Meso-scale Weathering of Cold Lake Bitumen/Condensate Blend

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Background

The physical properties of two diluted bitumen products were evaluated in 2005 to generate the necessary parameters for marine oil spill modeling (SL Ross 2005). The products tested were MacKay River Heavy Bitumen and Cold Lake Bitumen that were diluted with synthetic crude (Suncor Synthetic Light) and condensate (CRW condensate), respectively, to facilitate shipping. The 2005 analysis included exposing the oils in a wind tunnel to generate evaporated oil products under controlled conditions. This study investigates the weathering of one of the products, Cold Lake Bitumen diluted with condensate (CLB), under conditions more similar to a discharge to surface waters. The primary goal of the current study was to investigate the density change of the diluted bitumen product as it weathers under more realistic conditions than those used in the standard testing completed in 2005. The Cold Lake Bitumen diluted with condensate (CLB) was selected for testing because it is now the more commonly shipped product of the two previously tested, is expected to weather more quickly, and was readily available for testing. The primary concern being addressed in this project is the potential for the sinking or submergence of diluted bitumen products after prolonged exposure on water. The tank used in the testing is shown in Figure 1. This tank was recently fabricated and installed in the SL Ross laboratory for oil weathering studies.

Test Facility Description

The meso-scale oil weathering flume shown in Figure 1 consists of a channel 0.5 metres wide and 1.5 metres deep with a total centre-line length of 8.7 metres. A water depth of 1 metre was used in this test series. The inner and outer radii of the tank ends are 0.5 and 1.0 metres and the tank straight sections are 2.0 metres long. The tank footprint is 2.0 m wide by 4.8 metres long (including a wave generating section). The tank enclosure is covered by clear Lexan sheets to create an air chase above the water surface. Wind is circulated above the water using the fan shown in Figure 2. The flex hose shown in Figure 1 is attached to a ventilation fan that extracts vapours from the air space above the oil. Water currents are created using the thruster configuration shown in Figure 3. The water temperature is controlled using the chiller and heat transfer coil shown in Figure 4.

Ultra violet (UV) wavelength light is directed to the tank surface at one end of the tank using the fixture shown in Figure 5. A port has been cut through the aluminum tray and lexan cover to allow unimpeded light to irradiate the surface of the test tank. The UV light shines over approximately 1 m^2 of the tank surface area. To compensate for the limited coverage of the UV lamp (1 m^2 of a 4.36 m^2 test tank), it was run at high intensity for an average of 12 hours per day during testing, as opposed to 8 hours per day which is the solar simulator standard. The high intensity UV system emits an average of approximately 15 mW/cm^2. To put this UV light intensity in context, on a bright sunny June day in Ottawa (outdoor temperature reading of 30°C), approximately 5 mW/cm^2 of UV light was measured at noon.

For this test series the circulating oil was also subjected to a cascade of water using the arrangement shown in Figure 6. Water was pumped from the bottom of the tank from a location separate from the main flume (see Figure 4). The water cascade was implemented to impart energy into the system to accelerate weathering and emulsification tendencies of the oil.

Figure 1. Meso-Scale Oil Weathering Tank.

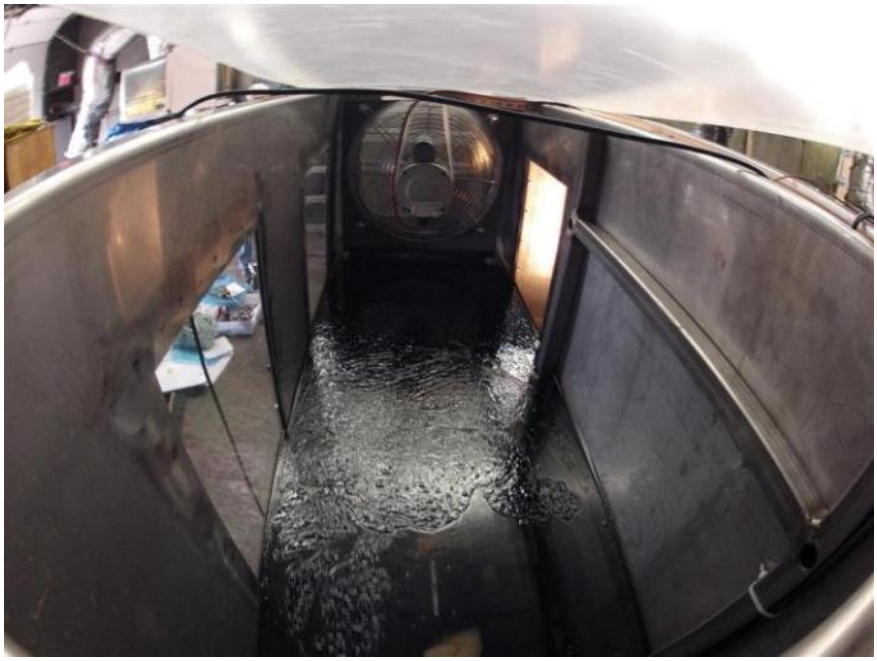

Figure 2. Air Space Fan.

Figure 3. Water Current Thrusters

Figure 4. Water Chiller Heat Transfer Coil and Water Cascade Pump Location

Figure 5. Ultra Violet Light mounted above Access Port.

Figure 6. Cascading Water.

Test Methods

Approximately 5L of oil (see Table 1) was placed in the tank and circulated around the tank via surface wind shear and water currents. In this test series the wind speed was set to 3.0 knots (1.5 m/s). The water velocity was set to approximately 0.5 knots (0.25 m/s). The velocities were set to generate as consistent as possible movement of the oil around the tank surface while minimizing the possibility of entrainment of the oil by the submerged water current thrusters shown in Figure 3. To further protect against entrainment, the upper thruster was shut down and the single lower thruster was used as the primary drive unit during testing. The tank was filled with fresh water to a height of 1.0 metres and the temperature was maintained at 15 °C ± 1 °C throughout the testing. Oil samples were taken periodically throughout the test duration to capture the change in oil properties with time. The collected samples were subjected to density, water content and viscosity measurements. Density measurements were made with an Anton Parr DMA 35 density meter operated within an environmental chamber. Viscosities were measured using a Brookfield DV-III+ viscometer using a cone and plate system with a computer controlled temperature bath. Water contents were determined by adding an emulsion breaker to a vial of the emulsion sample and placing the vial in a hot water bath overnight, maintained at 50°C, to break the emulsion. The heights of the separated oil and water layers were then measured to determine the water content. Micro-photographs of the samples were also taken to provide a qualitative assessment of the emulsified state of the oil over time. Digital video and still photographs were taken of the oil periodically and the behaviour of the oil was observed and recorded. Free-floating surface oil and oil adhered to the tank walls were collected and weighed to identify the percentage present in each of these compartments, at the end of each test. Oil on the tank bottom would have been collected and weighed if present.

Table 1. Total oil used in Tests

Sample ID	Description	2.5 L Input Container 1 (g)	2.5 L Input Container 2 (g)
Test #1	Oil Container - full	2711	2655
	Oil Container - empty	360	359
	Net Oil (g)	2351	2296
	Total Oil Input (g)		**4647**
Test #2	Oil Container - full	2778	2694
	Oil Container - empty	373	369
	Net Oil (g)	2405	2325
	Total Oil Input (g)		**4730**

Results

Two separate tests were conducted using the CLB. The primary differences in the two tests were the presence of the UV light, and the duration of the second test which was extended to determine possible longer term weathering issues. Summaries of the measured oil properties for the two tests are provided below in Table 2 and Table 3.

Table 2. Test Series #1 - Oil Property Summaries

Sample ID	Run Time (hr)	Density @ 20°C (g/cc)	Water Content (%)	Link to Emulsion Micro-Photo	Viscosity @ 15°C	
					(cP)	Shear rate (s^{-1})
T1S0	0	0.945		blank slide	3,300	2
T1S1	1.5	0.981	30	t1s1emul	20,000	2
T1S2	6	0.986	34	t1s2emul	70,030	1
T1S3	24	0.992	39	t1s3emul	116,000	1
T1S4	49	0.993	38	t1s4emul	168,000	1
T1S5	72	0.994	30	t1s5emul	190,500	1
T1S6	96.5	0.995	20	t1s6emul	200,000	1
T1S7	120.5	0.995	26	t1s7emul	206,500	1

Table 3. Test Series #2 - Oil Property Summaries

Sample ID	Run Time (hr)	Density @ 20°C (g/cc)	Water Content (%)	Link to Emulsion Micro-Photo	Viscosity @ 15°C	
					(cP)	Shear rate (s^{-1})
				blank slide		
T2S1	0	0.945	0	t2s1emul	3370	2
T2S2	0.5	0.968	26	t2s2emul	4370	2
T2S3	1	0.976	29	t2s3emul	15,480	2
T2S4	3	0.985	30	t2s4emul	38,300	2
T2S5	16.3	0.994	23	t2s5emul	145,000	1
T2S6	24	0.995	34	t2s6emul	193,000	1
T2S7	48	0.994	26	t2s7emul	244,500	1
T2S8	96	0.998	20	t2s8emul	400,000	1
T2S9	120	0.996	17	t2s9emul	420,000	1
T2S10	120	0.995	15	t2s10emul	442,000	1
T2S11	140	0.997	12	t2s11emul	382,000	1
T2S12	140	0.996	15	t2s12emul	550,000	1
T2S13	285	0.998	18		825,000	0.4
T2S14	285	0.997	13		665,000	0.4
T2S15	311	0.998	12		1,730,000	0.2
T2S16	311	0.998	17		1,090,000	0.2

Oil samples were taken every few hours at the beginning of the test and less frequently as the test progressed to capture the more rapid early change in properties. Samples were normally collected from the east end of the tank, near the UV light. Additional samples were also collected from the west end of the tank (near the chiller) as represented by samples T2S10, T2S12, T2S14, and T2S16. Weathered product viscosity and density did vary with sample location, but trends were generally consistent.

A summary of the measured properties is presented below.

