

## **Determination of Limits of Viscosity for Dispersant Use: Quantitative and Qualitative Assessment of the Dispersibility of Water-in-oil Emulsions at the Laboratory (IFP and MNS Tests) and in the *Polludrome***

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### **Abstract**

Various studies conducted over the last few years have increased the limits of viscosity for dispersant use. Many of these studies were based on efficiency measurements whereas the opportunity of applying dispersants can also be assessed on the quality of the dispersion. Dispersion characterization through oil droplets size distributions (key element in terms of behavior and fate in the water column) appeared therefore necessary.

In order to get a range of oils viscosity, an IFO 220 was emulsified at various levels, from 0 to ~ 60% water content, leading to products easily to poorly dispersible. Dispersibility was assessed considering two laboratory tests (IFP and MNS at two levels of energy). The same emulsions were also tested at the pilot scale in a flume tank, also regarding two levels of energy.

Efficiencies measured at the laboratory scale proved to decrease progressively as the viscosity increased, from 6000 to 35 500 cSt. Experiments performed at the pilot scale did not show such a clear trend, the amount of oil being transferred to the water column being significant for any condition of test. However, oil droplet size distributions demonstrated to be directly correlated to oil viscosity. The quality of the dispersion was ranked in 3 categories (good, uncertain, poor) corresponding to 3 growing ranges of viscosities. A relationship between laboratory efficiency and expected quality of dispersion was then established.

These results were in agreement with rules generally admitted for asphaltenic oils as regards the limits of viscosity for dispersant use. Emulsions characterized by a viscosity lower than 10,000 – 15,000 cSt were efficiently treated with dispersants while uncertainties remained in the range 15,000 – 25,000 cSt. Beyond 25,000 cSt, the probability of a successful treatment was low. Based on this work, threshold values, commonly used to predict an oil dispersibility at sea, were confirmed or updated for both IFP and MNS tests.

### **1 Introduction**

Following the *Deep Water Horizon* spill, the application of dispersants returned to the forefront of the panel of response techniques applicable in case of oil spill. Apart from the ecotoxicological issues, this technique is one of the most sensitive to environmental conditions and oil properties. The definition of a time-window of opportunity for dispersant use is of great concern in case of accident and at the preparation level in response plans. If modern dispersants have proved to be efficient on viscous products, many uncertainties remain as regards the definition of such a limit for use. Moreover, the dispersion itself is generally characterized from a quantitative point of view and only recent studies have focused on its quality through droplet sizes measurements.

The pilot scale devices developed at Cedre represent useful tools in order to predict the actual behavior at sea of spilled products, either chemicals or petroleum products. It is also possible to conduct dispersibility studies of oils, either combined with a preliminary weathering period or not. Among the various devices, the *Polludrome*, a flume tank, enables

a significant number of experiments, under realistic conditions but in a controlled system. In addition to that, various dispersibility tests have been developed at the laboratory scale, generally as part of a national approval procedure of dispersants. These tests were in a second step applied to the assessment of the dispersibility of one oil, potentially for various weathering degrees. Threshold values were defined in order to predict the efficiency of a treatment over time in real conditions.

Considering that this calibration work was previously performed only taking into account efficiency measurements, the objective of this study was to set up an experimental program in order to compare various laboratory and pilot scale tests. The innovative part of the work is to include a characterization of the quality of the dispersion through oil droplet sizes measurements. The low-energy IFP test (AFNOR, NF T90-345) and two levels of energy (low and high) of the MNS tests (Mackay and Szeto 1980) were chosen. Those tests are described in detail in the 2.1.1 section. As regards the pilot scale, two levels of energy were also recreated, leading to 5 different conditions of tests and energy.

An intermediate fuel oil IFO 220 (220 cSt at 50 °C) was emulsified at various levels in order to generate a wide range of viscosities, from dispersible to *a priori* non dispersible products. The final objective of this study was to confirm or to question the existing threshold values defined for each laboratory test.

## **2 Materials and Methods**

### **2.1 Test Protocols**

#### **2.1.1 IFP and MNS Laboratory Tests**

Oil dispersibility can be estimated from various laboratory tests which were mainly developed in the frame of dispersant approval procedures. Those tests are generally peculiar to the country where they have been designed. The WSL (Warren Spring Laboratory) test in the UK, the Swirling Flask or the EXDET (Exxon Dispersant Effectiveness Test) tests in the USA, the IFP (Institut Français du Pétrole) test in France and the MNS (Mackay-Nadau-Steelman) test in Norway are among the most commonly used. However, those tests can be inefficient when applied to weathered and emulsified oils. For example, the WSL efficiency drastically drops when oils get emulsified (around 20% water content) and does not further evolve (Guyomarch and Merlin, 2000).

The French procedure applied for the IFP test is in agreement with the AFNOR NF T 90-345 standard and is a low-energy system compared to other tests. The energy is generated by the vertical motion of a wave beater. The special feature of this test is to generate a dilution of the tank (where the dispersion is carried out) thanks to a continuous input of water (Figure 1). Theoretically, a water discharge located at the tank bottom allows the removal of smallest oil droplets. The volume of the dispersion tank is 5 liters; the dilution rate (maintained constant along the 1h test) is around 2.5 L/h. The test is run for 60 minutes.

The MNS test was described by Mackay and Szeto (1980). This test is characterized by a high energy generated by a wave initiated by a strong air flux flow. Several levels of energy can be simulated by varying the air flowrates (Table 1). Those air outputs are calibrated by measuring the difference of pressure between two points of a calibrated tube separated by a pressure limiter. The test is run for 10 minutes. For this study, two levels of energy have been simulated: low and high energy, corresponding to 25 and 40 mm H<sub>2</sub>O, respectively (Table 1).



