

PART II

BEHAVIOUR OF SUBSURFACE DISCHARGES
OF OIL, GAS AND DISPERSANTS

by

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ABSTRACT

This report contains descriptions of a number of research studies which culminated in the design of the discharge system for the dispersed oil spill in the Baffin Island Oil Spill Program (BIOS). Experimental data are reported on the oil droplet sizes resulting from laboratory discharges of

- (i) oil alone
- (ii) oil and gas mixtures
- (iii) oil and dispersant mixtures
- (iv) oil, water and dispersant mixtures.

The use of dispersants reduces oil droplet diameter from millimetres to approximately 10 μm . Test results used to assist the design of the BIOS dispersed oil discharge are described.

A simple method of estimating the particle size of oil-in-water emulsions is described based on observation of settling times. This method when applied to the BIOS discharge indicates that the oil droplet size produced was $10 \pm 5 \mu\text{m}$. Such drops have negligible buoyant velocity under the BIOS test conditions.

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1.0

INTRODUCTION

This report contains accounts of two sets of experiments which had quite different objectives but which concerned the same physical system, namely the discharge of non-aqueous fluids at relatively high velocity into water.

The first set of experiments were undertaken as an exploratory study of the behaviour of a subsea blowout of crude oil with and without gas present. When control is lost of an exploratory or production well, the high pressure oil and/or gas may flow as a two phase system through the well-bore at high velocity, the gas expanding as the pressure falls. Depending on the velocity and gas to oil volume ratios, several flow regimes may apply such as bubble, slug, transition or annular flow. These two-phase flow characteristics have been the subject of intensive study (for example, Oshinowo and Charles 1974 a,b, Govier and Aziz 1972 and Clark and Perkins 1981), When this fluid mixture jets into the water column at the sea bottom, the oil and gas streams fragment into small drops and bubbles of variable size which rise by natural buoyancy to the surface. The behaviour of this rising plume has also been extensively studied notably by Topham (1975), Ditmars and Cederwall (1974) and Fannelop and Sjoen (1980). A review of the status of technology which can be used to intercept and recover the hydrocarbons from this plume has been published recently by Meikle et al (1980).

An interesting aspect of this issue is that at the high pressures and low temperatures which may apply to blowouts in deep water, the gas may form solid hydrates thus reducing its specific volume and buoyancy characteristics (Bishnoi (1979)).

The entire issue of the behaviour of such releases in cold climates has been reviewed by Milne and Herlinveaux (1976) and many aspects of the problem have been discussed in papers in the Annual Arctic Marine Oilspill Program Technical Seminars (e.g. Environment Canada 1981). For the purposes of this work, it is sufficient to note that it is critically important to understand the range of likely oil and gas particle sizes which will be encountered in a blowout. Small particles will rise more

slowly, have greater surface areas and may drift for considerable distances and times before reaching the surface. Indeed, very small oil drops may never surface.

The first work described here was undertaken and reported as a bachelor's thesis project by Nilsson (1980) largely as an exploratory study of how velocity and the pressure of gas altered oil drop size distributions. The work was severely limited by difficulties in particle size measurement due to lack of suitable equipment. In this study, chemical dispersant was added to the oil (purely for interest) and the nature of dispersed oil plumes studied. It was shown that the addition of a small quantity of dispersant caused the oil drop diameter to fall from typically 1 mm to 10 μm resulting in a cloud of slowly rising oil particles which would be similar in characteristics to those formed during chemical dispersion of an oil spill.

This novel method of forming oil in water emulsions was subsequently adopted in modified form by the BIOS project as the method used to generate a defined dispersed oil plume. Further experiments were undertaken using a Coulter Counter for particle size measurement, specifically to obtain design data for the discharge.

A method was also devised for measuring the approximate oil particle size during the BIOS experiment, the method and results being reported here.

A major purpose of the BIOS project was to determine the difference in behaviour and effects of crude oil which impinges on an Arctic shoreline with and without chemical dispersion. An obvious approach is to spill two identical quantities of oil close to shore, disperse one and leave the other untreated, observe the behaviour and make measurements of concentration and the nature of oil in the water column, bottom and shoreline with complementary biological/ecological studies. In practice, this idealized system is not easily and reliably accomplished since it may be difficult to disperse the oil effectively with-

out disturbing the site and there is a risk that if dispersion was ineffective, or only partially effective (due, for example, to application problems), the results would be difficult to interpret. **Accordingly**, the approach in the dispersed oil case was to spill oil under artificial conditions such that dispersion is assured and is accomplished in a reliable, predictable manner.

There are two general methods of generating artificially dispersed oil. The first is to mix oil, dispersant and water in an agitated (eg. stirred) vessel then pump the mixture into the water through a pipe. Since it was decided to spill 15 m³ of oil and the dispersion in the tank should have a concentration no greater than 1000 ppm the volume of water processed must be 15000 m³. Since the aim is to create a plume of oil of concentration 10 ppm, this could involve pumping of the order of 1/100th of the volume of the water at the test site. This could result in severe local disruption of the water column since the dispersion can only be pumped into a small fraction of the area. If the residence time of the oil dispersion was 2 minutes in the mixing vessel and the total discharge time was 6 hours, the vessel volume must be 83 m³ or a 4.4 m cube (ie. 15000 in³ x 2 mins/360 reins). The pumping rate would be 42 m³/minute or 9000 lgal /rein which is an appreciable flow-rate. At a pipe velocity of 5 m/s, a pipe of area 0.14 m² would be required (diameter 42 cm).

A second, simpler and preferred method is to pump premixed oil dispersant and water from shore and discharge it through a series of jets directly into the water column. The jet will break up into a cloud of dispersed oil particles which, it is hoped will be close in particle size distribution to those obtained by application of dispersant to oil on the sea surface. The principal advantage of this system is that it is mechanically simple and involves pumping only 15 m³ of oil which has been premixed with 0.75 m³ of dispersant on shore and a volume of water which need not be stored.

In the first experiments, oil-dispersant mixtures were discharged

and in later tests, oil-dispersant-water mixtures were used. The water was included since it was feared that the relatively high viscosity could give rise to pumping difficulties and to excessive pressure drops which would result in uneven discharge from the perforated pipe which was ultimately used at BIOS. Essentially, the inclusion of water renders the entire design more reliable and robust. Ratios of 5:1 to 10:1, water to oil were contemplated.

Exploratory experiments were conducted to determine if the particle size distribution obtained from a jet is similar to that obtained on the surface and to provide a conceptual design for the delivery system. A Coulter-Counter was provided to measure particle size.

It is apparent from these studies that chemical dispersant can have a profound effect on the behaviour of subsea oil discharge thus enabling human intervention to substantially modify oil spill behaviour and thus effects. For example, dispersant could be injected into a subsea oil discharge resulting in a long delay in oil rise to the surface. Dispersant added to a leaking tanker cargo at the point of release would behave similarly. Obviously the full environmental implications of such measures would require assessment but there may be cases in which the use of dispersants in such circumstances is justified. Elimination of fire hazard, at least temporarily, is an example. Finally, the technique of forming dispersions by discharging oil-dispersant mixtures into water may be useful in toxicity studies where defined and controlled particle sizes are necessary.