Density

Oil densities were measured at 20°C and compared with the density of water measured at 20°C due to difficulties in obtaining density measurements of the extremely viscous oil samples at lower temperatures. This was a sample handling issue, specific to the technology used to obtain precise density measurements.

The measured densities for all emulsion samples never exceeded 0.998 and the density increase peaked after approximately 96 hours in both tests. Plots of emulsion density versus time for the two tests are provided in Figure 7.

In test 1 where there was no exposure to UV light, the emulsions generally remained buoyant throughout the entire 5 days. The emulsion densities never exceeded 0.995 g/cm^3 at 20 °C in this test whereas the density of the fresh water at the same temperature is 0.998 g/cm^3. Some oil was over-washed and temporarily submerged at the water cascade during the test.

When the oil was less viscous during the initial few hours of the runs, the water cascade sheared the oil into small droplets (1-4mm diameter, by observation). These drops submerged to a maximum depth of 10 cm and resurfaced within a metre of the water cascade (within 4 seconds). As the oil weathered, the water cascade was less effective at shearing the oil which resulted in larger particles that were not driven as deep into the water column.

Densities of the parent oil after the emulsions were broken were also measured. These data are also provided in Figure 7. In the first test, with no UV light exposure, the parent oil density was consistently less than that of the emulsion sample and reached a maximum of 0.993 g/cm^3. The water present in the emulsion increases the density of the emulsion over that of the parent oil.

In test 2, where UV light exposure was added, the emulsion densities reached 0.998 g/cm^3, remaining neutrally buoyant. After 48 hours of exposure, small oil droplets were visible throughout the water column and the water became cloudier with time indicating an ongoing natural dispersion of a small amount of oil. Figure 8 and Figure 9 show photographs with the oil drops present in the water column. The oil drops are on the order of 30 to 70 microns in diameter in these photos. This behaviour was not observed over the 120 hour duration of test 1 where the

oil was not exposed to UV light. Water samples were taken after 6 and 11 days of exposure and micro-photographed using the same setup as that used for emulsion photography.

The parent oil density increased more rapidly in the second test. This can be attributed to the UV light exposure. The measured parent oil and emulsion densities were very similar in test 2. This may be due to the more rapid increase in the parent oil density to a value near that of the water, the lower water content of the test 2 emulsions and the difficulty of injecting highly viscous samples to obtain density measurements.

The density meter had to be cleaned at a warm temperature (approximately 30°C) to reduce the viscosity of the sample. It was then left to reach equilibrium with the test temperature, and recalibrated after each oil measurement in order to obtain accurate measurements. Measurement values for water did not drift more than 0.2%.

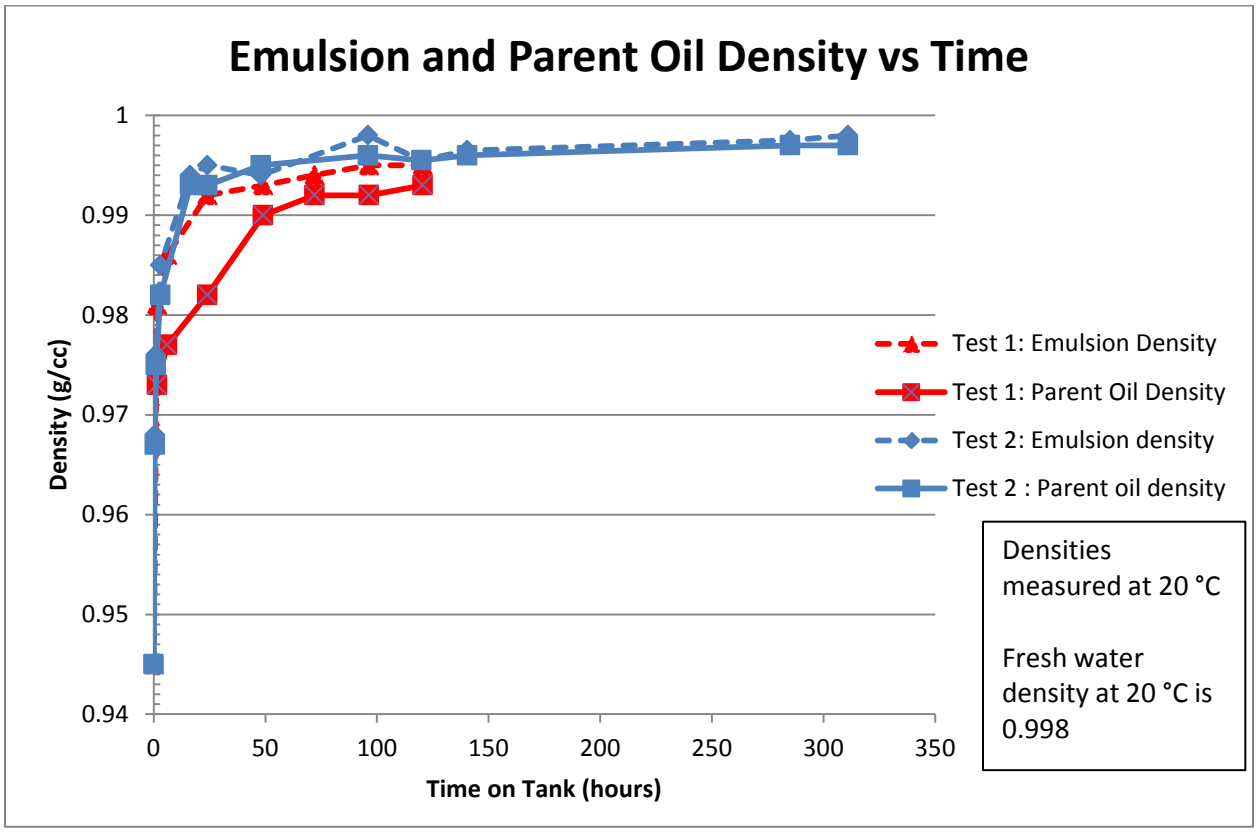

Figure 7. Emulsion and Parent Oil Density vs Time: Tests 1 & 2

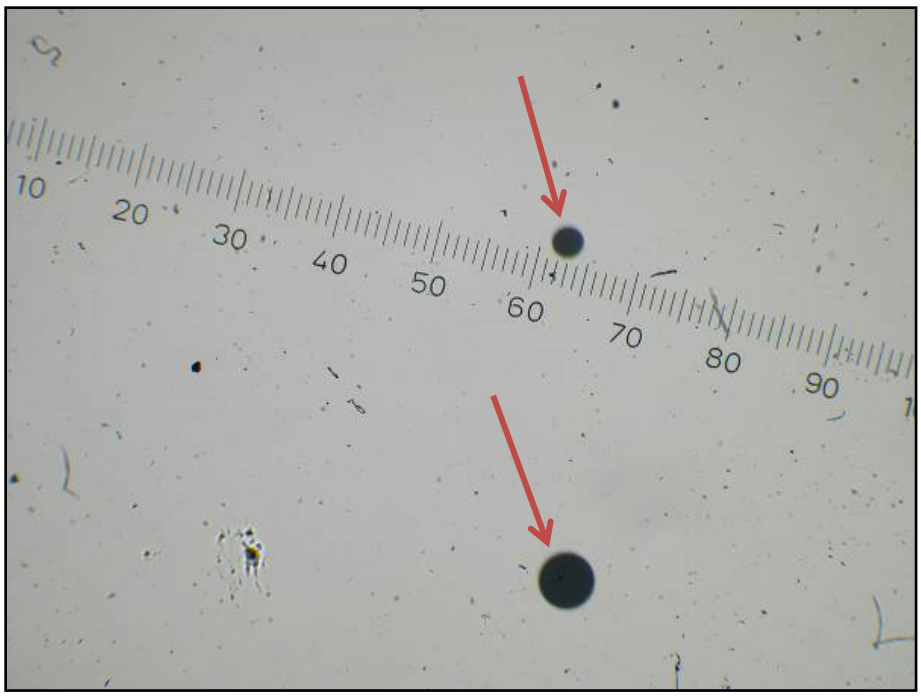

Figure 8. Dispersed Oil Drops in Water Column After 6 Days of Exposure with UV Light: Test 2 (scale: each small division represents 10µm):

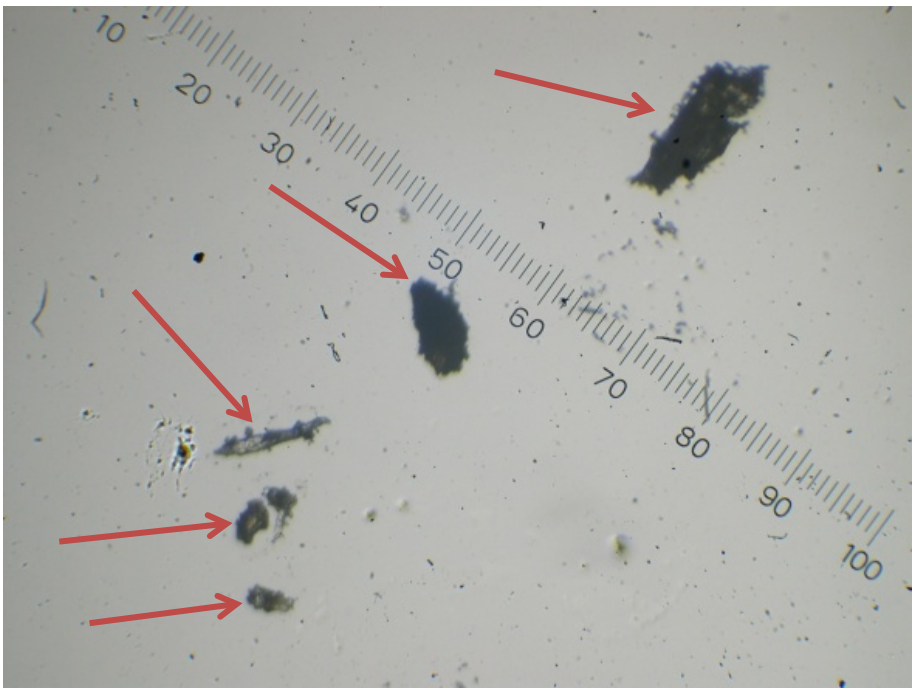

Figure 9. Dispersed Oil Drops in Water Column After 11 Days of Exposure with UV Light: Test 2

Water Content

The measured water contents for all samples never exceeded 39% and the water content peaked after approximately 24 hours in both test 1 and test 2 and then dropped with time in both tests. Plots of emulsion water content versus time for the two tests are provided in Figure 10. It should be noted that the emulsion samples contained considerable quantities of large drops of entrained water, which may inflate the emulsion water content measurement. Micro-photographs of the emulsion samples are provided in Appendix A and can be accessed through the hypertext links in Table 2 and Table 3. These photos were taken through a 10x eyepiece, fitted with a reticule, and 10x objective. A 1 mm x 100 division stage micrometer was photographed using the same microscope setup and camera zoom. This calibration indicated that each division on the eyepiece reticule (the scale shown in each photograph) is approximately 10 microns.

