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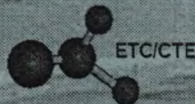
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# The Dynamics of Orimulsion Spills in Salt, Fresh, and Brackish Waters



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Environmental Technology Centre



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# **The Dynamics of Oil Spills in Salt, Fresh, and Brackish Water**

by

P. Jokuty, B. Fieldhouse, S. Whitticar, and M. Fingas

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## **EXECUTIVE SUMMARY**

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This report details a series of experiments performed to characterize the behaviour of two Orimulsion products, Orimulsion-100 and Orimulsion-400, in water under dynamic conditions. The variables in the experiments were salinity and depth of release (surface and sub-surface). A mesoscale apparatus was used, consisting of a 600-L test tank and a motor-driven hoop oscillating vertically beneath the water surface. The test tank was filled with 400 L of water, with salinity of 3.3% (salt), 2.0% (brackish), or 0.0% (fresh), with an Orimulsion product added at a nominal bitumen-to-water mass ratio of 1:1000. Energy was applied for up to 48 hours, with timed sampling from the top and bottom of the water column for analysis of particle size distribution and bitumen concentration.

In general, the two Orimulsion products behaved similarly. The main differences between the two products were the much higher removal rate of bitumen for the Orimulsion-400 test in salt water, and the large fluctuations in bitumen concentration in brackish water when Orimulsion-100 was released at the surface.

For both products, bitumen concentration decreased significantly within 48 hours for all tested water salinities, release points, and sampling depths. Bitumen concentration dropped as bitumen particles adhered to apparatus surfaces. For saline water, the main area of collection was surfaces in the zone of agitation. Sedimentation played a major role in bitumen removal from fresh water.

The Orimulsion release point (surface or subsurface) had a distinct effect on the salt water behaviour of both products. Much less bitumen was removed when the Orimulsion was released at the water surface compared to a release near the bottom of the test tank. Differences in bitumen concentration between top and bottom release in fresh and brackish water were much smaller.

Sampling depth did not appear to play a significant role in bitumen concentration for brackish and fresh water. For the salt water tests, however, surface samples had higher bitumen concentrations than bottom samples. It was also observed that Orimulsion-100 bitumen formed flocs that remained suspended near the surface after agitation ceased, but did not coalesce.

Salinity had a pronounced effect on changes in mean particle diameter as a function of time. In salt and brackish water, there was a very rapid increase in the mean volume diameter over a period of one hour, indicating coalescence of particles. The coalescence of bitumen was more rapid with Orimulsion-400, which also has a larger initial mean volume diameter. Coalescence was not observed in the fresh water tests, as the mean volume diameter decreased over time as the larger bitumen particles were removed from the water.

In general, the behaviour of the Orimulsion products is predictable in fresh and salt water, but can be very difficult to predict in brackish water.

## SOMMAIRE-RECOMMANDATIONS

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Le rapport expose dans le détail une série d'expériences visant à caractériser le comportement de l'Orimulsion-100 et de l'Orimulsion-400, dans l'eau, en conditions dynamiques. Les variables examinées étaient la salinité et la profondeur à laquelle survient le déversement (en surface et dans l'eau). On a utilisé un appareillage à moyenne échelle, constitué d'un bassin d'expérience de 600 L et d'un cerceau motorisé, oscillant verticalement sous la surface de l'eau. Le bassin a été rempli de 400 L d'eau de salinités diverses : 3,3 % (eau salée) ; 2,0 % (eau saumâtre) ; 0,0 % (eau douce). On y a ajouté l'Orimulsion de façon à obtenir un rapport massique nominal du bitume à l'eau de 1/1 000. L'agitation s'est poursuivie pendant jusqu'à 48 heures, avec échantillonnage minuté du sommet au fond de la colonne d'eau en vue de l'analyse granulométrique et du dosage du bitume.

En général, les deux Orimulsion ont eu un comportement semblable. Les principales différences ont été le taux plus élevé de disparition du bitume de l'Orimulsion-400 en l'eau salée et les fortes fluctuations de la concentration de bitume dans l'eau saumâtre à la surface de laquelle l'Orimulsion-100 avait été libérée.

Avec les deux produits, la concentration de bitume a considérablement diminué en moins de 48 heures, quelle que fût la salinité de l'eau, la profondeur de la libération de l'Orimulsion dans l'eau et la profondeur des prélèvements. La concentration de bitume a chuté en raison de l'adhérence des particules aux surfaces de l'appareillage. En eau salée, les principales zones d'adhérence étaient les surfaces dans la zone d'agitation. En eau douce, le dépôt au fond de l'eau a joué un rôle important dans l'élimination du bitume.

Le point de libération de l'Orimulsion (en surface ou sous l'eau) a nettement influé sur le comportement des deux produits en eau salée. L'élimination du bitume a été beaucoup moindre lorsque l'Orimulsion a été libérée en surface plutôt que près du fond du bassin. En eaux douce et saumâtre, les écarts entre la concentration de bitume libéré au sommet de la colonne d'eau et au fond étaient beaucoup plus faibles.

La profondeur du prélèvement ne semble pas avoir joué un rôle important dans la concentration du bitume dans l'eau saumâtre et douce. En eau salée, toutefois, les échantillons prélevés en surface renfermaient des concentrations de bitume supérieures aux concentrations du fond de l'eau. On a aussi observé que le bitume de l'Orimulsion-100 formait des flocs qui restaient en suspension près de la surface après la fin de l'agitation, mais sans subir de coalescence.

La salinité a exercé un effet prononcé sur l'évolution du diamètre moyen des particules en fonction du temps. Dans l'eau salée et saumâtre, le diamètre de volume moyen a augmenté très rapidement en une heure, signe de la coalescence des particules. La coalescence du bitume était plus rapide dans le cas de l'Orimulsion-400, qui possède aussi un diamètre de volume moyen initial plus grand. On n'a pas observé de coalescence dans les expériences en eau douce, puisque le diamètre de volume moyen a diminué graduellement, avec l'élimination des grosses particules de bitume de l'eau.

En général, le comportement des types d'Orimulsion est prévisible dans l'eau douce et l'eau salée, mais il peut être très difficile à prédire en eau saumâtre.

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## **1. INTRODUCTION**

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Orimulsion is a surfactant-stabilized emulsion of 70% bitumen in 30% water. Because of its unique composition, its behaviour when spilled is very different from that of conventional fuel oils. In the event of an Orimulsion spill, the selection and timely application of appropriate countermeasures depend on the ability to predict where in the water column the bitumen will be after a given elapsed time.

The purpose of this project was to provide quantitative information on the behaviour of Orimulsion spills in salt, fresh, and brackish water. A series of 12 experiments was undertaken to investigate the effects of surface and subsurface releases of two different Orimulsion formulations: Orimulsion-100, the currently available formulation, and Orimulsion-400, a new formulation that is under development. In each experiment, Orimulsion was added to a tank of water and timed samples were taken near the top and the bottom of the water column. Separate samples were taken for the determination of particle size distribution and bitumen concentration.



## 2. METHODS

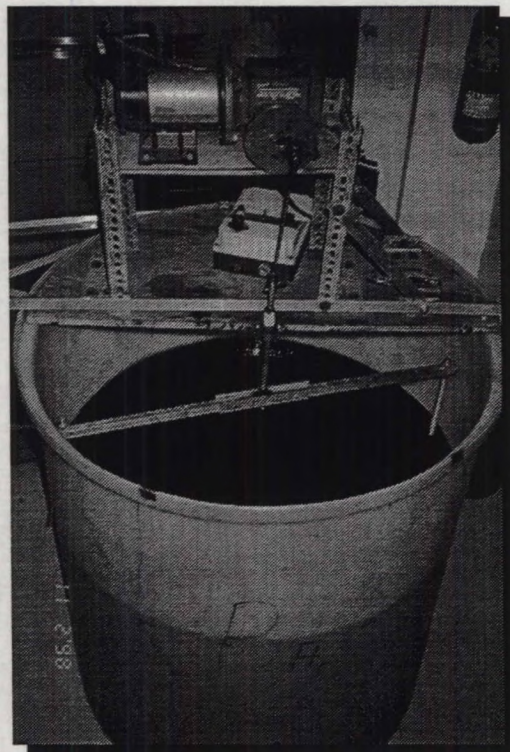
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### 2.1 Experimental Setup

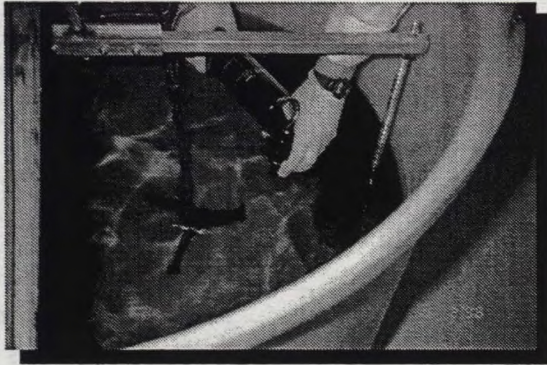
The apparatus consists of a cylindrical tank 90 cm in diameter and 106 cm in height and a vertically oscillating, flat, stainless steel hoop, 4.5 cm wide and 78 cm in diameter (Figure 1). The hoop was adjusted to oscillate between 6 and 18 cm below the surface of the water at a rate of 60 cycles per minute.

For each test, the tank was filled to a depth of 65 cm, yielding a volume of approximately 400 L of water. Salt was added as appropriate to obtain the desired salinity, nominally 0%, 2.0%, and 3.3%. Salinity was checked with a Horiba U-10 water quality tester. The temperature of the water was between 17 and 21°C for all tests.

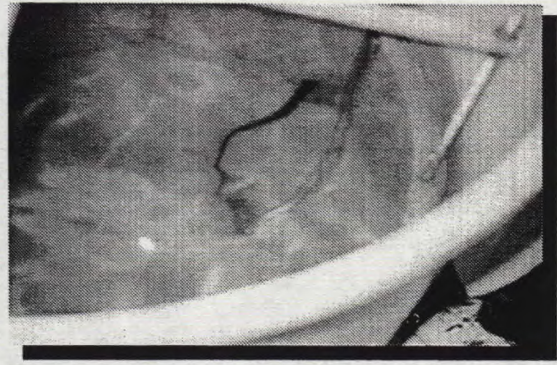
For each run, 600 mL of well mixed Orimulsion at 15°C was measured into a graduated cylinder and weighed. For top release runs, the Orimulsion was added at the surface, using a standard 60-mm diameter glass powder funnel (Figure 2). For bottom release runs, the same funnel was used together with a length of aluminum tubing, to direct the Orimulsion to the bottom of the tank (Figure 3). The funnel and tubing were rinsed with 500 mL of tank water. The graduated cylinder was weighed again and the mass of Orimulsion added was determined by difference. For all runs, the Orimulsion was added with the hoop in motion and timing of the run began as soon as Orimulsion was released into the water. Agitation was continued for 12 to 48 hours.



**Figure 1 Oscillating Hoop Apparatus**



**Figure 2 Top Release of Orimulsion**



**Figure 3 Bottom Release of Orimulsion**

At intervals, water samples were withdrawn from the tank for either particle size analysis or bitumen concentration determination. To ensure that samples were always collected from the same depth and location, a sampling jig was made by taping two pieces of plastic tubing to a ring stand so that the inlet of the longer piece of tubing was approximately 2.5 cm from the bottom of the tank and the inlet of the shorter piece of tubing was approximately 2.5 cm below the surface. Each piece of tubing extended above the surface of the water to allow for easy sampling. The ring stand was placed approximately midway between the centre of the tank and the tank wall. Samples were withdrawn using standard plastic syringes - 10-mL syringes for particle size samples and 60-mL syringes for bitumen concentration samples. Bitumen concentration samples were taken at the top and bottom of the tank at the same time interval. Because particle size analysis could be performed on only one sample at a time, samples were taken alternately from the top or bottom of the tank.

The Orimulsion-100 used for these experiments was a composite sample obtained from a shipment received at Dalhousie, New Brunswick in January, 1998. The Orimulsion-400 was from a 20-L sample supplied by Bitor America Corporation, received by ESD on August 7, 1997. A total of 12 experiments were run. The details of each experiment are summarized in Table 1. Data was obtained for of 192 concentration samples and 130 particle size samples.

## **2.2 Analytical Methods**

The methods used for determining the physical properties of the Orimulsion, the bitumen concentrations, and the particle size distributions can be found in Appendix A.

**Table 1 Summary of Experiments**

Experiment ID	Type of Orimulsion	Type of Water	Release Point	Salinity (wt %)	Initial Temperature (°C)	Nominal Bitumen-to-Water Ratio	Duration (hours)
O100ST	O-100	salt	top	NR	NR	1:999	48
O100SB	O-100	salt	bottom	3.25	20.1	1:1047	48
O100FT	O-100	fresh	top	0.01	20.8	1:1089	48
O100FB	O-100	fresh	bottom	0.01	20.1	1:996	48
O100BT	O-100	brackish	top	2.03	18.9	1:1049	24
O100BB	O-100	brackish	bottom	2.00	19.5	1:1075	24
O400ST	O-400	salt	top	3.26	17.6	1:985	48
O400SB	O-400	salt	bottom	3.30	20.9	1:1009	12
O400FT	O-400	fresh	top	0.01	20.0	1:995	24
O400FB	O-400	fresh	bottom	0.01	20.7	1:975	48
O400BT	O-400	brackish	top	1.99	21.6	1:1067	24
O400BB	O-400	brackish	bottom	2.00	20.6	1:1002	48

NR = checked but not recorded

### 3. RESULTS AND DISCUSSION

Some of the physical properties of the Orimulsion-100 and Orimulsion-400 are listed in Table 2. These properties indicate that the Orimulsion conformed to Bitor specifications (Intevep, 1993) and was also similar to Orimulsion previously analyzed (Jokuty *et al.*, 1995).

