Xia, L. S. Lu and G.Cao., "Stability and Demulsification of Emulsions Stabilized by Asphaltenes or Resins", *Journal of Colloid and Interface Science*, Vol. 271, pp. 504-506, 2004.

Yang, X. and J. Czarnecki, "The Effect of Naphtha to Bitumen Ratio on Properties of Water in Diluted Bitumen Emulsions", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 211, pp. 213-2227, 2002.

Yang, X., H. Hamza and J. Czarnecki, "Investigation of Subfractions of Athabasca Asphaltenes and Their Role in Emulsion Stability", *Energy and Fuels*, Vol. 18, pp. 770-777, 2004.

Yarranton, H.W., H. Hussein and J.H. Masliyah, "Water-in-Hydrocarbon Emulsions Stabilized by Asphaltenes at Low Concentrations", *Journal of Colloid and Interface Science*, Vol. 228, pp. 52-63, 2000.

Yarranton, H.W., D.M. Sztukowski and P. Urrutia, "Effect of Interfacial Rheology on Model Emulsion Coalescence: I Interfacial Rheology", *Journal of Colloid and Interface Science*, Vol. 310, pp. 246-253, 2007a.

Yarranton, H.W., P. Urrutia and D.M. Sztukowski, "Effect of Interfacial Rheology on Model Emulsion Coalesence: II Emulsion Coalesence", *Journal of Colloid and Interface Science*, Vol. 310, pp. 253-259, 2007b.

Zhang, L.Y., R. Lopetinsky, Z. Xu and J.H. Masliyah, "Asphaltene Monolayers at a Toluene/Water Interface", *Energy and Fuels*, Vol. 19, pp. 1330-1336, 2005.

Physical Properties of Oil-SPM Aggregates: Experiments with the NIST Standard Reference Material 1941b

Ali Khelifa and Carl E. Brown
Emergencies Science and Technology Division, Environmental Science and
Technology Centre, Environment Canada, Ottawa, Ontario, Canada
ali.khelifa@ec.gc.ca

Michelle Chun and Jonathon Lawrence Etue Eubank
Nanotechnology Engineering, University of Waterloo, Waterloo, Ontario, Canada

Abstract

Aggregation between suspended oil droplets and suspended particulate matter (SPM), which leads to the formation of oil-SPM aggregates (OSAs), is recognised as an important process affecting the fate of spilled oil in fresh and marine water systems. It affects, for instance, the sedimentation of dispersed oil as shown from previous works. However, very little is known about physical properties that control the fate of OSAs. A laboratory study was conducted to measure the size, density and settling velocity of OSAs formed under various mixing conditions. Both physically and chemically dispersed oils were considered in the study. OSAs were prepared using a previously discussed experimental procedure. This paper presents findings from experiments conducted using Standard Reference Material 1941b prepared by the National Institute of Standards and Technology, Arabian Medium and South Louisiana crude oils, and Corexit 9500 chemical dispersants. Two sediment-to-oil ratios of 0.5 and 1 were used. At sediment-to-oil ratio of 0.5, the results showed that oil-SPM interaction leads to formation of abundant negatively buoyant OSAs that settle at an average rate of 1 mm/s, their average effective density is about 60 g/L and their size varies from 30 to about 350 µm. The minimum effective density and settling velocity of OSAs measured in this study were 34 g/L and 0.3 mm/s, respectively. Slightly denser OSAs were obtained with chemically dispersed oil. Much less differences were obtained between physical properties of OSAs and those of sediment flocs when the sediment-to-oil ratio was increased from 0.5 to 1. Both the Stokes' Law and the modified one overestimate the settling velocity of OSAs and are not recommended for use in oil spill modelling.

1 Introduction

It is general knowledge for the oil spill community that naturally-dispersed oil droplets aggregate readily with suspended particulate material (SPM) such as clay minerals or organic matter to form oil-SPM aggregates (OSAs). Terminologies such as oil-clay flocculation, oil-SPM interactions, oil-mineral aggregates, and oil-fine interactions have been used to describe this natural process (Ali, 2006; Ajijolaiya, 2004; Khelifa et al. 2002, 2005a,b; Muschenheim and Lee, 2002; Omotoso, 2002; Owens, 1999; Owens and Lee, 2003; Payne et al., 2003; Stoffyn-Egli and Lee, 2002 for a review). The simplest form of OSA consists of an oil droplet coated with micrometer-sized solid grains. The oil spill response community has paid much attention to this process during the last three decades because of its potential to enhance natural dispersion of oil spilled in coastal waters and cleansing oiled shorelines. Many oil spill experts believe that this process enhances oil dispersion by preventing the droplets from sticking to each other and reforming oil slicks, and by enhancing their density to make them nearly neutrally buoyant and easily transportable by hydrodynamic currents away from the oiled sites (Bragg and Owens, 1994, Bragg and Yang, 1995; Owens 1999; Owens et al., 1994; Sergy et al. 1998, 1999, 2003; Lee et al., 2003; Le Floch et al., 2002; Owens and Lee, 2003). However, very little research has been conducted on measuring physical properties of OSAs and their settling ability to the seafloor. Furthermore, the oil spill response community has much less quantitative understanding regarding the formation and fate of OSAs with chemically-dispersed oil.

Experiments conducted by Guyomarch et al. (1999) in the Polludrome facility (the wave flume facility at CERDE, *http://www.le-cedre.fr/*) showed that 30 minutes of wave action on a chemically-treated oil were sufficient to disperse the oil. Almost 80 % of this oil was trapped as OSA and settled to the bottom of the flume. Moreover, OSA formation was closely related to the efficiency of treating chemical dispersant. Guyomarch et al. (2002) concluded that formation and transport of OSA must be studied further to determine whether it is beneficial to apply oil dispersant in coastal regions loaded with mineral particles. Previously, Mackay and Hussain (1980) found from their laboratory experiments that presence of suspended clay particles at moderate concentration accelerates sedimentation of chemically dispersed oil. They estimated the sedimented oil accounted for about 15% of the reacting oil. Recent laboratory experiments on size and fractal-dimension measurements conducted by Sterling et al. (2004) showed that OSAs form when artificially-weathered, Medium Arabian Crude oil is treated with Corexit 9500 and mixed with bentonite clay. The experiments were conducted in a shear reactor. Recently, Li et al. (2007) conducted a series of wave tank experiments to study oil dispersion with and without chemical dispersant and sediment fines. Formation of OSAs was observed when weathered Scotia Shelf Condensate was chemically dispersed with Corexit 9500 and mixed with kaolin sediment under breaking wave conditions. However, the fate the OSAs and their tendency to settle in the tank was not studied and not discussed in the study.