The micro-photograph of the fresh CLB is very similar to that for any crude oil or heavy fuel oil. The product has a uniform appearance with no bits or pieces of 'bitumen' suspended in a liquid phase, as is often an incorrect notion of the make-up of the diluted bitumen products. A micro-photograph of a sample of Intermediate Fuel Oil (IFO 550) is provided for comparison in Appendix A.

The emulsion photos show a progression of increased water uptake and a reduction of water drop size over the first few hours of the testing but this appears to stabilize after approximately 24 hours in test 2. This is consistent with the water content measurements.

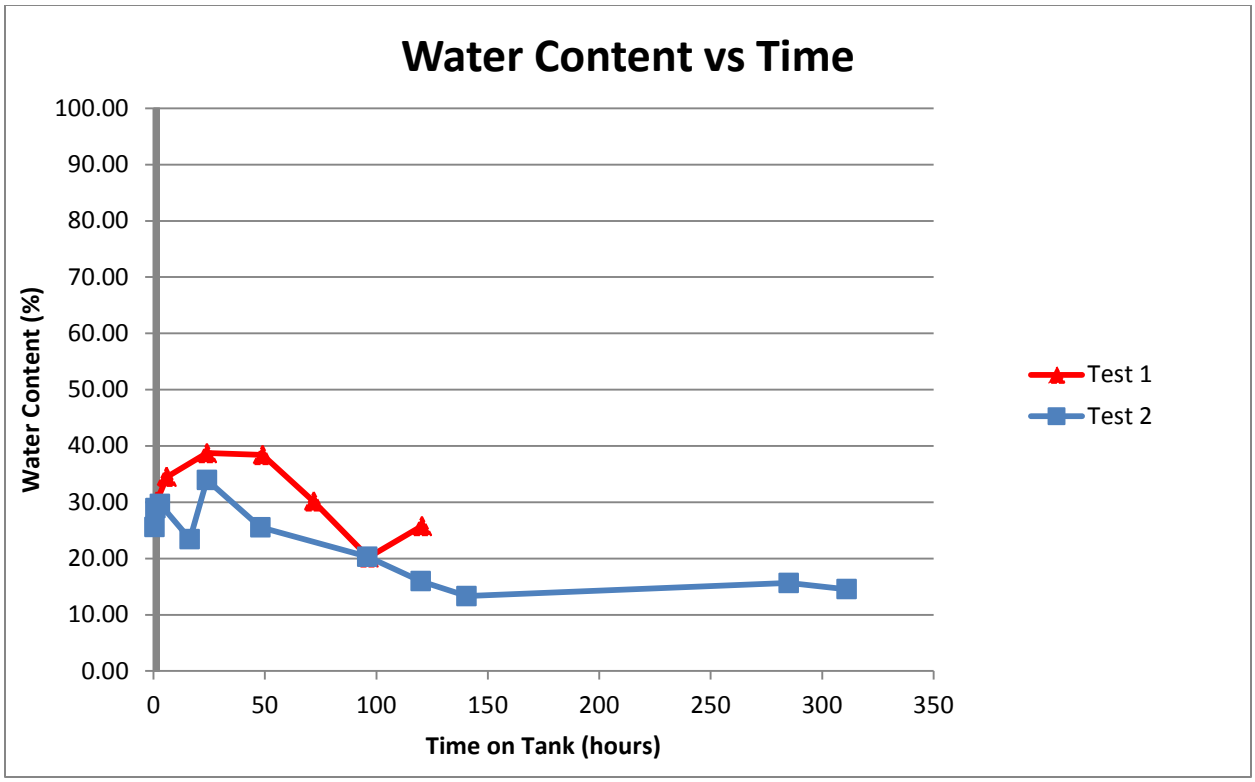

Figure 10. Water Content vs Time: Tests 1 & 2

Oil Viscosity

The oil/emulsion viscosity increased with UV exposure, evaporation, and dissolution as would be expected. The viscosity variations over time for the two tests are shown in Figure 11. The viscosity of the emulsion in test 1 peaked at about 200,000 cP by the end of the run. The viscosity of the emulsion in test 2 reached just above 400,000 cP within the same time period (120 hours). Ultimately, the viscosity of the emulsion in Test 2, where UV exposure was included, peaked in excess of 1,000,000 cP for the final samples taken around the 300 hour mark.

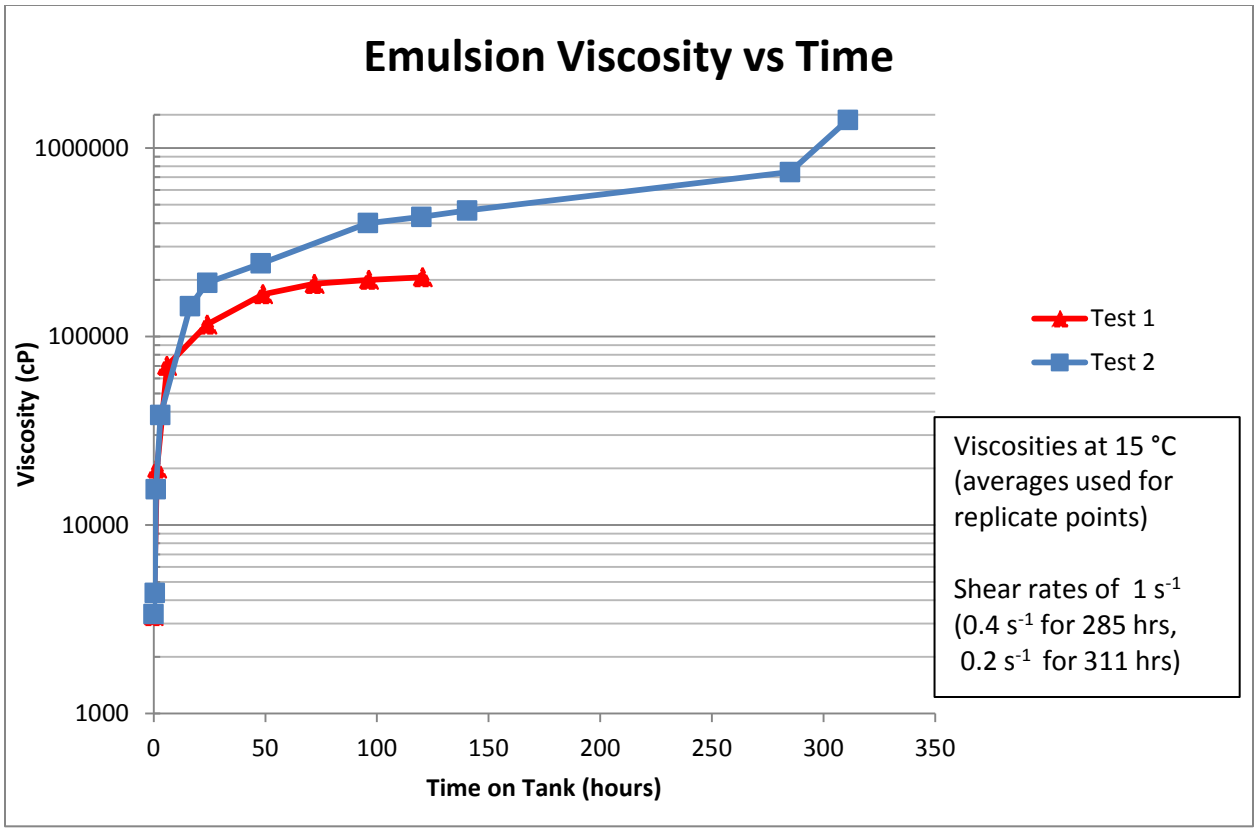

Figure 11. Viscosity vs Time: Tests 1 & 2

Oil Collection

Oil was collected following both tests to attempt to quantify the amount of oil remaining at the surface, at the subsurface, and oil sunk to the bottom of the test tank. The initial quantity of oil was measured by mass and documented. Following the tests, oil at the surface was first collected using sorbents and scrapers to clear the oil off of the walls of the tank. Oil down to a level approximately 10cm below the surface was collected and classified as "surface" oil. Oil in this region was typically smeared from the water interface. The second iteration of cleaning involved the manual collection of oil typically stuck to the walls and chiller cooling coils of the tank lower than 10 cm from the surface. Again scraping and sorbents were the primary means of removal. The results of the oil collection are indicated below in the tables. It should be noted that the mass of liquid collected surpasses the oil addition at the beginning of the test. Entrained water collected within the very viscous emulsion explains this difference

Table 4. Total recovered liquid

Sample ID	Description	Surface (upper 10cm) (g)	Subsurface (from tank wall below 10cm) (g)	Bottom of Tank (g)
Test #1	Total mass collected	6680	1754	0
	Sorbent + Container	1170	661	0
	Net recovered liquid	5510	1093	0
	Total recovered Liquid		6603	
	% of recovered Liquid	**83.4%**	**16.6%**	**0.0%**
Test #2	Total mass collected	5800	980	0
	Sorbent + Container	661	255	0
	Net recovered liquid	5139	725	0
	Total recovered Liquid		5864	
	% of recovered Liquid	**87.6%**	**12.4%**	**0.0%**