**Table 2 Physical Properties of Orimulsion**

Properties	Orimulsion-100	Orimulsion-400
Water Content	28.0 weight %	30.0 weight %
Median Particle Size (volume diameter)	15 $\mu\text{m}$	20 $\mu\text{m}$
Density at 0°C	1.0171 g/mL	1.0162 g/mL
Density at 15°C	1.0094 g/mL	1.0095 g/mL
Viscosity at 0°C (with SV1 sensor at shear rate 100/s)	744 mPa·s	1,065 mPa·s
Viscosity at 15°C	465 mPa·s	450 mPa·s
Pour Point	3°C	0°C
Flash Point	> 95°C	> 95°C

#### 3.1 Bitumen Concentration

Tables summarizing the results of analysis of water samples for bitumen concentration are collected in Appendix B. Tables B1 to B6 summarize the results for experiments with Orimulsion-100 and Tables B7 to B12 summarize the results for experiments with Orimulsion-400. The changes in bitumen concentration as a function of time are shown in Figures 4 to 9. Each figure is a composite, showing the results of two experiments (top release and bottom release of Orimulsion) in one type of water, with separate curves plotted for top and bottom samples.

##### 3.1.1 General Observations

The drop in bitumen concentration is due to removal of bitumen from the water column and its transfer onto various surfaces. The bitumen collects in four main zones: the vessel floor, the vessel wall at the wave zone, the vessel wall in proximity to the oscillating hoop, and on the hoop itself. There is minimal bitumen collection on vessel surfaces outside of these zones. This is true for both types of Orimulsion.

For experiments in salt and brackish water, the primary collection zones were surfaces where there was applied energy - the hoop, the wall along the hoop oscillation, and the wave zone. Most of the bitumen collected between the hoop and the vessel wall. Any floating bitumen patties appeared to have first accumulated on one of the surfaces where there was applied energy, then broken away. Sedimentation was not a factor for experiments with salt and brackish water.

In fresh water, the bitumen also collected on surfaces in the agitation zones, but most appeared to collect on the vessel floor due to sedimentation. This indicates that the density gradient between the bitumen and the water played a more significant role than the applied energy of mixing.

##### 3.1.2 Salt Water

In salt water, there was a marked difference in the rate and degree of bitumen removal from the water column, depending on whether the Orimulsion was added at the top or at the bottom. This effect was more pronounced with Orimulsion-400 (Figure 5) than with Orimulsion-100