**Figure 1** Experimental set-up used for the a) IFP and b), c) MNS tests.

**Table 1** Assessed relationship between wind speed, sea state and settings of the MNS apparatus.

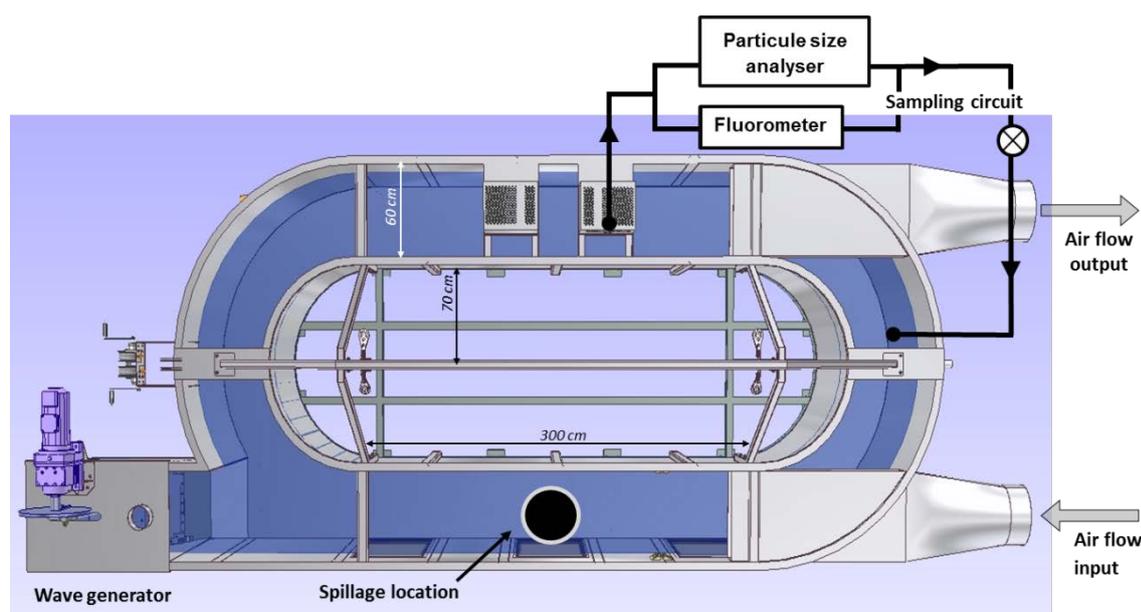
Wind speed (knots)	Beaufort scale	Sea state	MNS pressure drop (mm H <sub>2</sub> O)	MNS level of energy
1	0	0	5	-
1-10	1-3	1-3 (weak)	10	-
11-27	4-6	4 (medium)	25	low
28-40	7-8	5 (medium-)	40	high
41-47	9	6 (strong)	-	-

### 2.1.2 Polludrome Tests

Pilot scale tests were performed in a flume test canal, the *Polludrome*. This device, designed for weathering studies, has been modified to carry out dispersibility tests. It has been equipped with sampling and measurement systems (Figure 2). Parts suspected to generate shearing phenomenon (e.g. wave beater and current generator) have been changed. Water flow is induced by movable valves located on the wave beater: The generator pushes the water and avoids its suction back to the generator.

The wave shape is controlled by a deflector located in the front of the beater, allowing the formation of slightly breaking waves for the high-energy level.

The volume of seawater used for each test is 7.2 m<sup>3</sup>, leading to a water depth of 90 cm in the canal. 1 L oil is poured at the water surface, into a containment ring. The oil is let spreading for 5 min which allows also a thermal equilibrium. Continuous oil concentration measurements start at this point (see section 2.2). After 1 min, 40 mL of dispersant are sprayed over the oil for 20 seconds using a Wagner sprayer. The containment ring is lifted after 2 min (starting point for data collection); 25 seconds after, the wind is started and again 10 seconds after, the wave generator is started. The test is carried out for 1 hour. The droplet size is continuously measured with the Malvern (see section 2.2).



**Figure 2 Experiment set-up.**

Experimental biases have been minimized in order to ensure that only hydrodynamic energy generates dispersion. The different levels of energy have been chosen in order to induce significant variations of efficiency.

## 2.2 Measurement Equipment

Oil concentrations dispersed at the laboratory scale were quantified at the end of each test, after extraction with dichloromethane, drying on magnesium sulfate and analysis with a UV-visible spectrophotometer at 390 nm (Spectrophotometer Evolution 600 UV VIS., Thermo Scientific, Waltham, MA, USA). Oils dispersed during the *Polludrome* tests were measured continuously over 1h thanks to a field Turner Designs 10-AU spectrofluorometer SF-UV (Sunnyvale, CA, USA). The instrument is calibrated with oil solutions dispersed in seawater. A second calibration is performed at the end of each test by comparing a sample of theoretical known concentration measured by SF-UV to the oil concentration determined following the first method described. The calculated corrective coefficient was applied to the whole set of data.

The dispersion quality is evaluated thanks to droplet sizes measurements and their relative distributions. The laser particle size analyzer, a Malvern Mastersizer 2000 (Malvern, United Kingdom), determines the droplet size distributions with respect to number or to volume. The volume mode has been chosen as the objective of this qualitative study was to express a mass of dispersed oil in different class sizes. Those measurements were carried out at the end of each laboratory test and all along the *Polludrome* tests (0, 5, 10, 15, 20, 25, 30, 40, 50 and 60 minutes).

The viscosity of fresh or emulsified oils was measured by establishing the rheological curve using a Haake VT 550 viscometer at 15°C to get the evolution of the viscosity of the formed emulsions at dedicated shear rates (10, 20, 50 and 100 s<sup>-1</sup>). The viscometer was calibrated with a reference oil for each set of data.

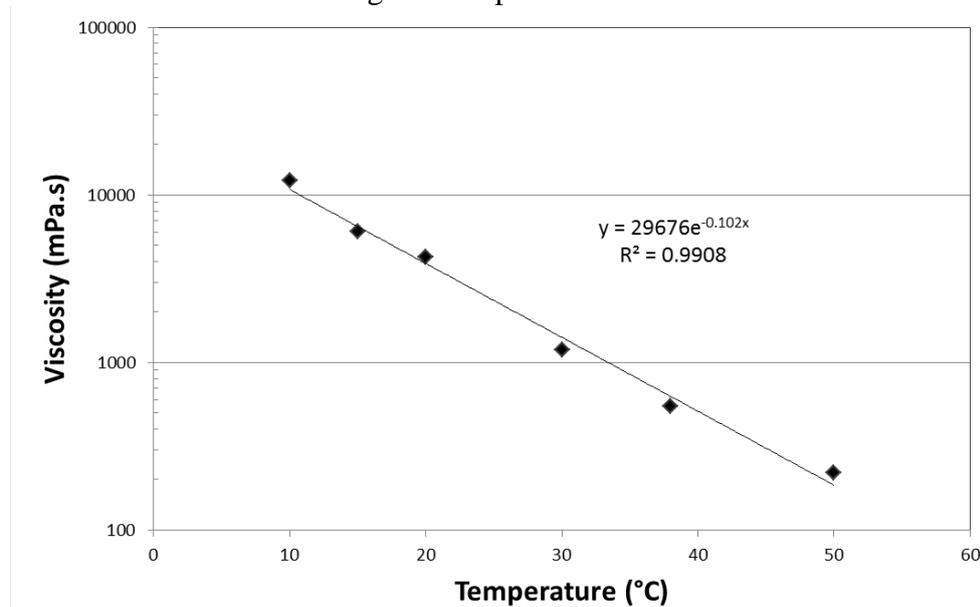
Asphaltenes content were measured on the residue obtained by distillation at 250 °C according to the IP-143/90 norm (1985): This gravimetric method is more reliable when applied to non-volatile oils, such as 250 °C residues. The result is then extrapolated to other residues and to the fresh oil by taking into account the evaporation rate measured following distillation. Wax content was measured on the same residue after the precipitation of asphaltenes (the measurement performed directly on the residue is liable to lead to co-

precipitation of asphaltenes and waxes). The protocol, which was described by Bridié et al. (1980), consists of a precipitation in a mixture of MEK (methylethylketone) and DCM (dichloromethane) 1:1 at -10°C.