Observations

Table 5. Observations from Test 1

Sample	Run Time (hr)	Observations
1	1.5	Approximately 5L of oil was poured into flume tank at beginning of run. Wind (fan) set at dial reading of 6.5, which equates to 1.5 m/s of air speed. Water was circulated using the lower mounted thruster set at a low speed (0.25 m/s or 0.5 knots). Tank chiller was set to 15°C. At 1.5 hours into the run a sample was taken (S1) for water content, viscosity, and density measurements. Oil blobs were observed circulating around the flume in the upper 10 cm of the water column. Oil was "shredding" into small clumps, while spherical drops were seen as well. Waterfall impact was driving oil approximately 10 cm into the water column before it resurfaced. Oil movement on surface was still good. (Figure 34)
2	6	Wind (fan) was increased to 2.5 m/s to assist the movement of surface oil. The thruster was temporarily (15 minutes) increased slightly to move oil past a "dead zone" on the surface; then turned back down to 0.25m/s. A sample was taken (S2) for water content, viscosity, and density measurements.
3	24	Wind (fan) was decreased back to 1.5 m/s to control flow of oil around tank (backpressure behind the fan was blocking the flow of oil). Thrusters were temporarily increased slightly to assist a cohesive mass of oil to move past the fan "dead zone". Remaining floating oil colour turning black. A sample was taken (S3) for water content, viscosity, and density measurements.

4	49	Oil basically in one viscous mass behind the fan with small pieces breaking off and circulating. A sample was taken (S4) for water content, viscosity, and density measurements.
5	72	Wind (fan) temporarily shut down (15 minutes) and thruster was increased slightly to move oil mass in front of fan and allow for its circulation around the tank. One neutrally buoyant oil drop (approximately 15 mm diameter) was observed in the water column, along with small (approximately 1 mm diameter) oil droplets occasionally being seen. A sample was taken (S5) for water content, viscosity, and density measurements. An air diverter was installed to assist in directing the flow of oil.
6	96	Oil started impacting and sticking to the upper walls of the flume tank (as submerged blobs near the surface throughout the flume). Occasional neutrally buoyant blobs of oil were seen floating near the surface in the water column and a partial dark brown film was evident on the surface of the flume. A sample was taken (S6) for water content, viscosity, and density measurements. (Figure 35)
7	120	Some blobs of oil were seen floating in the water column (<1% to <5% of the total oil volume by observation), while most oil remained at the surface either pooled or stuck to the side walls of the flume tank. A sample was taken (S7) for water content, viscosity, and density measurements.

Table 6. Observations from Test 2

Sample	Run Time (hr)	Observations
1	0	Approximately 5L of oil poured into flume tank at beginning of run. Wind was set to 1.5 m/s of air flow. Water was circulated using the lower thruster set to a low speed (0.25 m/s). Tank chiller set to 15°C, UV light started. Sample taken (S1) for water content, viscosity, and density measurements. Oil droplets were observed shearing off of surface oil at the waterfall. The oil droplets resurfaced and no oil droplets were observed downstream (>1m) of the water cascade. The water remained clear. (Figure 36)
2	0.5	Sample taken (S2) for water content, viscosity, and density measurements. Water column remains clear, no observable droplets downstream (>1m) of waterfall. Oil behaviour changing – droplets changing in size and shape as oil properties evolve. Oil started shredding into non-uniform blobs at this point in the test run (Figure 37)
3	1	Small oil droplets are seen circulating in the water column near the surface of the flume. Oil becomes more viscous, starts to stick to points along tank wall, waterfall has diminishing effect on oil slick passing underneath. Sample taken (S3) for water content, viscosity, and density measurements. (Figure 38)
4	3	Oil properties evolve as it continues to stick to points along tank wall, waterfall has diminishing effect on fragmented oil slick passing underneath. Sample taken (S4) for water content, viscosity, and density measurements. (Figure 39)
5	16.3	Oil sticking to sidewalls of tank, some larger oil drops seen floating within water column (blurred black circle in centre of picture, identified below). Sample taken (S5) for water content, viscosity, and density measurements. UV

		light cycled. (Figure 40)
6	24	More oil was observed adhering to tank sidewalls. Very tiny droplets of oil (less than 1 mm diameter) were observed in the water column (seen through 30 cm depth from the surface) Sample taken (S6) for water content, viscosity, and density measurements. (Figure 41)
7	48	Very tiny droplets of oil (most less than 1 mm in diameter, occasionally some up to approximately 10 mm) were observed in the water column at increasing frequency. Water column started to become slightly hazy. Sample taken (S7) for water content, viscosity, and density measurements. (Figure 42)
8	96	Droplets of oil in a range of sizes (from less than 1 mm diameter through approximately 20 mm diameter) were observed in the water column. Water column remains slightly hazy. Sample taken (S8) for water content, viscosity, and density measurements. (Figure 43)
9, 10	120	Frequency of droplets of oil in a range of sizes (from less than 1mm diameter through approximately 20 mm diameter) increased in the water column. Water column remains slightly hazy. Samples taken (S9, S10) for water content, viscosity, and density measurements. (Figure 44)
11, 12	140	Droplets of oil ranging in diameter from approximately 1 mm (many) through 20 mm (occasional) were observed floating in the water column. Water remains hazy. Samples taken (S11, S12) for water content, viscosity, and density measurements. (Figure 45)
13, 14	285	Droplets of oil in a range of sizes were observed floating in the water column. Samples taken (S13, S14) for water content, viscosity, and density measurements.
15, 16	311	Samples taken (S15, S16) for water content, viscosity, and density measurements.

Discussion

A range of interesting characteristics were observed during both tests. Of particular note was the peak of the oil sample density during the test runs. The oil subjected to the weathering tests was measured to have an ultimate density that approached but did not surpass that of the water. Samples were subjected to a simulated waterfall which had an overwash effect. Throughout the test duration, a small part of the oil slick (<1% to <5% by observation) was seen to submerge and hang in the water column as either neutrally buoyant droplets or blobs while the water circulated in the flume. At the end of the tests approximately 15% of the recovered oil was collected from the tank walls 10 cm below the water surface. This oil is assumed to be that which accumulated from the neutrally buoyant drops that were present during the test. The majority (approximately 85%) of the oil in both tests was found either at the surface or stuck to the side walls within 10 cm of the surface. At no point was oil found to submerge, sink, and stick to the bottom of the flume.

The UV light exposure did appear to have an impact in accelerating the degradation of the oil sample as shown by comparing viscosities over time in Test 1 and Test 2. After 96 hours the viscosity in Test 2 was measured at approximately 400,000 cP, effectively doubling the viscosity of the oil sample measured for Test 1 for the same run time. In addition, the haze within the water column witnessed during Test 2, from about the 48 hour mark and on, may be attributed, at least in part, to the introduction of the UV light system and its impact on degrading oil during the test run.

The low water content emulsions measured during Test 1 and Test 2 were determined not to be overly stable in that the water separated from the bulk emulsion as seen by the decreasing water content over the later part of the test runs.

Appendix A – Micro-Photographs of Emulsions

Test #1

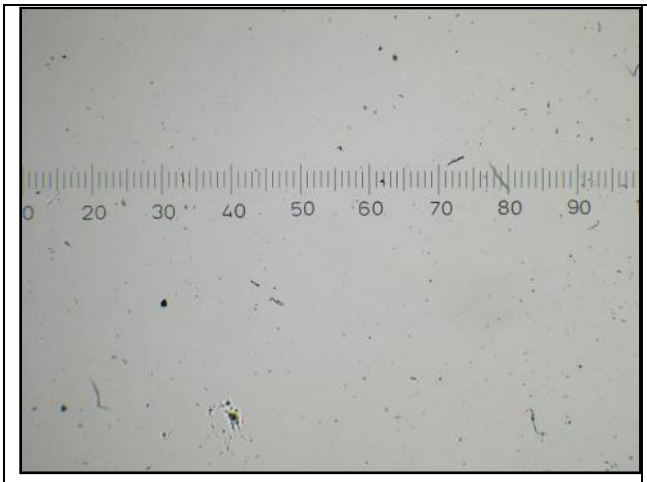

Figure 12. Blank Slide (showing artifacts on lens)

