, presentation of starting and ending data as presented in Table 4 can be informative.

633 Oil Sample Densities Before and After Rooftop UV Exposure All ρ's determined @ 21-23° C			
Sample #	Oil Description	Initial ρ, prior to UV (g/ml)	Final ρ, after UV (g/ml)
633-F01 (-UV1)	Fresh HOOPS crude oil	0.852	0.928
633-W01 (-UV2)	HOOPS extended weathering (24%)	0.905	0.926
633-W02 (-UV3)	HOOPS weathered to 10%	0.879	0.926
633-W03 (-UV4)	HOOPS weathered to 20%	0.897	0.926

Table 4. Densities of weathered samples of HOOPS prior to and after UV exposure

The density data after exposure to sunlight (UV) indicates that all samples seem to asymptotically approach a nominal density of 0.93 g/ml regardless of initial weathering treatment by air sparging in the laboratory. This of course is due to further weathering and loss of volatile fraction during the energetic exposure to sunlight. Recall that the long term (148 hours) weathered sample seemed to approach a final density of 0.91 g/ml. The higher terminal density of the UV exposed samples may indicate an affected chemical change that did not occur in the in the sample that was only air sparged. However, the difference could also lie within the margin of error in these determinations. This exercise was not designed to determine the actual effects of photooxidation due to exposure to sunlight. Investigation of this affect would require further investigation.

Lab-Scale Emulsification

Emulsification of the weathered, sunlight-exposed samples to five hours of agitation with saltwater in mason jars produced samples that were placed in separatory funnels to demonstrate emulsion stability. A combination of visual observation and measurement of the volume of

water separating from the emulsion over time were used to determine comparative stability.

Tables 5-7 list the results after settling times of 1:15 hours, 17:00 hours, and 24:45 hours.

1 Hour 15 Minutes Settling Time		
Sample Number	Sample Description	Water Decanted/Notes
633-F01-UV-E1	Fresh Oil/UV Exposed/5 hour Mixing	157 ml
633-W01-UV-E2	10% Weathered Oil/UV Exposed/5 hour Mixing	112 ml/ noted heavy slug of oil/solids in neck
633-W02-UV-E3	20% Weather Oil/UV Exposed/5 hours Mixing	153 ml
633-W03-UV-E4	Extended Weathering to 24%/UV Exposed/ 5 hours Mixing	77 ml

Table 5. Volume of water separating from emulsion after 1 hour 15 minutes settling time

17 Hours Settling Time		
Sample Number	Sample Description	Observations/Notes
633-F01-UV-E1	Fresh Oil/UV Exposed/5 hour Mixing	Density = 0.991 g/ml at 23.0º C
633-Wo1-UV-E2	10% Weathered Oil/UV Exposed/5 hour Mixing	• Density not possible • Heavily entrained water visible • Not homogenous enough to measure representative sample
633-W02-UV-E3	20% Weather Oil/UV Exposed/5 hours Mixing	• Density = 0.986 at 23.5º C • Some visible entrainment, but representative sample on non-entrained matrix was possible
633-W03-UV-E4	Extended Weathering to 24%/UV Exposed/ 5 hours Mixing	• Representative sample no possible • Heavily entrained water folded in throughout sample

Table 6. Volume of water separating from emulsion after 17 hours settling time

24 Hours 45 Minutes Settling Time		
Sample Number	Sample Description	Observations/Notes
633-F01-UV-E1	Fresh Oil/UV Exposed/5 hour Mixing	• Final density: 0.994 g/ml at 23.4º C • No water decanted • Sample was homogenous and visually stable
633-Wo1-UV-E2	10% Weathered Oil/UV Exposed/5 hour Mixing	• 61 ml of additional free water was decanted • sample not homogeneous • a lot of folded entrained water observed
633-W02-UV-E3	20% Weather Oil/UV Exposed/5 hours Mixing	• 22 ml of additional free water was decanted • a lot of folded entrained water observed
633-W03-UV-E4	Extended Weathering to 24%/UV Exposed/ 5 hours Mixing	• 108 ml of additional free water was decanted • sample was not homogeneous • a lot of folded entrained water observed