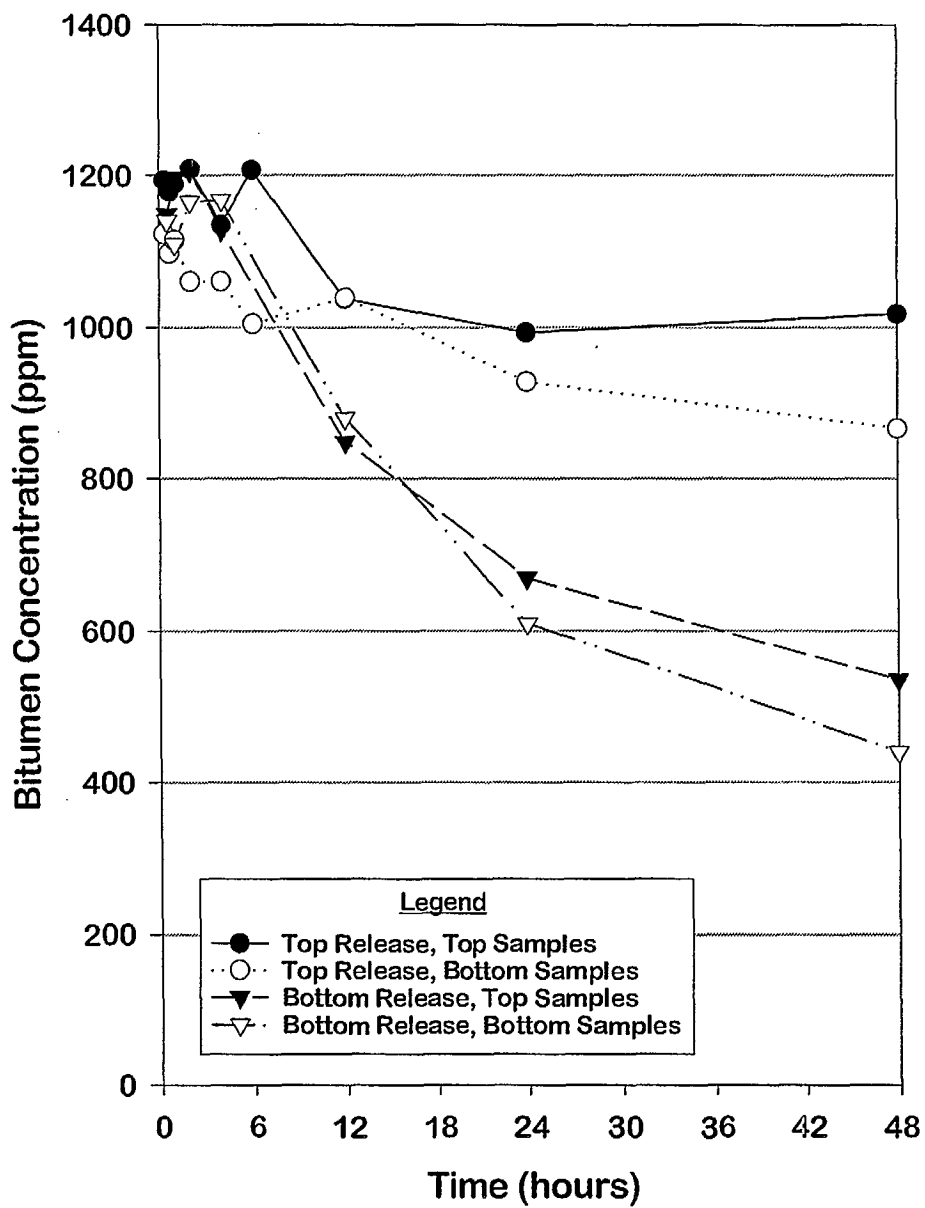


Figure 4 Orimulsion-100 in Salt Water

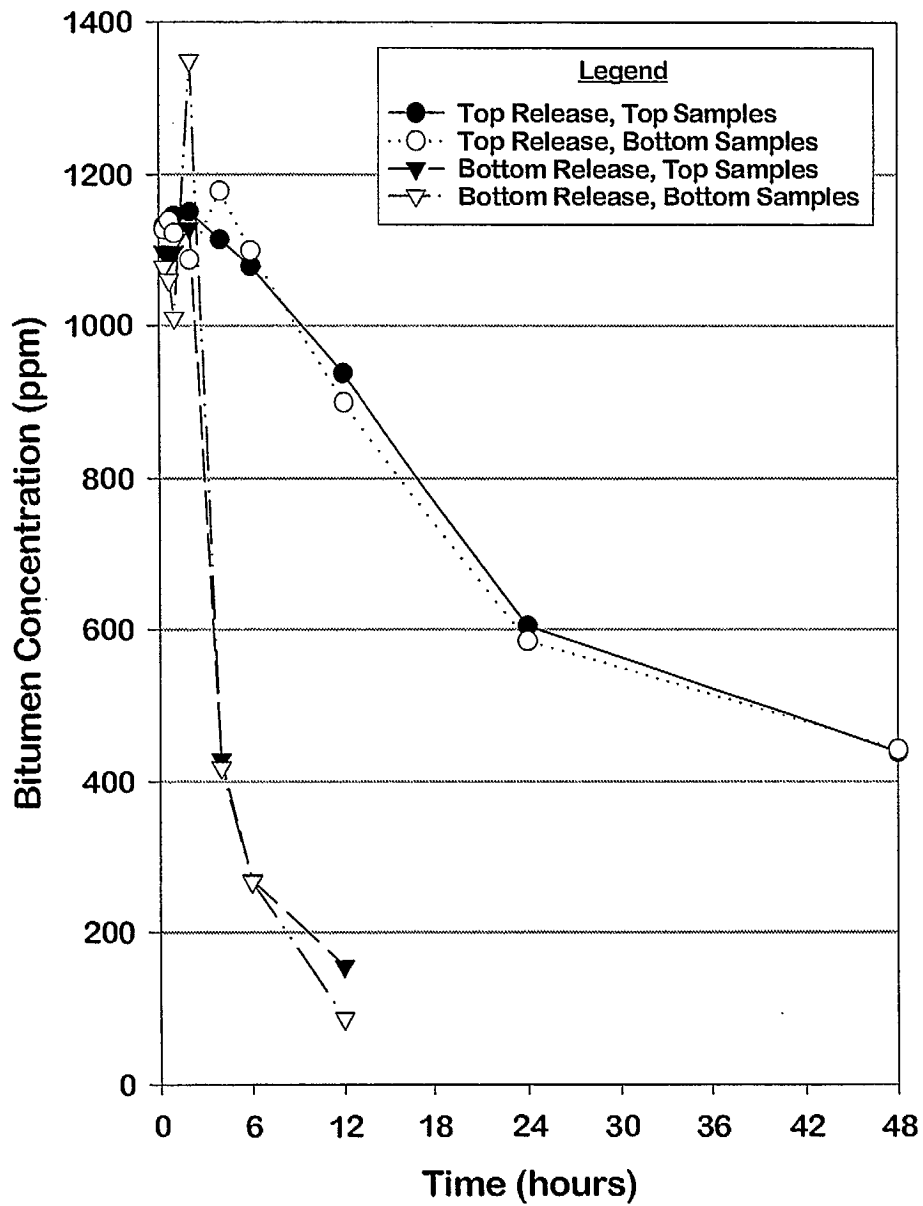


Figure 5 Orimulsion-400 in Salt Water

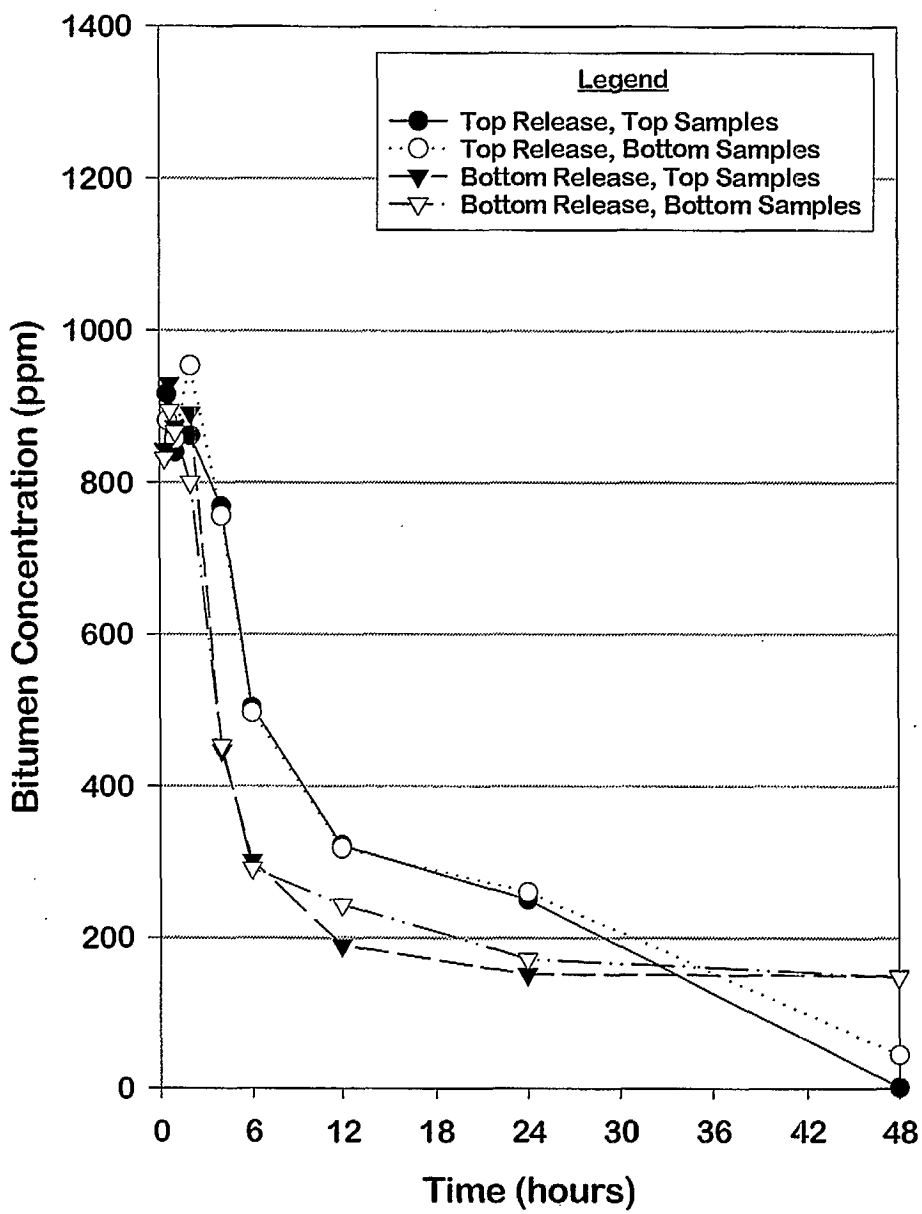


Figure 6 Orimulsion-100 in Fresh Water

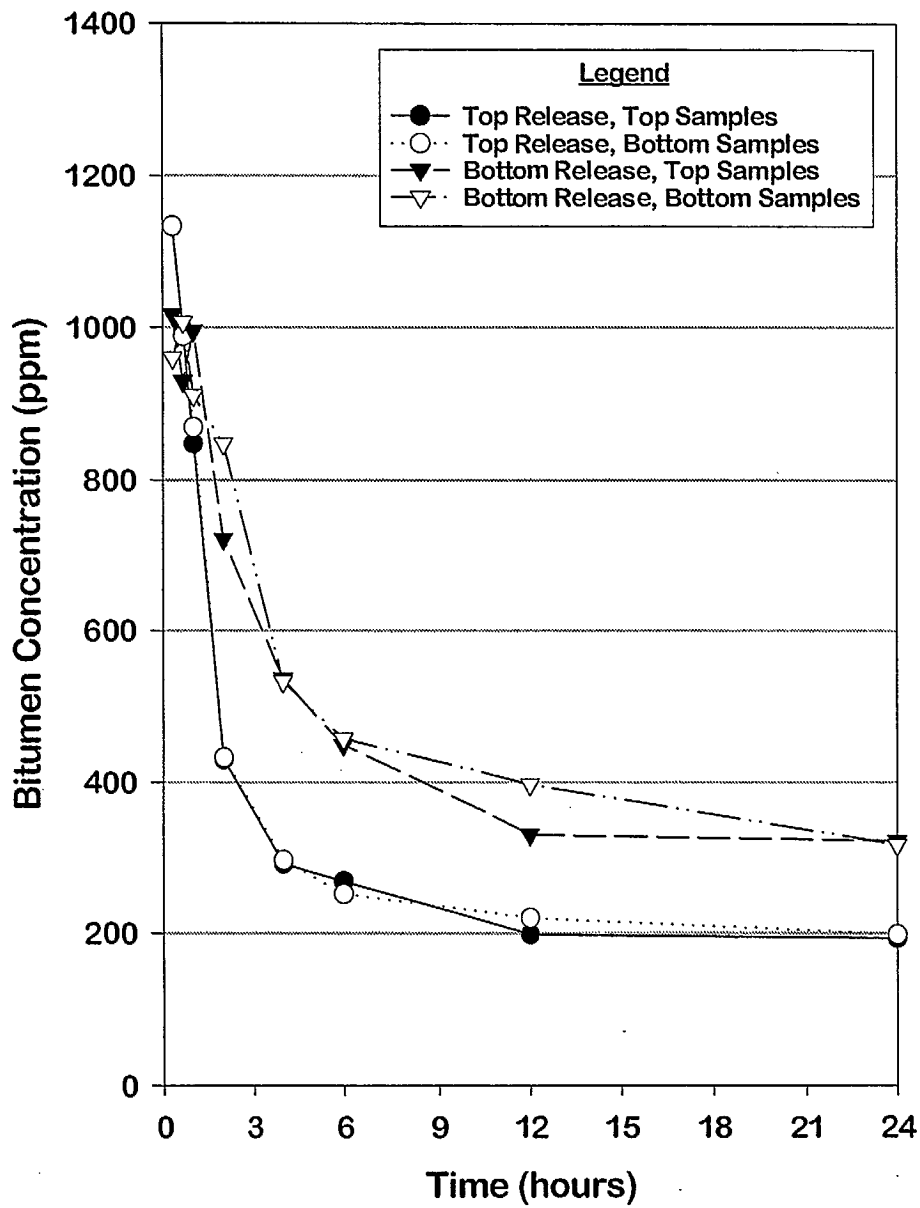


Figure 7 Orimulsion-400 in Fresh Water



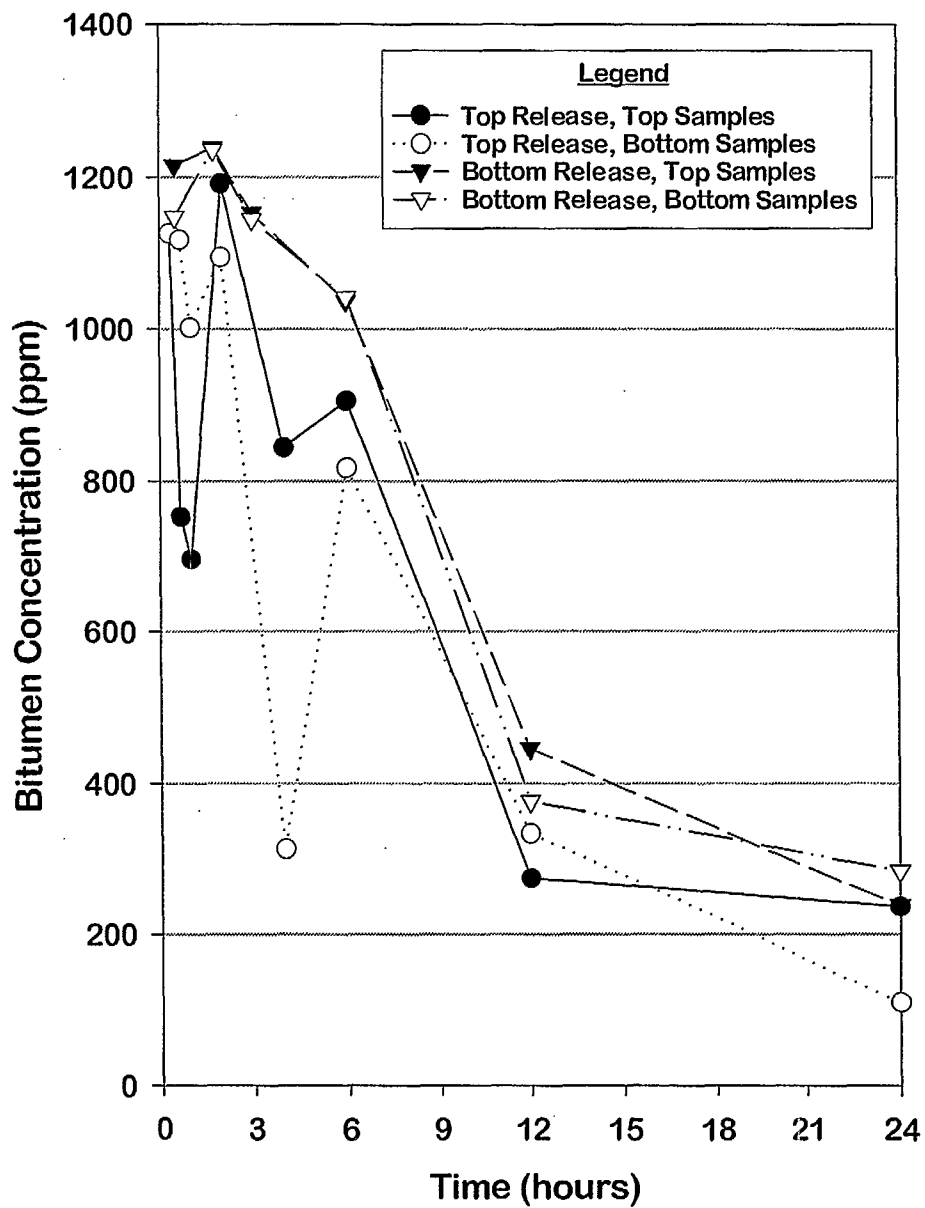


Figure 8 Orimulsion-100 in Brackish Water

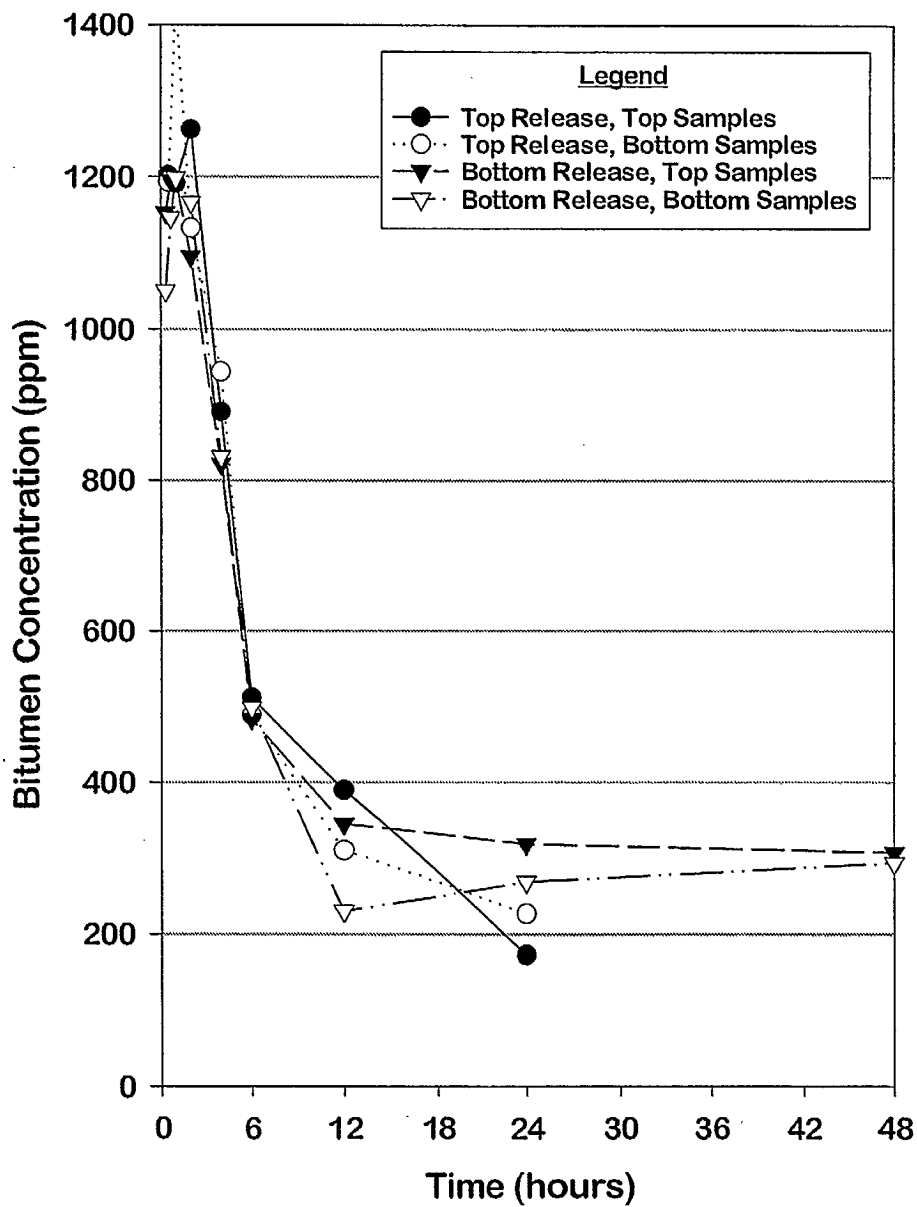


Figure 9 Orimulsion-400 in Brackish Water

(Figure 4). When Orimulsion-100 was added at the surface, there was a 20% decrease in bitumen concentration over 48 hours, compared to a 55% decrease in bitumen concentration over the same period of time when Orimulsion-100 was added at the bottom of the tank. When Orimulsion-400 was added at the surface, there was a 60% decrease in bitumen concentration over 48 hours and a 90% decrease in bitumen concentration over only 12 hours when Orimulsion-400 was added at the bottom of the tank.

During and after the salt water experiments with Orimulsion-100, it was observed that a lot of bitumen was suspended as small flocs (< 5 mm diameter). Even under static conditions (no hoop movement), these bits tended to rise to the surface, but not coalesce into a slick and when disturbed even slightly became resuspended. This behaviour was unexpected and may have been caused by a combination of temperature changes during the run (possibly as much as 5°C) and by the action of the hoop, as in salt water the bitumen droplets coalesce rapidly (see Section 3.2, Particle Size Distribution) and spend more time in the mixing zone as they rise toward the surface.

The more rapid decrease in bitumen concentration during the bottom addition experiments may be due to differences in surfactant concentration as the surfactant partitions into the water. This would be consistent with the very rapid change in concentration during the O400SB experiment, as the surfactant in Orimulsion-400 is different from the one in Orimulsion-100 and has been observed to be less stable in salt water (Jokuty *et al.*, 1999).

### 3.1.3 Fresh Water

In fresh water, much more of the bitumen is removed from the water column over a 48-hour period, compared to salt water. With Orimulsion-100, the bitumen concentration decreased by more than 95% during the top release experiment and by 80% during the bottom release experiment (Figure 6). With Orimulsion-400, the bitumen concentration decreased by 85% during the 24-hour top release experiment and by 65% during the 48-hour bottom release experiment (Figure 7). At the end of all fresh water experiments, bitumen formed a sediment layer on the bottom of the tank, which was clearly visible through the water column.

### 3.1.4 Brackish Water

In the brackish water experiments, the accumulation of bitumen between the hoop and the tank wall ended three of the four runs early, at 24 hours. Experiment O400BB went a full 48 hours. In all four experiments, the bitumen concentration decreased by roughly the same amount, 75 to 85%. When Orimulsion-100 was released at the bottom of the tank, the decrease in bitumen concentration was fairly smooth but when it was released at the surface, large fluctuations were measured in the bitumen concentration during the first six hours (Figure 8). The concentrations then stabilized and nearly paralleled the bottom release results. The concentration decrease in both Orimulsion-400 experiments was fairly smooth (Figure 9), with only one upward spike in the concentration during the early stages of the top release experiment. The observed concentration fluctuations are characteristic in brackish water (at 2.0% salt), where even small temperature changes have a critical effect on the relative densities of the water and the bitumen, making the movement of the bitumen within the water column somewhat unpredictable.

## 3.2 Particle Size Distribution

### 3.2.1 General Comments

When comparing results for different types of water, it must be noted that the limitations of the instrument were such that particles larger than  $45\ \mu\text{m}$  could not be measured and plugging of the orifice that the particles pass through ( $70\ \mu\text{m}$  diameter) determined the maximum time interval for which a distribution could be measured properly. When comparing results for the two types of Orimulsion, it should be recalled that the median particle diameter was  $15\ \mu\text{m}$  for the Orimulsion-100 and  $20\ \mu\text{m}$  for the Orimulsion-400.