### 2.3 Oil and Dispersant

The oil used is an IFO 220 (Intermediate Fuel oil with a viscosity of 220 cSt at 50°C). Physico-chemical characteristics of the oil, determined at Cedre, are presented in Table 2. The evolution of viscosity with the temperature is presented in Figure 3.

Samples of oils evaporated at various temperatures were obtained by distillation according to the protocol developed at IKU/SINTEF (Norway). The distillation technique is described by Stiver and Mackay (1984) as a modified ASTM D86/82 method. The objective of this protocol is not to get the distillation curve of an oil, as intended by the ASTM method, but to obtain oil residues at given temperatures.



**Figure 3 Evolution of viscosity of the IFO 220 oil with temperature.**

Samples with increasing viscosity were obtained by generating emulsions with water content of 0, 10, 20, 30, 40, 50 and 57%. Oil emulsification was achieved by using the modified Mackay-Zagorsky method using rotary funnels (Hokstad et al., 1993). The principle of the method is to form water-in-oil emulsions by rotating cylindrical separatory funnels containing water and oil. As an example; for the 10% water content emulsion, 30 mL of water and 270 mL of oil were mixed in a rotary funnel and let for rotating for 24 hours. The rotation simulates the mixing energy of the wave's activity at sea.

**Table 2 Physico-chemical properties of the intermediate fuel oil IFO 220.**

Parameters	IFO 220
Viscosity at 15 °C (mPa.s)	6 000
Density at 15 °C	0.987
Evaporation rate at 150/200/250°C (% vol.)	0.3 / 1.2 / 4.0
nC <sub>7</sub> -Asphaltenes (% wt.)	8.5
Paraffins (% wt.)	11.2

The dispersant used was *Finasol OSR 52* (Total Fluids, France) at a dosage rate of 5 % compared to the volume of IFO 2220 (emulsified or not).

## 2.4 Tests Matrix

The test matrix applied at the laboratory and *Polludrome* scales, is presented in Table 3. Trial reference is added in order to distinguish between the 2 levels of energy (for the MNS and *Polludrome* tests). An additional experimental condition has been added for the MNS test (40 % water content) at the end of the experiment in order to confirm a suspected trend.

**Table 3** Matrix of dispersibility tests. “Low” and “high” refers to the level of energy used in the tests.

Test % H <sub>2</sub> O	Polludrome		MNS		Trial reference		IFP
	Low	High	Low	High	#1	#2	
0	✓	✓	✓	✓	1 3	2 4	✓
10	✓	✓	✓	✓	5 8	7 9	✓
20	✓	✓	✓	✓	6 11	10 12	✓
30	✓	✓	✓	✓	13 15	14 16	✓
40			✓				
50	✓	✓	✓	✓	17 19	18 20	✓
57	✓	✓	✓	✓	21 23	22 24	✓

All the tests were carried out at approximately 15 °C. As the *Polludrome* tests require large amounts of water, no temperature regulation was considered in order to have a high frequency of testing. MNS and IFP tests were carried out in the same room with the same seawater, and all the tests were then conducted at the same temperature for a given emulsion. Viscosity was measured, for each sample preparation, at the same temperature as the one of the seawater used in the test.

The tests were carried out twice (duplicates). Results were compared qualitatively (evolution of oil concentrations and droplet size distributions with time during the *Polludrome* tests) and quantitatively (comparison of efficiencies, see section 2.5).

## 2.5 Efficiency Calculation

Dispersant efficiency was calculated relatively to the mass of oil used for each test. The mass of emulsion being constant (1 kg for the *Polludrome* tests, 10 g for the MNS tests and 5 g for the IFP tests), oil quantity decreases with the water content.

For the *Polludrome* and the MNS tests, efficiency was calculated as the ratio of the quantity of dispersed oil in the water column at the end of the test to the mass of IFO 220 initially poured in the tank. The quantity of dispersed oil was measured by determining the oil concentration in a sample considered as representative of the whole water volume.

IFP efficiency is based on the quantity of IFO 220 that has been flushed out from the tank. Efficiency is defined as the quantity of oil removed from the experimental tank related

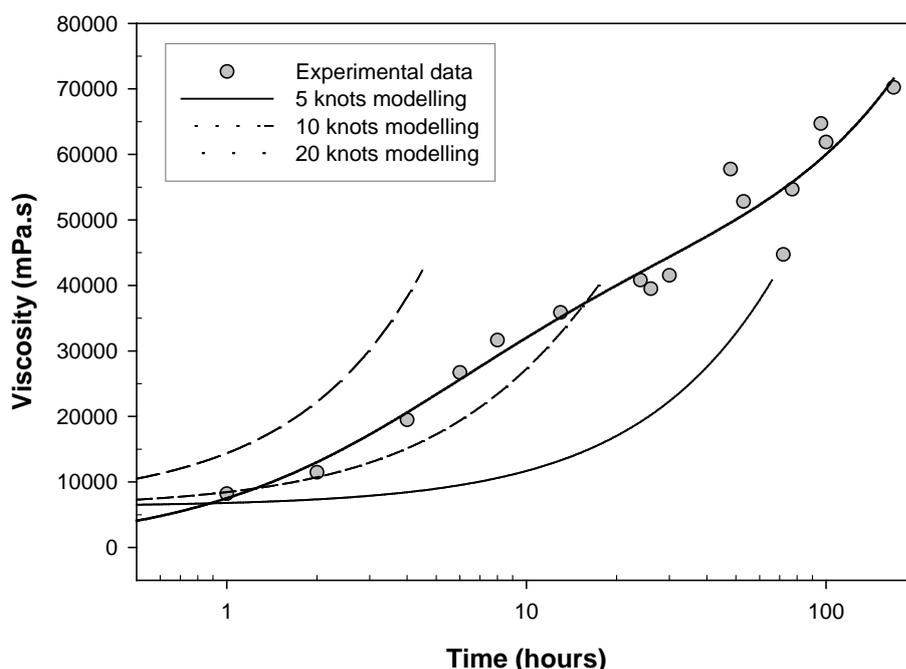
to the theoretical value obtained in the case of a fully solubilized oil and taking into account the water renewal rate.