This paper aims to present an experimental procedure developed to measure physical properties of OSAs including size, settling velocity and effective density, to discuss the first series of data obtained using two types of oils and the Standard Reference Material 1941b (SRM-1941b) prepared by the National Institute of Standards and Technology, and to show how application of chemical dispersant affects physical properties of OSAs and the resulting consequences on oil sedimentation in coastal waters.

2 Experimental Method

The experimental method developed to measure size, settling velocity and effective density of negatively buoyant OSAs includes several steps, as discussed in the following sub-sections. The steps include OSA preparation and isolation of negatively buoyant OSAs from the reaction chambers, measurement of size and settling velocity using a settling column apparatus and image analysis, and calculation of effective density using settling velocity data and a predefined model to describe the sedimentation process.

2.1 OSA Preparation

The first step in the experimental method used in this project was to prepare OSAs and isolate negatively buoyant ones from the reaction chambers. This is performed using experimental procedure described in details by Khelifa et al. (2007).

OSAs were prepared using a reciprocating shaker at a constant shaking speed rate of 126 cycles per minute and a constant stroke of 38 mm in a cold room at a controlled temperature of 15 °C. Erlenmeyer flasks (500 mL with silicone stoppers) containing 250 mL of sodium chloride solution at 33 ‰ salinity were used as reaction chambers. The solid phase (SRM-1941b sediment) was added dry to the seawater. The flasks were then shaken for 5 minutes before the addition of the oil phase. A pre-calculated volume of the test oil to deliver 50 mg of oil is added at the water surface using a syringe. For each test oil, the syringe was pre-calibrated to dispense 50 mg of oil. The flasks were then shaken (Figure 1) for a period of three hours and then left to settle overnight in the cold room (Figure 2a). Negatively buoyant OSAs were then separated with care from the oil/water/sediment suspension by removing the floating materials and water from the reactions vessels (Figure 2b). The OSAs were then used to measure their settling velocity and density.

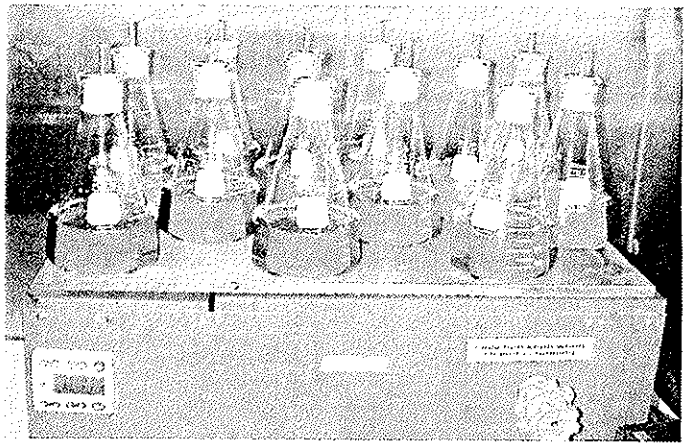

Figure 1 Reaction vessels set for the experiment on the reciprocating shaker

2.2 Settling Velocity

Settling velocity of negatively buoyant OSAs was measured using settling column procedure. The newly developed setup includes a 22 mm in diameter glass U-tube for a settling chamber, a back light illumination unit and a high resolution Sony HDR-HC3 camcorder (Figure 3a). OSAs are prepared first and isolated from the reaction chambers as discussed above. About 5 mL are withdrawn from the settling oil/seawater/sediment mixture (Figure 2b) and carefully introduced at the top of the U-tube filled with artificial seawater. OSAs settling in the U-tube were recorded after they travel about 73 cm down in the U-tube. The recordings last for 20 minutes from the time the first OSAs (large ones) reach the section where the measurements were taken. This long recording period was set to capture most of the size range of OSA population. Examples of images obtained with the setup are shown on Figures 3b and 3c.

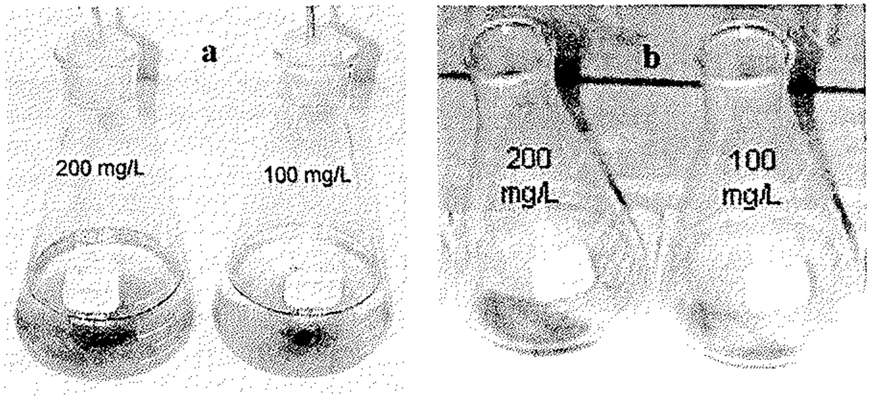

Figure 2 Reaction vessels after overnight settling (a) and after extraction of the floating materials and water (b): tests with SRM-1941b concentrations of 100 and 200 mg/L, as indicated on the Figures. Note oil-sediment mixtures sunken on the bottom of the vessels.

An image analysis program was developed using the Matlab platform and Image Toolbox to calculate size and settling velocity of OSAs from the movies. The smallest size that can be measured with the setup is about 2 μm. However, small particles that take more than 20 minutes (recording period set in this study) to settle in the settling column were not measured. The method used to measure the settling velocity was based on the particle tracking velocity technique. For each test, 150 images were processed. Preliminary tests were performed to validate the entire procedure to measure OSAs size and settling velocity. This is discussed in section 3 below.