2.0 EXPERIMENTAL AND RESULTS

2.1 Oil-Gas Dispersant Discharges

The experiments were undertaken in an aluminum column with a rectangular cross section (Figure 2.1) containing water and into which gas and oil were introduced through a pipe at the bottom. The column was equipped with three rectangular lucite windows through which the bubbles and drops were observed and photographed. The lucite tank and the outer plastic tubing were constructed to accommodate the currents which may occur along the side-walls downwards in the apparatus.

Oil and gas were introduced into the apparatus through glass tubes of 3 mm and 8 mm internal diameter (5 and 10 mm outside diameter). The distance between the outlet of pipe and the water level at the top of the apparatus was 2.15 m. The flowrate of gas was measured by a rotameter and of oil using a glass tube of cross section area 2.5 cm^2 , by measuring the distance which the oil interface moved during a measured time. The oil was forced through the glass tube by compressed air. All parts were connected by Tygon tubing.

When gas alone was introduced, the change of the water level in the tank was measured by a micrometer to estimate the average volume of gas bubbles in the apparatus, but this proved to be difficult since the change was of the order of 1 mm and could not be determined accurately.

The oil and gas experiments were carried out with tap water at a temperature of 20°C as the continuous phase. When dispersants were tested, salt water was used.

Air was used instead of natural gas for convenience and safety.

The first exploratory experiments were carried out with ke-

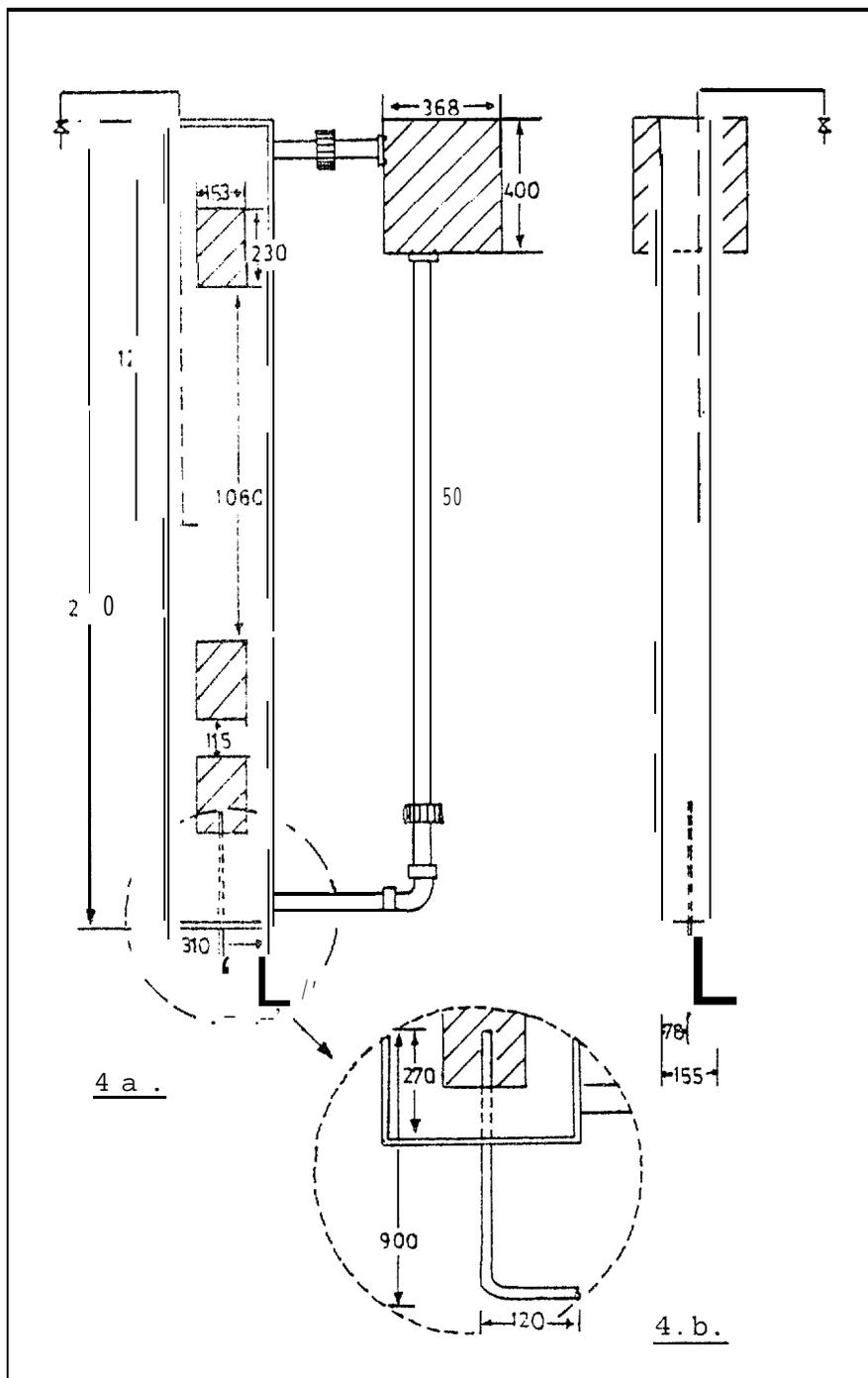


Figure 2.1 Apparatus.

rosene, coloured by red dye, (Sudan IV Red Dye), instead of oil. Kerosene is less viscous and easier to handle than most crude oil. Photographs were taken with an Olympus OM1 camera with a Vivitar 283 flash unit using 400 ASA film.

The crude oil was Alberta Sour Blend supplied by BP and the dispersant was Corexit 9527, which was premixed with the oil. Properties are given in Table 2.1.

TABLE 2.1 PHYSICAL PROPERTIES AT 20° FOR MATERIALS
USED IN THE EXPERIMENTS

MATERIALS	DENSITY kg/m ³	VISCOSITY (Pa s)x10 ³
Air	1.29	0.018
Water	998	1.06
Kerosene	801	2.00
Alberta Sour Blend	832	9.50
Corexit 9527	1010	0.68

Crude oil-water interracial tension was 24.1×10^{-3} N/m.

From the pictures, the number and the diameter of the bubbles were measured by a Tektronics particle size analyzer. Histograms showing the number of bubbles in different diameter ranges were prepared by a computer program and histograms showing the volume of bubbles in different diameter ranges were prepared from these diameter histograms by hand.

Drops of diameter less than 100 μm could not be reliably ob-

served, thus an attempt was made to estimate their number and volume by measuring the decrease in oil concentration with time after each experiment. The volume of drops in this diameter range and the amount of oil dissolved in the water can then be calculated from the rising velocities. The oil concentrations were measured by Horiba IR oil content analyzer.

Experiments with gas alone were performed at six different flowrates with two pipe diameters.

Bubble velocities obtained from the picture and the measurements in the upper tank were compared and the results are shown in Table 2.2 below.

TABLE:2.2 AVERAGE RISING VELOCITIES IN m/s FOR AIR BUBBLES:
OBTAINED PHOTOGRAPHICALLY FOR THE TWO PIPE DIAMETERS

Air Flow cm ³ /s	Pipe Inside Diameter	
	3 mm	8 mm
9.5	0.238	0.238
25.0	0.238	0.241
50.0	0.241	0.253
77.5	0.244	0.259
101.5	0.259	0.259
119.0	0.256	0.256

The velocities did not vary significantly with either air flow or source diameter being about 24 cm/s for a pipe diameter of 3 mm and 25 cm/s for a pipe diameter of 8 mm O.D.