Figures 10 to 21 show how the cumulative volume percentage of particle changes with time for each experiment. Figures 22 and 23 illustrate the effect of salinity on the median particle diameter during the first hour of the experiments for Orimulsion-100 and Orimulsion-400, respectively.

### 3.2.2 Salt Water

In salt water (Figures 10 to 13), the rapid shift toward larger diameter particles, on a cumulative percentage basis, indicates particle coalescence. The diameters of the largest particles exceed  $70\ \mu\text{m}$  within 30 to 45 minutes, becoming too large to pass through the aperture of the instrument. The particles remain too large to measure throughout the 48 hours of agitation. No significant differences were observed between the surface and subsurface releases of Orimulsion. The changes observed in particle size distribution were also similar for both types of Orimulsion.

### 3.2.3 Fresh Water

In fresh water (Figures 14 to 17), an increasing percentage of smaller particles contributes to the cumulative volume, as coalescence occurs to a much lesser degree and the larger particles settle out. This difference is due to the much greater stability of the surfactant in fresh water. Again, no significant differences in this decrease were observed as a result of the surface or subsurface addition of the Orimulsion and the changes observed in particle size distribution were similar for both types of Orimulsion.

### 3.2.4 Brackish Water

In brackish water, differences were observed between the top addition experiment and the bottom addition experiment with Orimulsion-100. When the Orimulsion was added at the top of the tank (Figure 18), the median particle size (50 volume percent) increased to nearly  $25\ \mu\text{m}$  within the first half hour, but by 24 hours, the median particle diameter had decreased to about  $11\ \mu\text{m}$  in the sample taken from the top of the water column and  $15\ \mu\text{m}$  in the sample from the bottom. When the Orimulsion was added at the bottom of the tank (Figure 19), there was very little difference between the distribution of particle diameters at 15 minutes and 24 hours for samples taken at the top of the water column, but the 24-hour sample taken at the bottom of the tank had a median particle diameter of approximately  $28\ \mu\text{m}$ , indicating that coalescence was still occurring. This difference between top and bottom again highlights the difficulty in precisely predicting Orimulsion behaviour in brackish water. No such differences were observed in the experiments with Orimulsion-400 (Figures 20 and 21), where the changes in particle size distribution are similar to those seen in salt water.