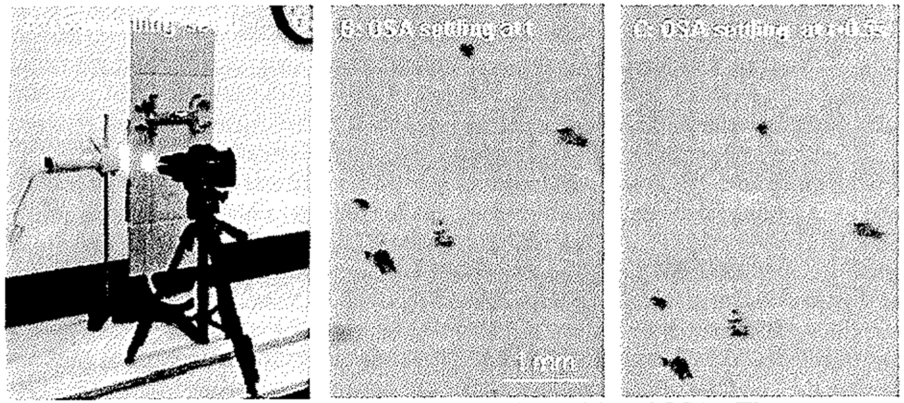

Figure 3 Setup to measure settling velocities and densities of OSAs. The setup includes a U-tube for settling chamber, a back light illumination unit, a high resolution Sony HDR-HC3 camcorder (A). With this setup, particles of about 2 μm and larger can be measured. Figures 3B and 3C show an example of pictures obtained with the setup at different times while OSAs were moving in the settling column.

2.3 Effective Density

The effective density of sinking OSAs was obtained using the measured size and settling velocity data and the modified Stokes' Law. For an OSA of size D_{OSA} and settling velocity W_{OSA}, its effective density $\Delta\rho_{OSA}$ is calculated using the following settling velocity equation:

$$W_{OSA} = \left(\frac{4}{3} g C_d^{-1} \frac{\Delta\rho_{OSA}}{\rho_w} D_{OSA} \right)^{0.5} \quad (1)$$

where g is the gravitational acceleration (m s^{-2}), C_d is the dimensionless drag coefficient, $\Delta\rho_{OSA}=\rho_{OSA}-\rho_w$ is the effective density (excess density) of OSAs (kg m^{-3}), D_{OSA} is the equivalent spherical diameter of OSAs (m) and ρ_{OSA} and ρ_w are OSA and water densities, respectively (kg m^{-3}).

The drag coefficient C_d shown in equation (1) is estimated using the following commonly used empirical relationship (Raudkivi, 1976):

$$C_d = \frac{24}{\mathrm{Re}}\left(1 + 0.15\mathrm{Re}^{0.687}\right), \quad (2)$$

where $Re=W_{OSA}D_{OSA}/\nu$ is the particle Reynolds number in which ν represents the kinematic viscosity of the water (m^2/s^{-1}).

3 Method Verification and Calibration

The method described above to measure size and settling velocity of OSAs was verified using sediment grains of known size and density. The sediment used was natural sediment sampled from Unalaska Island. Before use, the sediment was dry sieved. Sediment grains that passed through the 150 μm sieve and retained in the 100μm one (the finest grains forming this sediment) in size were used in the verification and calibration experiments. The bulk density of the sediment was measured to be 2.960 ± 0.003 g/mL. Results showing size and settling velocity of the selected sediment grains are shown on Figure 4a. The measured size varied from 79 to 162 μm. This range is slightly outside the size range initially defined by the sieving (100-150 μm). This slight difference was expected. Natural sediment grains are not spherical in shape and may have different lengths in the three dimensions.

Regarding verification of settling velocity measurements, the data were compared with the Stokes' Law known to reproduce very well settling process of small solid particles. As shown on Figure 4a, the measurements are in good agreement with the predictions. The corresponding calculations of the effective density of the sediment grains are shown on Figure 4b. The data showed variations from about 1000 to 4500 g/L. This is not surprising for natural sediment grains which may contain a wide variety of minerals and organic matters known to have different densities. However, the median value of the calculated effective density of sediment grains, 2055 g/L, compares very well with their bulk effective density measured to be 1940 g/L (solid and dotted lines on Figure 4b).

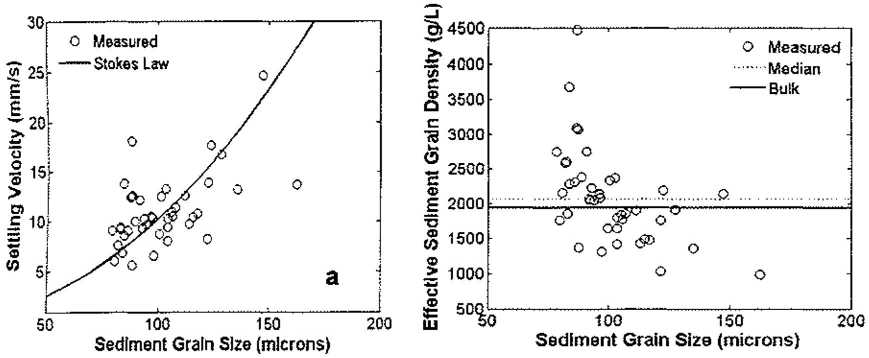

Figure 4 Verification of the methods used to measure settling velocity (a) and effective density (b) of OSA.

4 Experimental Conditions

In this study, OSA formation was studied using Standard Reference Material 1941b (hereafter referred by SRM) prepared by the National Institute of Standards and Technology, Arabian Medium and South Louisiana crude oils, Corexit 500 as chemical dispersant and the experimental methods described in section 2. Chemical dispersant was used at a constant dispersant-to-oil ratio of 1:10. Size distribution of the SRM grains is shown on Figure 5. The median grain size of the sediment is about 5.2 µm. The sediment contains about 56% of fines (sediment grains less than 5.3 µm in size) and 11% of organic matter (see Khelifa et al., 2008 for detailed characterisation of this sediment). Physical properties of the two crude oils and the experimental conditions are summarized in Table 1. Most of the experiments were run using sediment concentration of 100 mg/L (Sediment-to-oil ratio of 0.5). Only experiments with the Arabian Medium oil were repeated with 200 mg/L sediment concentration. All the experiments were run using constant oil concentration of 200 mg/L, at a controlled temperature of 15 °C and a constant mixing energy defined by a shaking speed of 126 cycles per minute and a stroke of 38 mm.