### 3 Results

#### 3.1 Weathering Simulation

Emulsions formed at the laboratory scale only vary from their water content. Evaporation processes were not taken into account as the loss of light fractions was considered negligible due to the low quantity of volatile fractions (maximum evaporation in volume of 4 %), the short duration of the experiment, and the rapid dispersion in the water column.

Characteristics of the IFO 220 oil were entered in the ADIOS 2 model (using wind speeds of 5, 10, 15 and 20 knots) in order to link emulsions with weathering stage at sea, particularly in terms of kinetics of emulsification. Thanks to the laboratory tests, a relationship was established between water content and corresponding viscosities at 15 °C. Evolution of water content with time provided by ADIOS 2 for the different wind speeds chosen were expressed in terms of evolution of viscosity. Modelling was stopped at the viscosity reached for the maximum water content emulsion tested. Figure 4 shows the evolution of viscosity with time, at 15 °C, for wind speeds from 5 to 20 knots. Results obtained at 15 knots being very close to the ones obtained at 20 knots, they are not shown in the figure for a question of clarity. It appears that the weathering in the flume corresponds to around 10-15 knots at sea.



**Figure 4** Evolution of the IFO 220 oil viscosity (in mPa.s) at 15 °C with time (in hours) modelled for various wind speeds (5, 10 and 20 knots) and compared to experimental data.

#### 3.2 Comparison of Efficiency

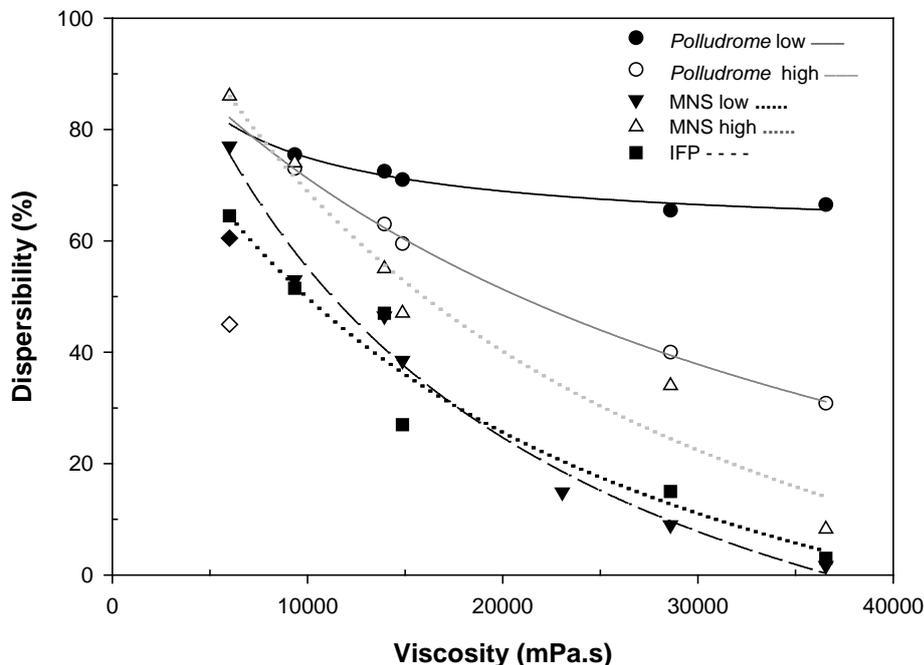
Mean efficiencies obtained for all the tests are presented in Table 4. Coefficients (data not shown) were used to correct SF-UV data from laboratory data. Viscosities shown in Table 4 are a mean of 4 measurements. The tests were carried out simultaneously following the 3 protocols. Emulsions were prepared 4 times for each water content in order to undertake twice the tests (duplicates) at low level of energy and twice the tests at high level. No test

without dispersant was carried out because weathering tests previously conducted on the IFO 220 oil did not show natural dispersion for any energy, temperature or salinity tested.

**Table 4** Efficiency measured for the various conditions of test. “Low” and “high” refers to the level of energy used in the tests.

% water	Viscosity (mPa.s)	<i>Polludrome</i>		<i>MNS</i>		<i>IFP</i>
		Low	High	Low	High	
0	6000	61	45	77	86	65
10	9337	76	73	53	74	52
20	13944	73	63	47	55	47
30	14858	71	60	39	47	27
40	23051			15		
50	28589	66	40	9	34	15
57	36552	67	31	2	8	3

Figure 5 shows the evolution of the efficiency calculated as a function of the viscosity, for all the protocols and conditions tested. Data obtained from the laboratory tests were modelled using a hyperbolic decay equation. Initial low values obtained for the tests carried out at the *Polludrome* scale were not taken into account in the model. A hyperbolic decay equation was also used to model those data.



**Figure 5** Evolution of the oil dispersibility (in %) according to viscosity (in mPa.s) for various test protocols and levels of energy (♦ and ◇ correspond to values obtained on the non-emulsified IFO 220 in the *Polludrome* at low and high energy, respectively).

Results obtained at the laboratory scale exhibit the same behavior (Figure 5), especially when considering the IFP and low-energy MNS tests. Efficiencies seem to be