Table 7. Volume of water separating from emulsion after 24 hours 45 minutes settling time

A major objective of the lab-scale tests was to determine if HOOPS could form stable emulsions, and if so, which weathering and UV exposed treatment scheme would be the best candidate to form emulsions on the Ohmsett tank. The stability testing seemed to indicate that the air-sparged weathered samples generally retained the most water and stability early (see 1:15 hour results). However, they all seemed to destabilize over time.   On the other hand, these tests indicated that fresh, unweathered HOOPS oil that was exposed to sunlight in the same manner that the weathered samples were, released the least amount of water, measured the highest density, and had enough uniformity to obtain a viscosity measurement.

Large-Scale Emulsion Study

To reiterate, the two overall objectives of this program were to establish the capability to provide stable, reproducible, saltwater in crude oil emulsions for use at the Ohmsett Facility; and, to support the BSEE remote sensing program by offering a large, open-air, W/O emulsion on saltwater venue for realistic observation and data collection by multiple remote sensing platforms. Accordingly, the lab- and mid-scale studies provided supportive data and operational experience in achieving the large-scale operational objectives. A general description of the execution of that operation has been described previously. Tabulated data for periodic sampling and analysis of the developing emulsion and background water analyses are provided below.

It should be noted that to accommodate the needs of the larger remote sensing program, and the operation limitations imposed by the need to cease wave operations during evening hours, adherence to a strict sequential time-line was not possible. However, the data, in conjunction with documentation of daily operations, does provide for some informative observations.

From 1130 hours on July 14, the time of initial deployment of 400 gallons of HOOPS crude oil onto the surface of the tank, until 1015 hours on July 15, the oil slick was allowed to move about on the surface exposed to the natural day and night elements without applying wave generation. During daylight operational hours, the slick was kept spread out as much as possible to provide surface area for natural exposure to sunlight. This was accomplished using the system of sprayers, booms, and current generators described earlier. Sampling of the slick during that wave-free time period indicates a constant increase in density and viscosity as would be expected of loss of mass due to weathering. Minimal emulsification or color change was observed during this period of no wave energy, other than surface ripples and capillary waves.

Generated waves with breaking field, as descried earlier, were applied starting at 1015 hours on July 18. For the next three days and eight hours, the same wave field was applied periodically. Waves were interrupted each evening, for a short time during sampling operations, and occasionally in response to the needs of the remote sensing program. However, during this time period significant emulsification was occurring. This was evidenced by the change in slick color and consistency, and the significant increases in density, viscosity, and water content. The observed variability in these physical quantities seems to correlate well with those documented times of no wave generation. Overall, density increase to over 1.0 g/ml, viscosity increase over 40 times to approximately 16,000 cP, and water content from nil to 84 percent by volume were observed. During times of no applied waves, quick filed determinations for water content indicated that water content of the emulsified oil could drop to less than 60% water by volume. This was empirically evidenced by the change in emulsion appearance to less "thick" and darker in color than when energetic waves were applied. It was also observed that, in time, the emulsified slick became streaked with different colors and consistencies. All of this is indicative

of an emulsion that is not fully stable without continued input of wave energy, and is in a transient stage of emulsification. Tables 8 and 9 list the test fluid properties measured during the large scale emulsion formation study.

TEST FLUID PROPERTIES NOMINAL OIL PROPERTIES @20C (PRE-TEST)					
TEST OIL:	SAMPLE #	ρ @ 20C (g/ml @ 20C)	VISCOSITY @ 20C (cP @ 20C)	WATER QUANITITATIVE SAMPLE #	% WATER
FRESH HOOPS	622-01	0.8508	16.5		
WEATHERED HOOPS	622-02	0.9183	178.8		
WEATHERED HOOPS	622-03	0.9243	289.6		
WEATHERED HOOPS	622-04	0.9287	390.7		
WEATHERED EMULSIFIED HOOPS	622-05	0.9817	15880.0	622-D01	79
WEATHERED EMULSIFIED HOOPS	622-06	0.9771	13490.0	622-D02	75
WEATHERED EMULSIFIED HOOPS	622-07	0.9768	16010.0	622-D03	84
WEATHERED EMULSIFIED HOOPS	622-08	0.9571		622-D04	82
WEATHERED EMULSIFIED HOOPS	622-09	1.0158		622-D05	75
WEATHERED EMULSIFIED HOOPS	622-10	1.0081		622-D06	74