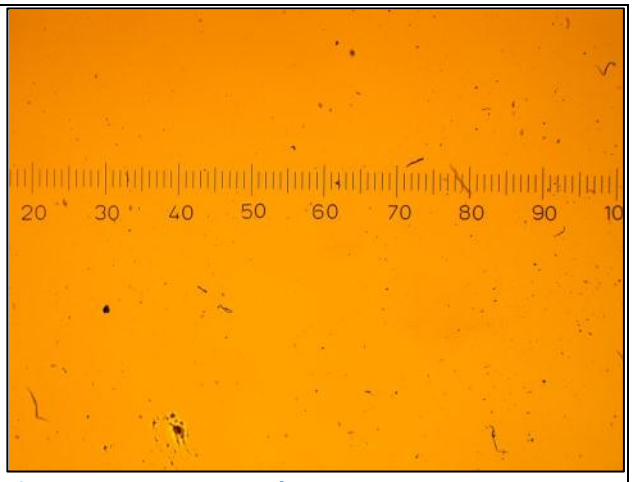

Figure 13. Test 1 Sample 1

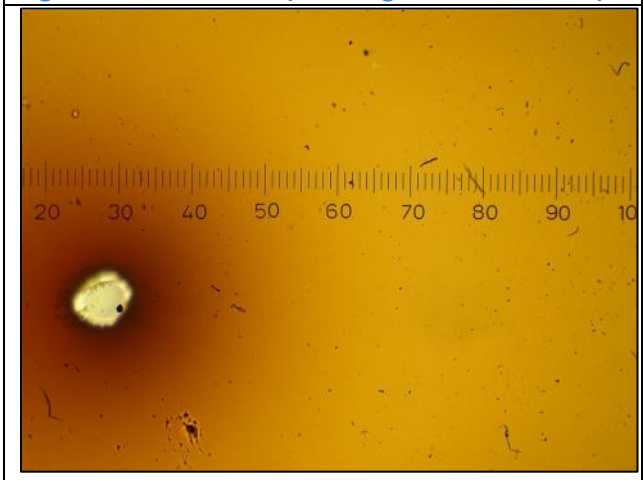

Figure 14. Test 1 Sample 2

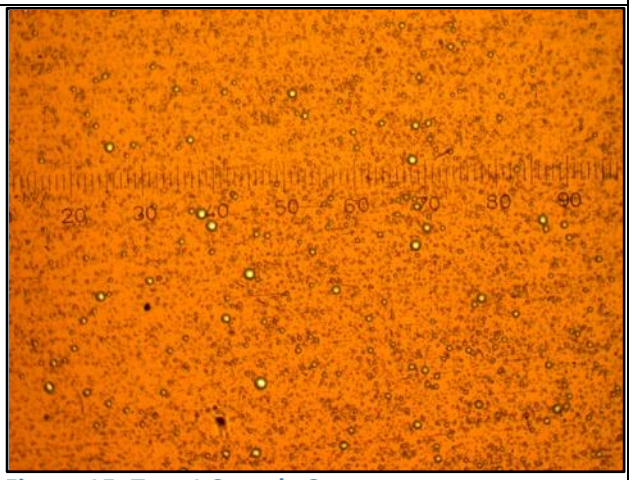

Figure 15. Test 1 Sample 3

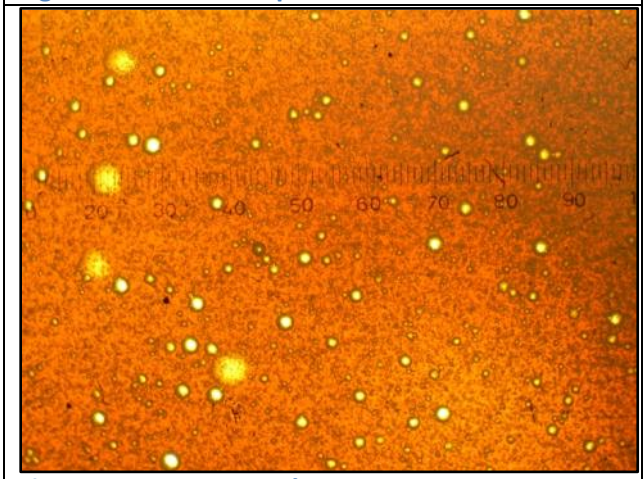

Figure 16. Test 1 Sample 4

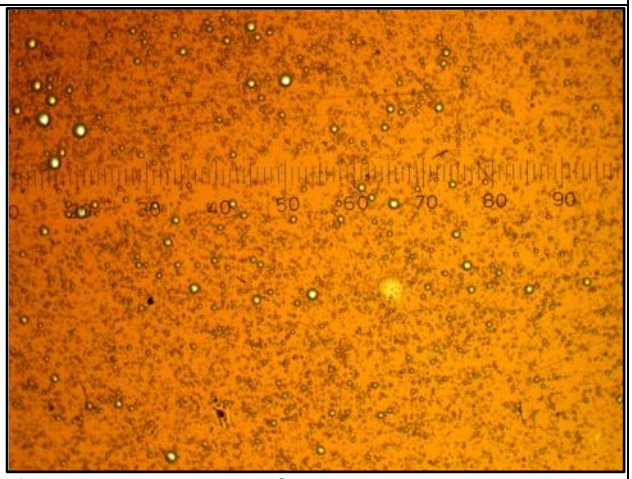

Figure 17. Test 1 Sample 5

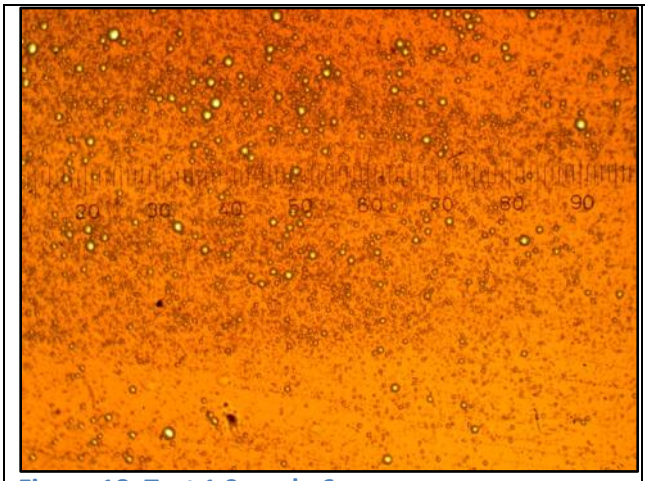

Figure 18. Test 1 Sample 6

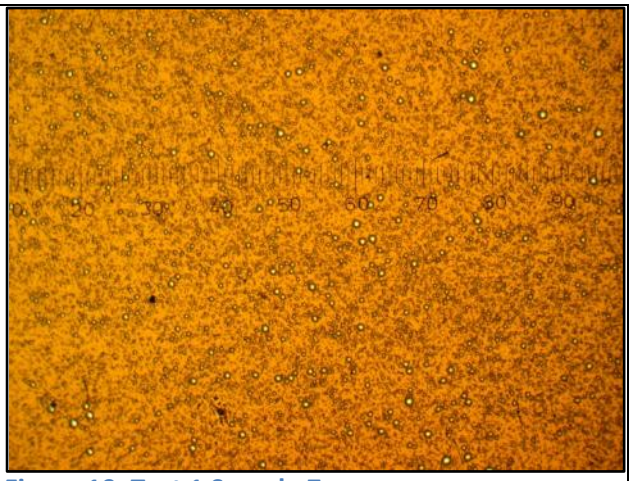

Figure 19. Test 1 Sample 7

Test #2

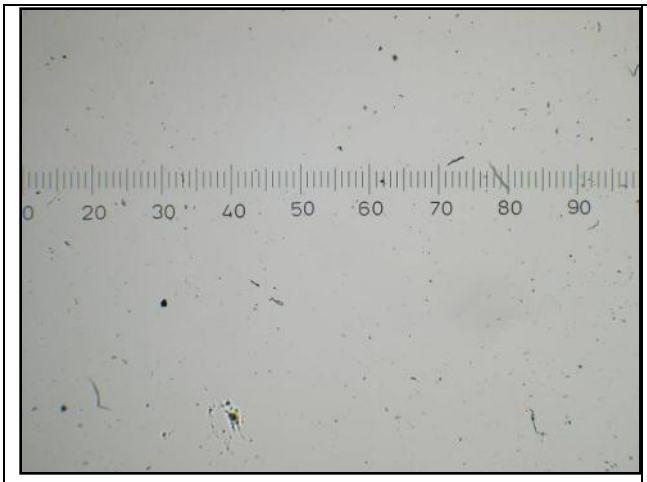

Figure 20. Blank Slide (showing artifacts on lens)

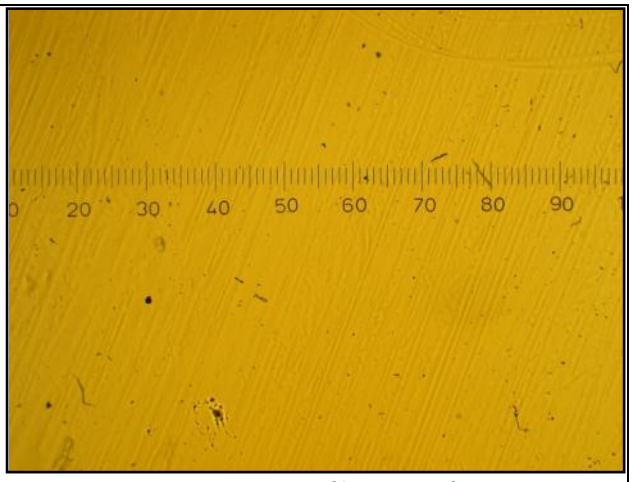

Figure 21. Test 2 Sample 1 (fresh CLB)

