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AN EXPLORATORY STUDY OF THE BUOYANCY BEHAVIOR OF WEATHERED OILS IN WATER

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ABSTRACT

An exploratory experimental study is described in which the behaviour of crude oil and fuel oil droplets was observed in a water column containing a known density gradient. Of particular interest is the buoyant behaviour of the oil because that behaviour influences the time period during which the oil may be submerged, and thus subject to dissolution, diffusion and advective processes in the water column. A system was developed in which a stratified water column was created in a glass-walled tank with a facility to measure density as a function of height using the "Westphal Balance" principle. Several oils were tested: fresh, weathered (evaporated) and emulsified (to form water in oil emulsions) and their behaviour observed, recorded and interpreted. A complementary theoretical treatment is presented.

It is concluded that a substantial quantity of oil can be submerged in the water column under steady state conditions. The extent of submergence is increased by

(i) a high oil density occurring naturally or induced by weathering.

(ii) the presence of significant surface turbulence to disperse the oil slick at an appreciable rate and induce water column mixing.

(iii) the formation of small oil drops.

(iv) the formation of emulsions of water in oil, especially those formed from high salinity water.

A complementary exploratory study showed that large oil masses which are slightly less dense than water may be essentially submerged, but remain close to the surface by virtue of their exposure to wind-induced water surface currents. These oil masses may be invisible to the eye or to remote sensing systems because they are continually awash with water.

There is also a possibility of density increase by association of the oil with mineral and organic matter in the water column.

It is suggested that as part of any environmental impact assessment process, an oil which may be produced in, or transported through, an environmentally sensitive region be subjected to an experimental protocol for determining its sinking potential. Such a protocol is suggested.

RÉSUMÉ

Description d'une étude expérimentale sur le comportement de gouttelettes de pétrole brut et de mazout observés dans une colonne d'eau contenant un gradient connu de densité. La flottabililité du pétrole est particulièrement intéressante parce qu'elle influence la période pendant laquelle le pétrole peut être submergé et se prêter ainsi à la dissolution, la diffusion et aux processus d'advection dans la colonne d'eau. Dans le cadre d'un système mis au point, une colonne d'eau stratifiée a été créée dans un réservoir à paroi de verre muni d'un instrument pour mesurer la densité en fonction de la hauteur, à l'aide du principe de la "balance Westphal". Plusieurs types de pétrole ont été testés : frais, altéré (évaporé) et émulsifié (pour former de l'eau dans des émulsions de pétrole) et leur comportement a été observé, relevé et interprété. Un traitement théorique supplémentaire est présenté.

Il a été conclu qu'une quantité considérable de pétrole peut être submergée dans la colonne d'eau dans des conditions de régime permanent. L'étendue de la submergence est augmentée par

(i) une forte densité de pétrole se produisant naturellement ou provoquée par l'exposition à l'air.

(ii) la présence d'une turbulence de surface importante qui disperse la nappe de pétrole à une vitesse

appréciable et provoque le mélange dans la colonne d'eau.

(iii) la formation de petites gouttes de pétrole.

(iv) la formation d'émulsions d'eau dans le pétrole, surtout celles qui sont formées par de l'eau à forte salinité.

Une étude exploratoire supplémentaire a montré que de grosses masses de pétrole qui sont légèrement moins denses que l'eau peuvent être entièrement submergées, mais demeurent proches de la surface en raison de leur exposition aux courants de surface provoqués par le vent. Ces masses de pétrole peuvent ne pas être décelées par l'oeil ou par les systèmes de télédétection parce qu'elles sont constamment à fleur d'eau.

Il est également possible que la densité augmente à cause de l'association du pétrole avec des matières minérales et organiques dans la colonne d'eau.

Il est suggéré que, dans le cadre de tout procédé d'évaluation des incidences environnementales, un pétrole qui peut être produit ou transporté dans une région sensible du point de vue environnemental soit soumis à un protocole expérimental visant à déterminer son potentiel de submersion. Un tel protocole est suggéré.

CONTENTS

1. INTRODUCTION.

1.1 Background.

There is an obvious incentive to develop the capability of predicting quantitatively the behaviour of crude oil and petroleum product spills on water. Such a capability is an essential component of environmental impact statements, of countermeasures plans, and of assessments of physical, biological and ecological impacts. It is also of considerable scientific interest. One aspect of oil spill behaviour which has been treated in only a cursory manner is oil sinking, or in general the formation of oil drops which are negatively buoyant, neutrally buoyant or near-neutrally buoyant. This process is important because if a substantial fraction of an oil slick is sunk, even temporarily, it removes the oil from sight and from access to surface containment, recovery or chemical dispersion. Further, sunken oil is likely to have a more significant effect on biota in the water column and possibly in the benthic zone. Clearly, if an oil has a tendency to sink, that tendency should be quantified, or at least elucidated.

Sinking is possible when one or more factors combine to create a downward velocity. This velocity may be the result of the oil having a density greater than that of water. It may also be the result of downward water currents generated randomly or by more defined circulations. The oil density may be increased by evaporative loss of less dense volatile material or by association of the oil with mineral or organic matter.

1.2 Literature Review.

Although it seems intuitively unlikely that oil will sink, there are several reports of submerged oil, especially following the Kurdistan incident in 1979 off Cape Breton Island. Vandermuelen (1980) edited a compilation of review papers on the incident among which are several references to "disappeared" or submerged oil.

While the spill occurred in mid March, the oil apparently disappeared from view until mid April. However, this could be largely attributed to ice floe interaction.

Tribs, Vandermeulen and Lawrence noted in their paper (Kurdistan Spill Movements) that there were reports of submerged oil in the Banquereau Bank area but they failed to elaborate on this due to a lack of knowledge of the oil submergence phenomenon. Also, Fingas, O'Neil, Thomson and Neville (Preliminary Results of Remote Sensing Overflights During The Kurdistan Operation) reported aerial sightings of "what appeared to be submerged pans of oil floating just below the sea surface". Its black colour indicated that it was probably not emulsified. There was also a report of the CCGS Daring motoring through and turning up submerged oil. This paper also noted that there was controversy during the spill as to whether the spill was submerging and resurfacing. Reimer (The Visual Identification of Bunker-C Oil in Dynamic Pack Ice) noted oil "pancakes" of about 30 cm diameter floating partially submerged in brash ice and suggested that they were in the process of being incorporated into the ice. Levy (Petroleum Residue Concentrations in Scotian Shelf Waters Following the Kurdistan Spill: Preliminary Results) noted the initial disappearance of the oil (i.e no aerial verification or shore evidence for several weeks) and acknowledged the possibility of dispersion of oil, as droplets or as solution, in the water column from wave action. He also noted that both oil forms were observed in the 1970 ARROW spill. Actual samples of sand-in-oil mixtures were collected, and oil concentrations in the water column of up to 1.45 micrograms per litre at 100 m depth were measured.

Reinson, Frobel, Taylor and Asprey (Observations on the Occurrence of `Bunker-C' Oil in the Cape Breton Shoreline, May 1979) observed oil sediments with sufficient sand content to lose their positive buoyancy and "act as sedimentary clasts". These were active in the swash zone of the waves and thus susceptible to retreat to the ocean.

There is thus a significant amount of circumstantial evidence of submerged oil, but little "hard" data.

A second report by Reimer (1981) on the same incident acknowledges the reports of subsurface oil and notes the interaction between oil and seaweed and other debris. This report's primary value (with respect to submerged oil) lies in its presentation of oceanographic and meteorological data over the duration of the spill. Assuming that some oil did submerge the report provides a complete set of data concerning ocean and air temperature as well as wave height over which oil may sink. In the area studied, between June and October of 1979, the ocean surface temperature varied from 7.5 deg.C in June to 13 deg.C in August returning to about 9 deg.C by October (with a standard deviation of about one degree). Over the same period the wave height varied between 0.39 m and 0.66 m with a standard deviation of about 0.1 m. Air temperature at the ocean surface varied from 4 deg.C in May to 16 deg.C in August and to 6 deg.C in October.

Thus, assuming that oil did submerge following the Kurdistan spill one can establish a framework of conditions within which submersion occurred. This paper also suggested that seaweed (kelp) and other debris were possible causes of oil submergence.

In a review of the sinking issue, Juszko et. al. (1983) showed that a case can be made for sinking oil by identifying the following occurrences:

1) 1966 ANNE MILDRED BROVIG - 125,000 bbl Iranian crude oil disappeared into the North Sea

2) 1971 SAN FRANCISCO HARBOUR - tanker collision caused incorporation of bunker C fuel oil into the near-bottom waters

3) 1978 AMOCO CADIZ - emulsified oil throughout the water column

4) 1980 HASTEB WELL BLOWOUT - off Saudi Arabia layers of oil were suspended several metres below the surface

It is recognized that while the specific gravity (SG) of oil is usually between 0.8 and 0.9,this may be increased by evaporation or dissolution of its light components, emulsion, absorption into particulates or bacterial growth. There is an example of Iranian and Kuwaitian crude having their SG increased from 0.869 to about 1.025 by weathering.

Surface density of the water (horizontal and vertical profiles) may be altered by temperature and salinity variations (typically at the surface by 0.5%). Salinity changes are caused by ice melts and river run-offs near the shore. Sharp pycnoclines (density gradients in shallow (less than 20 m) water, seasonal pycnoclines in 20 to 75 m water and deep permanent pycnoclines (between upper mixed and lower stable layers) all exist as a result of solar warming and lack of mixing. Thus, any mixing of the water column will alter the pycnoclines and the vertical density gradient. In areas containing banks, ridges, shallows and estuaries (common places for tanker spills) vertical fronts occur between mixed and non-mixed areas. This is important since a spill would behave differently on either side of the front. Such fronts are known to occur at regions of ice melt, shelves, and mouths of rivers.

By investigation of the various coastal areas of Canada the paper concludes that in general, the open ocean has a SG of approximately 1.027 except where input by fresh water may lower surface SG to as low as 1.005. This fresh water may be supplied by ice-melt at northern latitudes and river runoff at more southerly latitudes. However, this applies to only a small portion of the total ocean area and the major cause of density variation is temperature. Hence, where pycnoclines do exist, oil, depending upon its density, may be trapped between density layers and its subsurface movement will be dictated by water body movement and not by surface or wind factors.

There are two areas in which there is a notable lack of literature data. First, if an oil drop or pancake has a vertical dimension of one or more centimetres and lies partly submerged on a wind driven ocean surface it will span the vertical water velocity profile caused by the wind. It will thus be subject to a high velocity at the surface and a low velocity beneath and it seems likely that in this situation it may tend to submerge and allow water to wash over its surface. Its equilibrium location may be lower than that dictated by gravity. No data on this effect could be found.

Second, there is a lack of data concerning the density increase of crude oils and fuel oils when weathered. This is, in part, due to lack of a protocol or test procedure by which the density increase of an oil can be estimated. This issue is treated later in this report.

Although not considered here the issue of oil association with mineral or diatomaceous matter is clearly important. Recently Wong et. al. (1984) have shown that 2 days after a spill, following nutrient addition there was a high growth rate of diatoms and association between diatoms and oil drops with subsequent sinking. The diatoms were about 10 um in dimater and induced sinking in oil drops of comparable and smaller diameter. Approximately 21% of the oil spilled was estimated to have sedimented.

