Oil Interaction with Mineral Fines and Chemical Dispersion : Behaviour of the Dispersed Oil in Coastal or Estuarine Conditions

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Abstract

When spilled in the environment, especially in coastal systems like estuaries, oil frequently interacts with fine mineral particles to form aggregates. This process may enhance the effectiveness of chemical dispersant and influence the behaviour and fate of the pollutant. Understanding this process will help in deciding whether chemical dispersion is a good oil clean-up option in a particular environmental system.

This study investigates the influence of the oil-fines interaction on chemically dispersed oil. The study was conducted in two stages :

- First, in the laboratory, a study of the different parameters liable to take part in the aggregation process was conducted according to the WSL and IFP test methods. The minimal clay concentration required to form aggregates depended on several parameters : salinity, oil composition and type of clay. The maximum amount of oil trapped on clay was linked with the dispersant efficiency.
- Second, tests were performed in the Polludrome, Cedre's testing flume. The aim was to quantify the oil-mineral aggregation in realistic conditions and to observe the behaviour of pollutant and aggregates at different current speeds. The oil distribution in the water column was assessed and aggregates were found to settle only at very low current speeds.

1.0 Introduction

When spilled in the environment, especially in coastal systems, oil frequently interacts with fine mineral particles to form aggregates.This phenomenon is enhanced in estuaries, where the mineral load can be high. However, mixing energy is also a key factor in generating oil-mineral aggregates and, even if the appropriate conditions are combined, laboratory simulations have shown that only a small amount of oil could be trapped on the fines (McCourt and Shier, 1998).

The addition of surfactants can enhance the formation of aggregates in low-energy conditions. Some studies have confirmed this possibility with biosurfactants generated by natural biota (Wood *et al.*, 1998), but their influence remain at a low level (Jézéquel *et al.*, 1999). In the case of chemical dispersion, oil mineral aggregation may be a major process resulting in a new pollutant which behaves quite differently. The association of dispersed oil with mineral fines can prevent oil

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coalescence, thus stabilizing the dispersion. On the other hand, these aggregates may sediment depending on their size and density.

Estuaries are characterized by their very variable parameters : salinity, mineral load, mixing energy, current speed, etc... . These factors are likely to determine whether oil mineral aggregation occurs or not, and can induce changes in pollutant behaviour. Consequently, the decision on whether to use dispersants in coastal or estuarine conditions depends on these parameters.

To address this problem, the study was conducted in two stages :

- first, in the laboratory, the aggregation conditions were identified. Tests were performed according to the WSL and IFP test methods. The influence of several parameters was studied : type of clay, nature of oil, salinity and oil/clay ratio.
- second, in the Polludrome, Cedre testing flume, the behaviour of the dispersed oil in the water column when associated with clay particles was investigated.

2.0 Laboratory Studies

2.1 Materials and Analytical Methods

2.1.1 Oils

Different oils were used : Forties Blend crude, BAL 110 (an Arabian Light crude oil topped at 110°C to remove the most volatile components) and mixtures of Heavy Fuel Oil (HFO) and BAL 110 (FOREF is the mixture characterized by a 1000 cP viscosity at 20°C). Their physical and chemical properties are summarised in Table 1.

Density was determined at 20°C by the pycnometer method (French standard, NFT 66 007). Viscosity was measured at 15°C at a 10 s^{-1} shear rate using a Haake VT 550 viscometer.

Table 1. Physical and Chemical Properties of Experimental Oils

OILS	Density at 20°C	Viscosity at 15 °C (mPa.s)	Composition (%) Saturates/Aromatics/Resins/Asphaltenes
FORTIES BLEND crude	0.840	15	33 / 55 / 11 / 1
BAL 110	0.860	35	41 / 42 / 12 / 4
FOREF	0.965	1536	23 / 48 / 15 / 12
HFO / BAL 110 (96/4)	0.985	16500	19 / 50 / 16 / 15

2.1.2 Dispersant

Inipol IP 90 (CECA, France).

2.1.3 Clays

Two clays were used due to their differences of cation exchange capacities: Illite (Argiletz, France, 10-40 meq/100g) and Montmorillonite (80-155 meq/100g) (van Olphen and Fripiat, 1979). Montmorillonite (Clarsol®) was provided by CECA (France).

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2.1.4 Salinity

Salinity, as well as the nature of cations present, vary in estuaries. In this study, salinities ranged from 10 to 50 ‰ (10, 25, 35 and 50‰) (aquarium salt : Instant Ocean dissolved in distilled water) and an additionnal test was performed using a solution of $CaCl_2$ in distilled water (35 g/l).