Table 1 Experimental conditions

Reacting phase	Name	Density (g/mL)	Viscosity (mPa)	Surface tension (mN/m)	Oil-brine interfacial tension (mN/m)	Concentration (mg/L)
Sediment	SRM-1941b	2.57	-	-	-	100 & 200
Oil	Arabian Medium	0.876	28.1	26.5	20.0	200
	South Louisiana	0.859	13.3	26.5	16.2	

5 Results and Discussion

Examples of photomicrographs of negatively buoyant OSAs formed with Arabian medium oil and SRM-1941b sediment at 200 mg/L without and with chemical dispersant are shown on Figure 6. The photomicrographs are clear evidence that OSAs do form with both physically and chemically dispersed oils and the SRM-1941b sediment. OSAs formed with chemically dispersed oil contain many small droplets in their bodies and are more abundant than in those formed without chemical dispersant.

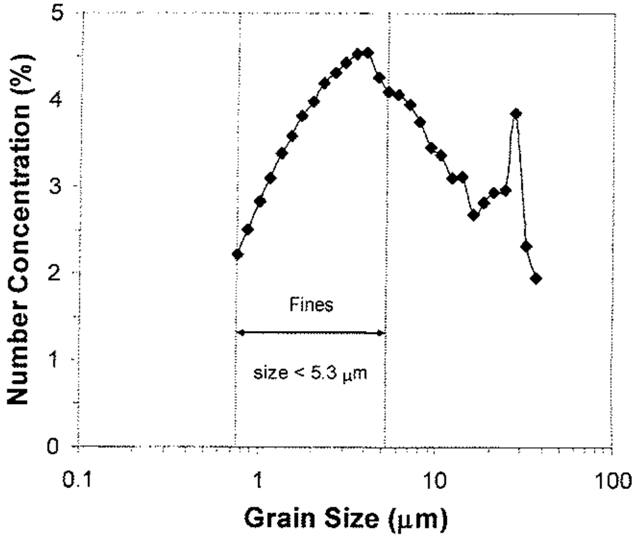

Figure 5 Size distribution of the SRM-1941b sediment. Fines are defined as sediment grains that are less than 5.3 µm in size. Fines in this sediment are abundant and represent 56% of the size distribution.

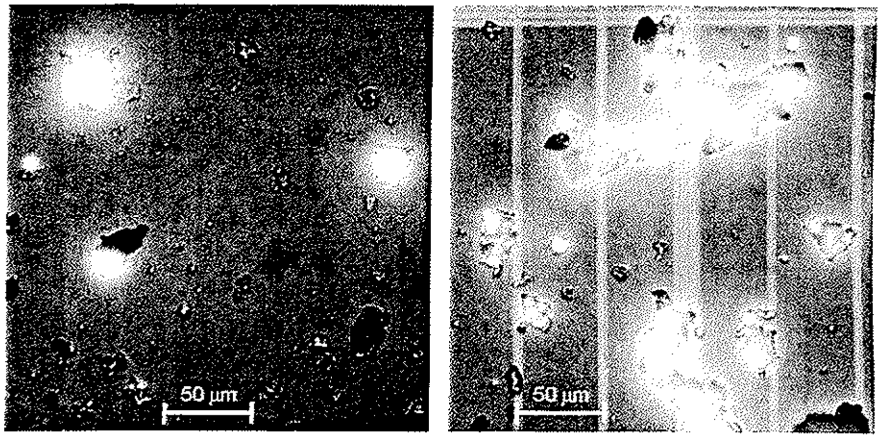

Figure 6 Photomicrographs of negatively buoyant OSAs formed with Arabian medium oil and SRM-1941B sediment at 200 mg/L without chemical dispersant (left) and with Corexit 9500 at 1:10 ratio (right). Oil droplets are fluorescent white particles surrounded and/or covered by dark sediment flocs.

Measured size distributions of OSAs formed without and with Corexit 9500 at 1:10 DOR are shown on Figure 7. The curves show typical distribution of sediment flocs (Khelifa and Hill, 2006). Compared to the no oil conditions, all the data show that OSA size distributions shift to large flocs (curves shown by solid lines shifting to the right side on Figure 7). The maximum size of OSAs increases from about 190 μm to 220 and 230 μm for Arabian Medium oil and to 340 and 320 μm for South Louisiana oil without and with chemical dispersant, respectively. This suggests that presence of small droplets in sediment flocs enhances growth of the flocs by enhancing their particle-particle stickiness. As shown below, the increase of OSA size enhances their settling velocity.

Guyomarch et al. (2002) studied variations of OSA size distribution with sediment concentration. The results they obtained with sediment concentration of 2.0 g/L (sediment-to-oil ratio close to 0.5 as in this study) compare well with those shown on Figure 7. However, OSA sizes measured in this study are not in the same range as those measured by Li et al. (2007) under breaking wave conditions. This is due, perhaps, to the difference in the mixing conditions used in the studies, as it is well established that mixing energy controls the size of sediment flocs in aquatic environment. It may also due to differences in the oil-to-sediment ratios that is much more difficult to control in a wave thank than in bench scale experiments.

Measured settling velocities of OSAs are shown on Figure 8. The data were compared with those obtained with sediment only without oil or chemical dispersant. The modified Stokes' Law, which is very often used to describe the settling process of natural particles, is also shown on this Figure for comparison. From the author's knowledge, data shown on Figure 8 represent the first information that exists in the literature regarding the settling process of OSAs. Analysis of the data shown on this Figure revealed that:

1) many OSAs have settling velocities very similar to those of sediment flocs of equal size (circle and triangle symbols shown in the area of the black dots on Figure 8). We believe that these OSAs contain no (sediment flocs) or very few oil droplets and, thus, they behave like sediment flocs. This interpretation is well corroborated by the UV fluorescence microscopy observations where OSAs of different oil (droplets) contents were observed under the same slide (Figure 6).
2) few OSAs settle faster than sediment flocs of the same size, as shown on Figure 8b with chemically dispersed oil (points shown by the triangle symbols above the black dots in the size range 50-200μm). We believe that these OSAs are sediment flocs similar to those discussed above. However, they may be OSAs that contain many small chemically dispersed droplets. Presence of these droplets in their body may have reduced their porosity and trapped many sediment grains due to enhancement of their stickiness. But, this needs further investigation.
3) a group of many OSAs (data shown by encircled circles and triangles symbols on Figure 8) can be distinguished from the pure sediment flocs (black dots). We believe that these OSAs contain many small and/or large oil droplets in their body, as shown on Figure 6. Reduction of their settling velocity compared to those of sediment flocs of the same size is caused by the low density of oil droplets (about 0.9 compared to about 2.6 g/mL for sediment grains) trapped into OSAs. The average size and settling velocity of the encircled data (OSAs) are about 150 μm and 0.8 mm/s for Arabian Medium oil (Figure 8a) and 180 and 1 mm/s for the South Louisiana oil (Figure 8b), respectively. In fact, the encircled data shows two sub-groups. The first one include OSAs in the same size range as sediment flocs, but with smaller settling velocity (encircled data less than about 190 μm in size). The average settling velocity of this sub-group of OSAs is about 0.5 mm/s for Arabian Medium oil and 0.6 mm/s for South Louisiana oil compared to 1 mm/s for pure sediment data. Their minimum settling velocity is about 0.3 mm/s for both oils. The second sub-group includes OSAs that are larger than the largest measured sediment floc (about 190 μm). As this type of OSAs were observed with both physically and chemically dispersed oils and with both Arabian medium and South Louisiana oils, we believe that those OSAs contain oil droplets and increase of their size is possibly due to enhancement of their stickiness. Their settling velocity is higher than those measured for sediment flocs. As shown on Figure 8, the increase is due to the increase of their size. This increase is well represented by the trend shown by the variations of settling velocity with the size of pure sediment flocs.
4) Stokes' Law is not an appropriate model to describe settling process of OSAs. It overestimates settling velocity of OSAs and sediment flocs. This finding is in agreement with recent findings related to modelling of settling process of sediment flocs (Khelifa and Hill, 2006).
5) settling velocity of OSAs increases with their size as it is well established for pure sediment flocs. On average, the data obtained in this study showed that OSAs and pure sediment flocs settle at a rate of 1 mm/s, which is very similar to what Hill et al., 1998) suggested for large sediment flocs.

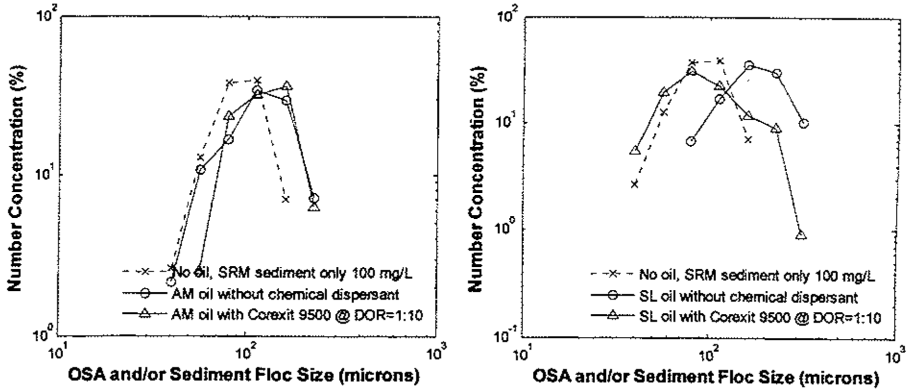

Figure 7 Measured size distributions of OSAs formed with the SRM-1941b sediment at 100 mg/L concentration and the Arabian Medium oil (left) or South Louisiana oil (right) without and with Corexit 9500 at 1:10 DOR.

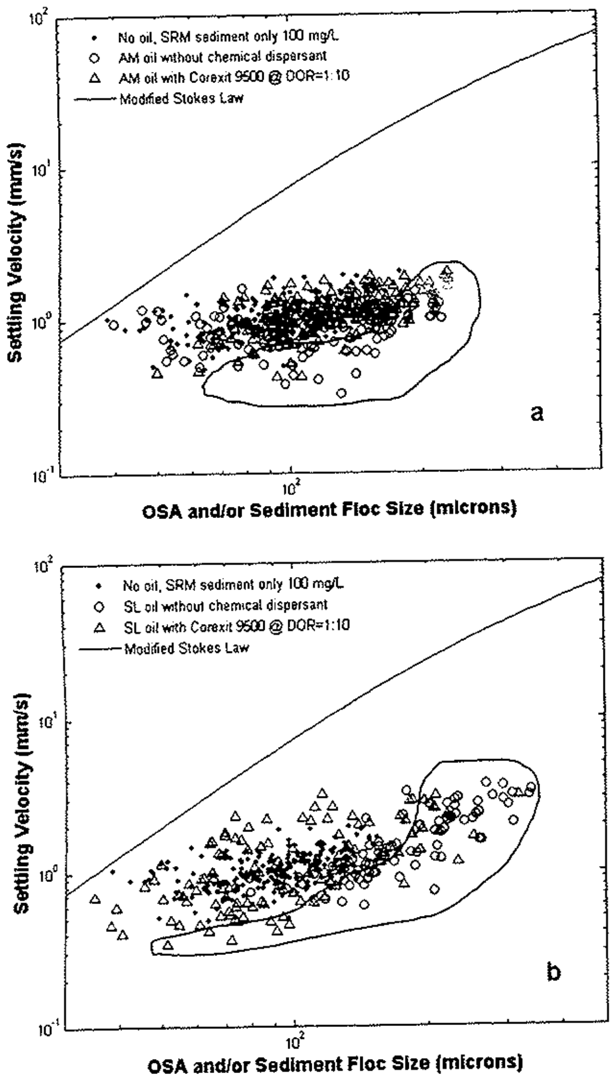

Figure 8 Measured settling velocities of OSAs formed with theSRM-1941b sediment at 100 mg/L concentration and the Arabian Medium oil (a) or South Louisiana oil (b) without and with Corexit 9500 at 1:10 DOR.