1.3 Theory.

Oil sinking is usually expressed in terms of Stokes' Law, a version of which can be stated as

$$Z = D^2 (Ro - Rw) g/18u + V = U + V$$

where

Z is the downward velocity (m/s)

D is the drop diameter (m)

Ro is the oil density (kg/m3)

Rw is the water density (kg/m3)

g is gravity (9.81 m/s2)

u is water viscosity (Pa.s)

U is the Stokes' Law velocity (m/s)

V is a water current velocity, vertically downwards (m/s)

The critical quantity is clearly the density difference term. This is usually negative and causes the oil drop to rise. Most crude oils have densities of 750 to 900 kg/m3 compared to the fresh water density of 1000 kg/m3 and saline water density of 1024 kg/m3. Some residual oils may have densities of approximately 1000 kg/m3, but three processes can enhance the oil density.

- The oil may weather (evaporate) thus causing the loss of the less dense components and an increase in the density of the residue.
- The oil may emulsify, i.e. form water-in-oil emulsions or "mousse" thus increasing the density of the combined two phase system.
- The oil may become associated with dense matter in the water column such as sediment, skeletal or diatomaceous material

resulting in a higher density.

In this study we consider the magnitude of the first two effects.

The water density may also fall due to temperature increase or a salinity decrease. A density gradient may exist in the surface waters arising from fresh water inflow from rivers, rainfall (which is not expected to be significant), and from melting ice. A temperature gradient may also enhance the salinity gradient.

A problem with Stokes' Law is that it is applicable only at low velocities, or more specifically at Reynolds Numbers less than about 2. The Reynolds No., Re, is (RwUD/u). It can be shown that Stokes' Law corresponds to the definition of a drag coefficient of 24/Re. At higher Reynolds Numbers flow becomes turbulent and the rising velocity is reduced, corresponding to the drag coefficient levelling out at a value of approximately 0.4 to 0.5. Significant deviations from Stokes' Law are expected for oil drops of diameter exceeding 0.2 mm after which the rising velocity is about 0.5 cm/s.

A convenient method of expressing a "corrected" Stokes' Law velocity in the turbulent regime is to define a correction factor C as the ratio of the actual to the Stokes' Law velocity. Plots of C versus Re have been prepared (e.g. Perry (1950) p1020). A simple curve fitting procedure gives the expression.

$$C = 1/(1 + (Re/35)^{0.5})$$

This is correct within 10% for Re as high as 1000.

For example, for a 1 mm oil drop of density difference from water of 250 kg/m3, in water of viscosity 0.001 Pa.s and density 1000 kg/m3. The indicated Stokes' Law velocity is 0.14 m/s and Re is 140. The correction factor C is thus 0.33 and the true velocity is 0.046 m/s. For a 1 cm oil drop the Stokes' Law velocity is 14 m/s, Re is 140000, the correction factor C is 0.015 and the true velocity is 0.21 m/s. We use this "Corrected Stokes' Law" equation in subsequent calculations i.e.

$$Us = D^{2}(Ro - Rw)g/18u$$

$$C = 1/(1 + (RwUsD/35u)^{0.5})$$

$$\text{and } U = CUs$$

Water current velocities may be the result of random eddies, of more defined circulations of the Langmuir type, or they may be attributable to breaking waves. Leibovich (1975) has discussed oil droplet dispersion in surface waters and has suggested that the eddy diffusivity may be estimated as

$$K = 0.00043W^{2} \text{ m2/s}$$

where W is the wind speed (m/s). This gives rise to the following diffusivities and velocities over a depth of 1 m (regarding diffusivity as the product of mean velocity and distance over which the velocity applies).

Wind Speed (W)		Diffusivity (K)	Velocity over 1m (V)	
m/s	km/h	m2/s	m/s	cm/s
1	3.6	0.00043	0.00043	0.043
2	7.2	0.0017	0.0017	0.17
3	11	0.0039	0.0039	0.39
5	18	0.011	0.011	1.1
10	36	0.043	0.043	4.3
20	72	0.17	0.17	17

Since breaking wave velocities are likely to be of the order of tens of cm/s they will cause appreciable migration downward.

It is interesting to compare these values with corrected Stokes' Law velocities. Assuming that the water and oil densities are 1024 and 824 kg/m3 (i.e. the density difference is 200 kg/m3) and that the water viscosity is 0.001 Pa.s, substitution in the corrected Stokes' Law gives the data in the following table from which the equivalent wind speed W can be deduced at which diffusive and rising velocities are approximately equal (i.e. U equals V).

Drop m	Diameter mm	Velocity U m/s	Velocity U cm/s	W m/s
1E-06	0.001	1.09E-07	1.09E-05	.016
3E-06	0.003	9.81E-07	9.81E-05	.048
1E-05	0.01	1.09E-05	1.09E-03	0.16
3E-05	0.03	9.72E-05	9.72E-03	0.48
1E-04	0.1	1.03E-03	1.03E-01	1.6
3E-04	0.3	7.60E-03	7.60E-01	4.2
0.001	1	0.039	3.9	9.6
0.003	3	0.096	9.6	15
.01	10	.19	19	21

It is clear that since wind speeds are rarely below 1.5 m/s and since there is always some residual wave motion, oil droplets of 0.1 mm and smaller will experience diffusive velocities which always exceed their rising velocities. They will be retained for long periods in the water column. This is consistent with Leibovich's deduction that a 50% probability of drop submergence is likely to occur for a 10 cm/s rising velocity drop (approximately 3 mm) at 12 m/s. The drops of primary interest here are thus those of diameter 1 mm and larger (which normally have an appreciable rising velocity of several cm/s) but which, in some cases, may have slower rising velocities because of high oil densities.

Considering a water column of depth L it is suggested that oil resurfaces at a rate dependent on L and U with a rate constant (U/L) or Ks with dimensions of reciprocal seconds or with a characteristic time (L/U) seconds. But a fraction of the oil which reaches the surface is immediately resubmerged by the diffusive velocity. It is postulated that this fraction is V/(U+V), thus the fraction which is permanently resurfaced is U/(U+V). The rate constant for permanent resurfacing is thus

$$U^{2}/(L(U+V) \text{ or } U/(L(1+V/U)) \text{ or } Ks/(1+Kt/Ks)$$

where Ks is the Stokes' Law rate constant (U/L) and Kt is the turbulent rate constant (V/L) and the characteristic time is

$$L(1+V/U)/U \text{ or } (1+Kt/Ks)/Ks$$

This has the correct properties that when U is zero the time becomes infinite, that when V is zero the time is L/U, that when V and U are similar in magnitude the time is approximately twice L/U, and that when V is very much larger than U the time increases accordingly. We later test this model experimentally. It is thus possible to deduce and tabulate these rate constants and characteristic times as a function of wind speed and drop size

Substituting various combinations of W and D gives the Table below for L of 1 m and a density difference of 200 Kg/m3

	Wind Speed			
	1 m/s	3 m/s	10 m/s	30 m/s
0.1 mm	0.4h	1.3h	11h	100h
0.3 mm	139s	198s	0.24h	1.9h
1.0 mm	25s	28s	53s	270s
3.0 mm	10s	11s	15s	50s
10.0 mm	5s	5s	6s	16s

Clearly large drops (1 cm) will resurface rapidly regardless of wind speed because of their high rising velocity. Drops of 0.3 mm and smaller will tend to be retained for long periods in the water except under very calm conditions. It is the intermediate range of 0.3 to 10 mm which is of greatest interest here.

These times will be displaced (increased) to some extent by oil density increase.

Accordingly, the experimental system developed here explores these characteristic times, but experimental constraints force the conditions to be of relatively low equivalent wind speed.

Specifically the experimental program described later is as follows.

1. Construction and operation of a glass walled tank in which a water column could be observed and a density (salinity) gradient

established and measured.

2. Introduction of turbulence by stirring near the surface to simulate wave action and observation of the effect of this stirring on the stability of the density gradient.

3. Measurement of the density of selected oils, fresh and "weathered" by evaporation and distillation.

4. Emulsification of some of these oils with water to form water in oil emulstions.

5. Dispersal of the oils in the apparatus and observation of the behaviour in the water as a function of droplet size, density gradient and turbulence.

2. EXPERIMENTAL SECTION.

2.1 Apparatus:

The principal equipment (shown in Figure 2.1) consists of a large glass tank of dimensions 47 cm x 47 cm x 120 cm high, reinforced at the corners by vertical angle-iron posts and reinforced horizontally by four tie rods. The tank has a single drain on the bottom without a valve but attached to a long tube which is maintained at a sufficient vertical height to avoid loss of fluid while the tank is full.

Resting on top of the tank is a wooden board upon which a Westphal Balance is mounted. The Westphal Balance is used to measure fluid density and operates on the principle that it weighs a 10 mL glass bulb which is submerged in the fluid. It is calibrated using liquids of known density. The apparent weight of the bulb is a function of the bulb volume and the difference in density between the bulb and the liquid. It is particularly advantageous for this study because it gives an in situ measurement which is relatively non-disturbing of the fluid. From the balance arm hangs a small pulley wound with a length of fishing line. The fishing line passes down through an opening in the board and supports the glass bulb. Using the pulley, the bulb can be raised and lowered to different depths within the tank. Also mounted on the board is a retort stand supporting a stirrer fitted with a long plastic Nalgene polyethylene impeller (3 blades of 44 mm diameter), used to agitate the water in the tank.