2.1.5 Measurements

Aggregates were separated from the water by filtration onto a 90 mm diameter, 1.6 µm pore-size glass microfibre filter (GF/A, Whatman).
The oil concentration in water was determined by solvent extraction with dichloromethane, filtration through anhydrous sodium sulfate and U.V. spectrophotometry at 580 nm.
The oil trapped on mineral fines was extracted by adding solvent on the glass microfibre filter. The amount of clay in the aggregates was measured by gravimetry (weight of the filter dried 4 hours at 80°C).
These quantifications led to the calculation of the Oil/Clay ratio of the aggregates and showed whether oil was associated with clay or not.

2.2 Experimental Methods

The test procedures used to evaluate oil-mineral fines interaction in the presence of a chemical dispersant are essentially those designed to assess the efficiency of a dispersant. These procedures were adapted from the WSL (Martinelli, 1984) and IFP (NFT 90 345, French standard) test methods. The seawater used in these tests contained various amounts of clays, montmorillonite or illite.

2.2.1 WSL Test Method

A 250 ml separatoty funnel was filled with 2 ml of oil and 200 ml of sea water containing various amounts of clay (from 0 to 8 g/l). The oil was then treated with 0.1 ml dispersant and the flask was rotated , end-over-end, at 30 revolutions per minute for 2 minutes. After a short waiting time (1 minute or 30 minutes), 50 ml of water was sampled from the bottom of the flask for the quantification of dispersed and/or trapped oil.
The temperature was kept at 15°C.

2.2.2 IFP Test Method

The IFP test method, used in France for dispersant use approval (NFT 90 345, French standard), is a low-energy test and is characterized by a dilution process. The maximum oil concentration is also much lower (570 ppm) than in the WSL test. In this series of experiments, the amount of trapped oil was calculated more precisely by quantifying and correcting for losses of oil that stuck on the wall flask and on the wave beater.

2.3 Results of the WSL Tests

2.3.1 Dispersion, Aggregation and Dispersant Efficiency

The first part of the study was the observation of the dispersed oil behaviour in the WSL test (Martinelli, 1984). For increasing clay concentrations, 2 different processes were observed, dispersion and aggregates formation :

- at low concentration, dispersion was the only phenomenon,
- for medium clay amounts, dispersion and aggregates formation were jointly observed,
- for high concentrations, there was no more dispersion and the totality of the oil was trapped on mineral particles; this process implied also the sedimentation of the pollutant.

To quantify the amount of dispersed and/or trapped oil, the protocol had to be modified. Dispersion was quantified by collecting samples after 1 minute in order to avoid coalescence of the dispersed oil (the 50 ml sample must be representative of the water column) while aggregates quantification required the completion of the sedimentation, considered as achieved after 30 minutes (all the trapped oil had to be collected in the sample). Consequently, the intermediate field of the medium clay concentrations could not be assessed from a quantitative point of view (Figure 1).

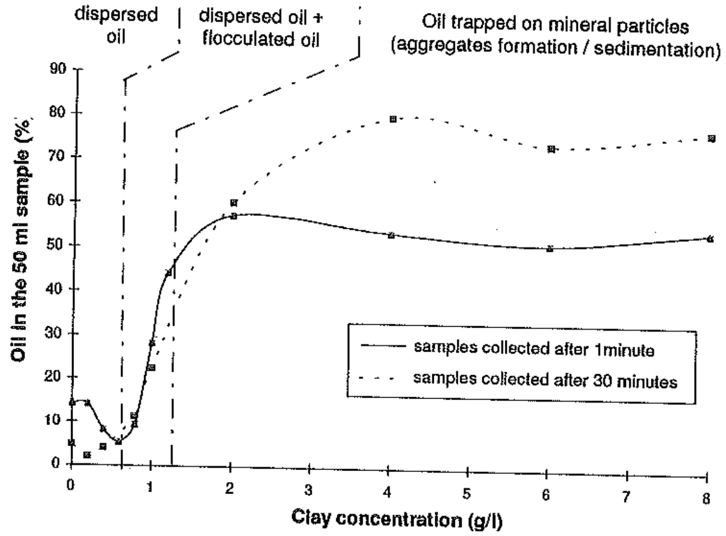

Figure 1. Influence of the Settling Time. Oil : mixture HFO/BAL 110 96/4, Salinity : 35‰, Clay : Montmorillonite.

For 8 g/l and a 30 minutes settling time, the percentage of oil was 77 ± 3 (95% confidence limit). The deviation was not higher for the other oils tested in the same conditions.

From the analytical data presented in Figure 1, the efficiency of the dispersant can be calculated as the percentage of oil removed from the water surface, either dispersed or settled. This parameter is plotted versus clay concentration in Figure 2.

