DISPERSANT EFFECTIVENESS AND TOXICITY—AN INTEGRATED APPROACH

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ABSTRACT: *An integrated approach to study chemical dispersant effectiveness and dispersed oil toxicity is presented. Conventional lab scale effectiveness tests generally provide a measure of overall dispersant effectiveness. However, chemical dispersion can be viewed as two processes: (1) dispersant-oil slick mixing and (2) oil droplet transport into the water column. Inefficiencies in either process limit the overall dispersant effectiveness. This laboratory study centered on the latter process and was conducted to focus on the impacts of water column hydrodynamics on the resurfacing of dispersed oil droplets. Using a droplet coalescence model (Sterling et al., 2002), the droplet coalescence rates of dispersed crude oil was determined within a range of shear rates. A controlled shear batch reactor was created in which coalescence of dispersed oil droplets were monitored in-situ. Experimental dispersion efficiencies (C/C_o) and droplet size distributions were compared to those predicted by Stokes resurfacing. Experimental C/C_o values were lower than that predicted from Stokes resurfacing. Experimental dispersion efficiency values (C/C_o) decreased linearly with increasing mean shear rates due to increased coalescence rates. These results suggested that dispersed oil droplet coalescence in the water column can adversely impact overall dispersant efficiency. To avoid high control mortality in toxicity testing, the toxicity exposure chamber was designed with separate compartments for scaled mixing and organism exposure, respectively. Chamber design includes continuous re-circulation between mixing and exposure chamber. A 1-minute exposure compartment residence time was determined from tracer studies indicating virtually identical oil concentrations in the mixing and exposure compartments. In addition, the 96-hour mortality of 14-day oil* Menidia beryllina *varied from 2% in the no-oil control tests to 87% in the dispersed oil (200 mg/L) tests. These results show the effectiveness of the integrated vessel for the characterization and toxicity testing of oil dispersions.*

Introduction

Chemical dispersants produce particulate oil down to micron diameters. This dispersed oil increases the surface area to volume ratio, which aids in the dissolution of soluble material from the droplets (Mackay, 1977; McDonald et al., 1984). Page et al. (2000) showed that the solubility of naphthalene compounds in crude oil were shown to agree well with Raoult's law and is thus proportional to the organic phase mole fraction and the solubility of the pure component.

Mixing energy in dispersant efficiency testing has been well documented. In a comparison of common dispersant effectiveness protocols, Daling et al. (1990) determined that the rotating flask (Labofina/Warren Spring Laboratory (WSL)) measurements yielded lower efficiencies than those of constant agitation tank tests (Mackay-Nadeau-Steelman (MNS)). A primary reason was that the WSL settling regime allowed droplets larger than 60 μm to resurface while the droplets smaller than 100-125 μm remained dispersed in the tank tests studied. Thus, the removal of entrainment energy before droplet characterization in the WSL leads to an artificially reduced efficiency. A rapid drop in dispersant effectiveness with increased settling time was also noted by Fingas et al. (1996).

The observed toxicity is a function of the oil's particle size distribution, oil concentration, and exposure duration. The particle size distribution has been shown to vary with time in laboratory tests (Sterling et al., 2002). In laboratory tests, dispersed oil droplets can coalesce into larger droplets. Thus, mixing energy is a critical factor affecting the chemically dispersed oil (CDO) exposure regime in toxicity evaluations.

The goals of this project were to develop a simple toxicity exposure system that incorporates scalable and quantitative mixing inputs with in-situ particle size analysis and traditional petroleum chemistry techniques to characterize the exposure regime. A second goal was to describe the kinetics of droplet coalescence in the toxicity chamber. The final goal was to demonstrate that the exposure system has the sensitivity required to determine petroleum toxicity with a juvenile test species.

Materials and methods

Experimental apparatus. The combined mixing-toxicity system is an adaptation to the vessel described by Sterling et al. (2002). The main adaptation to the reactor vessel is the addition of a toxicity exposure vessel (Figure 1). The toxicity chamber

was separated from the mixing chamber by a vertical Plexiglas partition. To prevent organism transport to the mixing chamber, a horizontal weir constructed of Plexiglas and stainless steel wire mesh was placed at the top of the toxicity chamber.