Velocities, corresponding to the bubble diameters obtained from the photographs, from the literature for single bubbles rising in a stagnant fluid are higher than those measured since, in the experiments, the air bubbles were rising as a plume. According to studies of air plumes done by Ditmars *et. al.* (1974) and Topham (1975), the rising velocity of a bubble in a plume exceeds the rising velocity of a single bubble. Similarity can only exist if the air bubbles are so small that their rising velocity relative to the induced plume is negligible.

The discharge of air bubbles into water creates a turbulent plume of an upward rising mixture of air and water by reducing the bulk density of water. The expansion of the rising air bubbles which causes the driving force for the system, buoyancy, to vary must be taken into consideration. The rising plume also entrains water from the depth until it reaches the surface.

The bubble diameters varied but most of the gas was in bubbles of 5 to 15 mm diameter.

Experiments with kerosene and oil individually were undertaken with two pipe diameters, 3 mm and 8 mm at five different flowrates, the average drop diameters being shown in Table 2.3. The drops are consistently in the 5 to 10 mm diameter range.

TABLE:2.3 AVERAGE DIAMETERS OF KEROSENE AND OIL DROPS FOR THE TWO PIPE DIAMETERS; WHEN INJECTED ALONE

	3 MM DIAMETER		8 MM DIAMETER	
	$m^3/s \times 10^6$	$m \times 10^3$	$m^3/s \times 10^6$	$m \times 10^6$
Kerosene	0.119	5.059	0.139	6.683
	0.229	5.227	0.257	6.718
	0.573	5.695	0.517	7.608
	0.912	4.997	0.848	8.081
	1.289	5.237	1.116	8.026
Oil	0.127	5.770	0.127	7.488
	0.257	6.038	0.271	7.423
	0.532	6.545	0.512	8.753
	0.863	6.628	0.851	9.037
	1.106	6.144	1.097	8.851

Experiments with oil or kerosene mixed with air were undertaken with the two pipe diameters at four flowrates. The volume ratio between the gas and liquid flowrates was approximately 100:1 but at one

gas flowrate ($12.0 \text{ cm}^3/\text{s}$), experiments were also carried out with a ratio of approximately 24:1.

The results, when using kerosene or oil and air, are shown in Table 2.4.

When oil and air were injected together, the oil was shattered into droplets within a short distance of the pipe exit, with an average diameter of approximately 1 mm which is similar to the results obtained by Topham (1975). The diameter of the oil drops was thus reduced by 5 to 10 when oil and air were injected together. The higher flow rate produced smaller droplet sizes, as did the larger pipe diameter for the same ratio (100:1) between the air and the oil flowrate. When the ratio decreased (24:1), the diameter of the oil droplets increased.

The experiments with kerosene gave the same results as for oil.

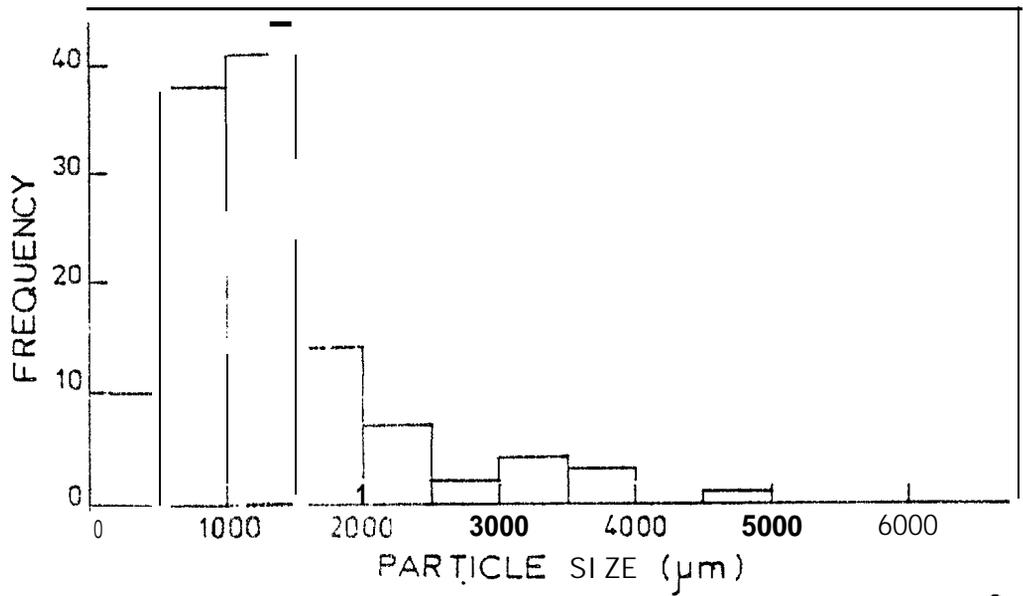
In the average diameters discussed above, the smallest particles (diameters less than $100 \mu\text{m}$) were not included. An attempt was made to estimate the distribution of smaller drops by observing the concentration changes on settling. It was apparent that a few percent of the volume of the oil is present as very small ($<100 \mu\text{m}$) drops.

The size distribution of the oil drops is very important for determining the rising time for the oil drops and of how far they will surface from the blowout. Graphs of the resulting droplet distributions are shown in Figures 2.2 to 2.4. Each sample consisted of a count of approximately 120 drops total. This sample size is rather small and the graphs should be regarded as indications of drop sizes rather than accurate determinations.

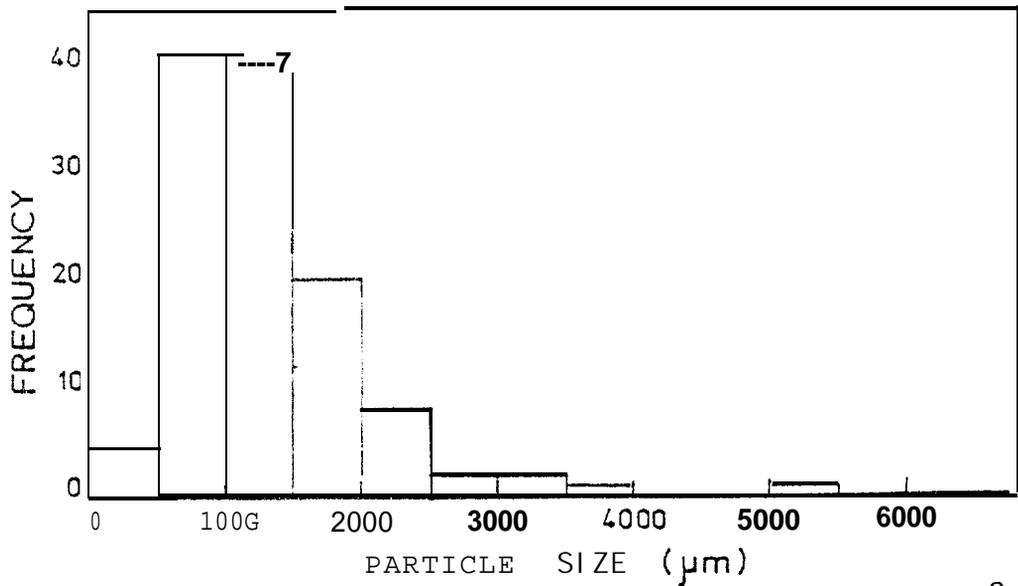
The histograms for different flowrates were similar. Topham (1975) found that there was a more marked difference between flowrates of $60 \text{ cm}^3/\text{s}$ and $450 \text{ cm}^3/\text{s}$. The reason for this is not known. In the histograms discussed here, the smallest particles (diameters less than