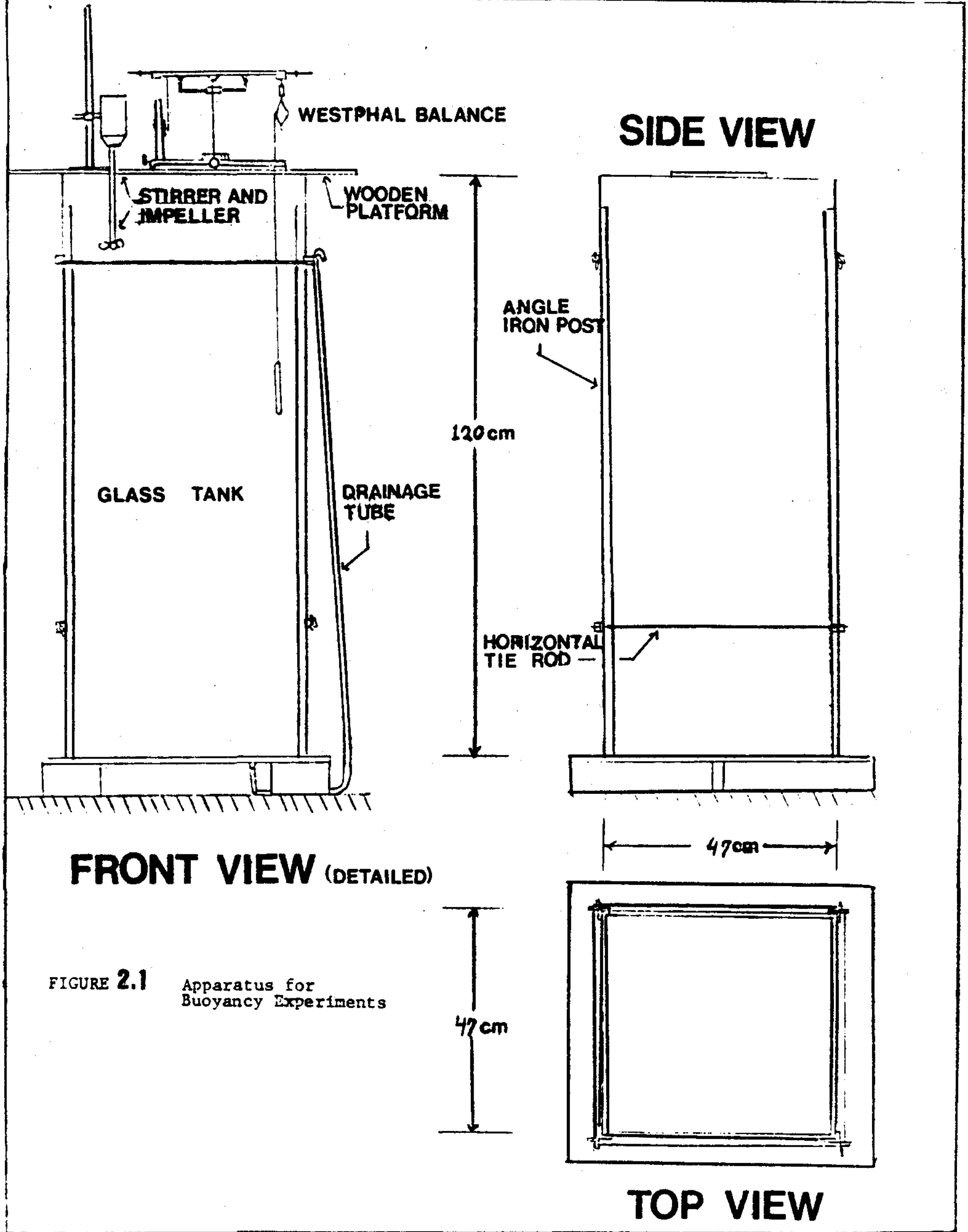


FIGURE **2.1** Apparatus for Buoyancy Experiments

2.2 Oil Weathering and Distillation.

Initial weathering of the various crude oils was performed in a wind tunnel of cross section 30 x 30 cm which maintains a wind velocity of approximately 4 m/s as measured by a pitot tube. Distillations (advanced weathering) of the crudes were done in a simple batch distillation apparatus using a heat mantle connected to a rheostat to vary the distillation rate. A magnetic stirrer was used to agitate the liquid. Dense and viscous oils with poor flow properties were warmed with a heat gun to facilitate their flow during transfer between containers.

Analysis of the composition of the different oil samples was performed using gas and liquid chromatography. All solvents were HPLC grade and obtained from Caledon Labs Ltd., Ontario. Liquid chromatography was performed using a Hyflo Super Cell (Fisher) and silica gel (100-200 mesh, Sigma) and Alumina (F-20, 80-200 mesh, Sigma). HPLC was conducted through a u Bondapak NH2, 3.9 mm I.D. x 30 cm column with particle size of 10 um connected to a LDC UV monitor (254 mu) and a Hewlett Packard 3380 A integrator. Samples were filtered through a multipore type HA 0.45 um filter. The pump used for the liquid chromatography was an Eldex Labs Inc. 60 cycle pump, model AA-100-S Duplex with a maximum flow rate of 10 mL/min and a minimum flow rate of 0.2 mL/min and a maximum pressure of 5000 psi. The gas chromatograph used was a Hewlett Packard 5700A with a Hewlett Packard 3390A integrator.

Photographs, slides and movies of the motion of the oil samples in water were taken using an Olympus 35 mm camera and an Elmo movie camera.

2.3 Procedure.

The overall experimental procedure consisted of;

i) The construction and operation of a glass walled tank in which a water column could be observed and a density (salinity) gradient established and measured.

ii) The introduction of turbulence into the water column by stirring near the surface to simulate wave action and the observation of the effect of this stirring on the stability of the density gradient.

iii) The measurement of the density of selected fresh and weathered oils.

iv) The emulsification of some of these oils with water to form water-in-oil emulsions.

v) Dispersal of the oils in the apparatus and observation of the residence time in the water as a function of droplet size, density gradient and turbulence.

The Westphal Balance was calibrated using salt water solutions containing 0, 5, 10, 20 and 30 g/L of salt. Specific gravity measurements, using the Westphal Balance and pulley apparatus were taken for each concentration of salt water at various depths below the surface of a water column in a plastic tube of approximately 5 cm diameter to a depth of 90 cm. The pulley arrangement was then removed and the balance restored to its normal functioning arrangement in order to take actual specific gravity measurements of the various salt water solutions at surface level.

It should be noted that with the pulley arrangement there were significant amounts of attached fishing line submerged. Because the fishing line has significant bouyancy which affects the apparent bulb weight, allowance for this effect was included in the calibration. Any air bubbles adhering to the bulb of the balance were shaken off.

During the course of the experimental work several rotational speeds of the impeller were used in order to obtain different degrees of agitation in the tank. To quantify the rotation rate the impeller was timed with a stop watch while a marker was stroked down the shaft of the impeller.

The experiments involved the formation of a vertical density gradient in the water column by locating a stratified layer of fresh water on top of salt water with an intermediate density gradient in the vicinity of the fresh - salt water interface. Initially, two batches of 30 g/L salt water solution were prepared in a separate tank and siphoned into the main experimental tank. This effectively filled the tank with salt water to a level of about 60 cm. A volume of fresh water equivalent to about half that of the salt water was placed in an adjacent tank and coloured with methylene blue dye in order to permit easy identification of the gradient (by the different shades of blue created by different degrees of mixing of the salt and fresh water). The fresh water was siphoned very slowly onto the salt water to minimize mixing. The result was a dark blue layer in the upper part of the tank, a light blue layer where some mixing had occurred and a clear underlying layer of 30 g/L salt water.

In order to obtain a crude oil of density greater than 1.0 g/L, various crude oils were evaporated in the wind tunnel in shallow trays to simulate the evaporation of an oil slick on the ocean. The evaporation was carried out at room temperature (20 degrees C) and with the following crude oils: Norman Wells Fresh, Norman Wells 20% Weathered, Aramco Weathered Gas Stripped, Arabian Heavy, Alberta Sweet Blend (EPS), and Cold Lake oils. However, after several days of weathering it became apparent that while the weathering was causing an increase in the density of the oils the rate was very slow. It was then decided that to obtain a heavy oil of density close to or greater than 1.0 with which to model subsurface oil behaviour, No. 6 (heavy bunker C) fuel oil would be distilled.

Initially, the specific gravity of No. 6 fuel oil was measured using a hydrometer (as were all measurements of specific gravity for fluids of specific gravity less than 1.000). The purpose of the distillation was to distill just enough of the No. 6 oil to leave a residual liquid of density between 1.0 kg/L and 1.024 kg/L (density of sea water), thus creating an oil that would sink in fresh water but float in salt water.

Using the distillate volumes and the specific gravities of the distillate and residual liquid from this distillation a general equation was derived to determine the appropriate quantity of distillate to take off in order to obtain a residual liquid density of approximately 1.0 kg/L. The equation used was essentially the addition of volumes

$$M1/D1 + (M-M1)/1.00 = M/D$$

where M1 = mass of distillate

M = mass of original sample of oil in pot

D1 = specific gravity of the distillate

D = specific gravity of the original oil

The same method of distillation was used to distill a sample of Alberta Sweet Blend oil until approximately 70% of the liquid had been distilled. As with the No. 6 fuel oil distillation the temperature, volume distilled and distillate specific gravity were recorded. By this method, combined with blending distillate with residue it was possible to obtain oils of any desired density.

2.4 Experimental Runs.

A number of experimental runs were performed in the stratified tank. The effect of different levels of agitation (different stirrer speeds) on the stability of the liquid density gradient and fresh to salt water interface was studied. Observations were made of the motion and relative level of disturbance of the gradient at various stirrer speeds. Specific gravity measurements were made at various depths within the tank and on either side of the interface (fresh to salt water) during the period of agitation (1 hour) and at a period of 24 hours after the cessation of the stirring.

Samples of oils of various densities were dropped into the tank, and their motion in the water column observed and photographed.

A sample of No. 6 fuel oil and dispersant (Corexit 9527) in the ratio of 50 g oil to 1 g dispersant was stirred into the water column in the tank and the motion of the small oil particles was observed and photographed.

A sample of 15% Cold Lake in Norman Wells oil emulsion was stirred in the tank and observed and photographed as well as timed for rate of particle rise with and without stirring.

It should be clear from the foregoing experimental discussion that much of the work was exploratory in nature in which various approaches were tried, and with varying success. Prior to the work it was not clear how the oil should be weathered to increase its density, how the density gradient should be created or its density measured, or how turbulence should be introduced. In answering these questions considerable experience has been gained about the preferred approach.

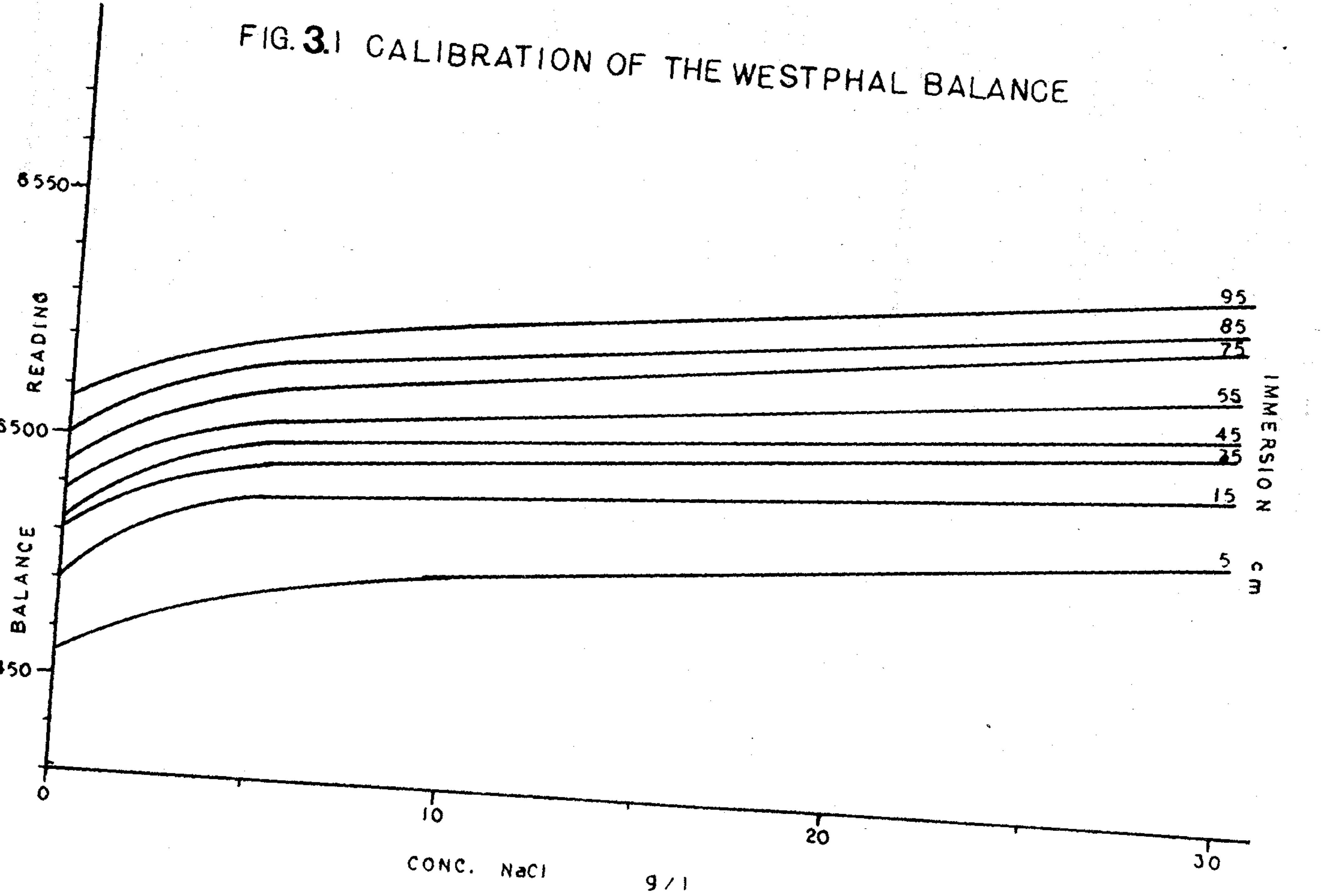
3. RESULTS.