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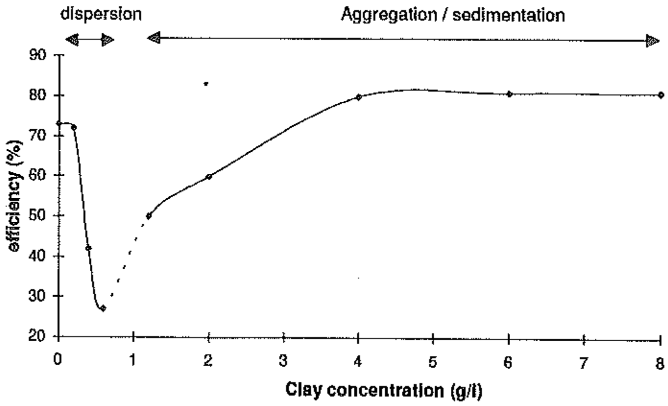

Figure 2. Oil Removed from the Water Surface. Oil : mixture HFO/BAL 110 96/4, Salinity : 35‰, Clay : Montmorillonite.

At clay concentrations below 1 g/l, dispersion efficiency decreased with increasing clay content of the water. For high clay concentrations, in the aggregation field, the efficiency increased with increasing clay content, resulting in lower oil concentrations in the water column. However, these differences of efficiency can not be separated from the fate of the oil. In this study, the efficiency represents either a dispersion commonly observed, either an aggregation/sedimentation.

2.3.2 Influence of Oil Composition

All the following tests focused on aggregates formation and samples were collected after 30 minutes. Data for the different oils are plotted in Figure 3.

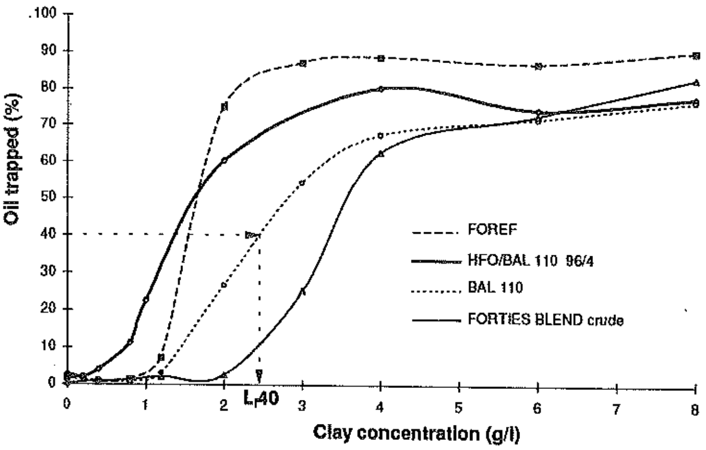

Figure 3. Oil Trapped Versus Clay Concentration. Salinity : 35‰, Clay : Montmorillonite.

Measurements and observations during the oil extraction showed that above 20% efficiency, the totality of the oil collected in the sample was trapped on mineral particles. In this study, the different tests carried out were characterized by the clay concentration required to get a 40% efficiency (oil removed from the water surface). This criterion was named L_f40 (Flocculation Limit 40%). For the FOREF, the 40% efficiency was also linked with an Oil/Clay ratio equal to 5.
There is an inverse correlation between the polar compounds content of the four oil types tested and the L_f40 as illustrated in Figure 4.

This relationship suggests that aggregates formation is the result of interactions between the polar compounds of the oil and the clay particles (negatively charged) by the intermediary of a cation, as proposed by Bragg and Yang (1993).

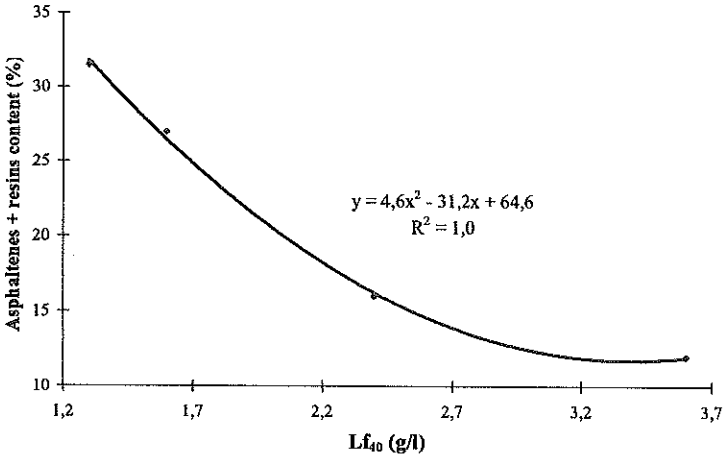

Figure 4. Correlation L_f40-Polar Compounds Content

The data points for 75 to 90% of oil trapped (maximum percentages of oil trapped) do not show significant differences according to the type of oil : this point may be due to the experimental protocol (high energies, high mineral load) and will be discussed further for the IFP tests.