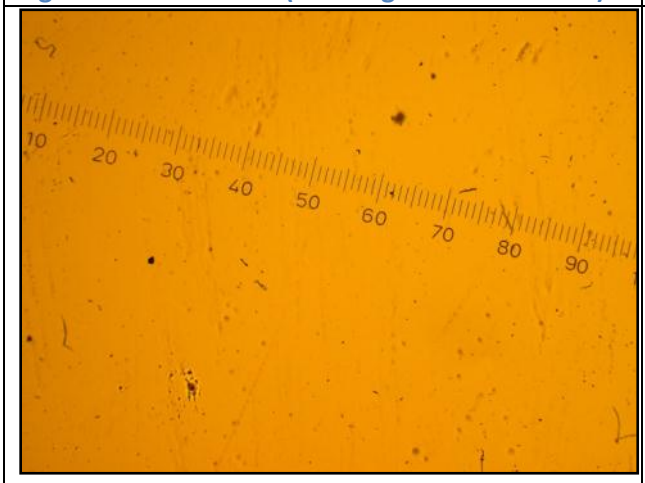

Figure 22. IFO 550 Fuel Oil

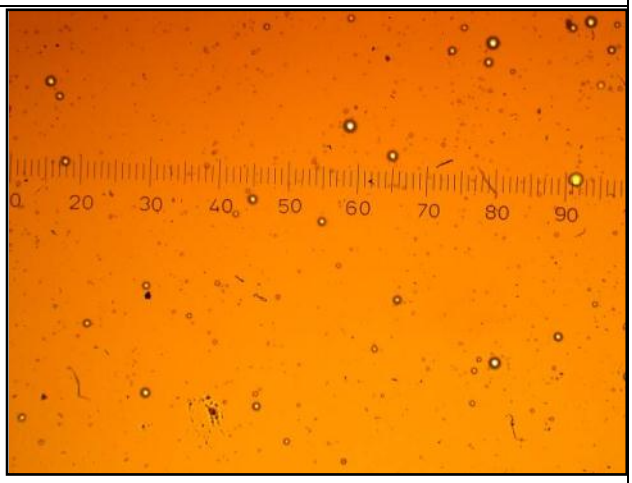

Figure 23. Test 2 Sample 2

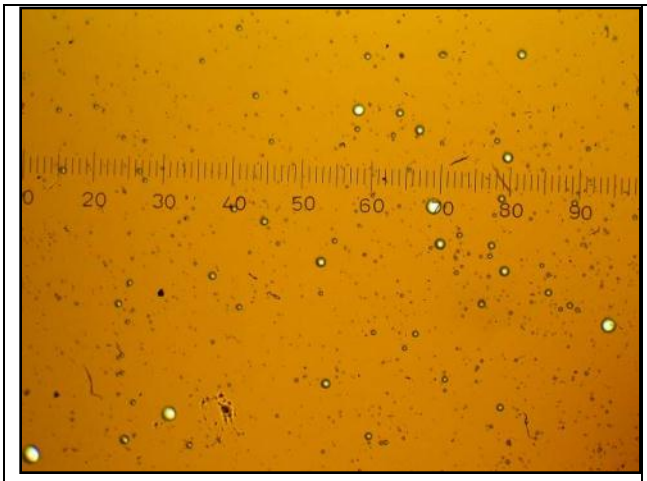

Figure 24. Test 2 Sample 3

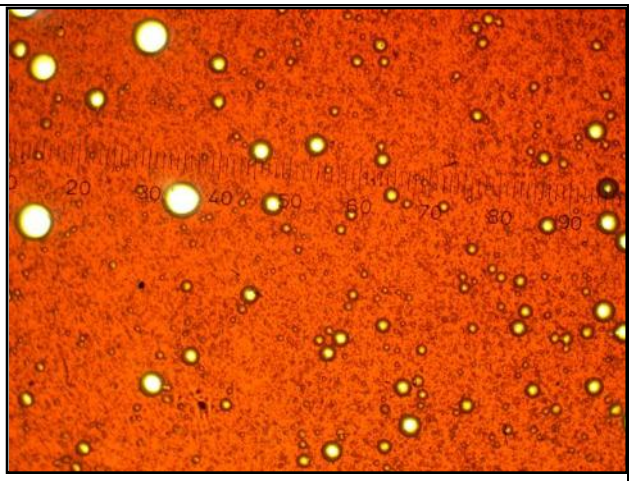

Figure 25. Test 2 Sample 4

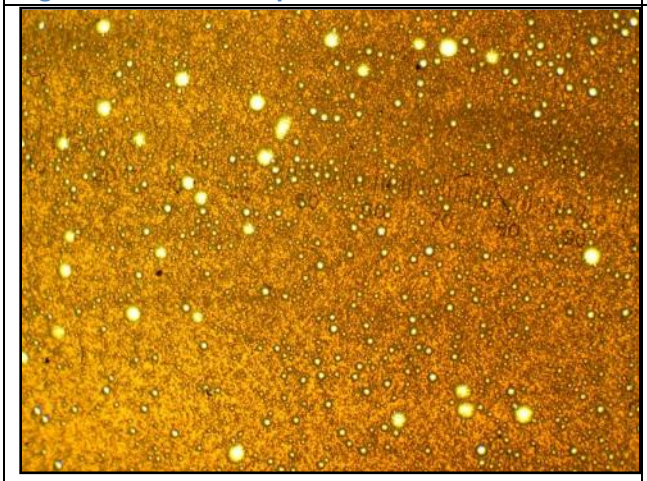

Figure 26. Test 2 Sample 5

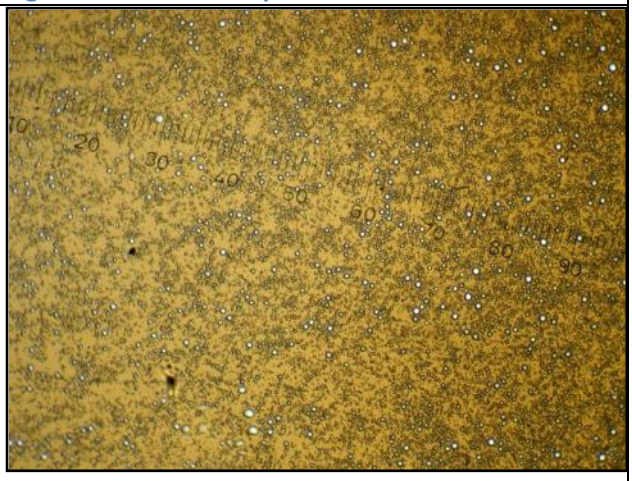

Figure 27. Test 2 Sample 6

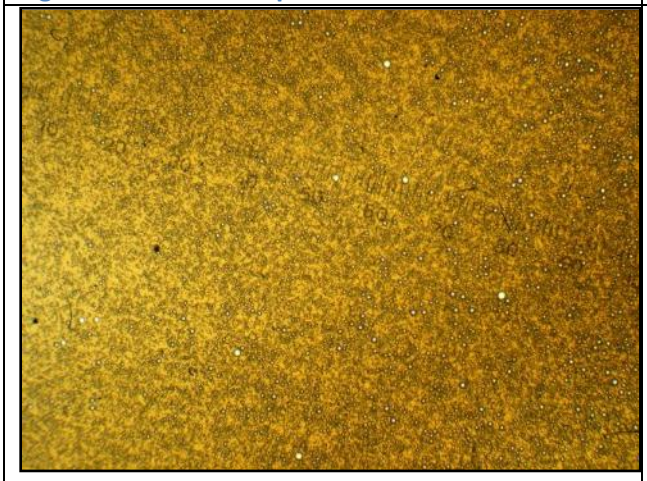

Figure 28. Test 2 Sample 7

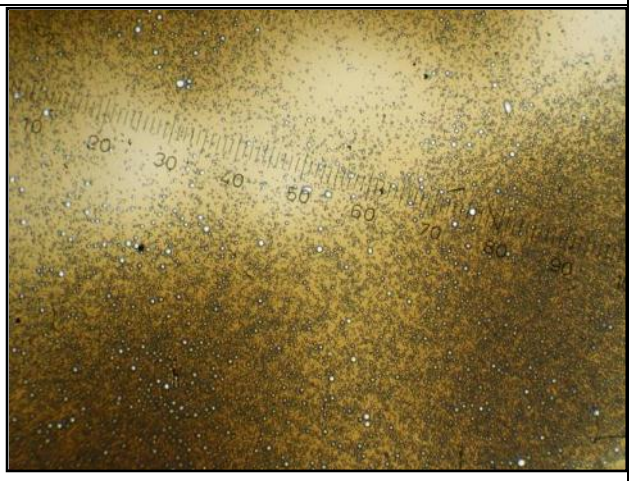

Figure 29. Test 2 Sample 8

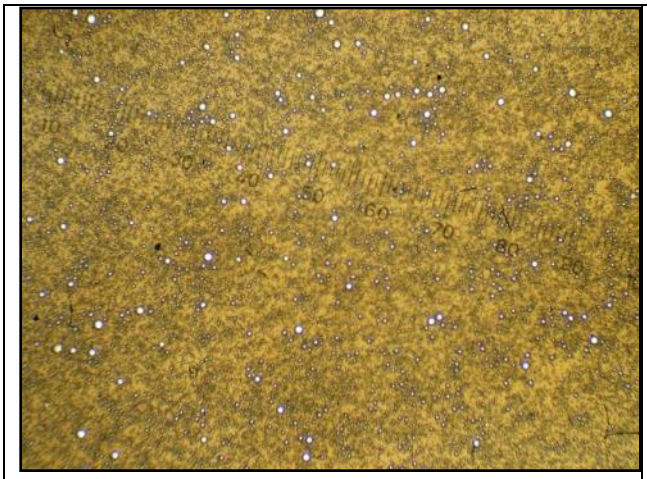

Figure 30. Test 2 Sample 9

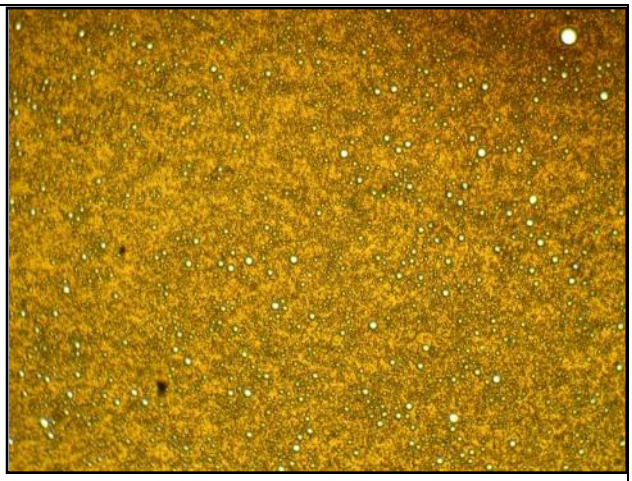

Figure 31. Test 2 Sample 10

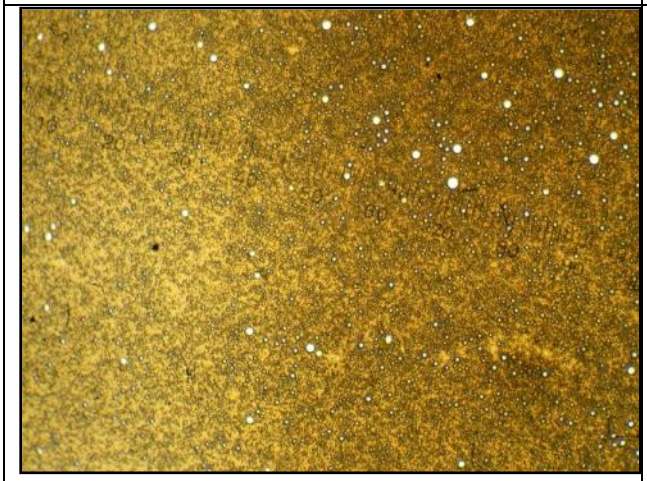

Figure 32. Test 2 Sample 11

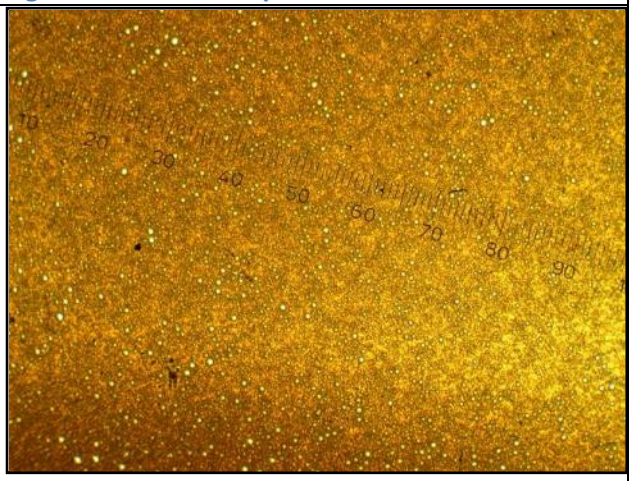

Figure 33. Test 2 Sample 12

Appendix B – Photographs of Flume Tank

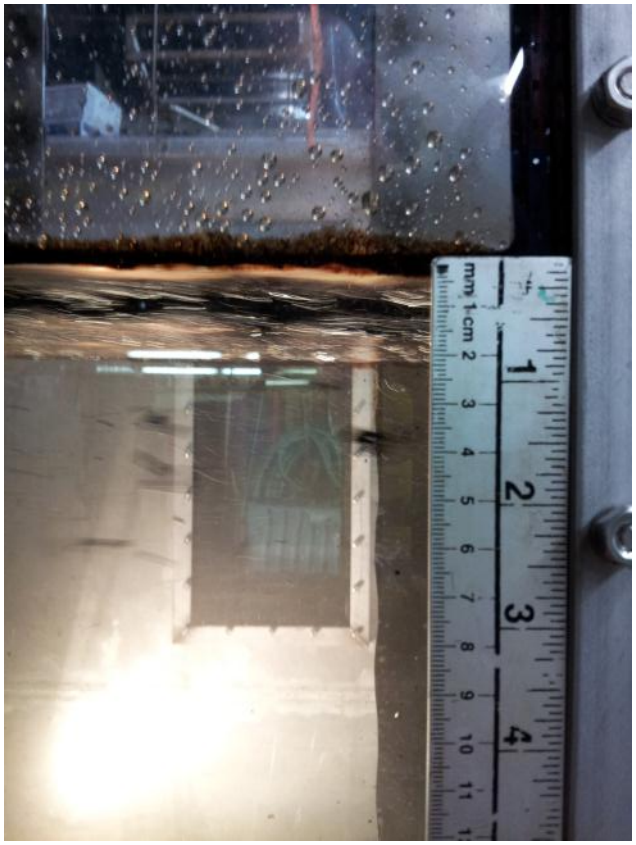

Figure 34. Test 1 Sample 1

Figure 35. Test 1 at 96 hours (Sample 6)