To provide simultaneous particle size measurements, the mixing side of the system was fitted with a port to accommodate the LISST-100 particle size analyzer. As with the jar test apparatus, this reactor system is agitated using a stainless steel mixing impeller. The mixing energy transferred to the reactor fluid by impeller rotation at a given speed was determined using a torquemeter. The impeller is composed of four cylindrical rods evenly staggered throughout the depth of the reactor. This impeller design, along with the addition of side baffles and internals of the reactor's ends increase the uniformity of reactor mixing.

An in-situ laser scattering particle sizer (LISST-100, Sequoia Instruments, Richmond, WA) was installed through one end wall of the reactor. This instrument can be used in bench scale as well as field scale measurements. Incorporating this instrument in the reactor design not only allowed the measurements of droplet size distributions without ex-situ sampling errors but also ensured consistent measurements between lab and field scale experiments.

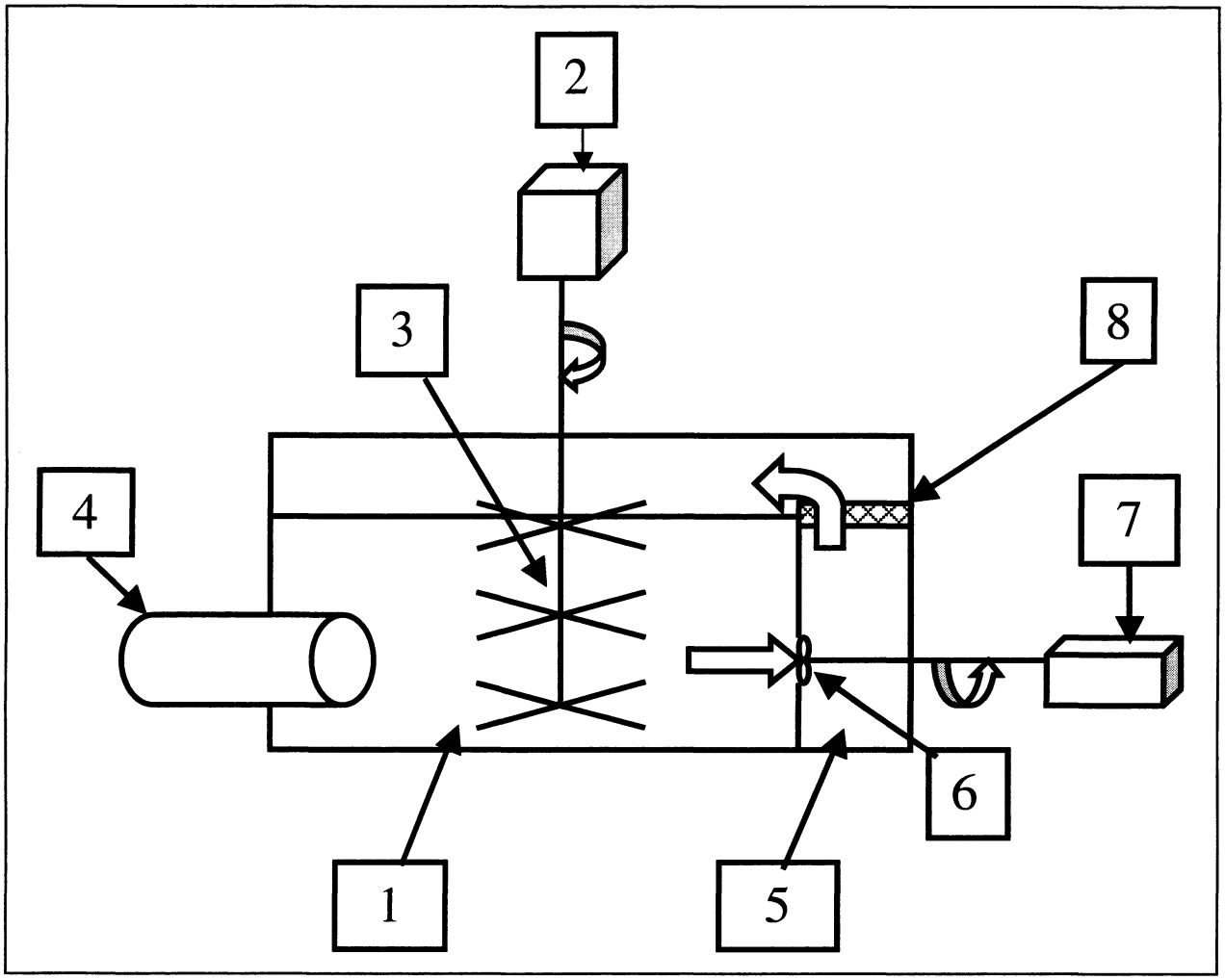

Figure 1. Integrated Effectiveness/Toxicity Reactor. (1) 40-L mixing chamber, (2) overhead mixing motor, (3) stainless steel impeller, (4) light scattering particle sizer (LISST-100), (5) organism exposure chamber, (6) re-circulation impeller, (7) re-circulation motor, and (8) outflow mesh screen.

Hydrodynamic characterization. A dye study using Rhodamine WT was conducted to assess the hydrodynamic characterization of the exposure side of the toxicity evaluation system. The absorbance of the dye in the exposure chamber was measured with an Ocean Optics® fiber optic spectrophotometer (S-2000) using a pulsed xenon lamp. Absorbance measurements were made in-situ using a fiber optic probe that was placed directly in the exposure side of the vessel.

A calibration curve showed that the Rhodamine WT absorbance was linear between 0-10 mg/L (r^2=0.9987). Therefore, a target steady state concentration in the whole volume of the testing system was set at 5 mg/L. When completely mixed conditions were visually established, approximately 25 ml of Rhodamine WT (10,000 mg/L) was added directly to the mixing chamber. The fluorometer was set to record the absorbance at a sampling interval of 10 sec. The experiment was terminated after the absorbance stabilized.