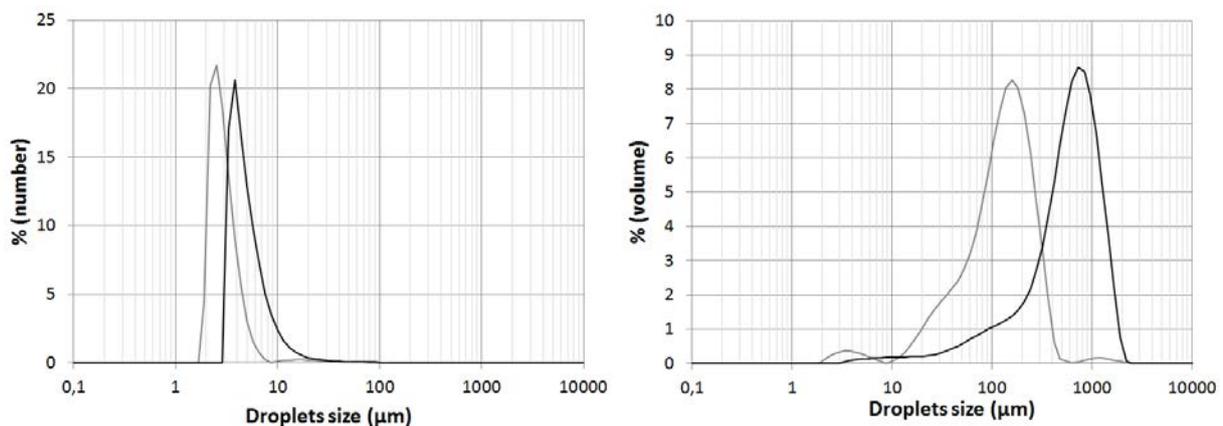
slightly higher for the high-energy MNS test. For all the conditions tested, efficiencies decrease with an increase of the viscosity, which is in agreement with dispersant action in this viscosity range (6000 – 36000 mPa.s). Surprisingly, results from the *Polludrome* tests do not show such a decrease. At high energy, even if a clear decrease is observed, final efficiency (31%) was not so different compared to the initial one (45%). At low energy, efficiencies are stable for all the viscosities tested, ranging between 66 and 76%.

Taking into account efficiency values only, those results allow a comparison between the different laboratory tests but do not allow to conclude about the representativeness of a real case. Droplet size distributions need to be studied in order to better evaluate the quality of a dispersion.

### 3.3 Droplet Sizes Comparison

#### 3.3.1 Distributions in Volume and in Number

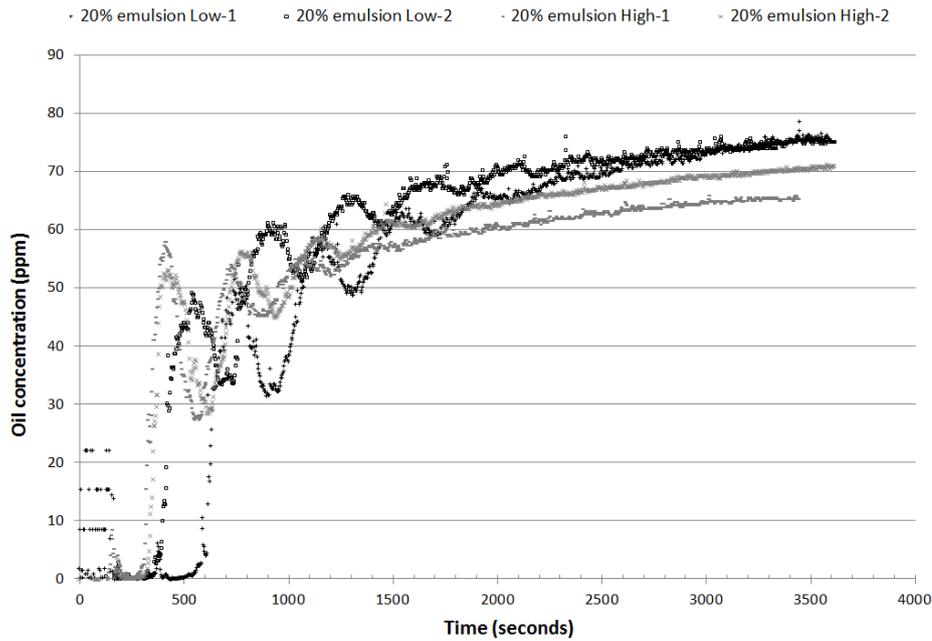
Laser particle size analyses provided droplet size distribution by calculating an abundance (%) in function of particle sizes. This abundance can be expressed either in number or in volume, leading to different results, as shown with the example of the 20% water content emulsion in Figure 6. On this figure, 2 particles of respectively 10 and 100  $\mu\text{m}$  have the same weight when comparing the abundance in number but differ by a factor 1000 when expressed in volume, and so in mass. As the objective of this qualitative study is to express a mass of dispersed oil in different class sizes, the analysis in volume was chosen.



**Figure 6** Droplet size distributions (in  $\mu\text{m}$ ) in number and volume for the IFP (grey) and low-energy MNS (black) tests for the 20% water content emulsion.

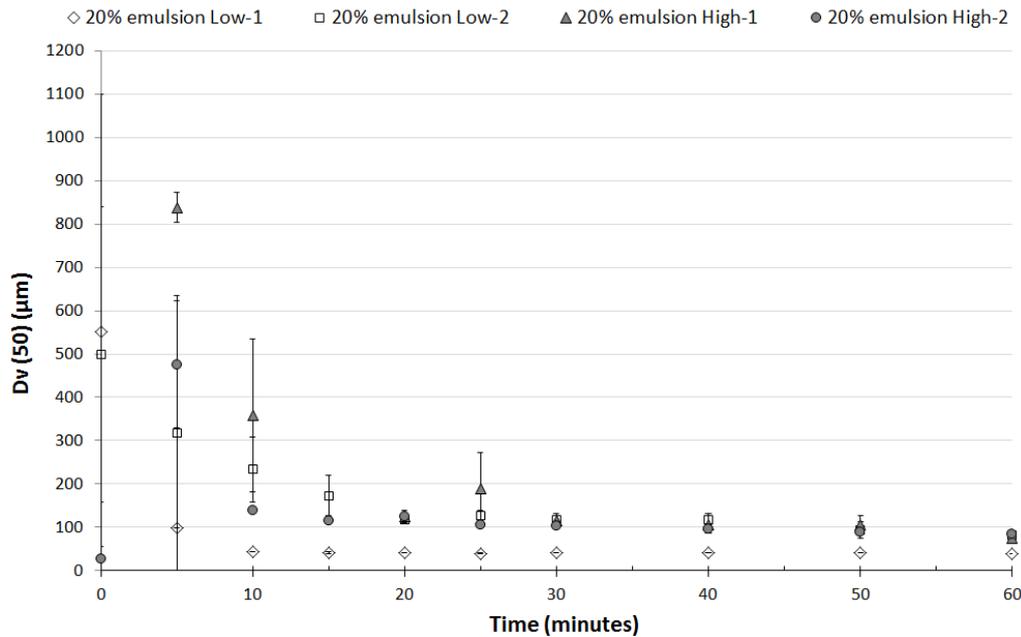
#### 3.3.2 Evolutions of Oil Concentrations and Droplet Sizes at the *Polludrome* scale

During the *Polludrome* tests, oil concentrations in the water column were continuously recorded using the SF-UV (Figure 7). During all the tests, oil concentrations increased with time before reaching a plateau. On the example detailed on Figure 7, corresponding to the 20 % water content emulsion, oil concentrations increase during the first 15 – 30 min before reaching a plateau at around 80 ppm and 55 ppm for the low and high energy, respectively.