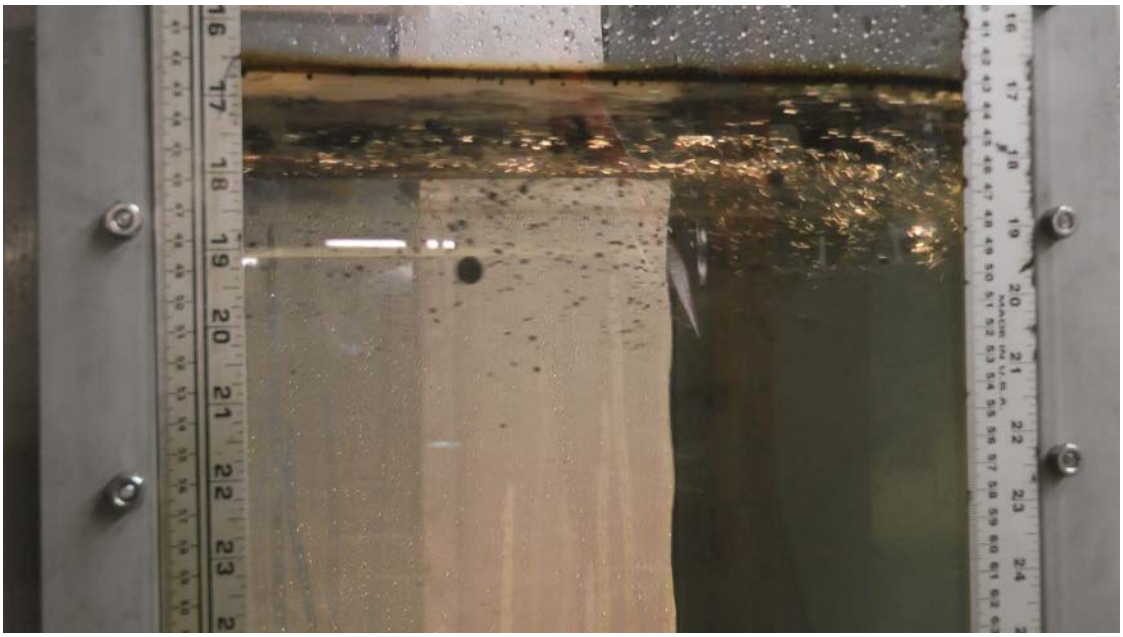

Figure 36. Test 2 Sample 1

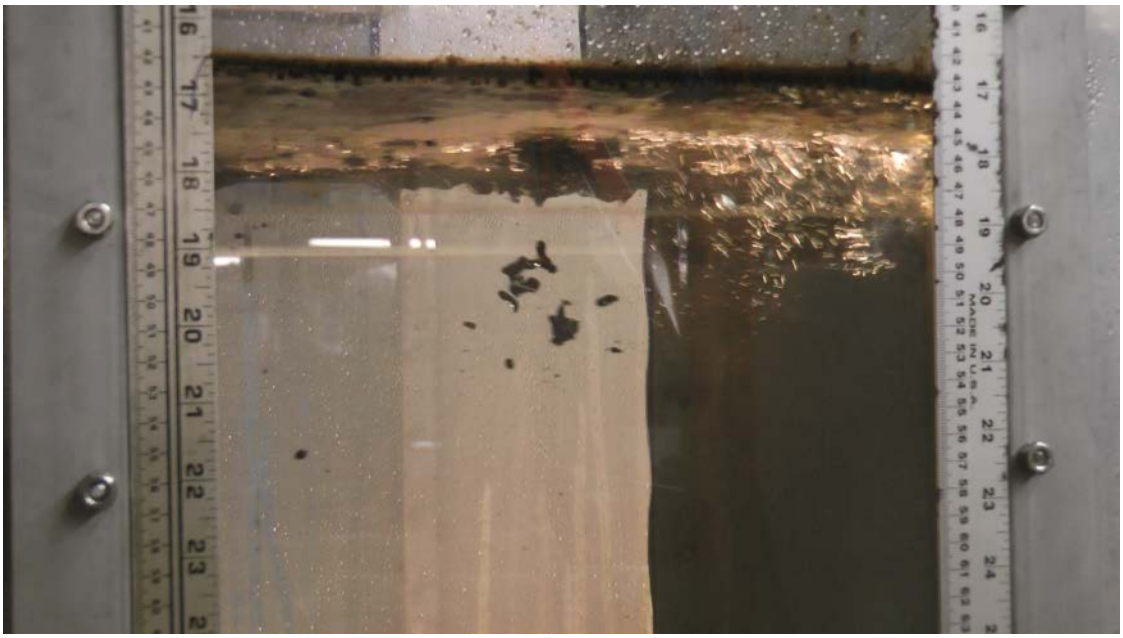

Figure 37. Test 2 Sample 2

Figure 38. Test 2 Sample 3

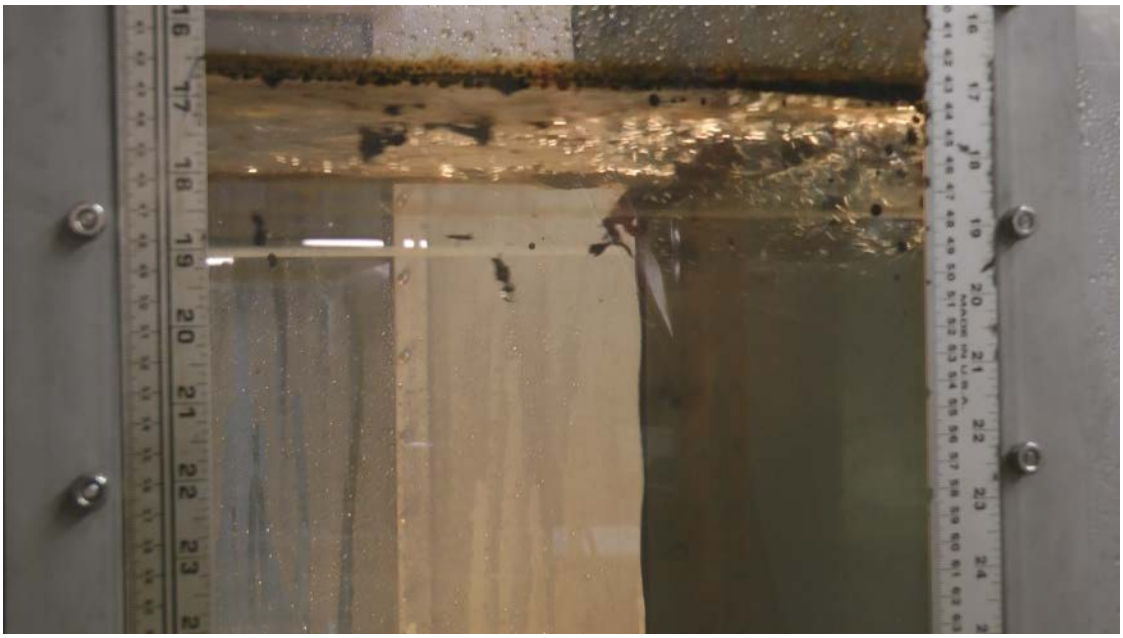

Figure 39. Test 2 Sample 4

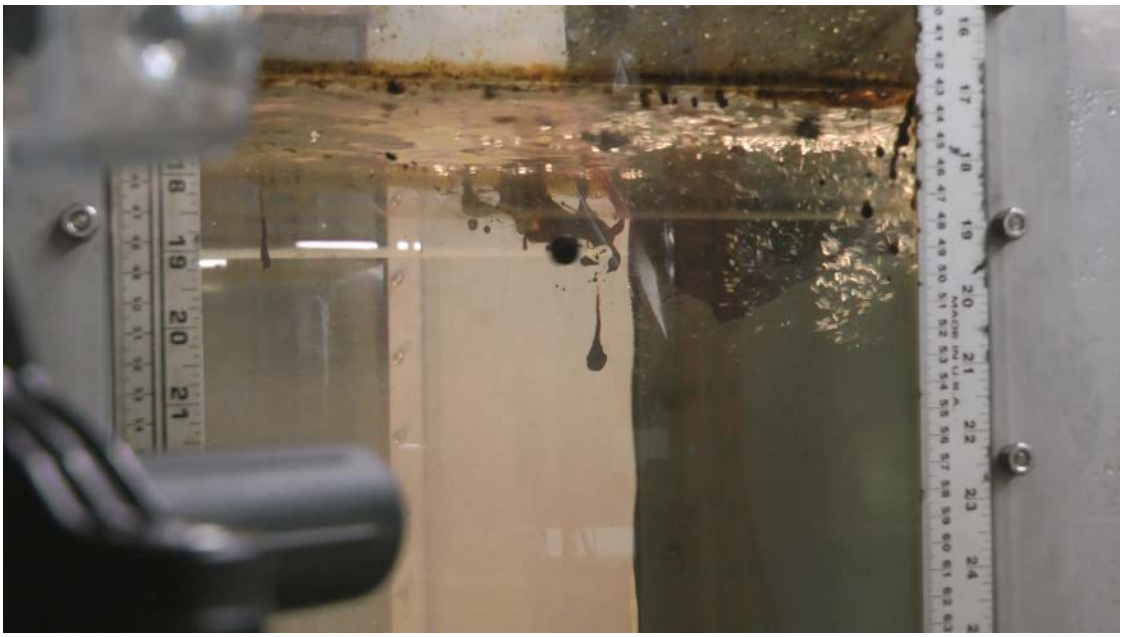

Figure 40. Test 2 Sample 5