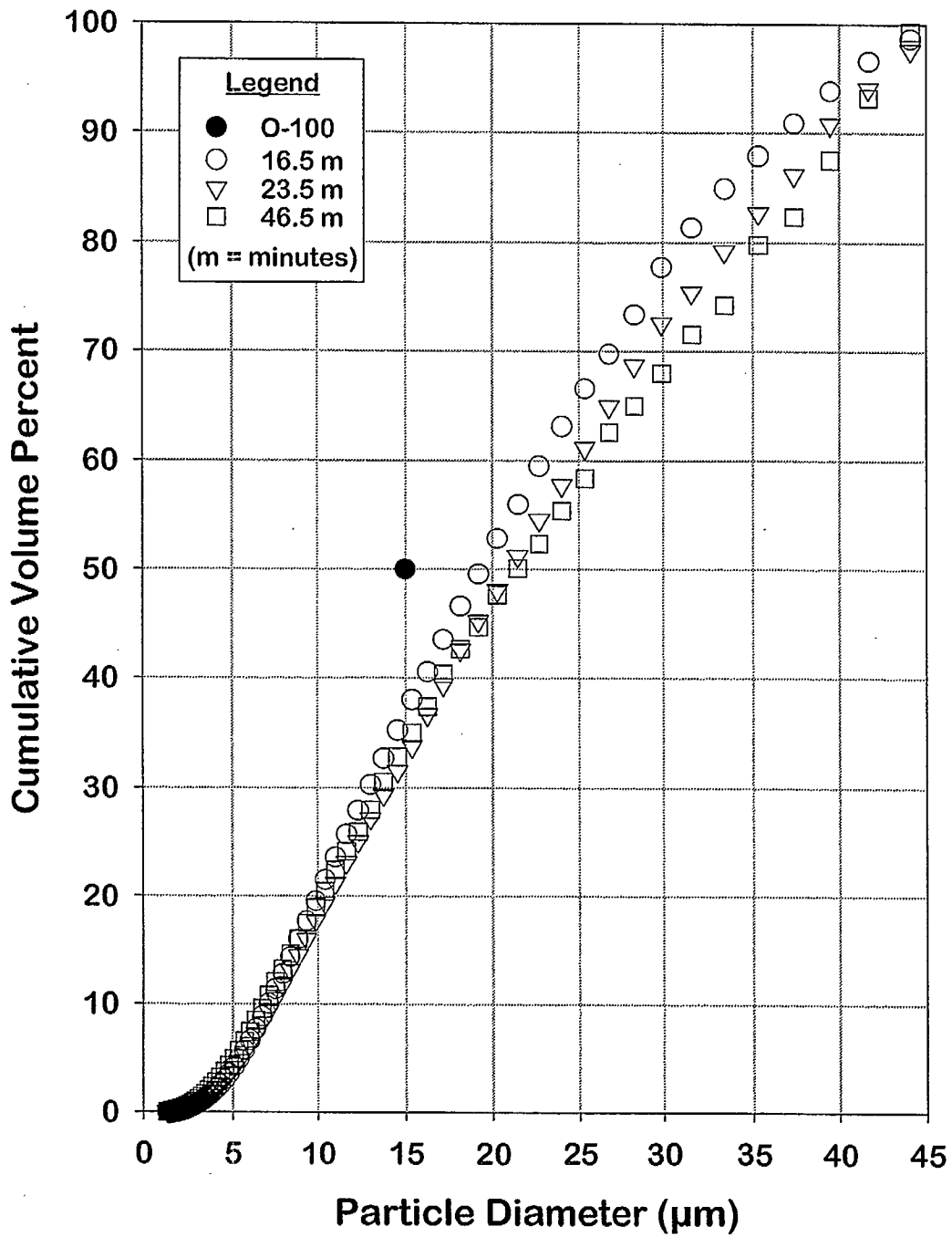


Figure 10 Particle Size Distribution - Experiment O100ST

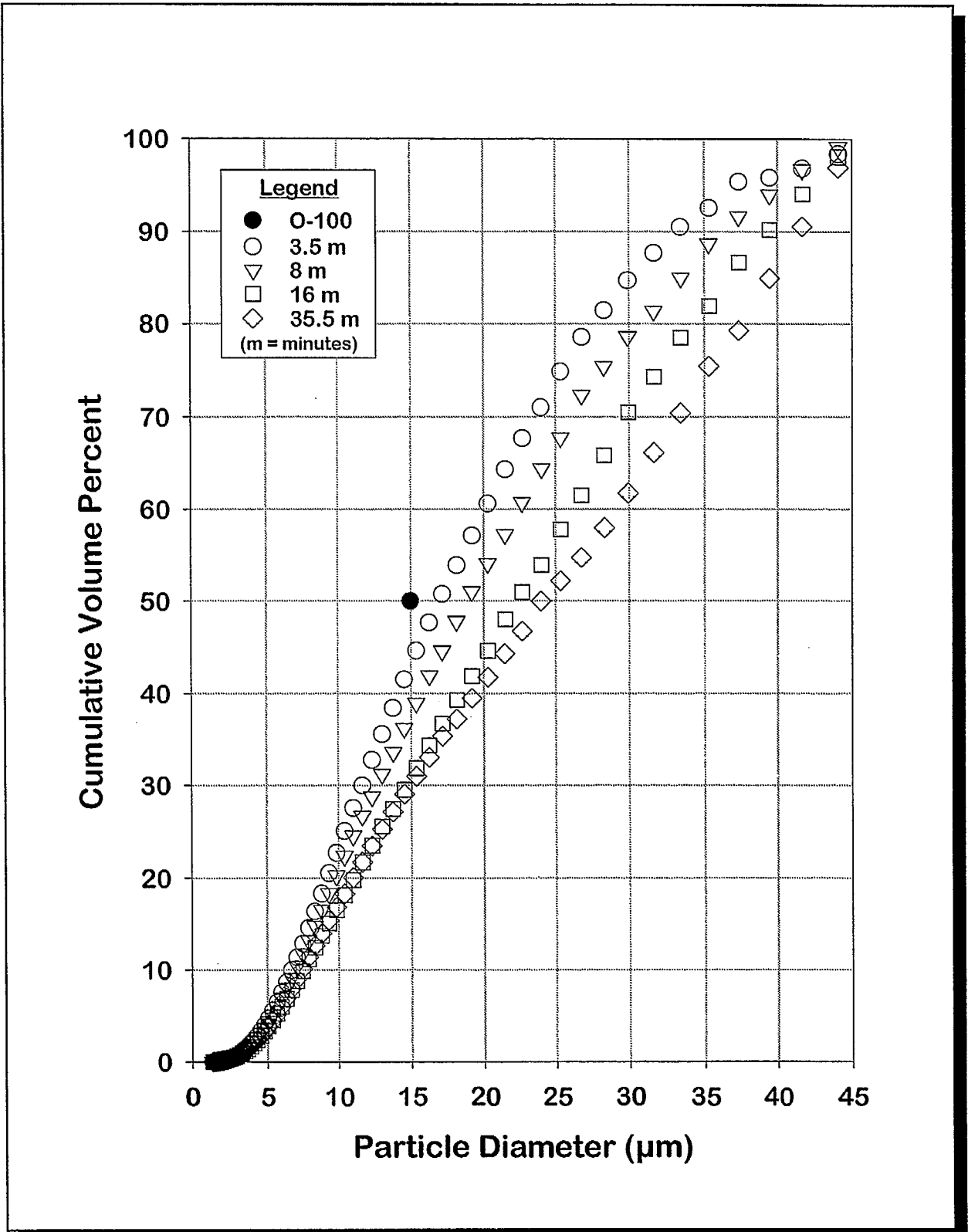


Figure 11 Particle Size Distribution - Experiment O100SB

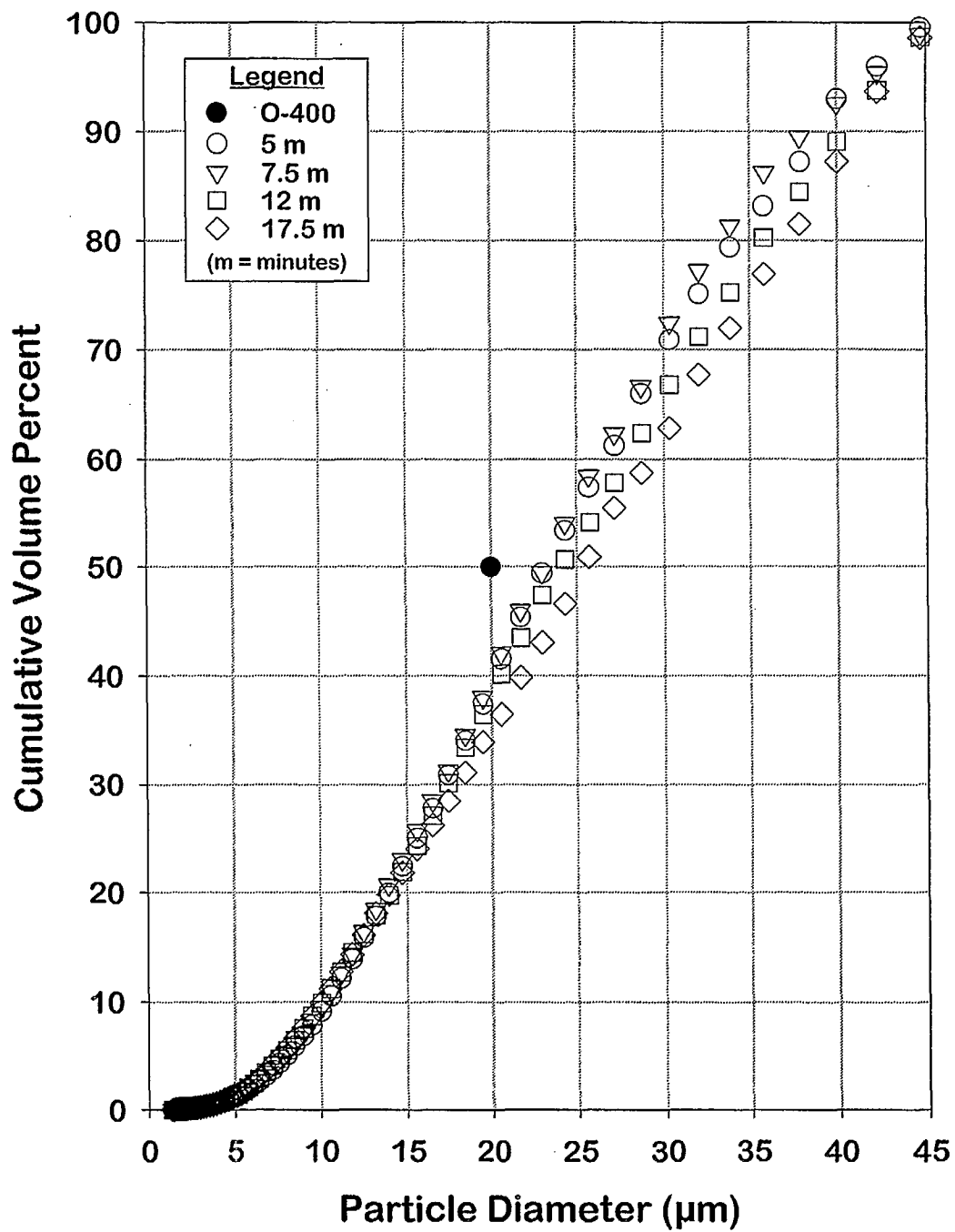


Figure 12 Particle Size Distribution - Experiment O400ST

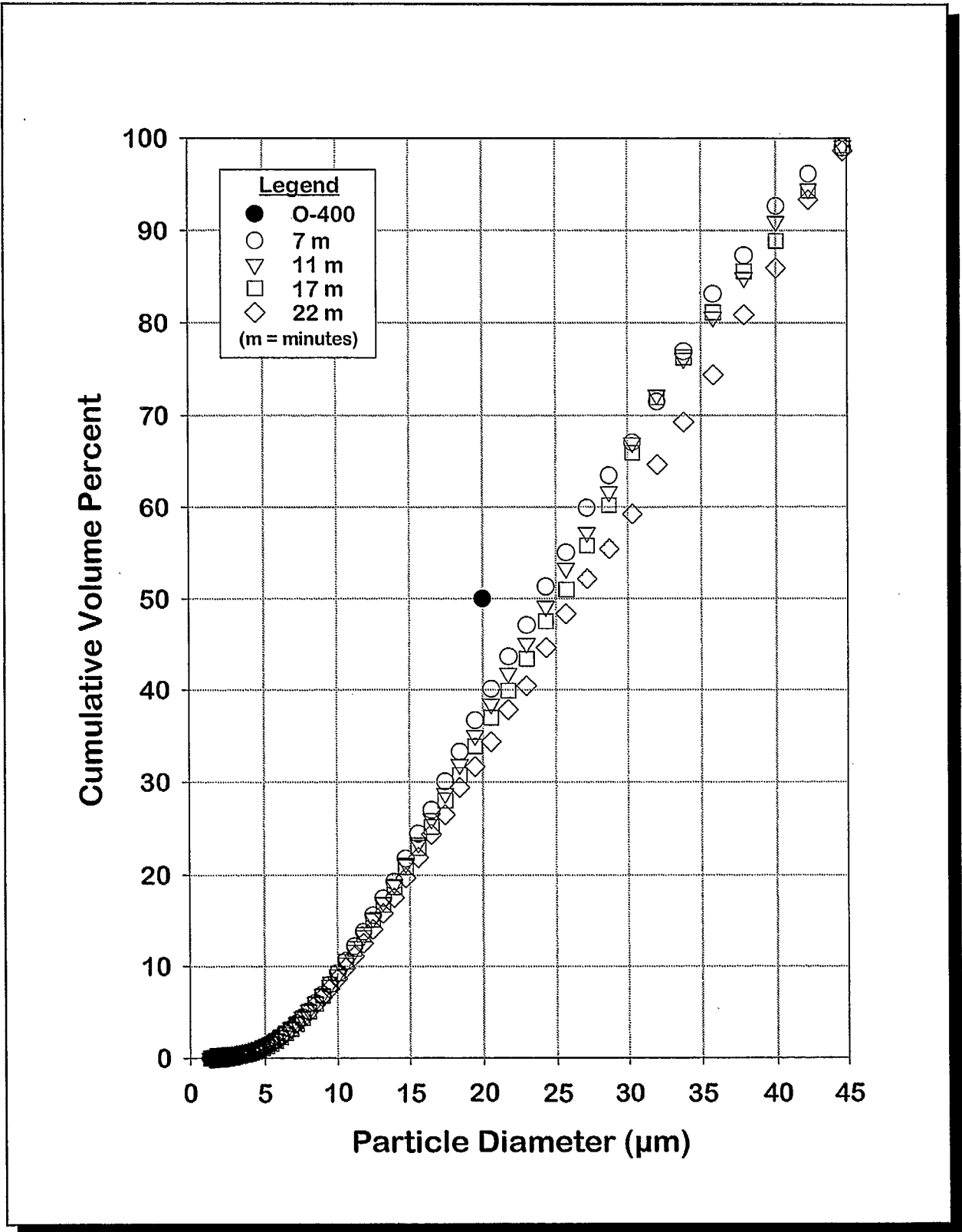


Figure 13 Particle Size Distribution - Experiment O400SB



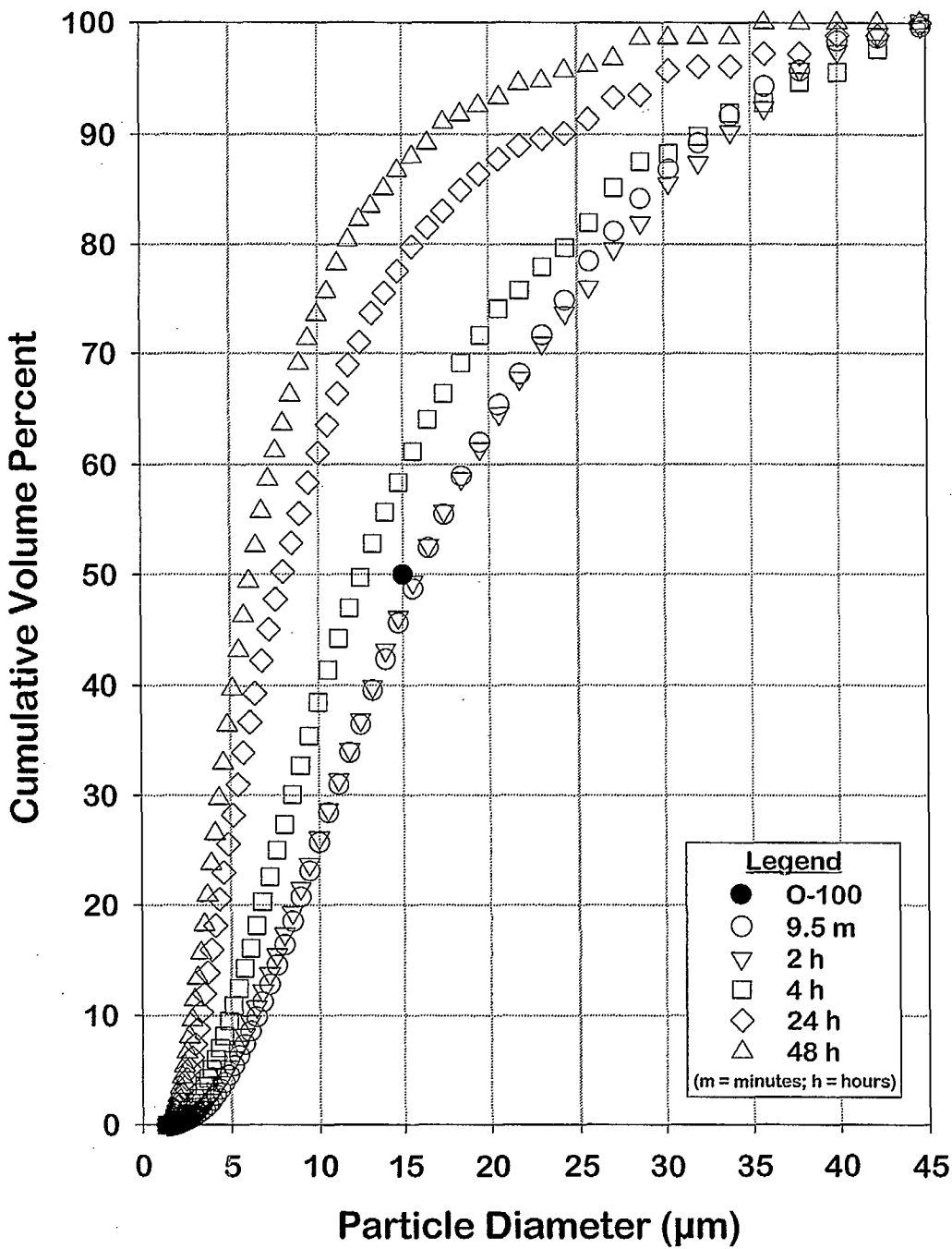


Figure 14 Particle Size Distribution - Experiment O100FT

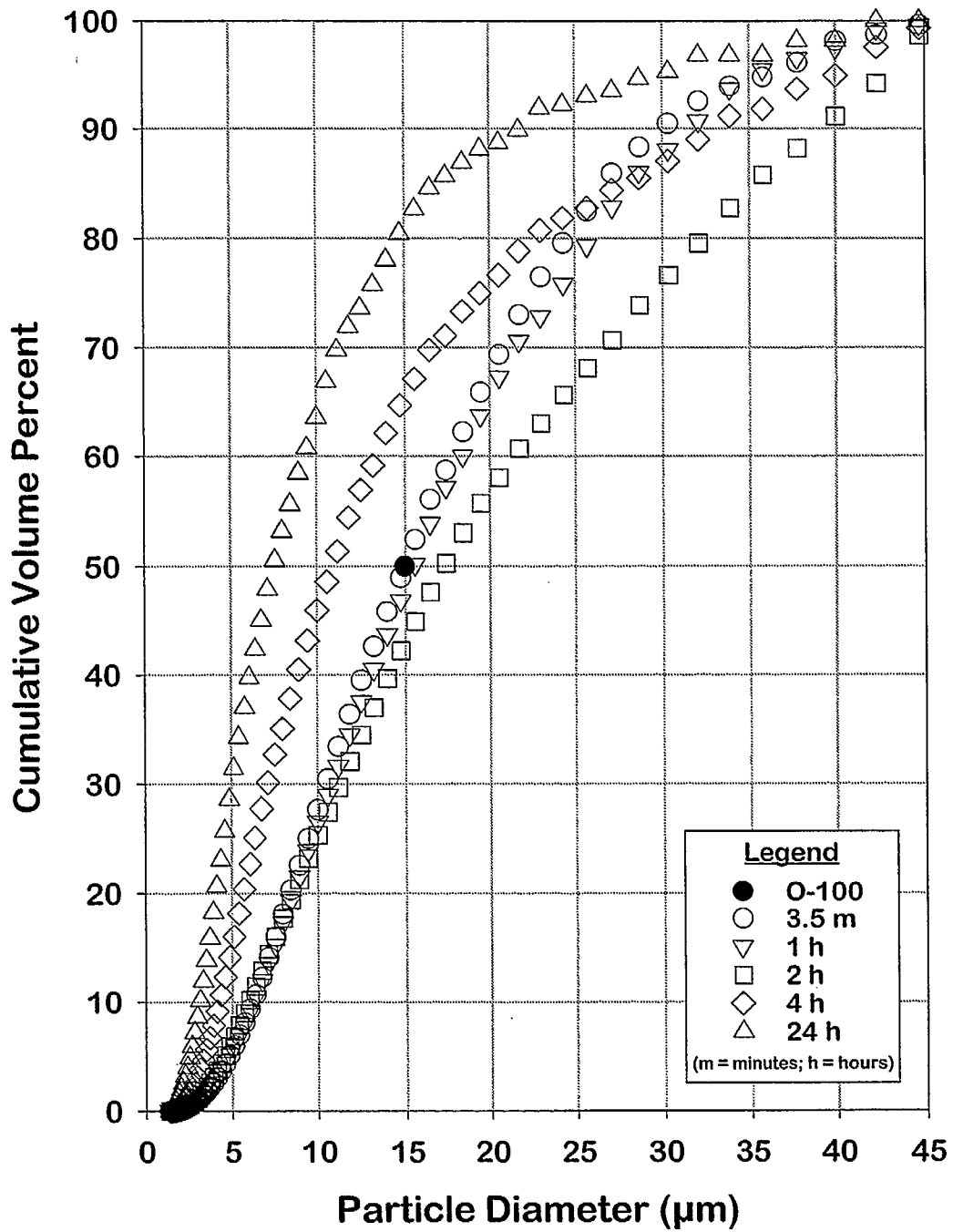


Figure 15 Particle Size Distribution - Experiment O100FB

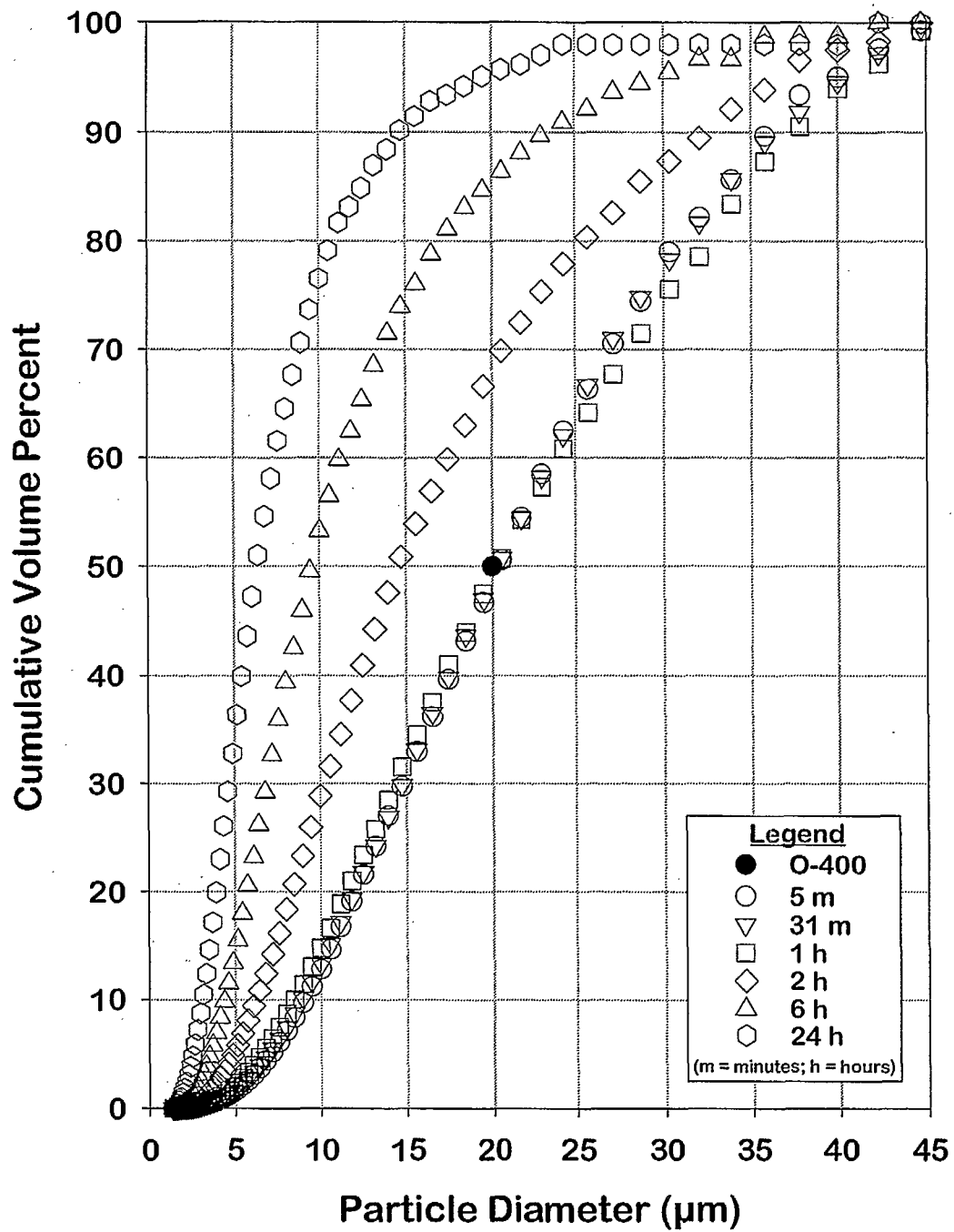


Figure 16 Particle Size Distribution - Experiment O400FT