3.1 Westphal Balance Performance and Calibration.

When studying processes in density gradients it is essential to be able to measure the gradient accurately by as non-disturbing a technique as possible. The ideal method is probably to use small coloured spheres of known density which can be dropped into the gradient and allowed to equilibrate. The only spheres available at a reasonable cost are for testing battery acid density which is much denser than seawater. Hence, the Westphal Balance principle was tested and found to be successful.

Calibration was performed using homogeneous standard sodium chloride solutions of 0 to 30 g/L in a long glass tube. The results are given in Figure 3.1 as a plot of balance reading versus concentration and density with depth of immersion as a parameter. This latter quantity is necessary because of the buoyancy of the line.

FIG. 3.1 CALIBRATION OF THE WESTPHAL BALANCE

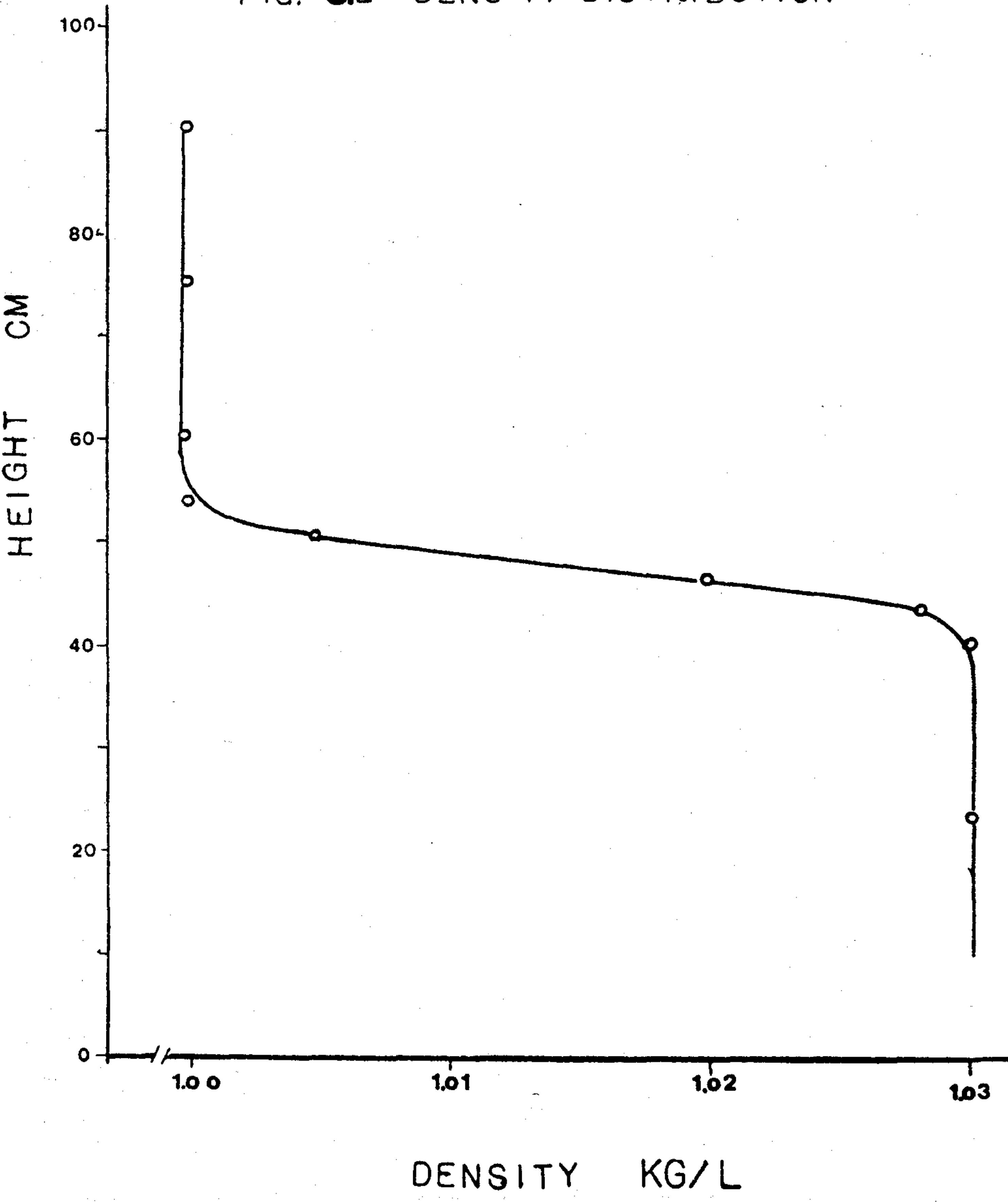


3.2 Density Gradient.

Density gradients were established, measured using the Westphal Balance and observed by using dyed fresh water lying over undyed salt water. Figure 3.2 is a plot of density versus height showing the gradient and figure 3.3 is a photograph of the system. The pycnocline depth was initially 43 cm from the surface and remained stable indefinitely if no stirring took place.

When stirring was started at 400 RPM with the impeller at a depth of 5 cm the pycnocline was observed to move downwards as salt water eddied up into the well mixed surface water. About 15 minutes after stirring started a distinct cirulation formed and the pycnocline moved downwards at a speed of about 8 cm per hour. Periodic density profiles were taken. Figure 3.4 shows a typical time course of density changes during stirring.

FIG. 3.2 DENSITY DISTRIBUTION



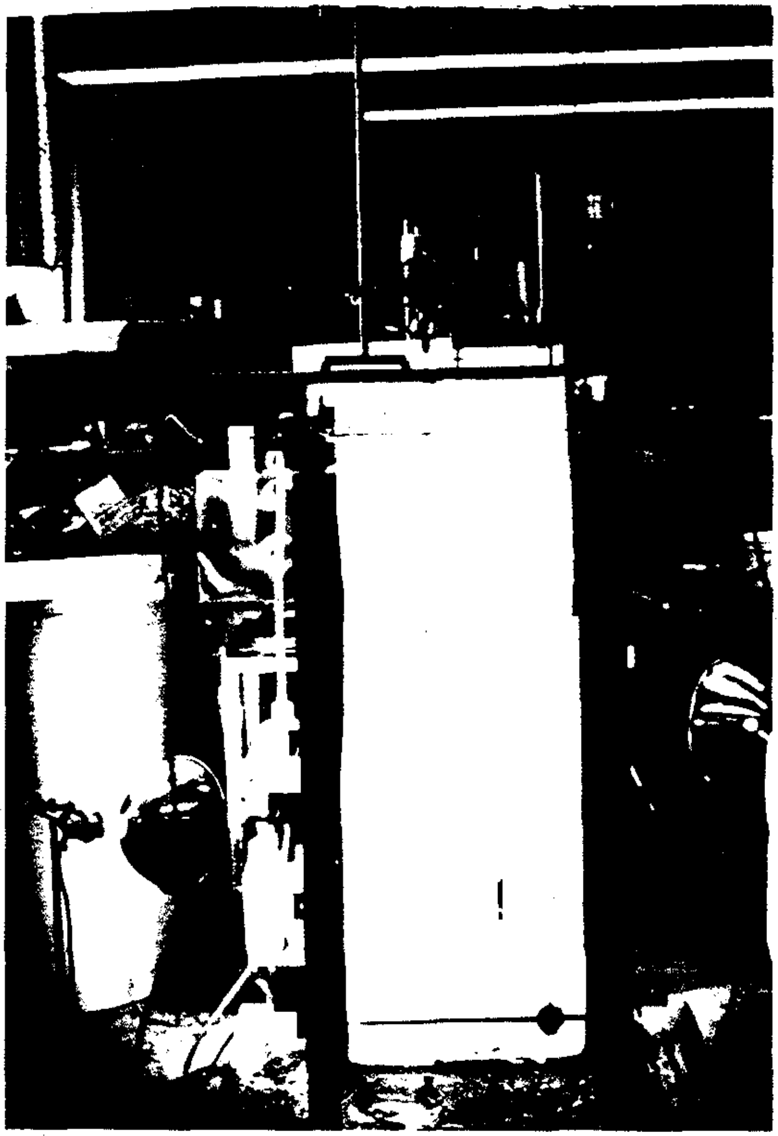
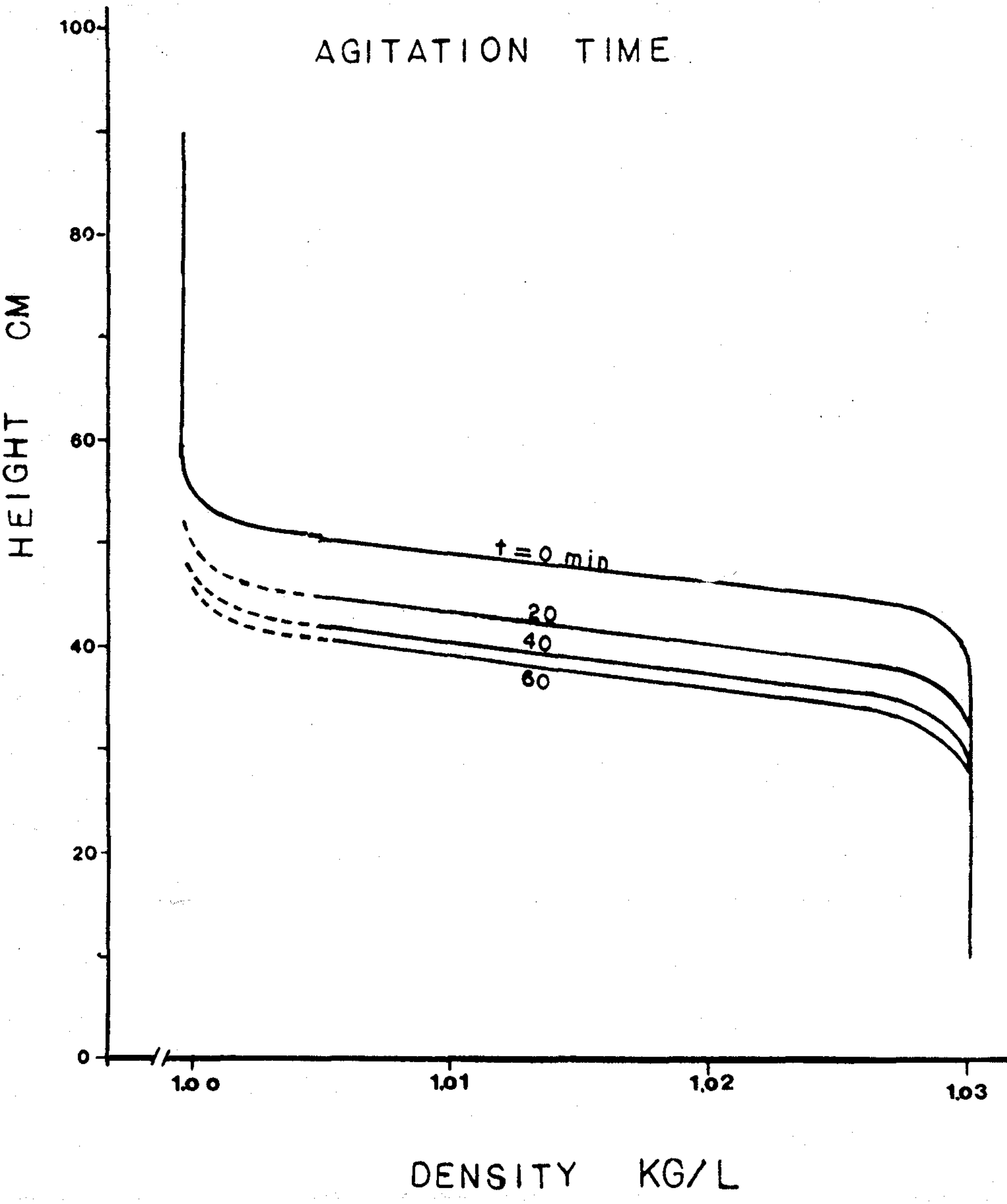