The settling velocity data shown on Figure 8 were processed using the procedure described in section 2.3 to obtain effective density of OSAs. The results were compared with those obtained with sediment only without oil and chemical dispersant (Figure 9). From the author's knowledge, data shown on Figure 9 represent the first information that exists in the literature regarding the effective density of OSAs. Because the effective density is almost proportional to the settling velocity, analysis of the data shown on these figures revealed similar observations as above. These include:

1) many OSAs have effective density very similar to those of sediment flocs of equal size (circle and triangle symbols shown in the area of the black dots on Figure 9). Once again, we believe that these OSAs contain no (sediment flocs) or very few oil droplets and, thus, they behave like sediment flocs.
2) few OSAs are denser than sediment flocs of the same size, as shown on Figure 9b with chemically dispersed oil (points shown by the triangle symbols above the black dots in the size range 50-200μm).
3) a group of many OSAs (data shown by encircled circles and triangles symbols on Figure 9) can be distinguished from the pure sediment flocs (lack dots), as for settling velocity data (Figure 8). As discussed previously, we believe that these OSAs contain many small and/or large oil droplets in their body, as shown on Figure 6. Reduction of their effective density compared to those of sediment flocs of the same size is caused by the low density of oil droplets (about 0.9 compared to about 2.6 g/mL for sediment grains) trapped into OSAs. The average effective density of the encircled data (OSAs) is about 60 g/L both Arabian Medium oil (Figure 9a) and South Louisiana oil (Figure 9b). As discussed for the settling velocity data, the encircled data shows two sub-groups. The first one includes OSAs in the same size range as sediment flocs, but with smaller effective density (encircled data less than about 190 μm in size). The average effective density of this sub-group of OSAs is about 70 mg/L for Arabian Medium oil and 100 mg/L for South Louisiana oil compared to 200 g/L for pure sediment data. The second sub-group includes OSAs that are larger than the largest measured sediment flocs (about 190 μm). As discussed above for the settling velocity data, we believe that those OSAs contain oil droplets and increase of their size is possibly due to enhancement of their stickiness. Their effective density is lower than those measured for sediment flocs. As shown on Figure 9, the decrease is due to the increase of their size. This increase is well represented by the trend shown by the variations of effective density with the size of pure sediment flocs.
4) the lowest effective densities of OSAs of 37 and 34 mg/L were measured with physically dispersed Arabian Medium oil and South Louisiana oil, respectively. The lowest effective densities of OSAs obtained with chemically dispersed Arabian Medium oil and South Louisiana oil were 55 and 42 g/L, respectively.
5) effective density of OSAs decreases with their size as it is well established for pure sediment flocs. On average, the data obtained in this study showed that OSAs and pure sediment flocs have an effective density of about 150 g/L.

Interpretation of the data shown on Figures 8 and 9 revealed that negatively buoyant OSAs settle at a rate slightly smaller (or equal) than the settling rate of sediment flocs of same size. The decrease in the settling rate is due to decrease of their effective density. The results showed also that two processes may affect the effective density of OSAs. The first one relates to introduction of oil droplets into OSAs which is expected to reduce their effective density as oil droplets are about 3 times lighter than sediment grains. This process is also expected to increase the effective density of OSAs because it decreases their porosity. The second process that causes decrease of the effective density of OSAs relates to the increase of OSA size

(Figure 7). It is well established that effective density of natural flocs decreases when their size increases (Khelifa and Hill, 2006).

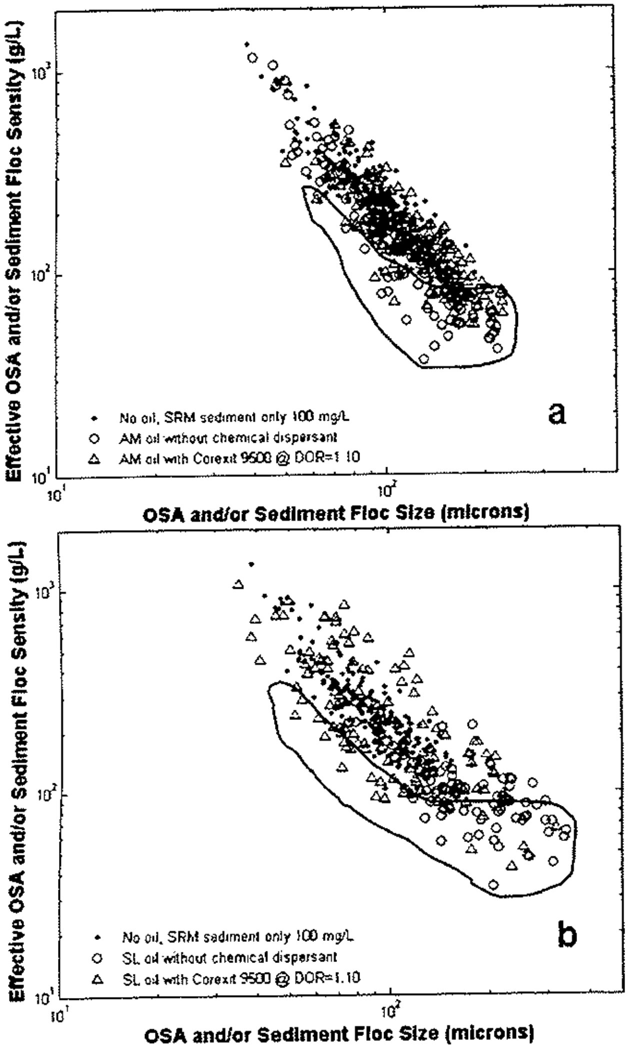

Figure 9 Measured effectives densities of OSAs formed with theSRM-1941b sediment at 100 mg/L concentration and the Arabian Medium oil (a) or South Louisiana oil (b) without and with Corexit 9500 at 1:10 DOR.

Physical properties of OSAs discussed so far were obtained with a small sediment concentration of 100 mg/L (sediment-to-oil ratio of 0.5), smaller than the background SPM concentration of many water systems. Additional experiments using a higher sediment concentration of 200 mg/L (sediment-to-oil ratio of 1) and Arabian Medium oil were run to verify the observations discussed above. Results showed that

abundance of suspended sediment makes OSAs size distributions very similar to those of pure sediment flocs (Figure 10a). Nevertheless, large OSAs were more abundant with chemically dispersed oil than without oil. The observations discussed above regarding settling velocity and effective density data are also valid for the new results obtained with sediment concentration of 200 mg/L (Figures 10b,c). However, the effects of oil are much less obvious that in the previous results obtained with 100 m/L sediment concentration. Higher sediment concentration enhances the density of OSAs. This is due possibly to enhancement of the sediment-to-oil ratio in the OSAs.