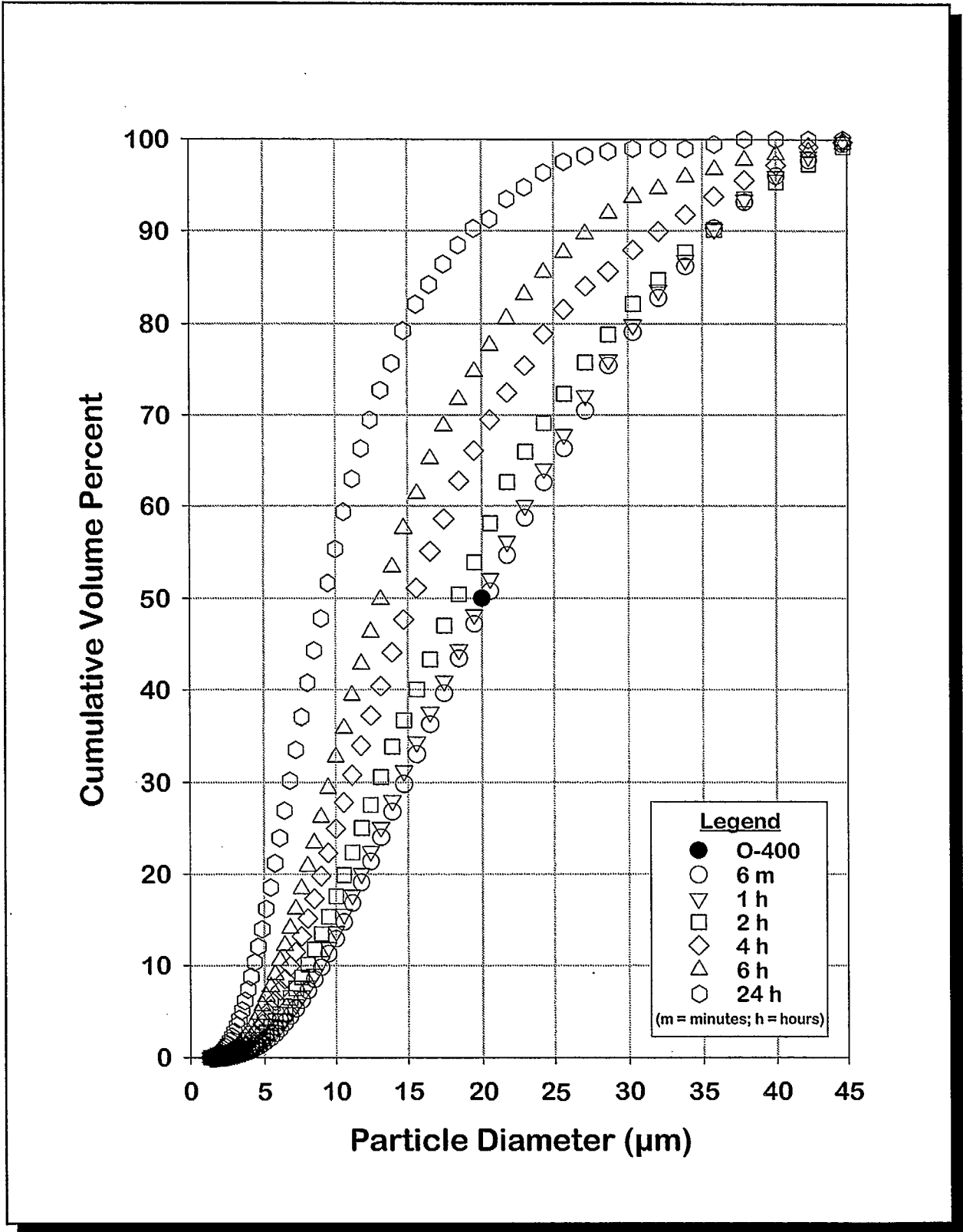


Figure 17 Particle Size Distribution - Experiment O400FB

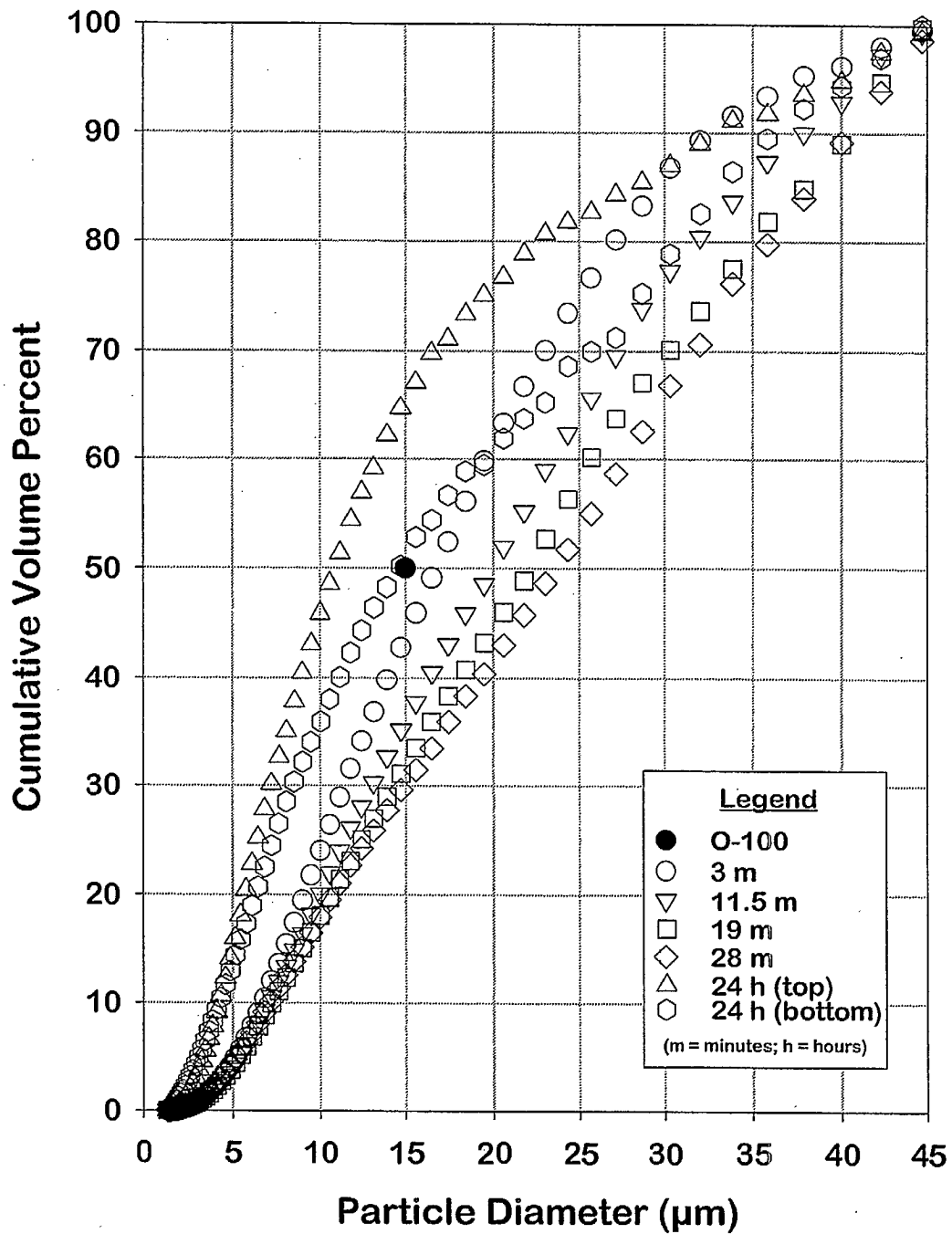


Figure 18 Particle Size Distribution - Experiment O100BT

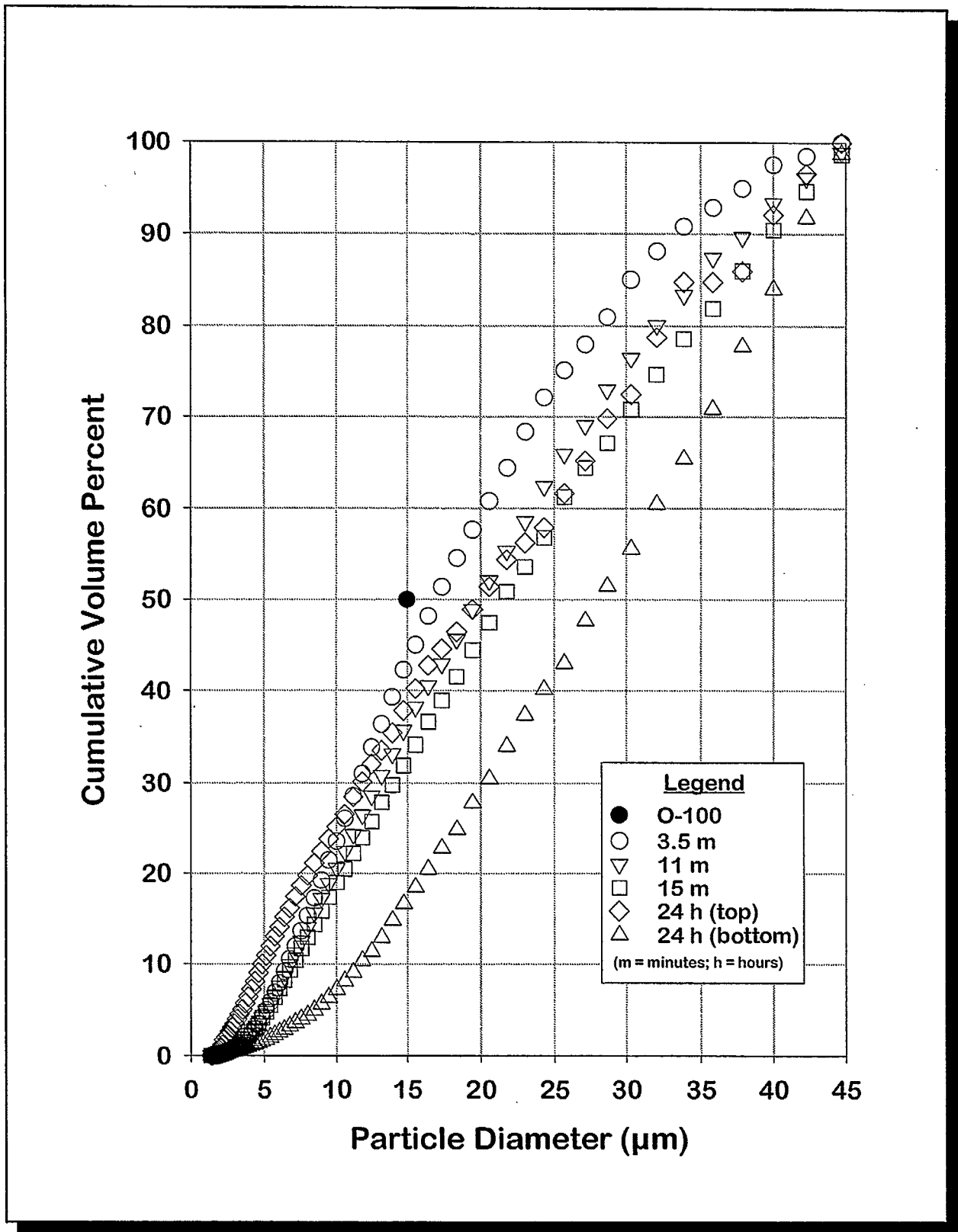


Figure 19 Particle Size Distribution - Experiment O100BB

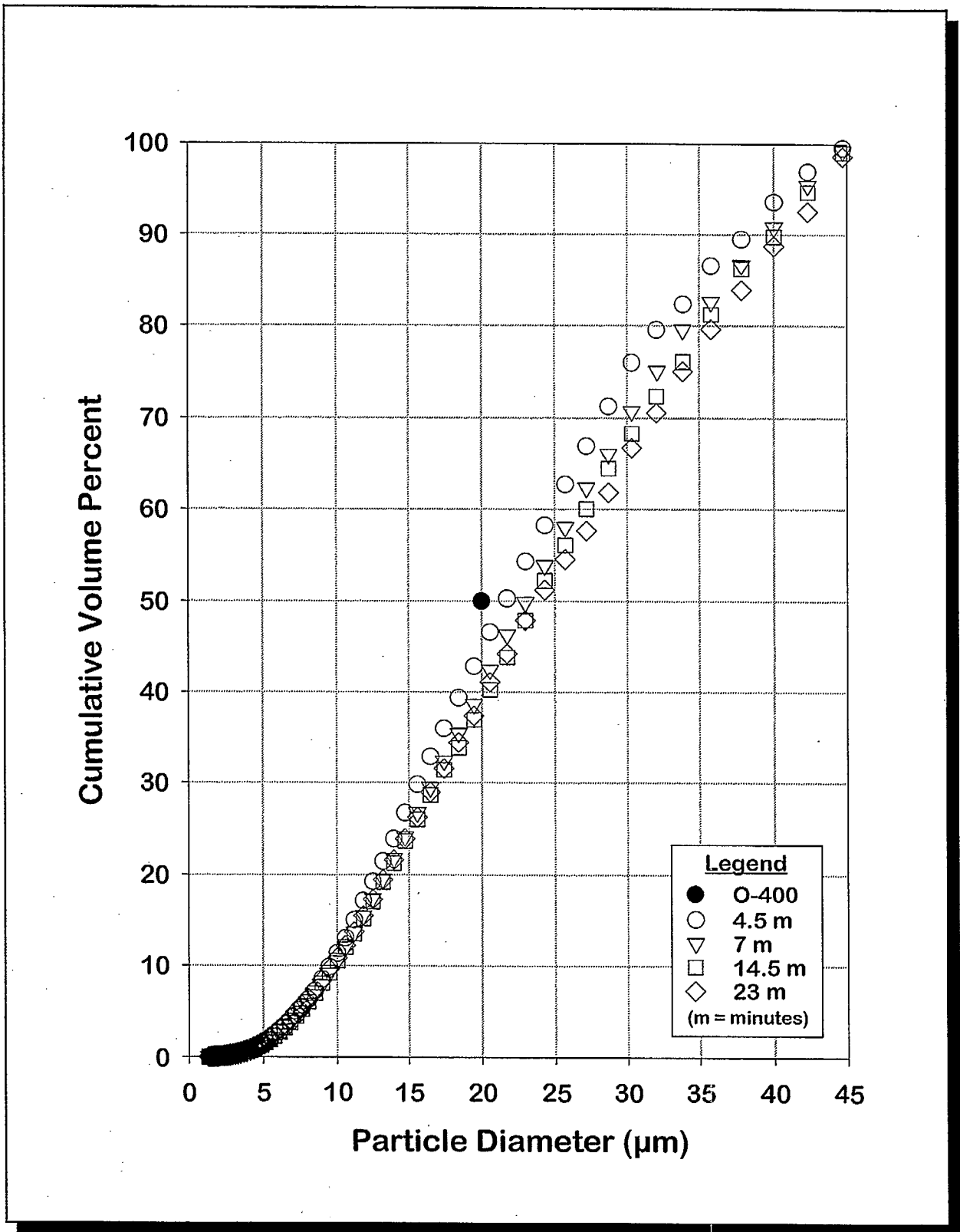


Figure 20 Particle Size Distribution - Experiment O400BT

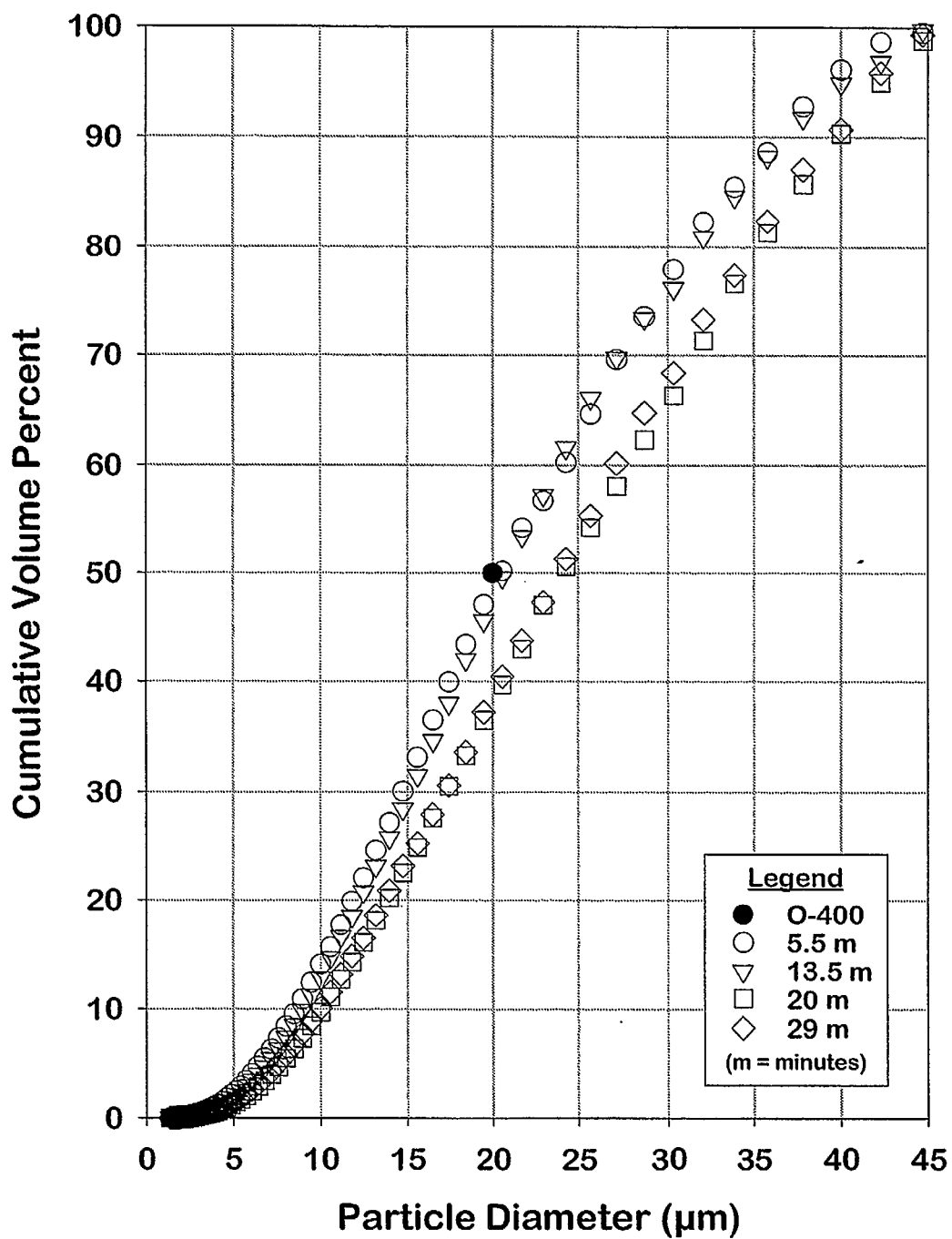


Figure 21 Particle Size Distribution - Experiment O400BB



### 3.2.5 Salinity Effects

The significant effect of salinity on median particle size within one hour, as shown in Figures 22 and 23, demonstrates that coalescence is occurring