**Figure 7 Evolution of dispersed oil concentrations (in ppm) over time (in seconds). Numbers 1 and 2 refer to the duplicate tests.**

In the flume tank, for all the tests performed, the first stage of dispersion consisted in the formation of big drops that fractionates the oil slick treated with dispersant, leading to a high mean size (few hundreds  $\mu\text{m}$ ). After this phase, the droplet sizes progressively decreased with time. Only the final distribution was taken into account on this graph, in order to compare pilot scale data with laboratory ones. An example, obtained with the 20% water content emulsion, is shown on Figure 8. On this graph, after 10 minutes, droplet sizes tend to stabilize around 100  $\mu\text{m}$  for the two levels of energy tested.



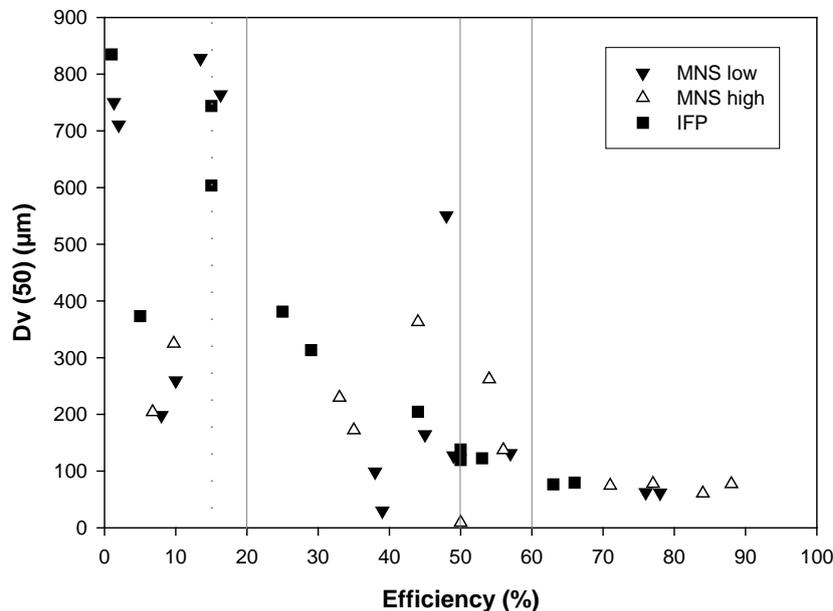
**Figure 8 Evolution of the droplet size distributions ( $D_v(50)$ , in  $\mu\text{m}$ ) with time (in minutes). Numbers 1 and 2 refers to the duplicate tests.**

### 3.3.3 Evolutions of Droplets Size at the Laboratory Scale

Droplet sizes were plotted over the efficiency obtained at the laboratory scale (Figure 9). Two vertical lines, at 20% and 50% of efficiency, were reported, referring to the IFP thresholds (above 50% an oil is considered as fully dispersible, below 20% it is considered as not dispersible). The 2 other lines refers to the MNS thresholds (15%, see conclusion, and 60%). Considering results obtained for the IFP test, droplet sizes greatly decreases with efficiency. For efficiencies above 50%, droplet sizes are around 80 – 120  $\mu\text{m}$ , and below 80  $\mu\text{m}$  for efficiencies above 60%. Considering the MNS tests, values are more variable up to 60% efficiency but, above this value, droplet sizes are nearly all below 70  $\mu\text{m}$ . Here again, below the 60% threshold, droplet sizes seem to stabilize around 60 – 80  $\mu\text{m}$ .

For both tests, droplets sizes are close or significantly greater than 300  $\mu\text{m}$  for efficiencies lower than 20%, with a great variability of the results ( $550 \pm 250 \mu\text{m}$ ).

Between these two domains, droplets sizes are around an average of  $220 \pm 150 \mu\text{m}$ , which shows the uncertainty of the dispersion quality.

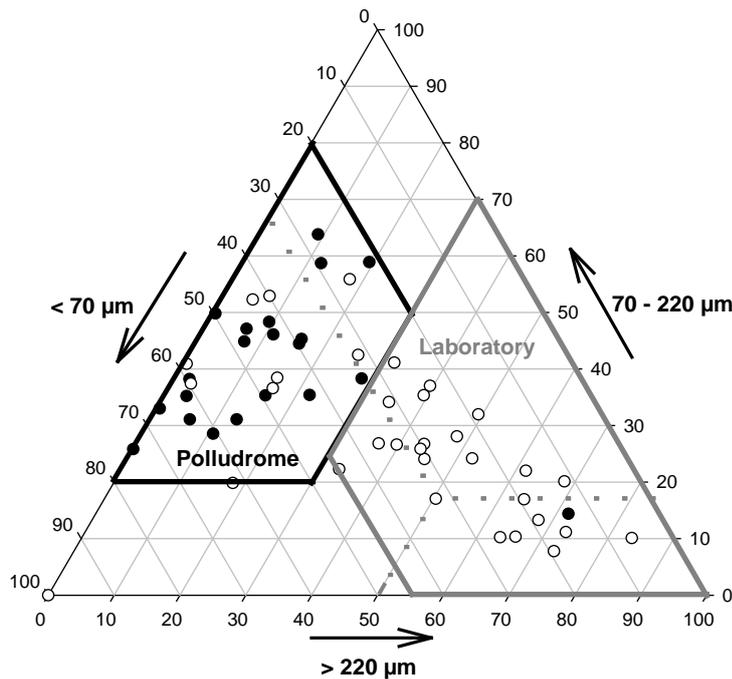


**Figure 9** Droplet sizes distribution (Dv(50), in  $\mu\text{m}$ ) over efficiency ( in %).

### 3.3.4 Comparison of Droplet Size Distributions (laboratory and *Polludrome*)

Analysis of the mean droplet sizes highlighted a qualitative trend between the size and the efficiency. Statistical study on size distributions for all the tests performed (laboratory and pilot scale tests), based on the maximization of differences between the different tests, allowed the definition of 3 classes defined thanks to 2 threshold values: 70  $\mu\text{m}$  and 220  $\mu\text{m}$ . Those classes allow then to better characterize the quality of the dispersions. Droplets smaller than 70  $\mu\text{m}$  are considered sufficiently dispersed and tend to stay dispersed in the water column. This value is in agreement with the threshold limit defined by Lunel et al. (1995) and Li et al. (2008, 2009) between dispersed and suspended droplets, suspended referring to droplets remaining in the water column only for sufficient turbulence conditions. The second threshold, determined at 220  $\mu\text{m}$ , has been inversely correlated to the efficiency. This value is in agreement with the 300  $\mu\text{m}$  limit determined by Lunel et al. (1995).