Chemically dispersed oil test. The effects of mean shear rate (5,10,15,20 s^{-1}) on the coalescence kinetics of chemically dispersed crude oil droplets. Other factors such as dispersant: oil

ratio, oil loading, and temperature were held constant throughout the study. Dynamic droplet size distributions were measured every 5 minutes using an in-situ laser scattering particle sizer (LISST-100, Sequoia Instruments, Richmond, WA). Daily water samples were extracted with methylene chloride and analyzed for petroleum hydrocarbons ranging from C10-C36. The analysis was conducted using the Gas Chromatography-Mass Spectrometer (GC-MS) method as previously presented by Mills et al. (1999).

For a subset of droplet coalescence studies, CDO bioassays were conducted. Toxicity tests used 14-day old *Menidia beryllina* obtained from Aquatic Biosystems in Fort Collins, Colorado. They were acclimated for 1 day in a glass aquarium with Instant Ocean®. The organisms were fed *Artemia* sp. Nauplii (24-48 hours old) *ad libitum*. In these tests, 100+ organisms were loaded into the exposure chamber that was partially filled with artificial seawater. Following organism loading, the wire screen weir was secured, the mixing/exposure vessel was filled, and the recycle flow was initiated in sequence. After 96-hour exposure duration, the surviving organisms were collected and counted.

As per USEPA (1994) guidelines, valid toxicity tests must demonstrate control mortality ratios below 10%. Therefore, a series of no-oil, -dispersant, control tests were conducted. The procedure followed that of the oil toxicity testing described above without the addition of oil-dispersant. All continuous flow tests were accompanied by a static no-renewal, -oil, -dispersant control test. The static tests were conducted in 1 liter beakers filled with 500 ml clean artificial seawater (Instant Ocean®). To each beaker, 10 organisms were loaded. The organisms were fed *Artemia* sp. nauplii daily. After the 96-hour test duration, the surviving and dead fish were collected and counted.

Results and discussion

Hydrodynamic characterization. Results from the Rhodamine dye study are shown in Figure 2. This data was used to calculate a mean hydraulic residence time (Clark, 1996).