Figure 3.3 Apparatus for Buoyancy Experiments on Weathered Crude Oils in a Fresh/Salt Water System.

FIG. **3.4** GRADIENT POSITION vs. AGITATION TIME



3.3 Oil Preparation.

As was discussed in Section 2 the evaporation of oil in the wind tunnel was abandoned after some initial measurements because it was too slow. Attention was then focussed on distillation to produce an oil termed "Fraction C" which is the backmixed or reconstituted sample of the residual oil from the third distillation of No. 6 Fuel Oil. This oil was used in many of the experimental tests. The densities (specific gravities) of the distilled and evaporated oils are given in Table 3.1.

Table 3.1

Oil	Specific Gravity
No. 6 Fuel Oil	0.962
No. 6 Fuel Oil (after 1st Distillation)	1.017
Distillate (after 1st Distillation)	0.862
No. 6 Fuel Oil (after 2nd Distillation)	0.988
No. 6 Fuel Oil (after 3rd Distillation)	1.022
"Fraction C" Oil	1.004
Alberta Sweet Blend Oil	0.865
Alberta Sweet Blend Oil (after 50 hours in Wind Tunnel)	0.894
Alberta Sweet Blend Oil (after Distillation)	0.937

Figure 3.5 shows the variation of density (specific gravity) of oil versus the volume fraction distilled or evaporated for the

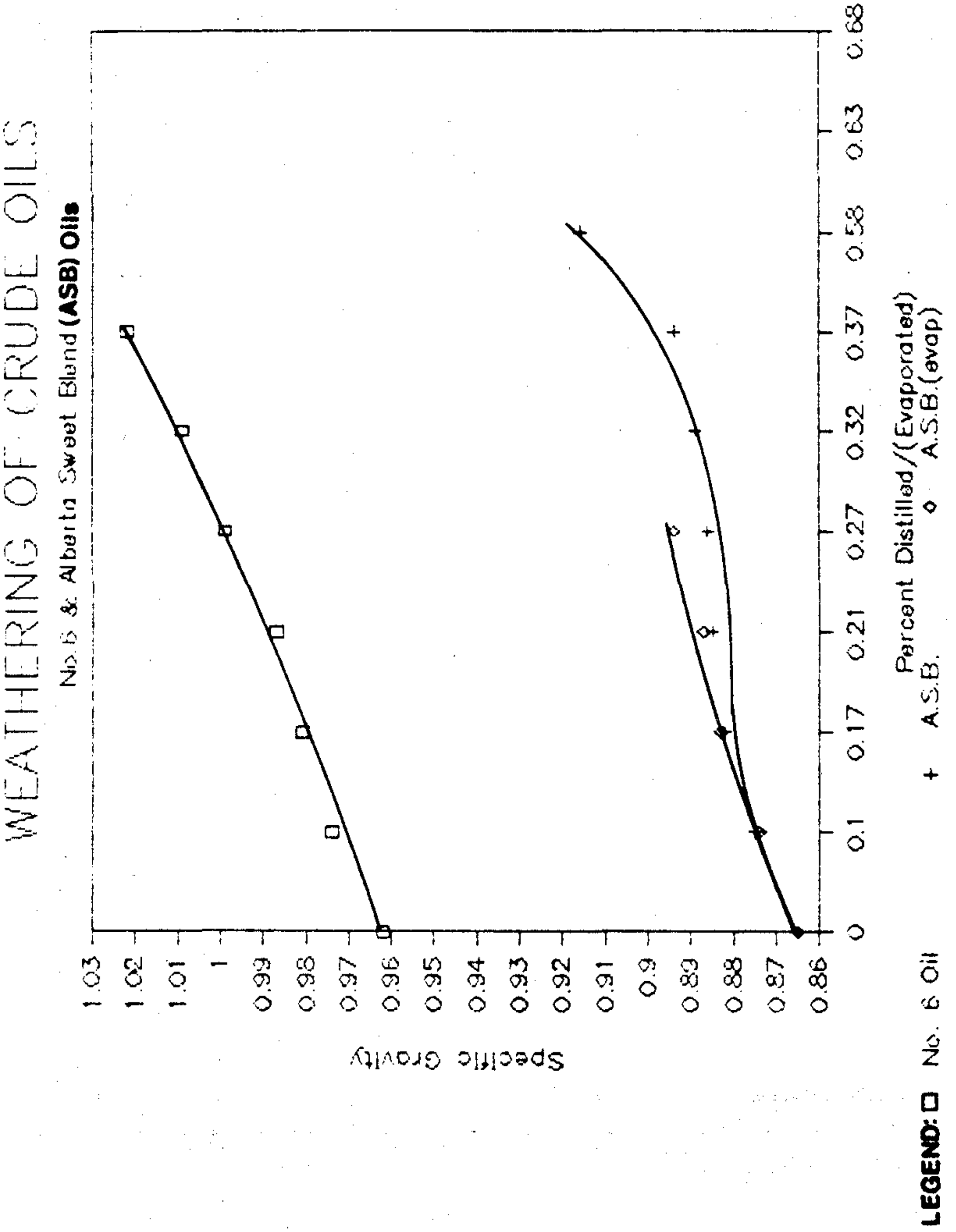


FIG. 3.5 SPECIFIC GRAVITY vs. % EVAPORATED

distillation of No. 6 fuel Oil and Alberta Sweet Blend Oil and the evaporation of Alberta Sweet Blend Oil in the wind tunnel. The initial result of the wind tunnel evaporation of the Sweet Blend Oil showed evaporation of 27% of the oil (at 18 deg. C) after 50 hours. From the plot it may be seen that the partial evaporation of Alberta Sweet Blend Oil in the wind tunnel closely resembles the first part of the curve for the distillation of the same oil and parallels the curve for the distillation of the No. 6 Fuel Oil. It seems likely that given sufficient time the wind tunnel evaporation would result in a level of weathering equal to that obtained by the distillation of Sweet Blend. Similarly, wind tunnel evaporation could possibly achieve the same density as distillation of No. 6 Fuel Oil (which achieved a specific gravity greater than 1.00) . Thus distillation may be considered as an acceptable accellerated weathering technique and provides evidence that sufficient weathering can indeed raise the density of an oil to that of water and even higher. However, the times required are probably so long (many weeks) that other processes such as stranding on shore, interaction with solid matter and photolysis will become more important determinants of oil density.

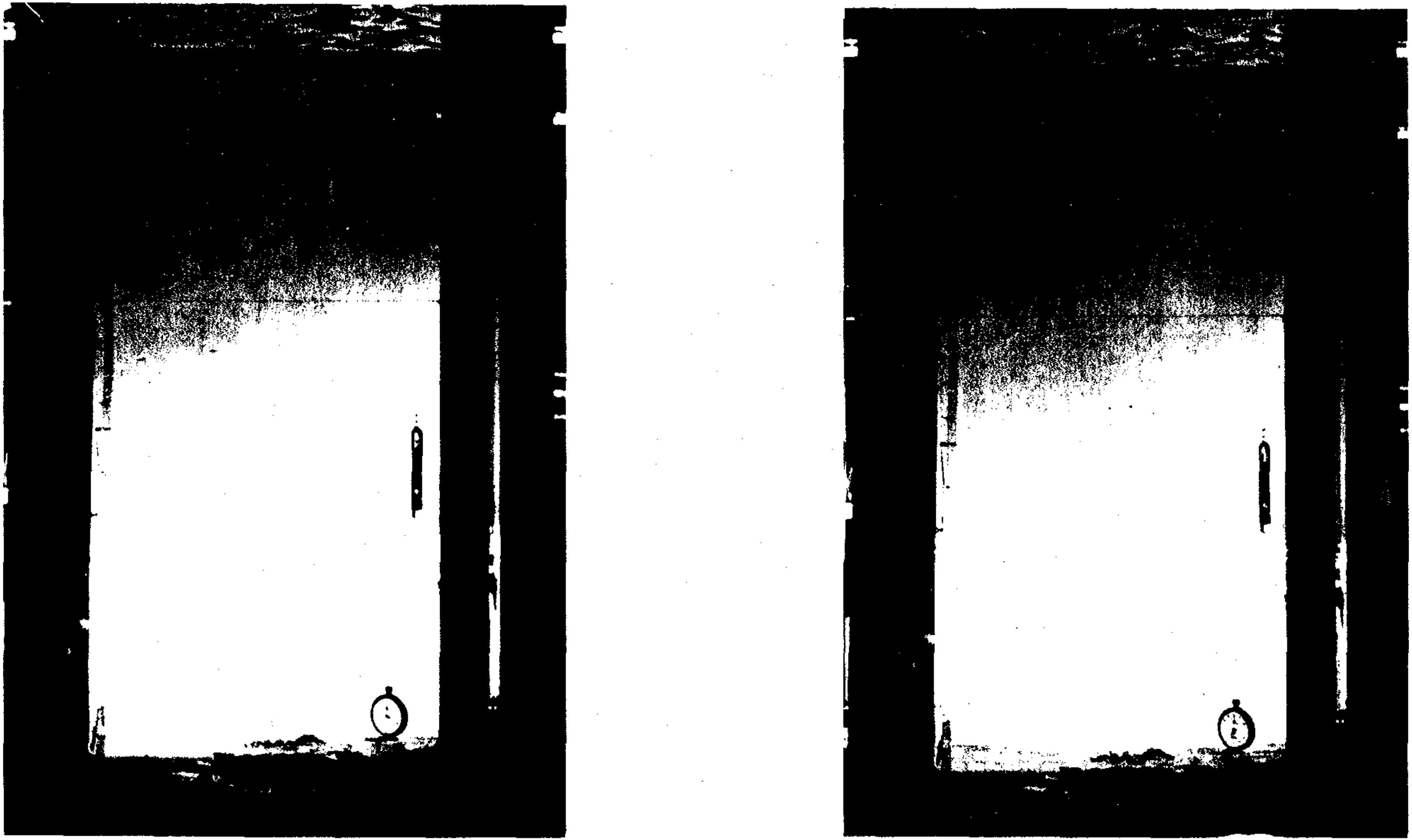
3.4 Tests with No. 6 Fuel Oil.