TABLE: 2.4 AVERAGE DIAMETER OF LIQUID DROPS FOR THE TWO PIPE DIAMETERS
WHEN KEROSENE OR OIL AND AIR WERE INJECTED TOGETHER

	$\frac{\text{GAS FLOW}}{\text{m}^3/\text{s} \times 10^6}$	$\frac{\text{LIQUID FLOW}}{\text{m}^3/\text{s} \times 10^6}$	<u>RATIO</u>	$\frac{\text{DIAMETER}}{\text{m} \times 10^3}$	$\frac{\text{GAS FLOW}}{\text{m}^3/\text{s} \times 10^6}$	$\frac{\text{LIQUID FLOW}}{\text{m}^3/\text{s} \times 10^6}$	<u>RATIO</u>	$\frac{\text{DIAMETER}}{\text{m} \times 10^3}$
	3 MM DIAMETER				8 MM DIAMETER			
Kerosene	12.0	0.530	23	1.089	12.0	0.495	24	1.129
	12.0	0.147	82	0.986	12.0	0.119	101	0.708
	50.0	0.517	97	0.860	50.0	0.495	101	0.762
	90.0	0.888	101	0.894	90.0	0.846	106	1.501
	120.0	1.086	110	0.761	120.0	1.069	112	1.043
oil	12.0	0.523	23	1.429	12.0	0.509	24	1.723
	12.0	0.127	94	1.200	12.0	0.122	98	1.294
	50.0	0.512	98	1.324	50.0	0.515	97	1.452
	90.0	0.879	102	1.339	90.0	0.871	103	1.254
	120.0	1.126	107	1.068	120.0	1.100	109	1.046



Air flowrate : $90 \text{ cm}^3/\text{s}$ Oil flowrate : $0,88 \text{ cm}^3/\text{s}$
Pipe diameter : 5 mm O.D.



Air flowrate : $90 \text{ cm}^3/\text{s}$ Oil flowrate : $0.87 \text{ cm}^3/\text{s}$
Pipe diameter : 10 mm O.D.

Figure 2.2 Size distribution of oil drops for different pipe diameters.

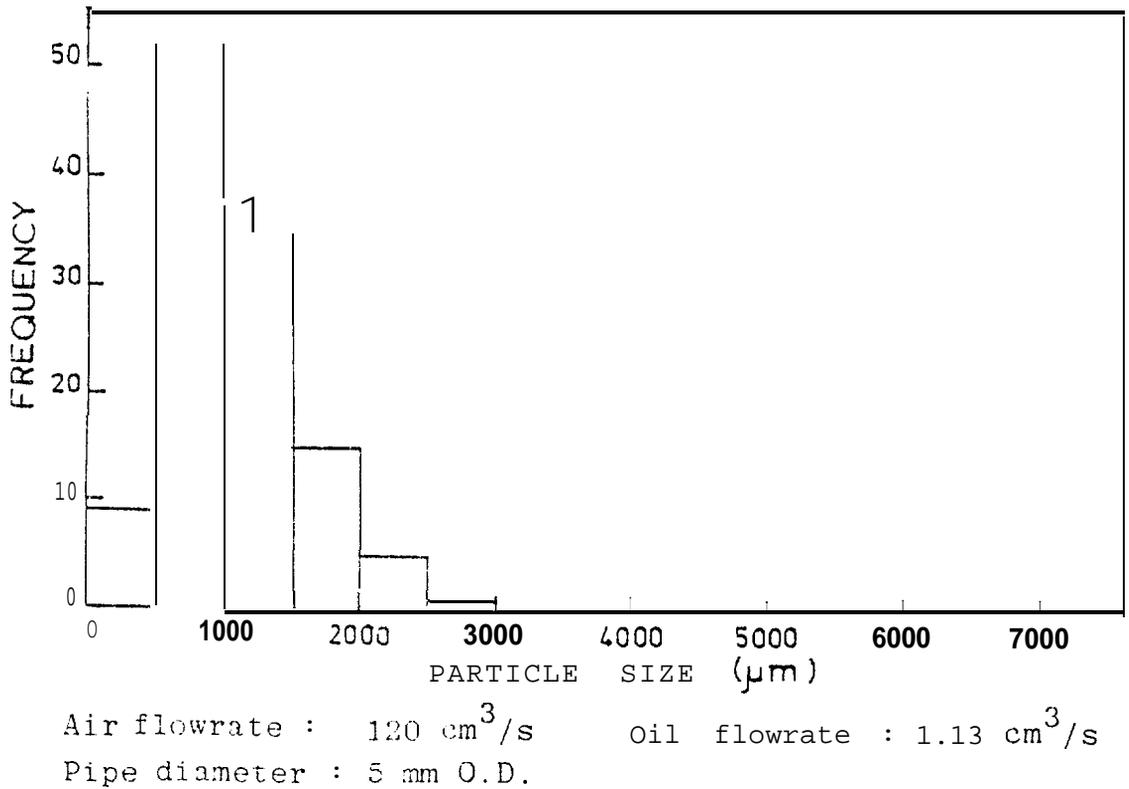
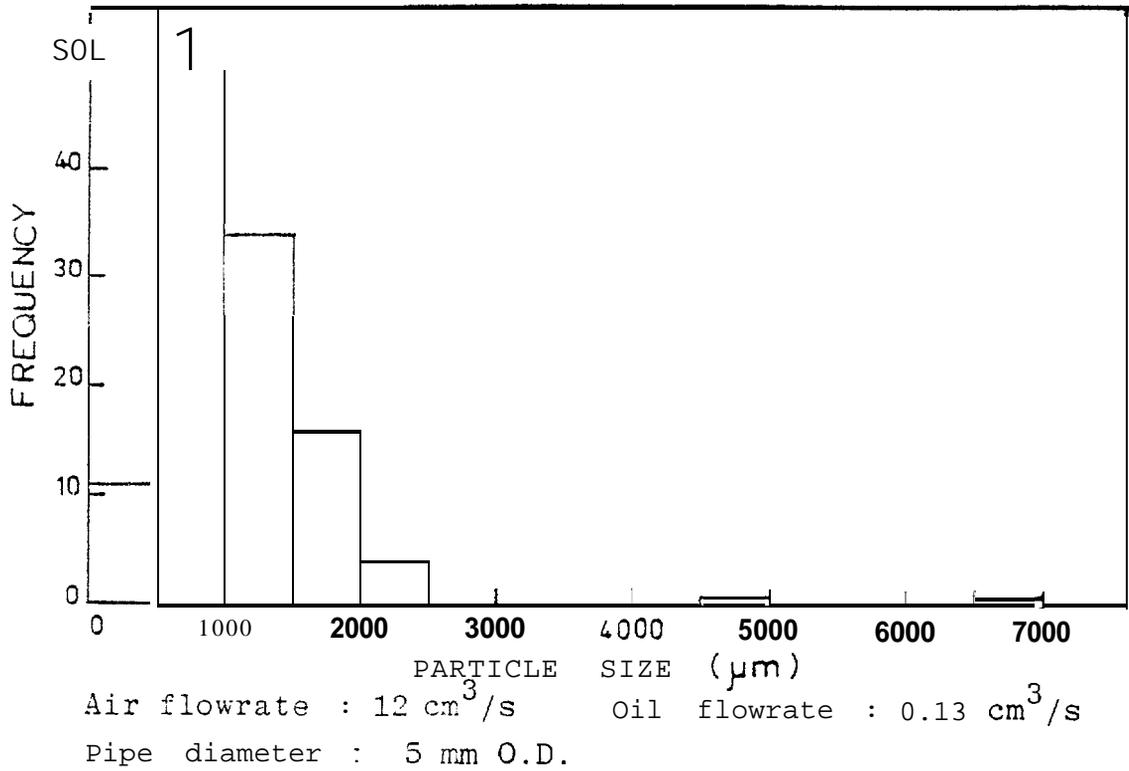


Figure 2.3 S . . . distribution of oil drops for different volumetric flowrates.