Figure 10 represents a ternary diagram showing the relative abundance of 3 size classes obtained during the *Polludrome* and the laboratory tests: < 70  $\mu\text{m}$ , 70 – 220  $\mu\text{m}$  and > 220  $\mu\text{m}$ . This graph represents the droplets size measured at the end of each test (i.e. at 60 min for the IFP and the *Polludrome* tests and 10 min for the MNS test).



**Figure 10** Droplet sizes distribution between 3 size classes:  $< 70 \mu\text{m}$ ,  $70 - 220 \mu\text{m}$  and  $> 220 \mu\text{m}$ . (●): data obtained during the pilot scale tests, (○): data obtained during the laboratory tests. The black and grey boxes roughly delimit the *Polludrome* and laboratory scale, respectively.

In order to clarify the reading of the graph, an example of determination of abundance is shown for one laboratory test using grey dashed lines: the parallel to each axis is reported on the graph and the percentage is read on the 3 axes. For this example, the abundance is of ~33% of fine small droplets ( $< 70 \mu\text{m}$ ) and 50% of  $> 220 \mu\text{m}$  droplets.

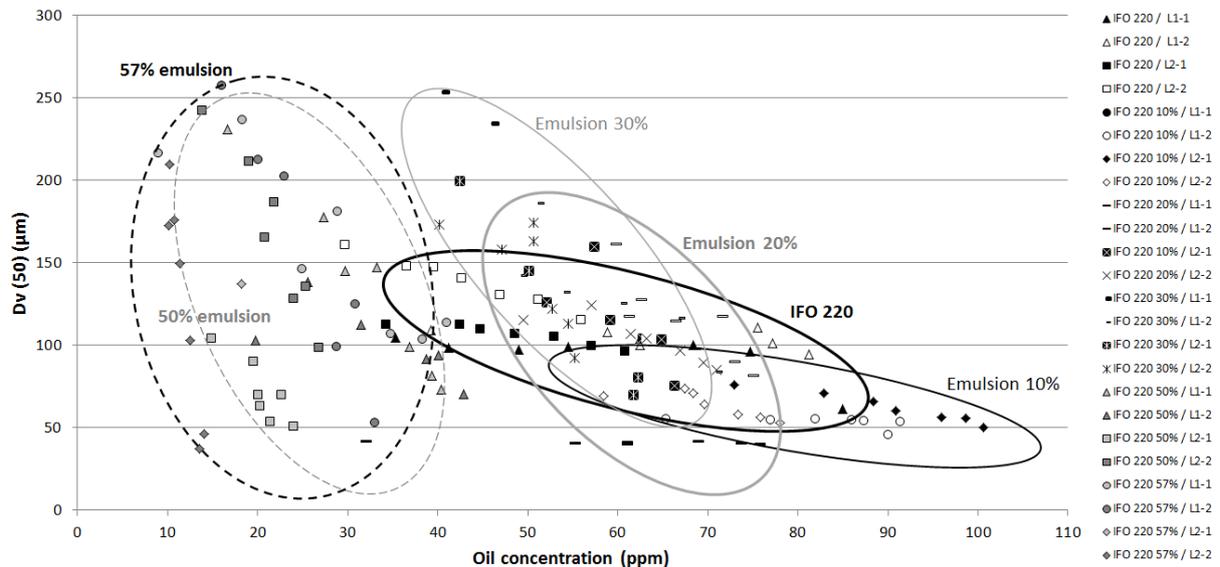
Taking into account all the data, a trend seems to emerge from the Figure 10. All the data (except one) obtained at the *Polludrome* are gathered in the same area of the graph (delimited by a black box). On the other hand, 75% of the data obtained at the laboratory fits in the grey box reported on the Figure 10. Following this grey box delimitation, the majority of the laboratory results are characterized by less than 45% (mainly 15 – 40%) of the smallest droplets ( $< 70 \mu\text{m}$ ) and more than 30% of “big” droplets ( $> 220 \mu\text{m}$ ). On the contrary, the majority of the *Polludrome* tests are characterized by smaller droplet sizes, with less than 30% of “big” droplets ( $> 220 \mu\text{m}$ ) and more than 40% of small droplets ( $< 70 \mu\text{m}$ ).

Those results do not allow to conclude about the quality of the dispersion between the different *Polludrome* tests but they highlight significant differences between laboratory and pilot scale tests. Comparatively to the laboratory tests, where the oils are transferred from the surface to the water column, the pilot scale experiment allows to simulate the dispersion in the water column, and especially allows the formation of particles, regularly exposed to wave energy, that have the capacity to stay in the water column under dynamic conditions.

### 3.4 Kinetic Evolution of the Droplets Size (*Polludrome*)

Figure 11 represents the kinetic evolution of the median droplet sizes in function of oil concentration measured by continuous SF-UV measurement. Data were collected after oil spillage (T0) and then at 5, 10, 15, 20, 25, 30, 40, 50 and 60 min after spillage. Figure 11 only refers to the data collected after 10 minutes of test. Few data were above  $300 \mu\text{m}$  in size.

Those values were either obtained at the early stage of the dispersion or are linked to experimental bias. Only droplets smaller than 300  $\mu\text{m}$  were presented on Figure 11. Each test is represented by a scatter plot characterized by a surface area (qualitatively determined) and by data dispersion. A slope (Table 5) can be determined from this dispersion. Variations of oil concentrations do not necessarily reflect differences of efficiency as the emulsions tested have the same volume but not the same water content (and so the same oil content). The main feature of this graph confirms a decrease of the droplet sizes, as already mentioned in 3.3.2.



**Figure 11** Distribution of droplets size/efficiency combinations measured during the *Polludrome* tests for the different emulsions tested.

Emulsions at 50 and 57% water content exhibit high mean droplet sizes and a high variability. The absolute values of the slopes characterizing those dispersions are high (Table 5), which means an important droplet sizes evolution over a narrow oil concentration range and so a larger uncertainty concerning the oil slick breakup. It appears that small droplets formation requires a longer mixing period. On the other side, emulsions at 10% tend to have low and more stable mean droplet sizes leading to an almost immediate effect of the dispersant. The same trend is observed for the fresh IFO 220 oil. Between those two extreme behaviors, corresponding to a poor and a good dispersion, respectively, a full range of emulsions (and so viscosities) exists. Those scenarios represent small droplet formations but with a non-immediate dispersion.