A gradient was set up with the pycnocline at a depth of 54 cm. After 90 minutes of stirring at 400 RPM a sample of No. 6 fuel oil of density 962.0 kg/m3 was added to the surface. To assist break-up of the oil 2% Corexit 9527 (a chemical dispersant) was premixed with the fuel oil. The subsequent motion of the oil was recorded photographically.

Round oil drops of 0.1 to 5 mm diameter and elongated drops of size 1 x 10 mm to 3 x 20 mm were formed. The elongated drops gradually became spherical under the influence of interfacial tension forces which tend to minimize the surface area. Figure 3.6 gives some photographs of the behaviour. Estimates of drop speed were obtained by photographing the drops with a slow shutter speed. The stirring was stopped and the drops allowed to rise. It was noted that as time progressed during stirring there was a steady increase in the number of small drops of less than 1 mm in the water column. No drops penetrated into the saline layer.

Under stirred conditions the droplets moved at velocities from 3 to 12 cm/s with most being in the range 3 to 6 cm/s. There was no clear dependence of velocity on drop diameter thus turbulent motion apparently dominated. A velocity of this magnitude is believed to be equivalent to a wind speed of the order of 36 km/h as discussed earlier, thus it reflects quite turbulent conditions. It can be concluded that under these conditions there will be substantial steady state retention of oil in the near surface waters.

Under stagnant conditions after stirring had stopped the observed average range of rising velocities were as follows.



t = 20 sec

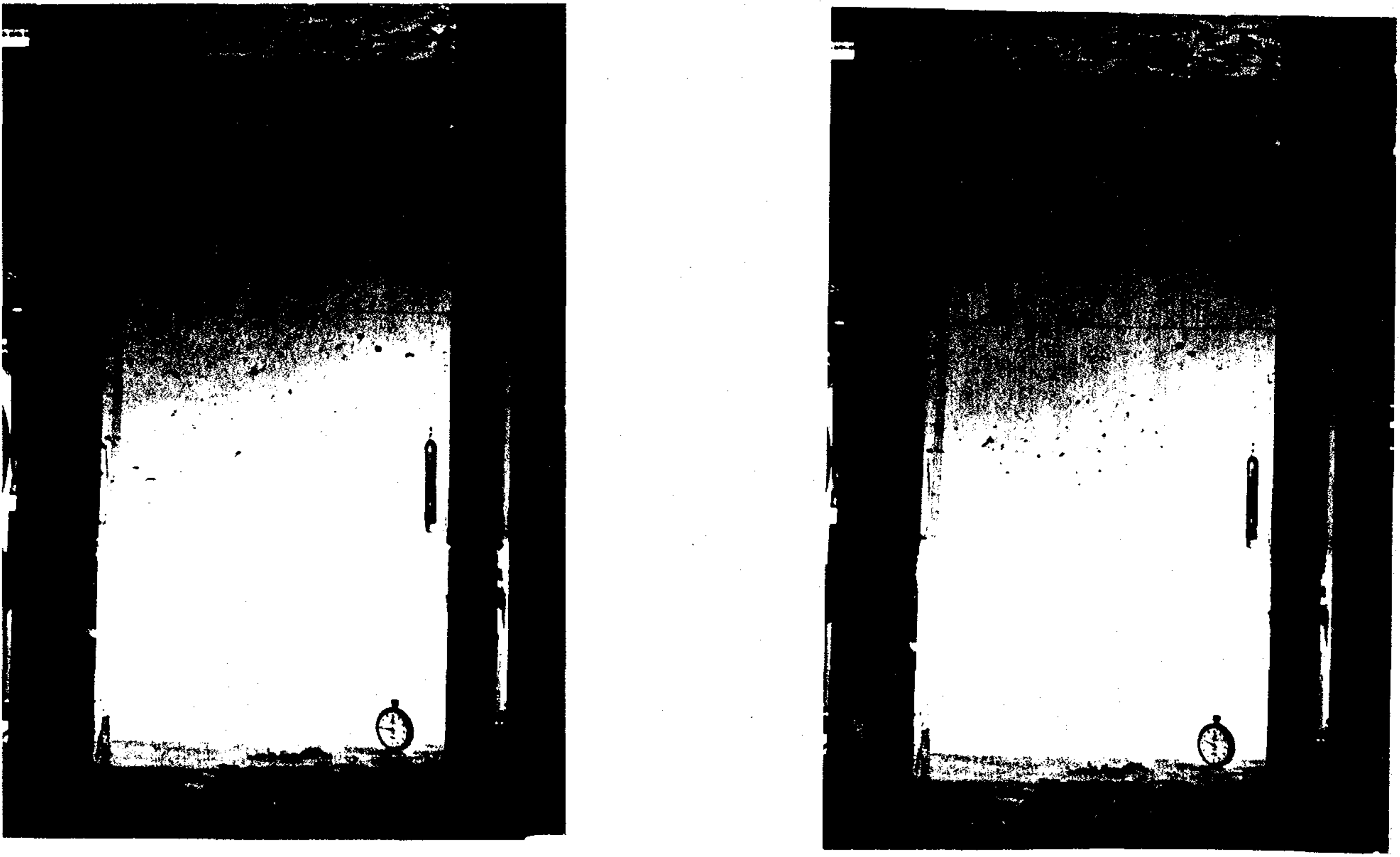
t = 35 sec

Figure 3.6A and B Dispersion of No. 6 Fuel Oil in a Fresh/Salt Water Tank

t = 38 sec

t = 40 sec

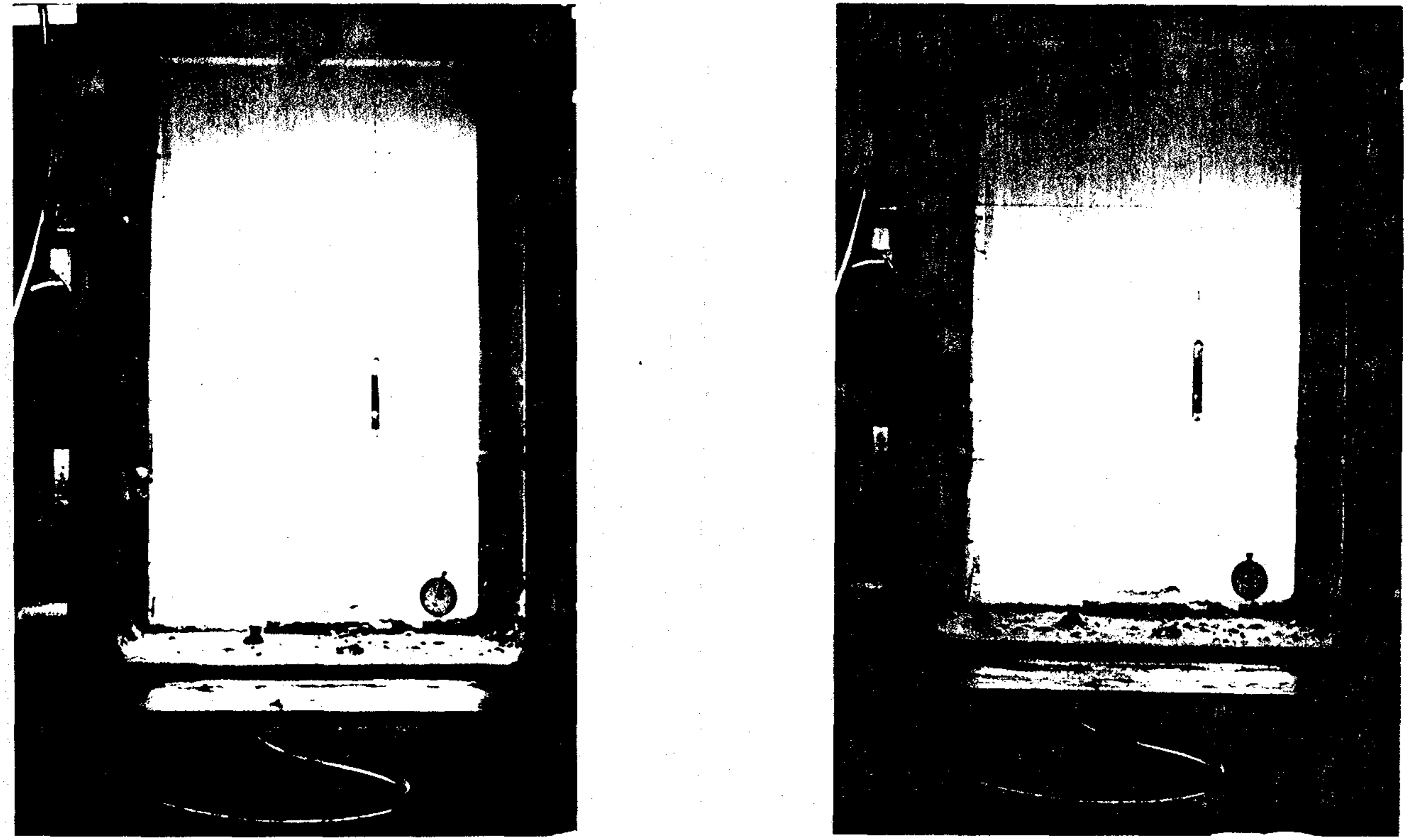
Figure 3.6C and D Dispersion of No. 6 Fuel Oil in a Fresh/Salt Water Tank



t = 45 sec

t = 47 sec

Figure 3.6E and F Dispersion of No. 6 Fuel Oil in a Fresh/Salt Water Tank



t = 0 sec

t = 1 min

Figure 3.7A and B Dispersion of a Residue C/Corexit 9527 Mixture in a Fresh/Salt Water Tank

diameter (mm)	Rising Velocity cm/s	Stokes' Law
0.1	0.33 (0.2-0.51)	0.02
0.5	0.57 (0.38-0.96)	0.41
1.0	0.86 (0.73-1.00)	1.2
2.0	1.54 (1.00-1.27)	2.6

The Stokes' Law velocity (based on a density difference of 38 kg/m3) is in fair agreement for the 0.5 mm drops but the smaller drops appear to rise faster than expected and the larger drops are probably out of the Stokes' Law range. The experimental difficulties of observing small drop velocity and estimating their diameters contributes to the discrepancy for the smaller drops. There were still slight currents remaining in the tank which may have increased the rising velocity of the small particles.