rapidly in salt and brackish water, but not in fresh water. The rate of change in median particle diameter appears to be similar for both types of Orimulsion, but as the initial particle size is larger in Orimulsion-400, it becomes unmeasurable sooner in salt and brackish water, compared to Orimulsion-100.

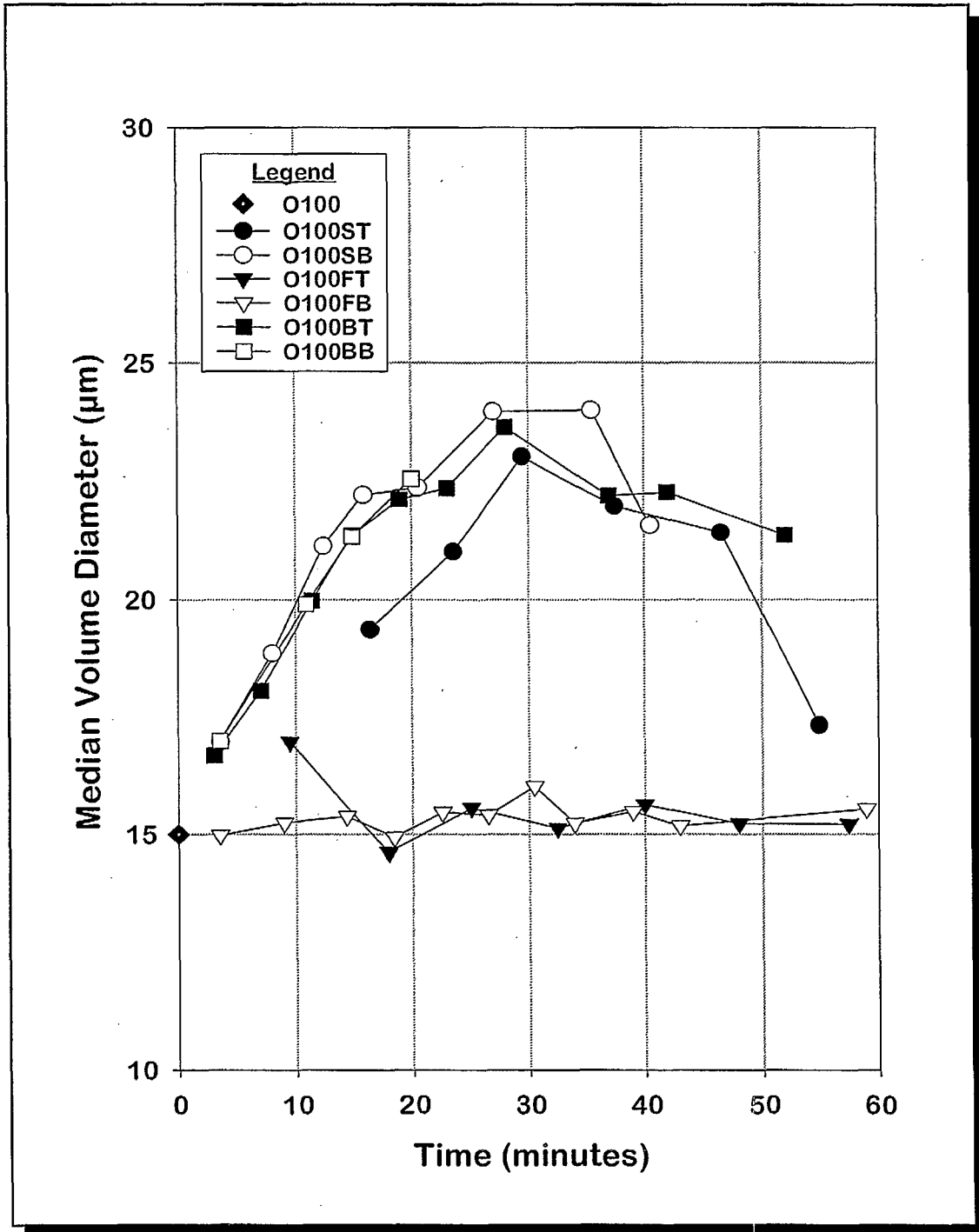


Figure 22 Effect of Salinity on Particle Diameter - Orimulsion-100 Experiments

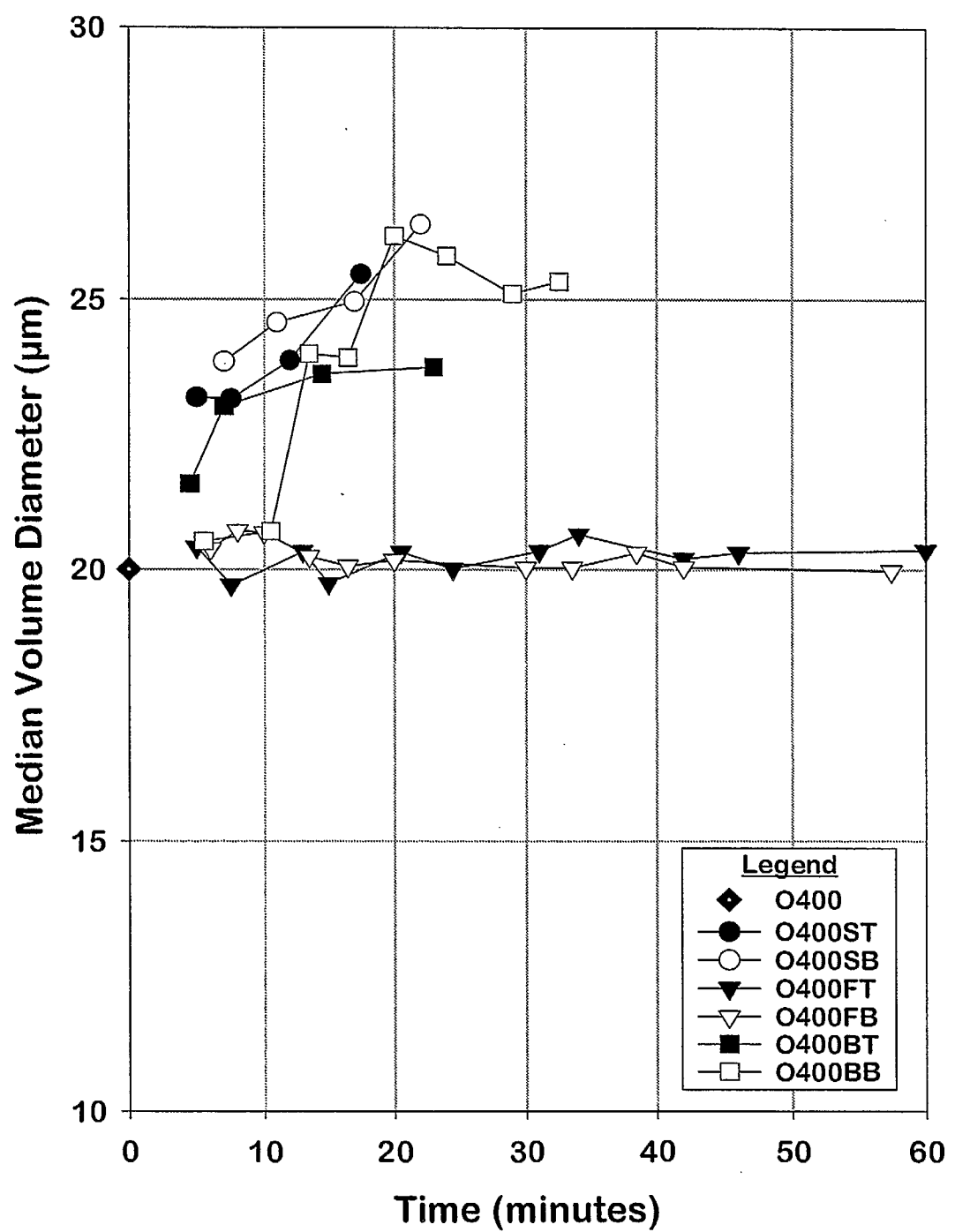


Figure 23 Effect of Salinity on Particle Diameter - Orimulsion-400 Experiments

## 4. CONCLUSIONS

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The following conclusions can be drawn from these experiments.