Those qualitative observations are confirmed by slope calculations of the droplet sizes evolution in function of the dispersed oil concentration (and so function of time). Table 5 summarizes the slope obtained for the different emulsions tested. Results confirm the differences observed for experiments carried out at low and high energy.

The differences observed in terms of efficiency at low energy can be qualitatively explained by a smaller droplet sizes evolution leading to a faster action of the dispersant. Globally, it can be observed that slopes are higher when viscosities increase which means a harder action of the dispersant.

**Table 5 Evolution of the droplet sizes versus oil concentrations for the various conditions tested at the *Polludrome*, for low and high energy.**

% water	Viscosity (mPa.s)	Slope		
		Low	High	average
0	6000	-	-	-0,3
10	9337	-	-	-1,1
20	1394	-	-	-2,3
30	1485	-	-	-5,7
50	2858	-	-	-7,5
57	3655	-	-	-

#### 4 Discussion

This study generated important qualitative and quantitative data and raised new questions about chemical dispersion at sea. The *Polludrome* tests, conducted at low and high energies, led to contrary results to what was expected as a higher efficiency was observed for the low-energy test. The difference of efficiency between low and high energies increases when emulsions become viscous and so, in theory, more difficult to disperse.

The study of droplet sizes distribution can explain those observations. To be efficient, dispersion needs time (to allow a sufficient contact between the oil and the dispersant). The more viscous an oil is, the more time is needed for the dispersion to be achieved. At high energy, the interaction between the emulsions and the water is reduced, which can lead to a loss of part of the dispersant in the water column and so to a lower efficiency of the treatment. On the other side, at low energy, the mixing is sufficient enough to generate a dispersion and allows an extended contact time between the oil and the dispersant.

The *Polludrome* tests simulate simultaneous natural processes in a more realistic way than laboratory tests. The two level of energy tested (low and high) have to be considered simultaneously as they are representative of the different seawater stages encountered during treatment with dispersants. However, conditions may be too controlled compared with real conditions: the containment of the slick in the ring during the application of the dispersant may, for example, overestimate the efficiency obtained in this study.

Determination of threshold limits of efficiency is fundamental to help in the decision to use chemical dispersion as response technique. Considering dispersant application as a technique that should lead to a complete treatment of the oil slick (in order to avoid issues linked with incomplete dispersed oil slicks arriving on the shoreline), the 6 dispersions characterized in this study can be qualified as:

- *Optimized* for the 10% water content IFO 220 emulsion
- *Uncertain* for the 20 and 30 % water content IFO 220 emulsion
- *Poor* for the 50 and 57 % water content IFO 220 emulsion

The word *Uncertain* gathers an efficiency slightly lower than the optimized conditions and a significant effect of mixing time on the droplet size together. The word *Poor* means a high droplet size evolution with time, combined with an efficiency that can be divided by two in comparison with *Optimized* dispersion considered as total.

Table 6 presents the summary of the qualitative and quantitative data obtained in the frame of this project.

**Table 6** Quality of the dispersion in the *Polludrome* and efficiencies measured at the laboratory.

% water	Viscosity (mPa.s)	<i>Polludrome</i>	<i>MNS</i>		<i>IFP</i>
			Low	High	
0	6 000	<i>Good</i>	77	86	65
10	9 300		53	74	52
20	14 000	<i>Uncertain</i>	47	55	47
30	15 000		39	47	27
40	23 000		15		20 (calc.)
50	28 500	<i>Poor</i>	9	34	15
57	36 500		2	8	3

Taking into account those results, it appears that threshold values can be defined for the IFP and MNS tests for the low level of energy tested (the high one does not allow to observe any sufficient efficiency difference when the quality of the dispersion decreases). Those threshold values, presented in Table 7, are close to the previous estimations determined at Cedre but allow to reevaluate the threshold usually found in the literature for the MNS test (15% in this study compared to the 5% usually encountered).

**Table 7** Proposition of threshold values for the IFP and MNS tests.

<i>Dispersibility</i>	<i>MNS</i>	<i>IFP</i>
<i>Good</i>	$E > 60\%$	$E > 50\%$
<i>Uncertain</i>	$15\% < E < 60\%$	$20\% < E < 50\%$
<i>Poor</i>	$E < 15\%$	$E < 20\%$

## 5 Conclusion

The objective of this study was to determine if laboratory tests can serve to predict oils dispersibility in real conditions and to define threshold values for each test protocols. Accordingly to general practicing, IFP and MNS were chosen as dispersibility tests. Concerning the MNS test, two levels of energy reported in the literature have been chosen (low and high). The experimental set up in real conditions being difficult for technical reasons (emulsion preparations, control of viscosity, application of dispersant, efficiency estimation ...) and administrative reasons, pilot scale experiments were carried out.

Increasing viscosities (6000 – 36500 mPa.s) were obtained by forming emulsions from an IFO 220 (Intermediate Fuel Oil of maximum viscosity 220 mPa.s at 50 °C) at water content from 0 to 57%.

Laboratory tests showed expected decreasing efficiency. *Polludrome* tests carried out at low-energy level could not be differentiated when using the efficiency criterion alone. Evolutions of droplet sizes distribution collected for all the tests, linked with efficiency values, allowed to evaluate the quality of the dispersions, which have been classified in 3 categories: *Good*, *Uncertain* and *Poor*. Threshold values have been redefined for the MNS tests.

Finally, those results are in agreement with viscosity thresholds generally accepted for the treatment with dispersant for asphaltenic oils. Emulsions of viscosities lower than 10 000 – 15 000 mPa.s can be efficiently treated with dispersant. Uncertainties persist concerning the range 15 000 – 25 000 mPa.s. Above 25 000 mPa.s, emulsions are poorly dispersible.

Further studies should be undertaken in order to better understand the mode of action of chemical dispersants. Three main research axes should be especially explored:

- Pilot scale experiments have shown that efficiency seems not to be directly related to the level of energy simulated. Experiments including additional intermediate level of energy should be considered. More realistic conditions could also be reached with, for example, the way the slick is contained at the beginning of the tests.
- The viscosity range obtained during this study corresponds to the same asphaltenic oil emulsified at different water contents. Experiments with other type of oils and with different ranges of viscosity should be considered (paraffinic and naphthenic oils for example).
- Tests in real conditions, combining droplet sizes / oil concentration measurements in the water column and the use of sensors (to characterize the oil slick on the surface), would allow to better estimate the representativeness of tests carried out at the laboratory and pilot scale.

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