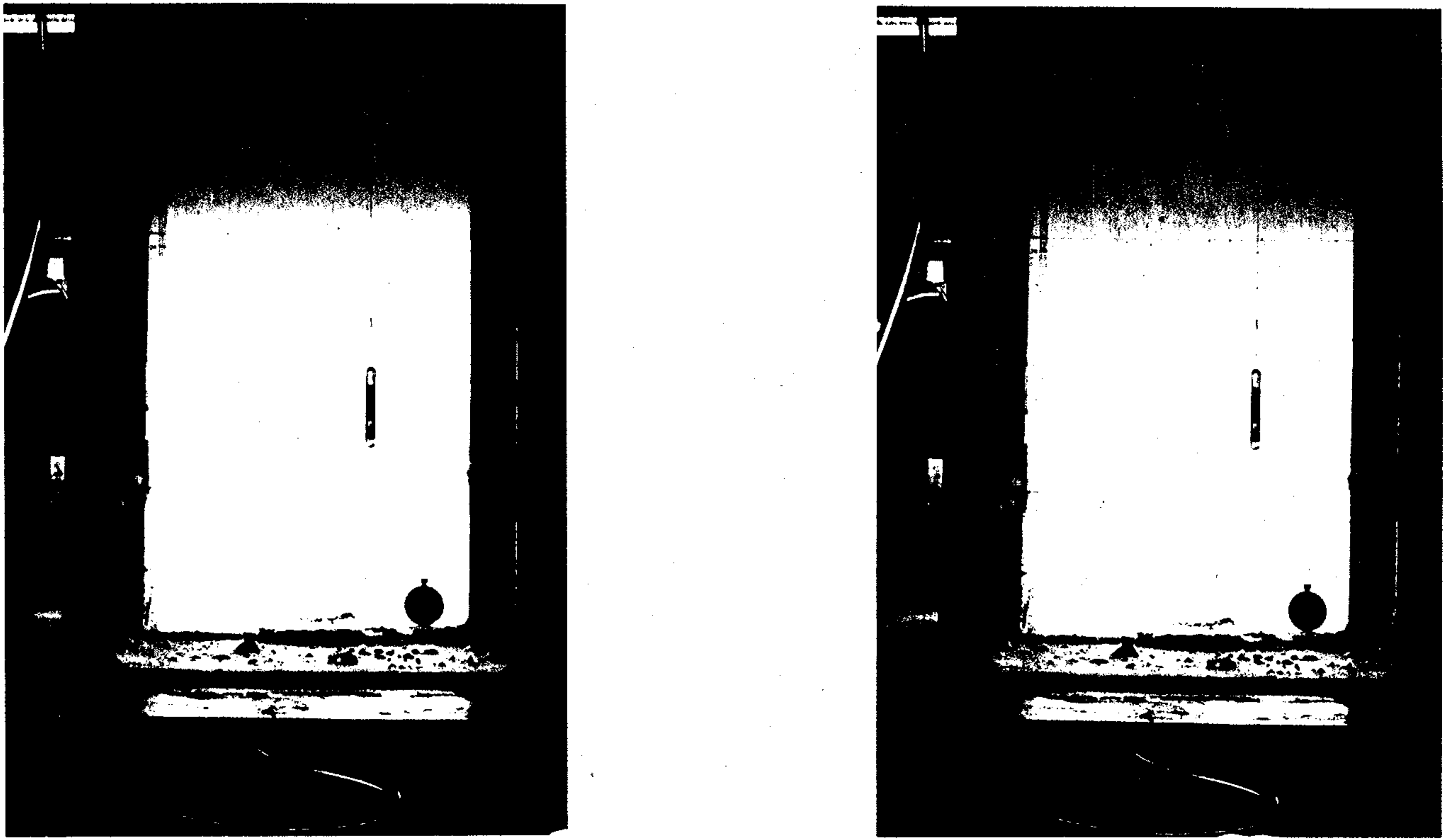
It thus appears that a typical oil droplet rising velocity in the 0.1 to 1.0 mm range is 0.5 cm/s plus or minus a factor of two. This is about a factor of ten less than the turbulent velocities expected under moderate wind speed conditions.

3.5 Tests with Weathered Crude Oil.

A gradient was set up with a pycnocline at 65 cm, stirring was started, then a mixture of distilled oil (Fraction C) of density was 1004.8 kg/m3 was added, again with a small quantity of Corexit 9527 dispersant. Spherical and elongated drops were formed but few drops were smaller than 0.5 mm. After about 8 minutes drops of diameter 0.2 - 2 mm began to accumulate at the pycnocline and remained there in a stagnant condition. Figure 3.7 illustrates this phenomenon. Some were recovered later for GC analysis.

The experiment was repeated without the use of Corexit 9527. Fewer smaller drops were formed and drops again accumulated at the pycnocline.

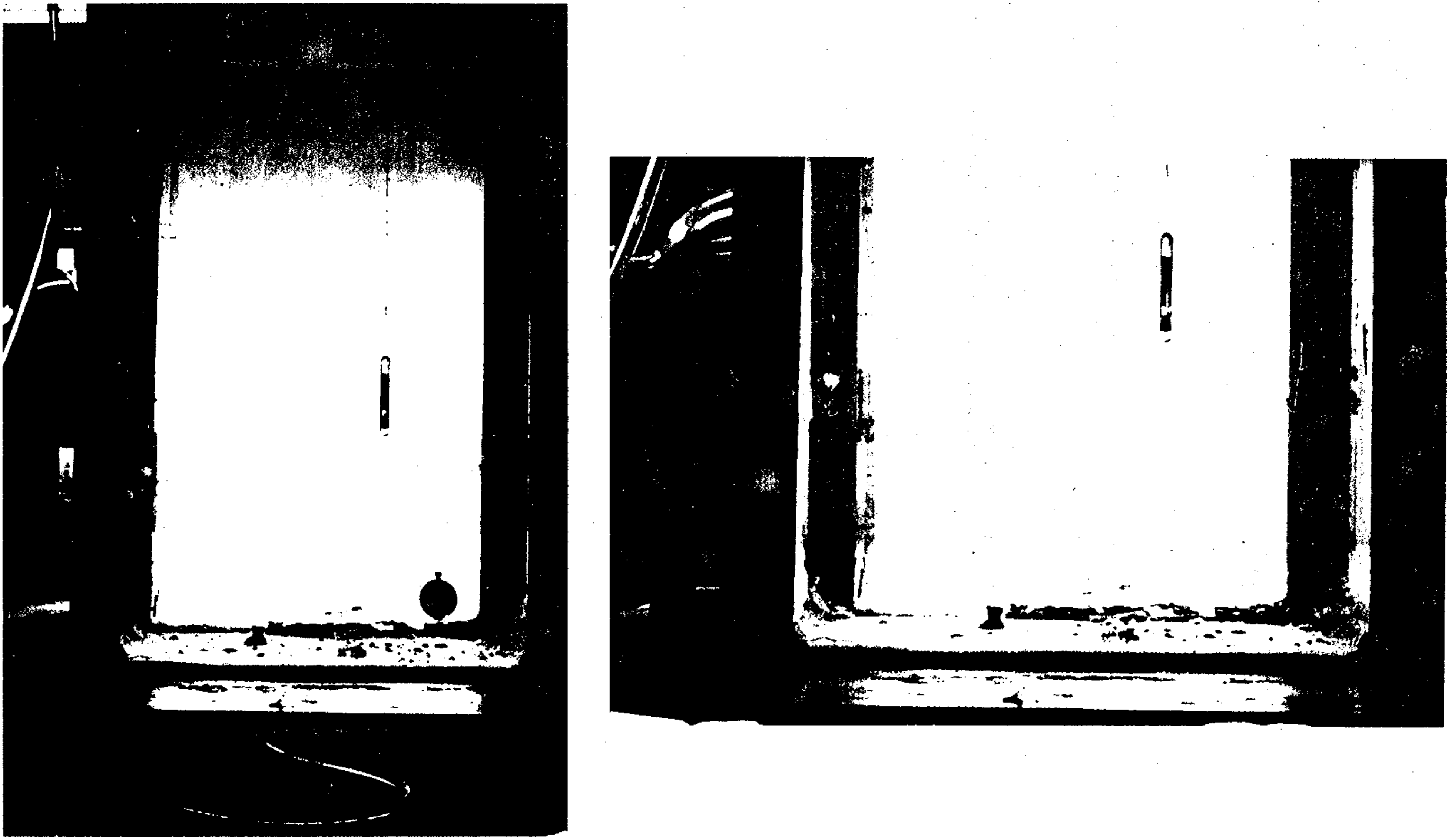
Clearly there is a tendency (as expected) for dense oil drops to fall until they achieve neutral buoyancy.



t = 8 min

t = 11.5 min

Figure 3.7C and D Dispersion of a Residue C/Corexit 9527 Mixture in a Fresh/Salt Water Tank



t = 31.5 min

Final Stages

Figure 3.7E and F Dispersion of a Residue C/Corexit 9527 Mixture in a Fresh/Salt Water Tank

3.6 Tests with mixture of Fuel and Crude Oil.

An experiment was conducted with a mixture of 15 g No. 6 fuel oil and 10 g fraction C. Similar results were obtained to those described above with oil drops accumulating at the pycnocline.

A water-in-oil emulsion was prepared from a mixture of Norman Wells and Cold Lake crude oils And seawater. A small quantity of Corexit 9527 was added and the mixture dispersed into the tank. After stirring was stopped all oil drops of 1 mm or greater rose to the surface within 1 minute and after 10 minutes only drops of less than 0.2 mm remained. A number of "water-in-oil drops" were observed consisting of a spherical skin of oil (like air in a balloon with the water replacing the air and the oil replacing the rubber). This behavior is illustrated in Figure 3.8. They tended to accumulate at the pycnocline indicating that their net density exceeded that of the fresh water, presumably because they still contained salt water incorporated during their formation.

This illustrates the importance of the density of the water used to create emulsions in determining the emulsion net density.