6 Conclusion

A laboratory setup and procedure were developed and tested to measure size, settling and effective density of OSAs. The data discussed in this paper were obtained using Standard Reference Material 1941b prepared by the National Institute of Standards and Technology, Arabian Medium and South Louisiana crude oils, Corexit 9500 chemical dispersants, and for sediment-to-oil ratios of 0.5 and 1. We conclude tha the hypothesis stating that OSAs are neutrally buoyant and do not settle to the seafloor is not valid. Overall, it appears that OSAs behave as sediment flocs commonly observe in coastal waters. As such, it is legitimate to using the extensive knowledge established by experts on sediment transport regarding formation of sediment flocs to predict physical properties of OSAs. Of course more work is needed to understand how physical properties of OSAs vary with many controlling factors. But it appears from thi study that the well recognized variability in physical properties of natural flocs is wide enough to make OSAs hardly distinguishable from these flocs, especially at sediment-to-oil ratios of 1 and higher.

From an oil spill response perspective, we conclude also from this study that application of chemical dispersant in coastal waters rich in SPM could be problematic because it may enhance oil sedimentation and contaminate the seafloor. There are two supporting evidences for this statement. The first relates to the fact that application of chemical dispersant enhances OSAs formation as shown from our recent study (Khelifa et al. 2008), while the second one relates to the fact that OSAs are negatively buoyant and behave as natural sediment flocs, as just discussed above. However, further researc is needed to evaluate the effects of other key factors controlling the fate of OSAs that were not studied and/or not discussed in this study. For instance, the effect of mixing energy is well known to have strong control on the size and, hence, the settling process of natural flocs. More specifically, given the results discussed in this paper, it is important to investigate on what would be the minimum mixing energy required to keep the OSAs in suspension. It is also important to quantify the minimum hydrodynamic shear, induced by tide currents and/or waves, required to re-suspend OSAs from the seafloor that can then be transported away from the oiled sites by local flows. Much research is also needed to study toxicity and biodegradation of OSAs formed with chemically dispersed oil.

Additional results related to effects of sediment type and chemical dispersant on formation and fate of OSAs will be published in coming papers.

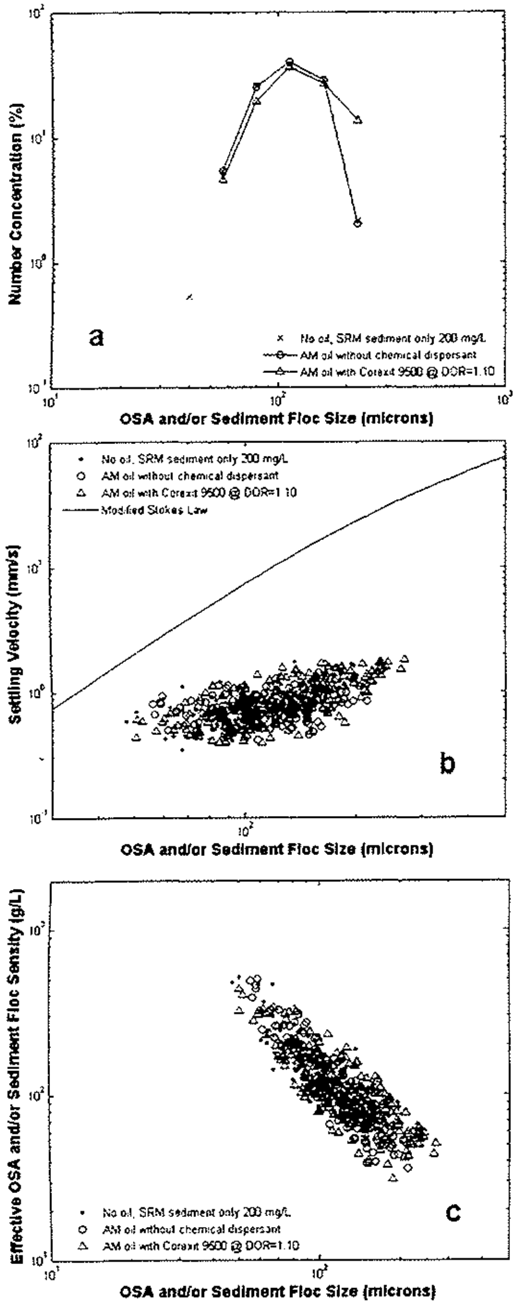

Figure 10 Measured size (a), settling velocity (b) and effective density (c) of OSAs formed with theSRM-1941b sediment at 200 mg/L concentration and the Arabian Medium oil without and with Corexit 9500 at 1:10 DOR.

7 Acknowledgements

Funding for this project was provided by the Coastal Response Research Center www.crrc.unh.edu

8 References

Ali, M., *Effect of Sediment Size on Oil-Mineral Aggregation*, Master Thesis, Department of Civil Engineering, Faculty of Engineering, Dalhousie University, Halifax, NS, Canada, 83 p., 2006.

Ajijolaiya, L.O, *The Effects of Mineral Size and Concentration on the Formation of Oil-Mineral Aggregates*, Master Thesis, Department of Civil Engineering, Faculty of Engineering, Dalhousie University, Halifax, NS, Canada, 80 p., 2004.

Bragg, J.R. and E.H. Owens, "Clay-Oil Flocculation as a Natural Cleansing Process Following Oil Spills: Part 1 – Studies of Shoreline Sediments and Residues From Past Spills", in *Proceedings of the Seventeenth Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1-23, 1994.

Bragg, J.R. and S.H. Yang, "Clay-Oil Flocculation and its Role in Natural Cleansing in Prince William Sound Following the Exxon Valdez Oil Spill", in *Fate and Effects in Alaskan Waters*, ASTM STP 1219, Peter G. Wells, James N. Butler, and Jane S. Hughes, Eds., American Society for Testing and Materials, Philadelphia, PA, pp. 178-214, 1995.

Guyomarch, J., F.-X. Merlin, and P. Bernanose, "Oil Interaction With Mineral Fines and Chemical Dispersion: Behaviour of the Dispersed Oil in Coastal or Estuarine Conditions", in *Proceedings of the Twenty-Second Arctic and Marine Oilspill Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 137-149, 1999.