Table 8. Tank-scale test fluid properties

TANK WATER PROPERTIES				
WATER SOURCE	DATE	ρ@TEMP (g/mL @C)	SALINITY @TEMP (ppt @C)	IFT (dynes/cm)
TANK WATER SURFACE SAMPLE	7/14/2016	1.0203 @ 22.6	29.0 @ 20	27.8
TANK WATER SURFACE SAMPLE	7/15/2016	1.0193 @ 25.8	29.0 @ 20	28.9

TANK WATER SURFACE SAMPLE	7/18/2016	1.0191 @ 25.0	29.0 @ 20C	29.0
TANK WATER SURFACE SAMPLE	7/20/2016	1.0189 @ 24.1	28.9 @ 20C	29.3

Table 9. Tank-scale water properties

CONCLUSIONS

The intent of this study was to develop a method for the Ohmsett Facility to create large quantities of stable, reproducible water-in-oil emulsions without tying up the large Ohmsett tank for weeks at a time. Concurrent to this study was the BSEE remote sensing project which required large quantities of realistic emulsions and a fly-over friendly venue; hence, results from that effort were incorporated into the overall lessons learned. At all three test scales, increases in viscosity and density were consistent with weathering prior to emulsification. Mass loss from evaporation in time eventually approached an exponential relationship with an asymptotic leveling off consistent with the literature for most crude oils (there is no mention of weathering or emulsification of HOOPS in the literature). Evaporative weathering at higher temperature shifted this relationship accordingly.

Once emulsification began, the general trend did indicate higher values of density and viscosity that followed the overall trend of increased water content in the emulsion. The on-tank emulsion density data differed slightly from what the analyzed water content would predict on a calculated mass and volume basis. In the early phases of emulsification, resultant densities were less than the calculations based on constituents would predict, albeit only by a few percent. Later in the on-tank emulsification process, that trend reversed with measured densities being slightly higher than calculated values would predict. This could be due to the interaction of water and the crude oil components that may produce an expansion or contraction of the

composite material not explainable by volumetric considerations alone. However, the differences are within the error of scale and sampling, and controlled, small-scale studies would need to be performed to elucidate such a phenomenon. Accordingly, emulsification proved quite fleeting and obtaining representative samples across the tank within the emulsion thicknesses themselves proved problematic. Related was the reality that the stability of the emulsions changed during transport of samples from the tank to the nearby on-site lab. Later viscosity measurements were not possible given the instability of these sample emulsions. Moving forward, investigation of existing in-situ instrumentation to measure water content, density, and particle size distribution of water droplets in the emulsion could prove valuable The practice of production and study of emulsions by other industries, such as cosmetics and coatings, could be useful in this concern.

The stability of emulsions formed in the environment are based on the complex interaction of a number of constituent and energetic factors over time. In the present study, it was observed that the emulsion slick would persist as long as waves continued to supply shear energy. However, once waves stopped, the emulsified slick would break down non-homogeneously. Water content would readily drop from the 70 to 80% by volume range to under 50%. Streaks of what appeared to be more "oil like" material were observed. The low asphaltene content as well as high ambient temperatures during the tank-scale tests in mid-July most likely led to the instability of the emulsions. Asphaltene stability through interaction with other constituents may also have contributed.

This study focused on the creation of water-in-oil emulsions using HOOPS oil, and all oils are different; therefore, strict standardization is impossible. However, valuable insight into necessary weathering, photo oxidation, and mixing energy was gained to move forward in order to create reproducible, stable emulsions for testing at Ohmsett.

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