3.7 Tests on Floating Block Submergence.

It was suspected that floating oil masses may appear to be submerged because they are awash with water. To investigate this a short exploratory test was done in which a wooden block 30 cm by 20 cm by 5 cm thick was weighed with metal plates until its net specific gravity was approximately 0.9. It was then placed in a wind-wave tank and subjected to a wind velocity of approximately 13 m/s. The water depth was 60 cm. It was observed and photographed. As expected, in

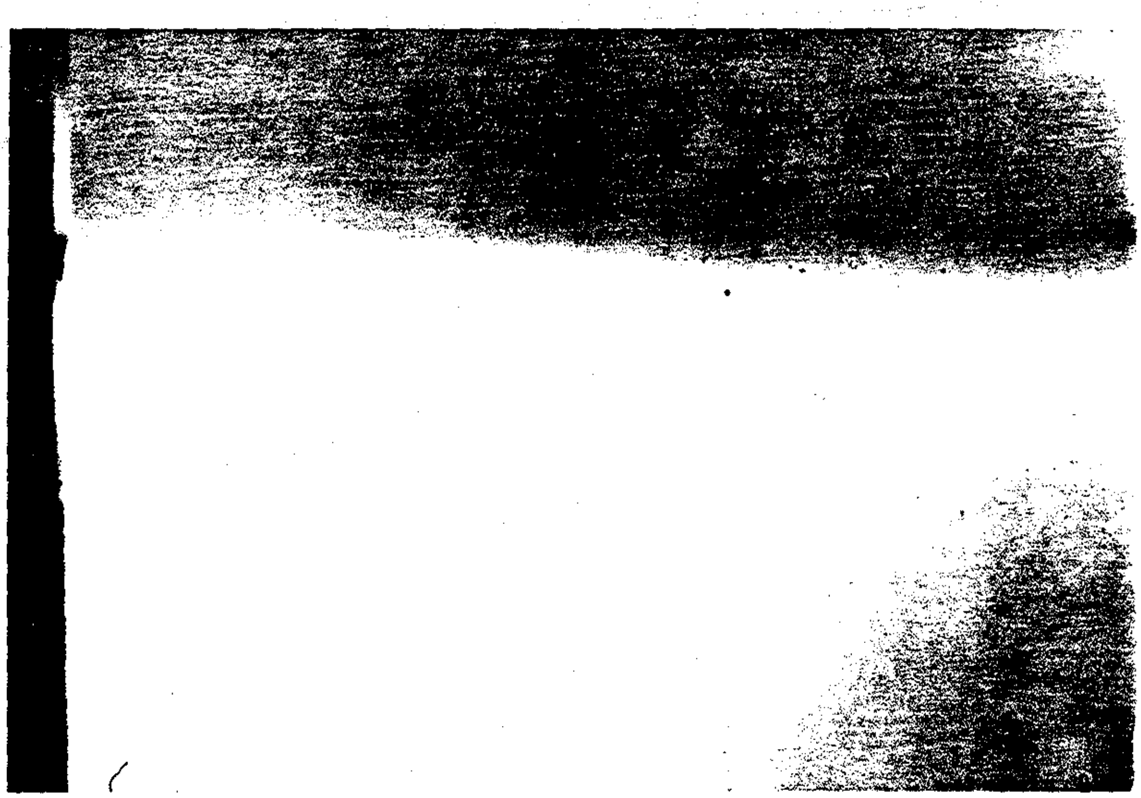


Figure 3.8 Buoyancy Experiment, Water-in-Oil Droplets, Norman Wells/Cold Lake/Corexit 9527 Mixture.

quiescent conditions it lay 90% submerged but in the wind field it was continuously awash with water. It was not clear if it had actually moved vertically downwards but it was essentially 100% submerged. This may be the explanation of the Kurdistan oil behaviour.

4. DISCUSSION.

The results of this exploratory study have shown that substantial quantities of oil can be incorporated into the water column, especially when the surface waters are of low salinity. It is possible to create salinity gradients in the laboratory under stagnant conditions, and with turbulence present in the surface layer. Methods have been devised by which the stratification can be observed, photographed and measured. The introduction of turbulence by stirring simulates to some extent the dispersion of oil by wave breaking, thus it is possible to investigate these phenomena in the laboratory for a period of some hours while the pycnocline moves steadily downwards. It may be possible to create a turbulent agitated regime which can be more closely related to oceanic wind speeds but it unlikely that oceanic conditions can be closely simulated.

The long term buoyant behaviour of oil drops is consistent with a Stokes' Law analysis with dense oils accumulating at the pycnocline or in an extreme case passing through into the saline layer. The theory presented in Section 1 is thus regarded as a reasonable method of estimating the residence time of oil droplets in surface waters.

The behaviour of water-in-oil emulsions is interesting. It appears that when a droplet of emulsion is dispersed it tends to be retained in the water column for a prolonged period because its density is close to that of water. But water-water coalescence may occur within the emulsion (especially if it is only partly stable) giving rise to a water-in-oil-in-water drop. This drop has a large diameter and a density essentially that of the water which was incorporated during emulsification. It may therefore sink when the emulsion moves from an area of high salinity to one of lower salinity. These drops are quite large and may be particularly prone to accumulating detrital material, thus further increasing their net density.

It is clear that at the ocean surface a steady state can exist in which a considerable amount of oil can be present in the surface water. It is convenient to view this process in terms of a series of rate constants or characteristic times (i.e. reciprocal rate constants).

First is a dispersion rate constant Kd equivalent to the fraction of the surface oil which is dispersed into the water per unit time. It may have a value of 10 to 50% per day or perhaps 0.5 to 2.0% per hour, i.e. 0.005 to 0.020 reciprocal hours or 0.01 plus or minus a factor of two.

Second is the Stokes' Law rising rate constant Ks which is the rising velocity divided by the surface depth. For an oil drop of 0.50 mm, of density 40 kg/m3 less than that of seawater, Ks is 5 cm/s divided by 100 cm or 0.005 reciprocal seconds or 18 reciprocal hours. It is equal to U/L discussed earlier.

Third is the turbulent rate constant Kt, as discussed earlier, which is a function of wind speed and may be 5 cm/s divided by 100 cm or 0.05 reciprocal seconds or 180 reciprocal hours. It is equivalent to V/L discussed in Section 1.

If all drops formed were of the same diameter and if it is assumed that the net resurfacing rate is Ks/(1 + Kt/Ks), then a steady state will be reached in which the rates of dispersion and resurfacing are equal. Now if the total oil volume is V and a fraction F is in the water (amount is VF) then the amount on the surface is V(1-F) and

$$V(1-F)Kd = VFKs/(1 + Kt/Ks)$$

$$\text{or } F = Kd/[Kd + Ks/(1 + Kt/Ks)]$$

For example if Kd is 0.01, Ks is 18 and Kt is 180 (reciprocal hours) F is 0.006, (i.e. 0.6% is in the water column). Only when Kd is large compared to Ks, and especially when Kt exceeds Ks will F be large. For small oil drops this condition does exist and it can be expected that when small drops are formed they remain for prolonged periods in the water. Indeed, if a fraction of the oil dispersed is small in size then that fraction will tend to accumulate in the water. It will be difficult to measure this at sea because of the displacement of the oil slick from the water due to wind drift.

It is thus concluded that only under turbulent conditions will an appreciable fraction of the oil be submerged, unless there has been water-in-oil emulsification.

It seems inconceivable that large oil drops (1 cm diameter or more) will be permanently retained in the water but they may appear to be submerged if they are continually washed with water from surface drift currents. No experimental work (apart from the brief tests conducted here) has been reported on this topic and a more detailed study would be interesting. It would involve measurement of the vertical location of a slightly buoyant body in a wind driven velocity field, preferably in a wind wave tank. It is noteworthy that these oil masses would possibly not be visible from the air by eye or by remote sensing devices because they would be continually awash.

This work has shown that there is a need for development of a standard method for weathering oils, specifically aimed at determining their tendency to sink. Recently Stiver and Mackay (1984) have described methods of weathering oils experimentally by tray evaporation, stripping and distillation. Clearly, for these purposes distillation is preferred because it is rapid and because the evaporated oil can be collected and various oils reconstituted from the distillates. The following procedure is suggested.

A large volume of oil (possibly 2 L) is batch distilled under appropriately safe conditions and the distillation temperature measured at the liquid surface. The distillate is taken off in 50 mL fractions, and individual densities and viscosities are measured. The distillation should continue until a temperature of about 300 C is reached or pyrolysis starts. The density and viscosity of the residue are also measured.

The distillate fractions are then progressively mixed back with the residue (last first) to reconstitute the oil, measurements of density and viscosity being taken after each mixing. It is then possible to prepare a plot of oil density and viscosity versus volume fraction evaporated (distilled) and boiling temperature. Samples can also be analysed by GC. The points can be identified when (or if) the oil density exceeds that of fresh and salt water. It is also possible to estimate the "evaporative exposure" (as described by Stiver and Mackay 1984) corresponding to these points and hence the time necessary for these points to be reached during sea-surface weathering. For most oils this time may be much longer than the slick lifetime, but it is suspected that in some cases with heavy crude oils and with fuel oils it may be reached in a few days.

It is also possible to calculate the density of an emulsion (mousse) of, for example, 80% water and 20% oil (by volume) which is,

$$0.8\ (\text{water density}) + 0.2\ (\text{oil density})$$

and compare this with typical seawater densities. If the emulsified water is salt (e.g. 1024 kg/m3) and the oil density is 904 kg/m3 then the emulsion density will be 1000 kg/m3 and the oil will be neutrally buoyant in fresh water. It is thus concluded that when an oil density exceeds 900 kg/m3 the potential exists for sinking under these conditions. A No. 6 fuel oil is almost certain to sink under salt-water emulsification conditions with subsequent movement into fresh water.

It is suggested that in view of the importance of sinking from countermeasures, remote sensing and environmental impact viewpoints that any oils produced or transported in a region should be subjected to a "potential-for-sinking" analysis as described here. This will be particularly relevant in areas of commercial fisheries in which there is potential to foul nets and introduce benthic contamination.

6. CONCLUSIONS.

An experimental system has been devised and tested in which a salinity gradient can be established, measured and observed. Agitation can be introduced to simulate to a limited extent near-surface wind derived turbulence.

The system can be used to determine and illustrate the sinking behaviour of fresh and weathered crude oils, fuel oils and emulsions. Results are presented.

A protocol has been suggested by which an oil can be subjected to a "potential-for-sinking" analysis by a distillation procedure.

An elementary theoretical analysis is presented in which the influence of turbulence on oil droplet rising is treated. This analysis leads to a tentative expression for fraction of oil retained in the water column under steady state conditions.

It is concluded that a substantial quantity of oil can be submerged in the water column under steady state conditions. The extent of submergence is enhanced by

i) a high oil density occurring naturally or induced by weathering.

ii) the presence of significant turbulence to disperse the surface oil at an appreciable rate and induce water column mixing.

iii) the formation of small oil drops.

iv) the formation of emulsions of water in oil especially involving high salinity water.

There is a possibility, which has not been investigated in sufficient detail experimentally, that large oil masses which are slightly less dense than water may be essentially submerged by virtue of their exposure to water surface currents. These oil masses may be invisible to the eye or to remote sensing systems because they are continually awash with water.

Finally, there is also a possibility of density increase by association of the oil with mineral and organic matter in the water column.

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