Guyomarch, J., S. Le Floch, and F.-X. Merlin, "Effect of Suspended Mineral Load, Water Salinity and Oil Type on the Size of Oil–Mineral Aggregates in the Presence of Chemical Dispersant", *Spill Science and Technology Bulletin*, 8(1), pp. 95-100, 2002.

Hill, P.S., J.P. Syvitski, E.A. Cowan, and R.D. Powell, "In Situ Observations of Floc Settling Velocities in Glacier Bay, Alaska". *Mar. Geol.*, 145, pp. 85-94, 1998.

Khelifa, A., and P.S. Hill, "Models for Effective Density and Settling Velocity of Flocs *Journal of Hydraulic Research*, Vol. 44 (3), pp. 390-401, 2006.

Khelifa, A., P. Stoffyn-Egli, P.S. Hill, and K. Lee, "Characteristics of Oil Droplets Stabilized by Mineral Particles: The Effect of Oil Types and Temperature", *Spill Science & Technology Bulletin*, 8(1), pp. 19-30, 2002.

Khelifa, A., P.S. Hill, P. Stoffyn-Egli, and K. Lee, "Effects of Salinity and Clay Composition on Oil-Clay Aggregations", *Marine Environmental Research*, 59, pp. 235-254, 2005a.

Khelifa, A., P.S. Hill, and K. Lee, "The Role of Oil-Sediment Aggregation in Dispersion and Biodegradation of Spilled Oil", in Oil Pollution and its Environmental Impact in the Arabian Gulf Region. A. Al-Azab, W. El-Shorbagy, and S. Al-Ghais, Editors, Amsterdam, pp. 131-145, 2005b.

Khelifa, A., B. Fieldhouse, Z. Wang, C. Yang, M. Landriault, M.F. Fingas, C.E. Brown, and L. Gamble, "A Laboratory Study on Formation of Oil-SPM Aggregates using the NIST Standard Reference Material 1941b", in *Proceedings of the Thirtieth Arctic and Marine OilSpill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 35-48, 2007.

Khelifa, A., M. Fingas, and C.E. Brown, "Effects of Dispersants on Oil-SPM Aggregation and Fate in US Coastal Waters", *Final Report submitted to the Coastal Response Research Center*, University of Hampshire, NH, 53 p. and Annexes, 2008.

Lee, K., P. Stoffyn-Egli, G.H. Tremblay, E.H. Owens, G.A. Sergy, C.C. Guenette, R.C. Prince, "Oil–Mineral Aggregate Formation on Oiled Beaches: Natural Attenuation and Sediment Relocation", *Spill Science and Technology Bulletin*, 8(3), pp. 285-296, 2003.

Le Floch, S., J. Guyomarch, F.X. Merlin, P. Stoffyn-Egli, J. Dixon, and K. Lee, "The influence of salinity on oil–mineral aggregate formation". *Spill Science and Technology Bulletin*, 8(1), pp. 65–71, 2002.

Li, Z., P. Keplay, K. Lee, T. King, M. Boufadel, and A.D. Venosa, "Effects of Chemical Dispersants and Mineral Fines on Crude Oil Dispersion in a Wave Tank under Breaking Waves, *Marine Pollution Bulleting*, 54, pp. 983-993, 2007.

Mackay, D., and K. Hussain, "Studies of Oil Sedimentation", in: *Proceedings of the third Arctic Marine OilSpill Program Technical Seminar*, Environment Canada, Ottawa, ON, Canada, pp. 120-125, 1980.

Muschenheim, D.K., and K. Lee, "Removal of Oil from the Sea Surface Through Particulate Interactions: Review and Prospectus", *Spill Science and Technology Bulletin*, 8(1), pp. 9-18, 2002.

Omotoso, O. E., V.A. Munoz, and R.J. Mikula, "Mechanisms of Crude Oil–mineral Interactions", *Spill Science and Technology Bulletin*, 8(1), pp. 45–54, 2002.

Owens, E.H., "The Interaction of Fine Particles with Stranded Oil", *Pure Appl. Chem.*, 71(1), pp. 83-93, 1999.

Owens, E.H., and K. Lee, "Interaction of Oil and Mineral Fines on Shorelines: Review and Assessment", *Marine Pollution Bulletin*, 47(9-12), pp. 397-405, 2003.

Owens, E. H., J. R. Bragg, and B. Humphrey, "Clay–Oil Flocculation as a Natural Cleansing Process Following Oil Spills: Part 2 – Implications of Study Results in Understanding Past Spills and for Future Response Decisions", in *Proceedings of the Seventeenth Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, ON, Canada, pp. 25–37,1994.

Payne, J.R., J.R. Clayton Jr., and B.E. Kirstein, "Oil/Suspended Particulate Material Interactions and Sedimentation", *Spill Science and Technology Bulletin*, 8(2), pp. 201-221, 2003.

Raudkivi, A.J., "Loose Boundary Hydraulics", 2nd Edn., Pergamon, New York, 1976.

Sergy, G.A., C.C. Guenette, E.H. Owens, R.C. Prince, and K. Lee, "The Svalbard Shoreline Oilspill Field Trials", in: *Proceedings of the Twenty-first Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, ON, Vol. 2, pp. 873-889, 1998.

Sergy, G., C. Guennette, E.H. Owens, R. Prince, and K. Lee, "Treatment of Oiled Sediment Shorelines by Sediment Relocation", in: *Proceedings of the 1999 International Oil Spill Conference*, Seattle, Washington, USA, pp. 549-554, 1999.

Sergy, G.A., C.C. Guenette, R.C. Prince, and K. Lee, "In-situ Treatment of Oiled Sediment Shorelines", *Spill Science & Technology Bulletin*, 8(3,) pp. 237–244, 2003.

Sterling, M.C., J.S. Bonner, A.N.S. Ernest, C.A. Page, and R. L. Autenrieth, "Characterizing Aquatic Sediment-Oil Aggregates Using In situ Instruments", *Mairine Pollution Bulletin*, Vol. 48, pp. 533–42, 2004.

Stoffyn-Egli, P., and K. Lee, "Formation and Characterization of Oil–Mineral Aggregates", *Spill Science and Technology Bulletin*, 1, pp. 31-44, 2002.