1. Orimulsion coalesces in salt (3.3%) and brackish (2%) water. The coalescence is rapid, resulting in a significant increase in median particle diameter within one hour. Orimulsion does not coalesce in fresh water, as the median particle diameter remains the same.
2. In general, the concentration of bitumen in the water column decreases significantly within 48 hours. This is true for all salinity levels. In salt water, surface releases of Orimulsion result in much slower rates of bitumen decrease than subsurface releases. Orimulsion-400 is removed much more rapidly from salt water than is Orimulsion-100, but decreases in bitumen in fresh and brackish water are comparable for both types of Orimulsion.
3. For salt and brackish water, the bitumen from the water column accumulates mainly at surfaces in zones of agitation. For fresh water, sedimentation plays a major role.
4. The behaviour of Orimulsion in salt water or fresh water is fairly predictable, but in brackish water Orimulsion behaviour can be very difficult to predict.

## 5. REFERENCES

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- Intevep, *Characterization of Orimulsion® Quality Control Manual Version 2.0*, Bitumenes Orinoco, S.A., Venezuela, 1993.
- Jokuty, P., S. Whitar, Z. Wang, K. Doe, B. Fieldhouse, and M. Fingas, "Orimulsion-400: A Comparative Study", Manuscript Report EE-160, Environmental Protection Service, Environment Canada, Ottawa, ON, 1999.
- Jokuty, P., S. Whitar, M. Fingas, Z. Wang, K. Doe, D. Kyle, P. Lambert, and B. Fieldhouse, "Orimulsion: Physical Properties, Chemical Composition, Dispersibility, and Toxicity", Manuscript Report EE-154, Environmental Protection Service, Environment Canada, Ottawa, ON, 38 p. 1995.

## **Appendix A - Analytical Methods**

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### **Water Content**

Water content was determined by Karl Fischer titration, as in ASTM method D 4377 (ASTM, 1999a), with the following modifications. A Metrohm 701 KF automatic titrator was used and the sample was dissolved in a pre-titrated 1:1:2 volume mixture of methanol/chloroform/toluene. Samples were run in triplicate and the mean water content is reported.

### **Density**

Density was measured using an Anton Parr DMA 48 digital density meter and following ASTM method D 5002 (ASTM, 1999b). Samples were run in duplicate and the mean density is reported.

### **Viscosity**

Dynamic viscosity was determined using a HAAKE RV20 Rotovisco with the M5 measuring system, SV1 sensor, and HAAKE RC20 Rheocontroller. Although this type of instrument is widely used in industry, there are no ASTM standard methods for the determination of viscosity using concentric cylinder rotational viscometers. The following procedure was used. An aliquot of Orimulsion was obtained using a 10-mL disposable syringe (no needle). The excess was wiped from the outside of the syringe and the sample cup was carefully filled. The sample was allowed to equilibrate for approximately 15 minutes at 0°C or for 5 minutes at 15°C. Samples at both temperatures were only slightly non-Newtonian and were measured at a single shear rate of 100/s. The shear rate was ramped up 5 minutes, held 5 minutes, and ramped down 5 minutes. Samples were run in duplicate and the mean viscosity is reported.

### **Pour Point**

The Orimulsion was poured into test jars meeting the specifications of ASTM method D 97 (ASTM, 1999c). The test jars were fitted with stoppers and ASTM-designated thermometers and warmed in a water bath to 50°C. The samples were removed from the bath and allowed to cool to room temperature. For additional cooling, the samples were moved sequentially to a cold room maintained at 5°C and a freezer at -25°C. While cooling, the sample was checked periodically as per ASTM method D 97, but not necessarily at multiples of 3°C. When the pour point was reached, 3°C was added to the temperature recorded from the thermometer, as specified in the ASTM method. This value is reported as the pour point. Samples were run in duplicate and the mean pour point is reported.

### **Adhesion**

This method requires the use of an analytical pan balance capable of weighing to 0.0001 g, with provision for weighing from below the pan and a standard penetrometer needle as described in ASTM method D 5 (ASTM, 1999d), adapted for hanging below the balance. Adhesion measurements were made according to the following protocol.

The balance was prepared for measurement by hanging a penetrometer needle, for which the surface area of the stainless steel section had been calculated, from the balance hook and allowing the weight to stabilize. The weight of the clean needle was recorded. Approximately

80 mL of sample was placed in a 100-mL beaker and elevated, using a lab jack, until the top of the stainless steel needle met the top of the oil. The needle was left in the oil for 30 seconds and then the beaker was lowered, allowing the needle to hang undisturbed. After 30 minutes, the weight of the needle plus oil was recorded. The needle was cleaned with dichloromethane and allowed to dry before the measurement was repeated.

Five replicate measurements were made. The oil adhesion was calculated as the weight of oil remaining on the needle divided by the needle's surface area. The mean value  $\pm$  one standard deviation is reported.

### **Particle Size Distribution**

Particle size distribution was determined using a Coulter Counter Multisizer with AccuComp software. The Coulter Counter determines particle size by measuring the increase in voltage as a particle passes through a small aperture between two electrodes. The particles are suspended in an electrolytic solution that is drawn by vacuum suction through a small aperture separating two electrodes under applied current. As a particle passes through the aperture, there is an increase in resistance between the electrodes that results in a voltage pulse. The magnitude of the voltage pulse is proportional to the volume of the particle passing through the aperture. The voltage pulses are scaled and counted by the AccuComp<sup>R</sup> software package, which can then mathematically manipulate the data to provide particle size distribution information.

### **Bitumen Concentration**

Each water sample was extracted in a 125-mL separatory funnel with three 25-mL portions of dichloromethane. The dichloromethane was collected in 125-mL boiling flasks and the solvent recovered by rotary evaporation. The bitumen remaining was weighed and the concentration calculated as parts-per-million of bitumen in water.

### **References**

- ASTM (American Society for Testing and Materials), "D 4377 Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration", in *Annual Book of ASTM Standards - Section 5 Petroleum Products, Lubricants, and Fossil Fuels*, American Society for Testing and Materials, West Conshohocken, PA, 1999a.
- ASTM (American Society for Testing and Materials), "D 5002 Test Method for Density and Relative Density of Crude Oils by Digital Density Meter", in *Annual Book of ASTM Standards - Section 5 Petroleum Products, Lubricants, and Fossil Fuels*, American Society for Testing and Materials, West Conshohocken, PA, 1999b.
- ASTM (American Society for Testing and Materials), "D 97 Test Method for Pour Point of Petroleum Products", in *Annual Book of ASTM Standards - Section 5 Petroleum Products, Lubricants, and Fossil Fuels*, American Society for Testing and Materials, West Conshohocken, PA, 1999c.
- ASTM (American Society for Testing and Materials), "D 95 Test Method for Penetration of Bituminous Materials", in *Annual Book of ASTM Standards - Section 4 Construction*, American Society for Testing and Materials, West Conshohocken, PA, 1999d.

## Appendix B - Bitumen Concentration Data

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Table B1 Concentration Data for Experiment O100ST

Time (hours)	Sample Point	Bitumen Concentration (ppm)
0.33	top	1,193
0.67	top	1,173
1	top	1,188
2	top	1,208
4	top	1,135
6	top	1,207
12	top	1,038
24	top	993
48	top	1,018
0.33	bottom	1,123
0.67	bottom	1,098
1	bottom	1,115
2	bottom	1,062
4	bottom	1,062
6	bottom	1,005
12	bottom	1,040
24	bottom	928
48	bottom	867

Table B2 Concentration Data for Experiment O100SB

Time (hours)	Sample Point	Bitumen Concentration (ppm)
0.5	top	1,148
1	top	1,197
2	top	1,205
4	top	1,128
12	top	848
24	top	670
48	top	535
0.5	bottom	1,140
1	bottom	1,110
2	bottom	1,165
4	bottom	1,167
12	bottom	880
24	bottom	610
48	bottom	440

**Table B3 Concentration Data for Experiment O100FT**

<b>Time (hours)</b>	<b>Sample Point</b>	<b>Bitumen Concentration (ppm)</b>
0.5	top	917
1	top	840
2	top	862
4	top	768
6	top	503
12	top	323
24	top	252
48	top	2
0.5	bottom	882
1	bottom	857
2	bottom	953
4	bottom	757
6	bottom	497
12	bottom	320
24	bottom	262
48	bottom	45

**Table B4 Concentration Data for Experiment O100FB**

<b>Time (hours)</b>	<b>Sample Point</b>	<b>Bitumen Concentration (ppm)</b>
0.33	top	843
0.67	top	930
1	top	873
2	top	892
4	top	447
6	top	303
12	top	190
24	top	152
48	top	150
0.33	bottom	832
0.67	bottom	895
1	bottom	867
2	bottom	800
4	bottom	453
6	bottom	293
12	bottom	245
24	bottom	172
48	bottom	148



**Table B5. Concentration Data for Experiment O100BT**

<b>Time (hours)</b>	<b>Sample Point</b>	<b>Bitumen Concentration (ppm)</b>
0.33	top	1,127
0.67	top	753
1	top	697
2	top	1,192
4	top	843
6	top	905
12	top	275
24	top	237
0.33	bottom	1,127
0.67	bottom	1,118
1	bottom	1,002
2	bottom	1,095
4	bottom	315
6	bottom	817
12	bottom	335
24	bottom	110

**Table B6 Concentration Data for Experiment O100BB**

<b>Time (hours)</b>	<b>Sample Point</b>	<b>Bitumen Concentration (ppm)</b>
0.5	top	1,215
1.75	top	1,238
3	top	1,153
6	top	1,037
12	top	445
24	top	238
0.5	bottom	1,148
1.75	bottom	1,235
3	bottom	1,145
6	bottom	1,042
12	bottom	377
24	bottom	285

**Table B7 Concentration Data for Experiment O400ST**

<b>Time (hours)</b>	<b>Sample Point</b>	<b>Bitumen Concentration (ppm)</b>
0.33	top	1,132
0.67	top	1,133
1	top	1,145
2	top	1,150
4	top	1,113
6	top	1,078
12	top	937
24	top	605
48	top	438
0.33	bottom	1,127
0.67	bottom	1,138
1	bottom	1,122
2	bottom	1,087
4	bottom	1,178
6	bottom	1,098
12	bottom	898
24	bottom	585
48	bottom	442

**Table B8 Concentration Data for Experiment O400SB**

<b>Time (hours)</b>	<b>Sample Point</b>	<b>Bitumen Concentration (ppm)</b>
0.33	top	1,097
0.67	top	1,092
1	top	1,097
2	top	1,128
4	top	428
6	top	268
12	top	155
0.33	bottom	1,077
0.67	bottom	1,060
1	bottom	1,010
2	bottom	1,348
4	bottom	418
6	bottom	267
12	bottom	87

**Table B9 Concentration Data for Experiment O400FT**

Time (hours)	Sample Point	Bitumen Concentration (ppm)
0.33	top	1,133
0.67	top	997
1	top	848
2	top	430
4	top	292
6	top	268
12	top	198
24	top	193
0.33	bottom	1,133
0.67	bottom	988
1	bottom	870
2	bottom	433
4	bottom	297
6	bottom	252
12	bottom	220
24	bottom	198

**Table B10 Concentration Data for Experiment O400FB**

Time (hours)	Sample Point	Bitumen Concentration (ppm)
0.33	top	1,017
0.67	top	930
1	top	995
2	top	722
4	top	537
6	top	450
12	top	330
24	top	322
48	top	307
0.33	bottom	960
0.67	bottom	1,007
1	bottom	912
2	bottom	848
4	bottom	533
6	bottom	458
12	bottom	397
24	bottom	317
48	bottom	372

**Table B11 Concentration Data for Experiment O400BT**

<b>Time (hours)</b>	<b>Sample Point</b>	<b>Bitumen Concentration (ppm)</b>
0.5	top	1,202
1	top	1,192
2	top	1,263
4	top	892
6	top	513
12	top	390
24	top	173
0.5	bottom	1,193
1	bottom	1,437
2	bottom	1,133
4	bottom	945
6	bottom	490
12	bottom	310
24	bottom	227

**Table B12 Concentration Data for Experiment O400BB**

<b>Time (hours)</b>	<b>Sample Point</b>	<b>Bitumen Concentration (ppm)</b>
0.33	top	1,153
0.67	top	1,195
1	top	1,198
2	top	1,095
4	top	822
6	top	485
12	top	345
24	top	318
48	top	307
0.33	bottom	1,050
0.67	bottom	1,147
1	bottom	1,198
2	bottom	1,167
4	bottom	832
6	bottom	500
12	bottom	230
24	bottom	268
48	bottom	293

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