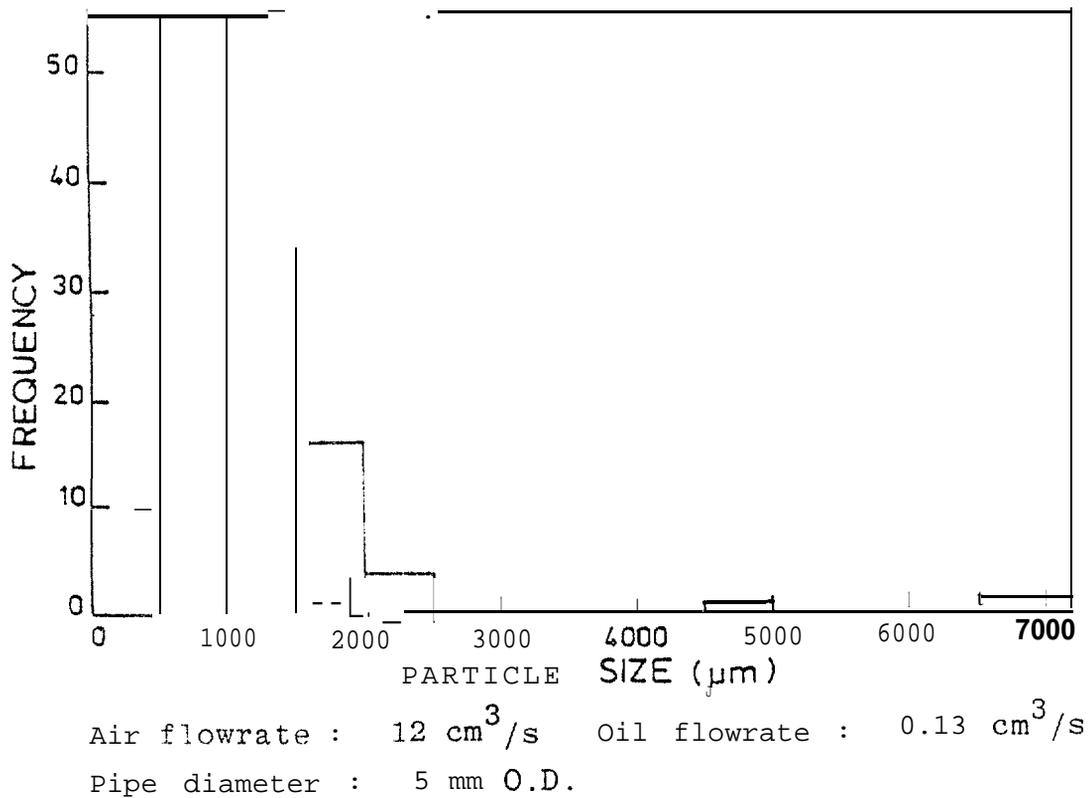
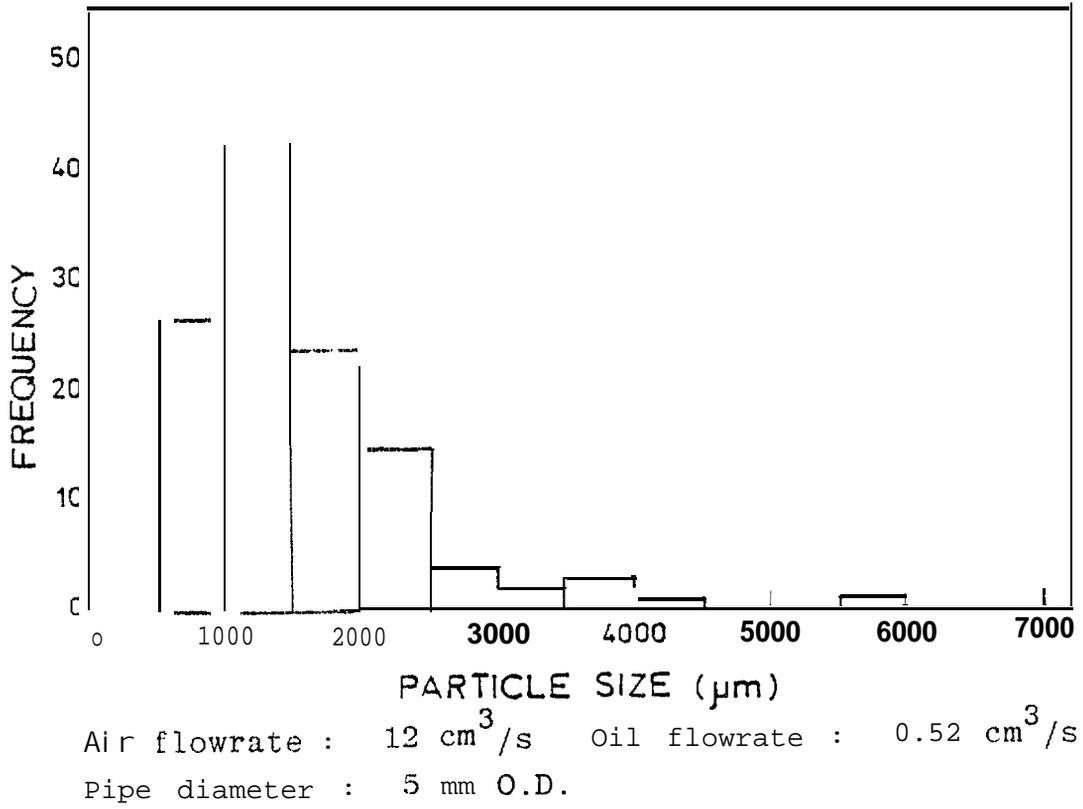


Figure 2.4 Size distribution of oil drops for different flowrate ratios air/oil.

100 μm) were not included.

A small portion, of the order of 3% of the oil injected, forms drops of less than 100 μm diameter and these could be mixed downwards at the outer edges of the plume and from there be carried away with small ocean currents.

Most of these small droplets were within the diameter range **10** μm to 50 μm and the distribution for the two diameters were similar.

A small part of the order of 0.2% of the oil injected dissolved in the water.