Figure 41. Test 2 Sample 6

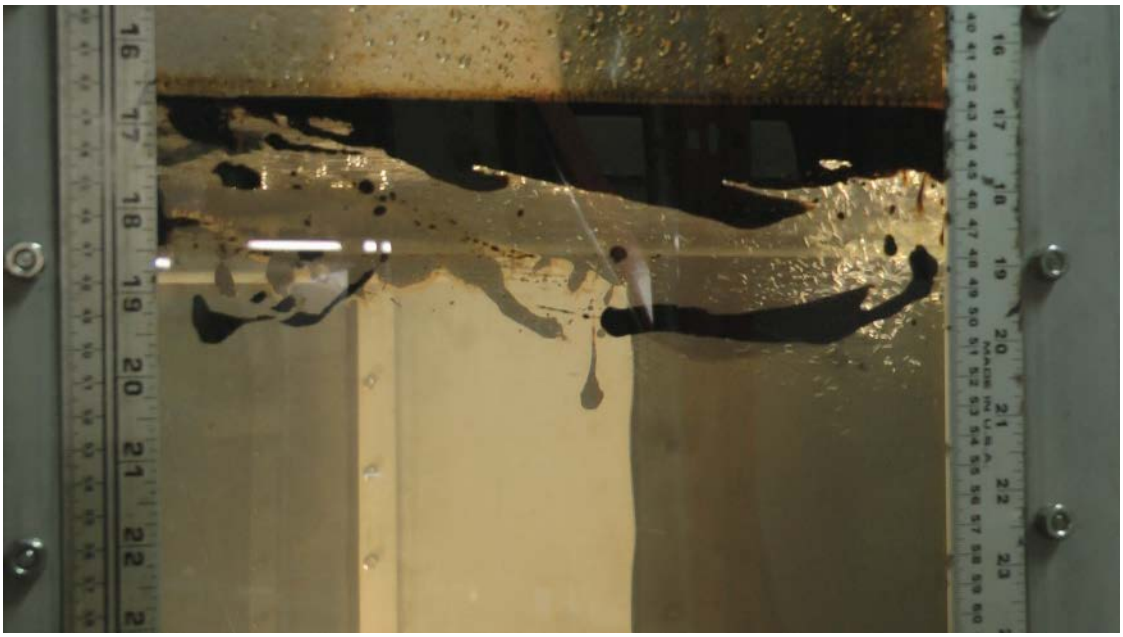

Figure 42. Test 2 Sample 7

Figure 43. Test 2 Sample 8

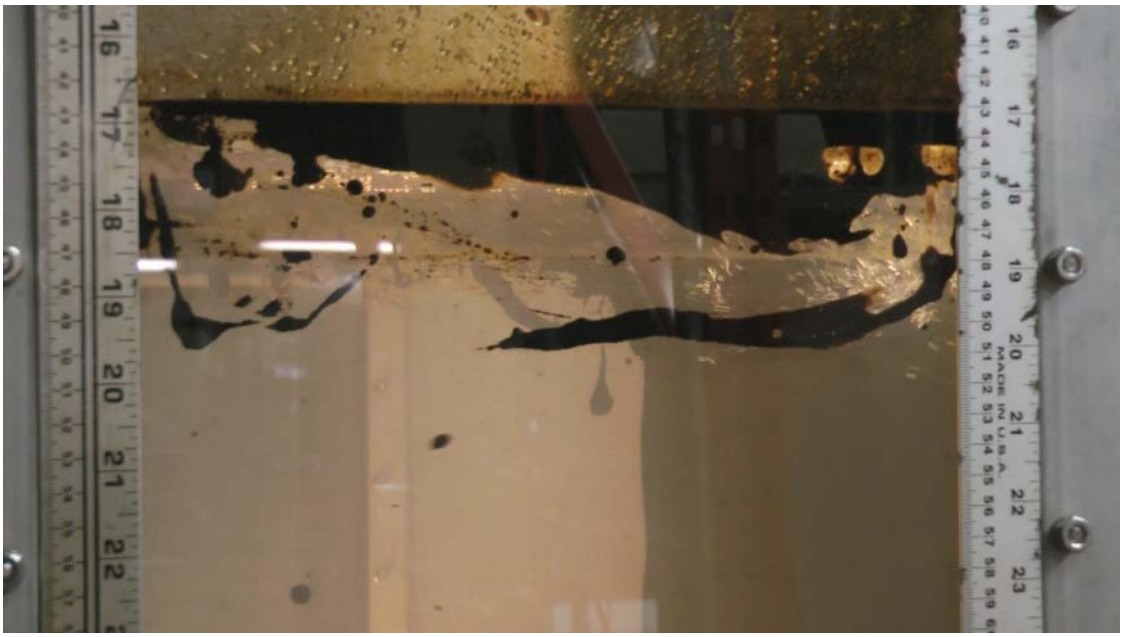

Figure 44. Test 2 Sample 9, 10

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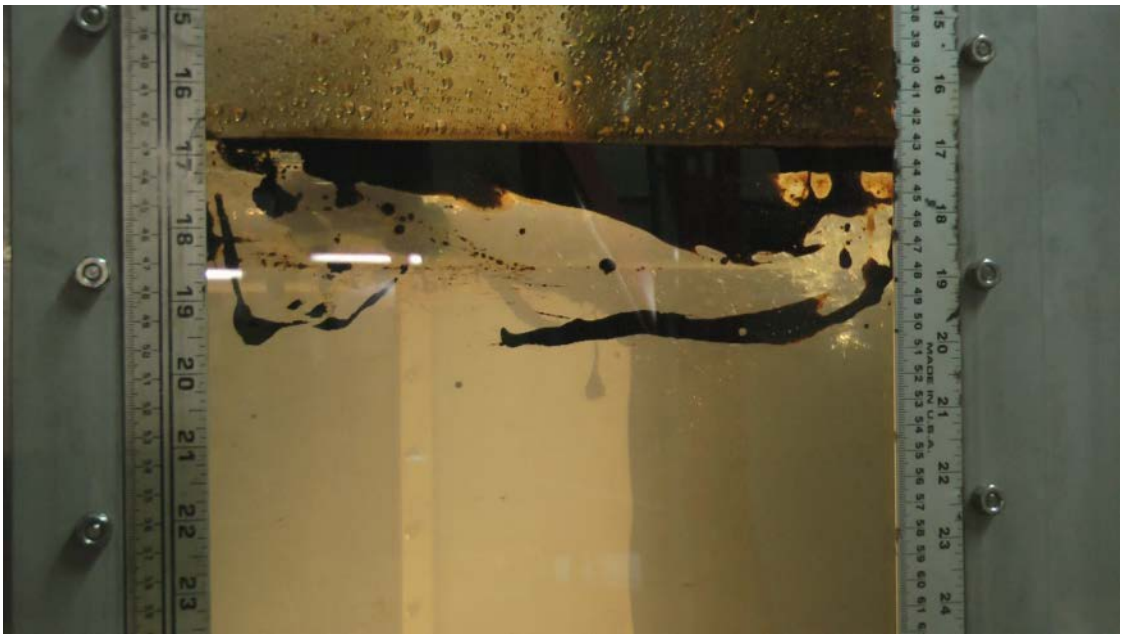

Figure 45. Test 2 Sample 11, 12