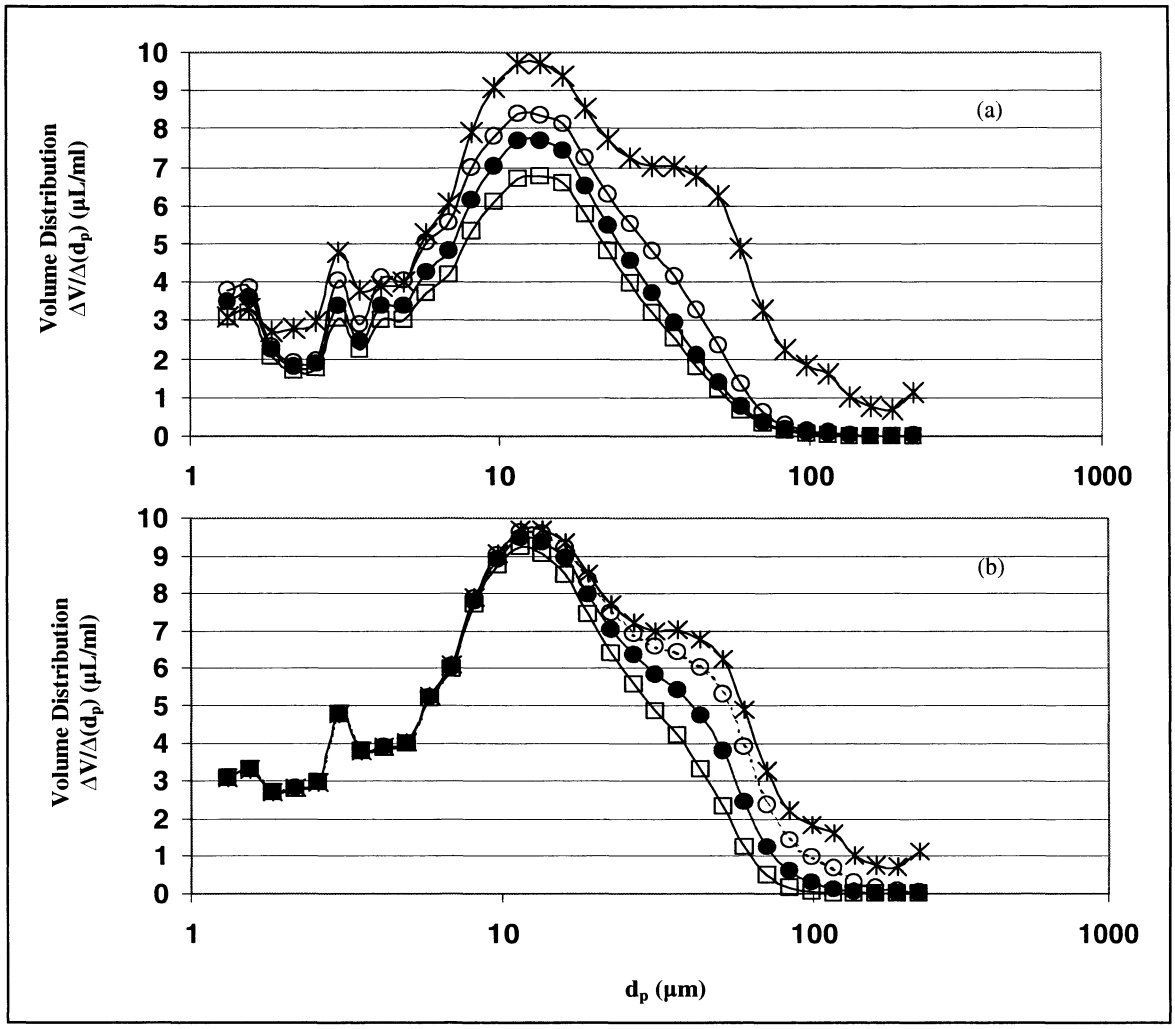

Figure 2. Observed (a) and non-coalescence predicted (b) volume distribution at G_m = 10 s^{-1} at middle depth. Each line represents a different sample time in minutes: 0.0 (*); 60 (○); 120 (●); 240 (□).