The configuration of the oil/gas mixture within the exit pipe was expected to be of some importance in influencing drop size. This flow regime is known to be a function of the superficial oil and gas velocities. The flow conditions used here resulted in different flow regimes for the two pipe diameters. In the 3 mm I.D. case, the flow was expected to be of the annular type and for the flow conditions corresponding to 8 mm I.D., the flow was expected to be of the slug flow pattern. As the use of different pipes results in different flow patterns, it may be necessary to adjust the flow rates to give the same superficial velocities and consequently the same flow pattern if accurate results are to be obtained. In practice, the flow obtained in the experiments was in the slug flow region for both diameters.

The experiments with dispersant were carried out with the smaller pipe (3 mm I.D.) at four different flowrates. The ratio between the gas and the liquid flowrates was approximately 100:1 and at one gas flowrate, 12.0 cm^3/s , experiments were also carried out with a ratio of approximately 25:1.

Both oil and kerosene were used and the dispersant was mixed with the liquid before it was injected. The volume ratio of oil to dispersant was 30:1.

The volume of the mixture was 430 cm³ when the mixture was used individually and 640 cm³ when the mixture and air was injected together.

It was very difficult to observe any particles by eye since the dispersant scattered the liquid drops to very small particles and it is believed that the oil droplets were in the diameter ranges less than 100 μm . After some time, the oil plume spread throughout the whole apparatus turning the water opaque and it was impossible to see any flow through the windows. This may indicate that for a real oil blowout, the oil would have been spread over a larger volume than when dispersant is absent.

When oil with dispersant and air were injected together, there were apparently more particles in the lower diameter ranges than when oil with dispersant was introduced alone since the oil settled more slowly.

It is apparent that when oil is injected into water at moderate velocities, the drop size is of the order of 5 mm and is controlled largely by surface tension considerations. When gas is injected simultaneously, the drop size falls to of the order of 1 mm probably because (i) the kinetic energy is higher thus the energy available for new surface formation is larger and (ii) the oil leaves the jet as small particles or slugs separated by gas bubbles. When dispersant is added thus reducing the oil-water interracial tension from approximately $24 \times 10^{-3} \text{N/m}$ (or 24 dyne/cm) by a factor of probably 50 to 500 the oil shatters into very small drops varying below 100 μm . It would be satisfying to propose a correlation between diameter and velocity, Reynolds No. and interracial tension but this is presently impossible since the latter are not known for the cases in which dispersant is present.

2.2 BIOS Oil Dispersant Discharge

2.2.1 Background

The general aim in these experiments was to simulate to the maximum extent conditions as would apply at the BIOS discharge. Further, it is desirable to ensure that the oil drop sizes produced are typical of those which occur following dispersion on a sea surface. These tasks are rendered difficult by a number of conflicting requirements and by lack of some basic information, thus the experiments done were necessarily designed within certain constraints and contain elements of compromise. It is useful to document the bases for defining the nature and conditions of the experiments.

(a) Coalescence at high concentrations

It is believed that high concentrations of dispersed oil particles may coalesce to form larger particles thus giving atypical results. A concentration of approximately 1000 ppm (which is equivalent to one 10 μm oil drop in every drop of water 100 μm in diameter) is regarded as the maximum tolerable which can be stored under mild turbulent conditions. Ideally, the concentrations should be lower since at a 1000 ppm concentration drops are separated by only nine drop diameters of water.

The approach adopted was to tolerate high concentrations only for a short period of time and under turbulent conditions then dilute rapidly to establish concentration of 10 to 30 ppm.

(b) Lack of Oceanic Particle Size Data

To our knowledge, there have been no studies of dispersed oil particle sizes following dispersion of oil at sea. This may be difficult since there is a considerable background of biotic and mineral matter, especially close to the surface.

It was thus necessary to simulate this process in the laboratory using a small scale dispersant effectiveness test system. Two such systems were available, the "Mackay-Nadeau-Steelman" apparatus using 6 litres of water (Mackay & Szeto 1981) and a hoop apparatus using 20 litres of water in which radially inward-moving waves are generated, this latter system having been used in aerial application trials.

(c) Volume Constraints on Oil, Water and Dispersant

The effectiveness systems use 6 and 20 litres of water. If a concentration of 10 ppm is sought, the oil volumes become 0.06 cm³ and 0.20 cm³ which at a thickness of 0.1 mm would cover areas of 6 and 20 cm². Administering 0.006 or 0.02 cm³ of dispersant accurately (to give a 1:10 dispersant to oil ratio) is clearly impractical. The only feasible approach is to premix the oil and dispersant then add this mixture to the water surface in the effectiveness systems. As is discussed later, the addition of 0.06 cm³ of oil to the Mackay-Nadeau-Steelman system proved to be difficult since this small volume could be swept to the side and smeared onto the vessel walls. After some experimentation, a volume of 1 cm³ was adopted which gives a concentration of 167 ppm which is recognized as being unsatisfactorily high but is unavoidable.

In the laboratory jet apparatus, the maximum volume of water which can be conveniently handled in a single test is approximately 200 litres (44 I gallons). It should be noted that this requires 6 kg of salt to achieve 30 parts per thousand. If the 10 ppm maximum concentration is used, the oil volume becomes 2 cm³ per test. It is impossible to discharge this small volume at a rate of 5 to 20 cm³/s as appears to be necessary if an excessive number of jets is to be avoided. For example, 15 m³ in 6 hours is 694 cm³/s. The minimum discharge time is 3 seconds thus the volume of oil discharged must be 15 to 60 cm³ which in 200 litres of water gives concentrations of 75 to 300 ppm which is in the same range as those obtained in the effectiveness apparatus. Again it is essential to premix the oil and dispersant.

It was thus concluded that the effectiveness systems should be operated by dropping of the order of 1 cm³ of premixed oil and dispersant onto the turbulent water surface. In the jet system, a volume of 15 to 60 cm³ of oil should be discharged in 3 seconds into 200 litres of water. In both cases, concentrations within a factor of two of 150 ppm should be achieved.

(d) Temperature

The ideal test temperature is approximately 0°C but this is not practical in the laboratory especially for the large scale system for which no cooling system exists. It is believed that a ~~tempera-~~
~~ture~~ below 3°C would be satisfactory.

(e) Coulter Counting

For highly accurate counting, it is necessary to filter the water to remove particles of dust and microorganisms. This is impractical for large volumes of water thus a "background subtraction" method must be used, with some attendant loss in accuracy. Considerable sample dilution was necessary to avoid coincident counting.

As a result of these considerations, a jet system was designed and built and complementary effectiveness tests were done in the Mackay-Nadeau-Steelman and hoop systems.

2.2.2 Experiments

Jet System

The apparatus consisted of the aluminum tank containing two plexiglass windows described in Section 2.1. A second all glass tank was also used. Oil was injected through a bulkhead fitting at the base. Provision was made to permit water recirculation from top to bottom to facilitate mixing. The volume of water used was 150 L of 30 parts per thousand salinity. The temperature was reduced to 1 to 3°C by adding ice and mixing. Temperature rise was reduced by insulating the outer surface with polystyrene slabs. Sampling was from the bottom, middle or top using taps or syphons.

The first oil discharge system was a 50 mL plastic syringe which was driven by an air cylinder activated by compressed air, the flow and pressure of the air being controlled by valves. A quick-opening valve was used to start and stop the air flow. The duration of the discharge was timed manually with a stop watch.

The jets used were glass tubing of internal diameter 3 mm and 5 mm. Samples were taken after discharge and 1 hour later.

Mackay Nadeau Steelman (MNS) Effectiveness Apparatus

This apparatus has been described by Mackay and Szeto (1980) and consists of a 30 cm diameter glass vessel containing 6 L of water which is swirled with a tangential air flow of variable velocity, thus giving a variable turbulence level. It is believed that this system simulates to some extent natural turbulence at the ocean surface.

The system is normally operated by dropping dispersant onto 10 mL of oil held in a containment ring. In the present work the ring was removed and 1.0 mL of premixed oil and dispersant was added to the water surface. Samples were taken after 10 minutes turbulence and 1 hour later after settling.

Hoop Apparatus

This apparatus has been described by Mackay and Hossain (1980). It consists of a plastic vessel 40 cm in diameter containing 20 L of water which is agitated by a hoop vertically oscillating at 360 strokes per minute creating waves which move radially inwards thus tending to collect the oil at the centre. A volume of premixed oil and dispersant was added to the surface and samples taken after 10 minutes agitation and 1 hour later after settling.

Oil-Water Discharge

In these tests, premixed oil and dispersant (volume ratio 10:1) was pumped at 500 to 900 cm³/min along $\frac{1}{4}$ inch pipe into a tee junction along with a flow of water of 3000 cm³/min and the mixture passed through 2 m of $\frac{1}{4}$ inch pipe before discharging into 204 L of salt water in a glass tank 100 cm high by 47.5 cm square. The plume was photographed and sampled for particle size measurement.

Particle Size Measurement

The oil particle sizes were measured with a Coulter Counter Model TA II which had variable orifices of 100, 200 and 400 μm and gave particle sizes by number and volume distribution. The samples were diluted in an electrolyte solution (300 mL) which was passed through the counter over a period of several minutes. The counting rate was kept low enough to avoid coincident counting errors. All samples had a background which was partly electronic and partly real in nature. To subtract this background identical volume samples were run in sequence with and without oil sample addition, the particle numbers subtracted, then each number was multiplied by the cube of the mean particle diameter for each channel thus giving the volume distribution. These were totalled and normalized to 100% to yield volume distributions. The results were expressed graphically or as the volume median diameter i.e. the diameter above and below which half the volume of particles was distributed. The number median diameter was of

course lower and is regarded as a less useful figure. The upper and lower quartile diameters were also estimated.

Materials

The oil used was "aged Lago Medio" crude oil obtained from EPS Halifax, as used in the BIOS experiment.

The dispersant used was Corexit 9527 supplied by Imperial Oil Ltd. Sarnia.

Salt water was made by dissolving commercial salt in Toronto tap water at a concentration of 30 g/L.

2.2.3 Oil-Dispersant Discharge Results

General

When dispersant was mixed with the oil, it became impossible to use visual or photographic methods to estimate particle size. A cloud of coffee-coloured oil-water mixture rose and expanded to fill the entire system. In some tests, air was injected as well and similar results were obtained. Only with the use of a Coulter Counter was any reasonable data obtained.

When recording these data, the most useful format is to give the median and the lower and upper quartile diameters on an oil volume basis. Thus 7/10/18 μm is a statement that 25% of the oil is less than 7 μm , 25% is between 7 and 10 μm , 25% is between 10 and 18 μm and 25% is above 18 μm .

The Coulter Counter results are distorted by two effects. First the orifice size controls the particle size "window" which is observed. Obviously no particles larger than the orifice are observed and particles less than 1 to 3% of the orifice are not detected. A 100 μm orifice was used in most of this work thus a large population of sub μm drops would not be detected nor would a few large drops. Ideally, the sample should be analysed by several orifices but this was beyond the scope of the present project. The results should thus be taken as semi-quantitative and not as precise determinations.

MNS and Hoop Effectiveness Apparatus

The results shown in Table 2.5 indicate that the MNS apparatus gives smaller particle sizes than the Hoop apparatus but the effect is not large. Most oil in both cases is in the 4 to 18 μm range. These particles rise with a velocity such that the rise 20 cm takes 38 to 2 hours thus they are essentially permanently dispersed. A few quite large and visible drops also form of diameter approximately 200 to 500 μm but

TABLE 2.5 RESULTS OF PARTICLE SIZE DISTRIBUTION MEASUREMENTS IN TEST SYSTEMS EXPRESSED AS LOWER QUANTILE, MEDIAN AND UPPER QUANTILE DIAMETERS IN μm

MNS Apparatus (2.5 cm H₂O pressure drop)

t = 0 4/9/11 (i.e. after 10 minutes mixing)

t = 10 min 4/6/10

t = 60 min 4/6/10

Hoop Apparatus

t = 0 7/10/18 (i.e. after 30 min mixing)

t = 60 4/8/12

t = 120 4/8/10

Jet Apparatus

Jet Diameter mm	Flow cm ³ /s		
	10	20	30
2	Re = 60 t = 0 3/4/10 t = 60 3/4/18		
3	Re = 40 t = 0 3/5/12 t = 60 3/4/10	Re = 80 t = 0 3/5/12 t = 60 3/5/10	Re = 120 t = 0 4/7/8 t = 60 3/7/8
4	Re = 30 t = 0 9/16/20 t = 60 5/10/16		

they rise rapidly to the surface in a minute or two.

Jet Apparatus (Oil-Dispersant)

Five experiments were undertaken as illustrated in Table 2.5 to investigate the effects of pipe diameter and velocity. The Reynolds Numbers are given and seem to correlate with the particle size, high Reynolds Number tending to give smaller particles. The particle sizes span the range covered by the effectiveness tests thus it appears that similar distributions are obtained in both systems.

Jet Apparatus (Oil-Dispersant-Water)

Similar results were obtained in the two tests which took place with water to oil ratios of 3:1 and 6:1 and total flows of 65 and 58 cm³/s. The discharge Reynolds Numbers were of the order of 5000 which is much higher than the tests with oil alone. The reasons are the higher velocities and the lower viscosity. The drops are formed however in the pipe at the tee not at the orifice thus the distribution of particle sizes is presumably a function of this mixing process.

The particle size distribution was difficult to estimate but was quantitatively similar to the jet system being estimated to be (2 to 5)/(10 to 15)/(15 to 20). There appeared to be some larger particles present which may have been formed early or late in the pumping when mixing was incomplete.

In the BIOS discharge, the drop size distribution was established similarly in the pipe at comparable Reynolds Numbers thus it was expected that particle sizes in the range of 5 to 20 μm would occur. It is noteworthy that the BIOS pipe is much longer thus some additional large drop breakup may occur.

2.3 Field Particle Size Measurement

2.3.1 Background

It is useful to have a method of estimating the oil particle size distribution during the BIOS oil-dispersant spill. Such an estimate is of potential value in assisting interpretation of the oil plume behavior. The possibility of installing a Coulter Counter at the site was considered but was rejected for reasons of cost, uncertain reliability after transportation and the complication of counting natural particulate matter in the water column. Two surrogate measurements were investigated, photographic recording and a settling test.

The principle of the photographic test was that a small volume of water containing the dispersed oil was spread on a sheet of unexposed film with the assistance of a wetting agent. The film was then exposed to an electronic photographic flash at a convenient distance of approximately 1 m and developed. The oil particles appeared as white spots on the negative and could be counted and, it was hoped, the size of the particles determined. The system worked satisfactorily for larger oil particles, i.e. greater than 50 μm but became less satisfactory for small particles because of a combination of problems associated with scattering of light around the particle and grain size of the film. Unfortunately, the particles of interest which are in the 1 to 10 μm range could not be detected reliably. It is noteworthy that since the wavelength of light is only slightly less than 1 μm this provides an ultimate limit to optical methods.