$$A_{norm} = 1 - \frac{A_t}{A_{t,\max}} \quad (1)$$

First, the raw absorbance was normalized by giving maximum and minimum A_{norm} values of unity and zero, respectively. A_t is the raw absorbance at t=time and $A_{t,max}$ is the maximum absorbance observed during the test. The area under the A_{norm} vs time curve was calculated by the following

$$Area = \sum \left[\frac{A_{norm}(t_{i+1}) + A_{norm}(t_i)}{2} \right] * [t_{i+1} - t_i] \quad (2)$$

where t_i, t_{i+1} are time points in a discrete time series. The discrete residence-time density function, $f(t_i)$, was then calculated by equation 3.

$$f(t_i) = \frac{A_{norm}(t_i)}{Area} \quad (3)$$

Finally, the discrete approximation of the mean residence time, t_{RTD}, was calculated by equation 4.

$$t_{RTD} = \sum \left[\frac{(t_i + t_{i+1})}{2} \right] * \left[\frac{f(t_i) + f(t_{i+1})}{2} \right] * [t_{i+1} - t_i] \quad (4)$$

The discrete t_{RTD} was calculated to be approximately 67 seconds. This short residence time indicates that the dispersed oil concentrations in the exposure side of the chamber follows those of the mixing chamber with a resolution of about 1 minute. Thus, organism exposure to the dispersed oil closely follows the dispersed oil characteristics observed in the mixing chamber.

Coalescence kinetics. The significance of coalescence in determining the efficiency of chemical dispersion is illustrated in Figure 2, which compares the mass of oil dispersed in the water with and without droplet coalescence. In both the coalescence and non-coalescence models, the disappearance of the largest droplets results due to resurfacing. In addition to resurfacing, smaller droplets combine to form larger droplets that subsequently resurface. The loss of dispersed oil mass is illustrated by the decreasing area under the droplet size distribution curve at later times. Figure 2 highlights how the mean droplet size changes over time. In coalescence and non-coalescence models, the mean droplet size initially decreases as the rate of resurfacing is greater than the rate of coalescence. While the mean droplet size continues to decrease in the non-coalescence model after the first hour, the mean droplet size in the non-coalescence model increases. This highlights that the rate of coalescence becomes greater than the rate of resurfacing in the latter case.

Toxicity tests. Mortality in no-oil, dispersant control test ranged from 2-6% and satisfied the guidelines for acceptable control mortality (USEPA, 1994). These results indicate that the exposure chamber does not subject the test organisms to harmful stresses resulted from the continuous flow conditions. Simultaneous static no-oil control tests resulted in 0% mortality.

Results from the CDO test resulted in 87% mortality with an initial C10-C36 concentration of 68 mg/L. Simultaneous static no-oil control tests resulted in 0% mortality. Use of a single data point precludes accurate determination of a median lethal concentration (LC50), but the observed response is comparable to the LC50 of 31 mg/L (C10-C36) reported for 10-day old M. *beryllina* in declining exposure evaluations (Fuller, 2001). These results demonstrate that the protocol and system has the sensitivity required to evaluate CDO toxicity.

Conclusions

The most important aspect of this integrated system is the use of continuous and scalable mixing energy to prepare and maintain the CDO suspension. This allows scaling the experimental energy inputs to energy inputs observed or expected in the coastal water column. Thus, physical conditions responsible for the transport mechanisms in the water column were accurately quantified such that the loss of chemically dispersed oil suspensions in the lab system can be described mathematically. This has resulted in a declining exposure regime that is dependant on natural and characterized processes instead of producing a declining exposure based on arbitrary dilution rates.

The results of this study demonstrate that the methodology and apparatus are suitable for chemically dispersed oil toxicity evaluations using juvenile marine species. As indicated by the hydrodynamic tracer studies, conditions in the exposure chamber closely follow those of the mixing chamber. Toxicity tests with no-oil (control) showed low mortality. Conversely, toxicity tests with CDO showed results comparable to previous declining exposure tests.

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Biography

Michael Sterling is a doctoral candidate in the Civil Engineering department at Texas A&M University, College Station. He earned his Master of Science degree in Agricultural Engineering at Texas A&M and his Bachelor of Science degree in Chemical Engineering from the University of Oklahoma, Norman.

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