A settling system was then devised and tested. A glass tube 20 cm long by 1.0 cm internal diameter was filled with the dispersion and both ends sealed with stoppers. The tube was mounted vertically and allowed to settle. Photographs were taken periodically using a Polaroid camera at a distance sufficient to fill the entire frame. A paper background of black horizontal lines was placed behind the tubes.

As the dispersion settled, the lines became visible in sequence until ultimately the tube became almost clear with only a slight haze. The "settling time" is controlled by the oil particle size as determined by the Stokes' Law velocity.

The concentration of oil in the water was approximately 10% by volume but diluted samples gave better resolution. The oil to water volume ratio could be readily determined after settling was complete.

The recommended procedure is thus to take a sample of the oil-dispersant-water mixture of 100 mL. One tube is filled with this mixture. A second tube which has been prefilled to half volume (i.e. to 10 cm) with the same water is then filled. A third tube prefilled to 15 cm is treated similarly. This gives a fourfold dilution. A duplicate set can also be filled. The tubes are then sealed, inverted a few times to mix the contents then stood vertically in front of the background. Polaroid photos are taken at regular time intervals, say at 0, 2, 4, 8, 16, 32, 64, 128, 256, 512 and 1026 minutes.

From these photos, an approximate particle size analysis can be done using Stokes' Law

$$U = gD^2(\rho_w - \rho_o)/18\mu$$

$$g = 9.81 \text{ m}^2/\text{s}$$

D = particle diameter (m)

$$\rho_w \cong 1017 \text{ kg/m}^3$$

$$\rho_o \cong 850 \text{ kg/m}^3$$

$$\mu \cong 1 \text{ CP or } 10^{-3} \text{ Pas}$$

thus

$$u = \frac{9.81 (1017 - 850)}{18 \times 10^{-3}} D^2 = 9.1 \times 10^6 D^2 \text{ m/s}$$

The time to travel 20 cm is thus 0.2/U seconds. A table of velocities and times can thus be assembled and used to interpret the results as tabulated below.

Oil Particle Diameter D			Rising Velocity U		Time to travel 20 cm		
m	mm	μm	m/s		s	m in	hours
10⁻⁶	10⁻³	1	9.1X10 ⁻⁸	0.33mm/h		37000	610
3X10 ⁻⁶	3X10⁻³	3	8.2x10 ⁻⁷	3.0mm/h		4070	68
10 ⁻⁵	10⁻²	10	9.1X10 ⁻⁶	3.3cm/h	22000	366	6.1
3X10 ⁻⁵	3X10⁻²	30	8.2x10 ⁻⁵	30cm/h	2441	40.7	0.67
10 ⁻⁴	10⁻¹	100	.00091	330cm/h	219	3.7	
3X10 ⁻⁴	3x10⁻¹	300	.0082	30 m/h	24.4	0.41	
10 ⁻³	1	1000	.091	330 m/h	2.2		

This shows that within 4 minutes, all particles greater than 100 μm will have settled. Within 40 minutes, particles greater than 30 μm will have settled. After 6 hours, particles greater than 10 μm will settle. The growth in length of the oil layer at the surface can be used as an indication of the distribution of particle sizes. For a 10% by volume oil sample, this layer should become 2 cm long but normally the layer contains trapped water and the interface may be indistinct.

The photographic record provides a characterisation of the particle size distribution which can be reproduced in the laboratory, the same sample being subjected to Coulter Counting to obtain a breakdown of particle size. Some difficulty may arise from coalescence, especially for the more concentrated samples, thus the Stokes' Law analysis may not apply. Further, the settling velocity of the particles is influenced by the settling of other particles in the water column, and the bulk water density is in some doubt. The Stokes' Law calculations must thus be taken as indicative of the particle size and not as an accurate determination.

2.3.2 BIOS Discharge Results

The discharge took place on 27 August 1981 over a period of 6 hours 25 minutes. The oil-dispersant flow average 41 L/rein and the water flow 200 L/rein giving a ratio of 4:9. Samples were taken of the mixture initially but at a time when there was a flow rate reduction, then after 3 and 6 hours. Since these latter two samples were taken from a "dead end", it is possible that they represent oil which had resided for some time in the pipe and had coalesced.

Samples were placed in the tube rack and photographed periodically for 70 hours. From the photographs, the "settling time" in the water was observed and compared with similar data obtained in the laboratory. The "half times" for settling was estimated to be 10±3 hours for the initial set of three replicate tubes, 1, 3 and 5 hours for the 3 hour samples and 2, 2 and 1 hour for the final set. Accordingly, the oil particle sizes are believed to be as follows.

Initial set	10 μm \pm 5 μm
3 hour set	10 to 30 μm
6 hour set	20 to 30 μm

It is believed that no more than 5% of the oil was less than 3 μm since settling was essentially complete by 70 hours. The initial set results are regarded as most reliable. A 10 μm oil drop will rise at a rate of approximately 3.3 cm/hour or less than 1 m per day thus during the time of the experiment, vertical buoyant motion is almost completely insignificant compared to horizontal drift. Further, any movement of oil to the bottom or surface will be controlled by eddy diffusion rather than buoyancy.

It is possible that the plume as a whole may be slightly buoyant as a result of thermal effects and the presence of oil but the magnitude is likely to be quite small especially as the bulk of the plume will consist of entrained "local" water which will be drawn into the jet.

It **is** thus concluded that the overall performance of the system was as expected and a non-buoyant plume of oil particles was generated, most of which were in the 5 to 15 μm range.

3.0 CONCLUSIONS

When oil alone is discharged through an orifice of diameter 5 to 10 mm at flowrates of 0.1 to 1.2 cm³/s, the drop diameters formed are typically 5 to 10 mm.

When gas is discharged with the oil under these conditions at a volumetric flowrate some 20 to 100 times that of the oil, the oil drop diameter becomes smaller ranging from 1.0 to 1.8 mm.

In both cases, but especially when gas is present, a population of very small i.e. less than 0.1 mm drops is also formed but they are responsible for only a small fraction, possibly 3% of the oil volume.

Higher flowrates result in smaller drops being formed, probably as a result of the greater energy availability.

When oil-dispersant mixtures (volume ratio 20:1) are discharged, drops of the order of 5 to 20 μm are formed. This provided a convenient method of preparing oil-in-water emulsions. Higher Reynold's Numbers result in smaller particle sizes.

When water is discharged simultaneously with the oil dispersant mixture, similar size distributions result, although the distribution is probably established in the mixing section of the pipe. A system of this type was used to provide design data for the BIOS experiment.

A method of estimating oil droplet size in the field has been devised based on observation of settling times in tubes. When applied to the BIOS test conditions, it was concluded that the oil particle size generated was 10 μm ± 5 μm. Such particles have negligible buoyant velocity under the test conditions.

It is believed that this method of preparing emulsions may find application in toxicological studies of dispersed oil and that the principle of injecting dispersant into oil which is being released under environmental blowout or vessel leakage conditions may be desirable under certain circumstances.

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