2.3.3 Inluence of Salinity

The aggregation processes depend on cation concentration (e.g. salinity, Na^+ concentration) and cation type (e.g. Na^+/Ca^{2+}).
Figure 5 illustrates the curves obtained at various salinities and for different "flocculating" cations. The effect of a high salinity was negative (L_f40 doubled for an increase of salinity of 10 to 35 g/l). Oil was also less trapped for high ionic strenghts achieved with $CaCl_2$. A previous study conducted in the laboratory showed that aggregates formation was enhanced for increasing salinities up to 10 g/l. Above this value, a slight decrease was observed.
A correlation was also established between the salinity and the L_f40 (Figure 6).

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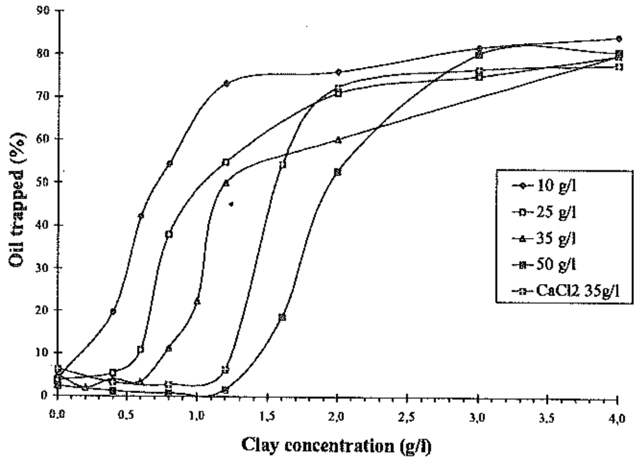

Figure 5. Influence of the Salinity. Oil : mixture HFO/BAL 110 96/4, Clay : Montmorillonite.

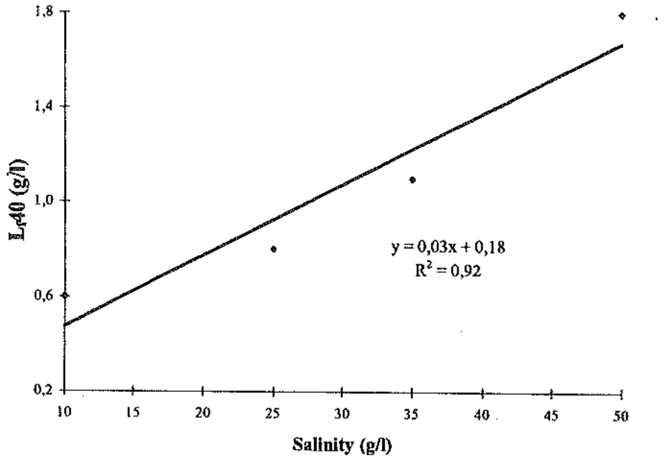

Figure 6. L_f40 versus Salinity

2.3.4 Oil/Clay Ratio

For high polar compounds content, aggregates were formed at low clay concentrations and lead to structures defined by a high oil/clay ratio. At high clay concentrations, the aggregates oil/clay ratio tended to a constant value independent of the type of oil (Figure 7).

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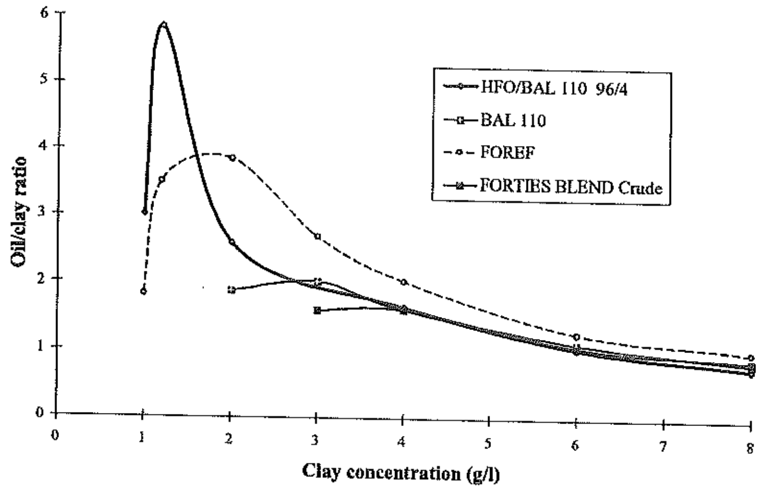

Figure 7. Aggregates Oil/Clay Ratio Versus Clay Concentrations for Various Oils. Salinity : 35‰, Clay : Montmorillonite.

2.3.5 Type of Clay

There is no significant differences between Illite and Montmorillonite as illustrated in Figure 8. Only two oils have been tested, but even using a larger panel of clays and oils, studies have shown that it is difficult to establish a correlation between the amount of oil trapped and the the cation exchange capacity of the clay (Wood *et al*, 1998).

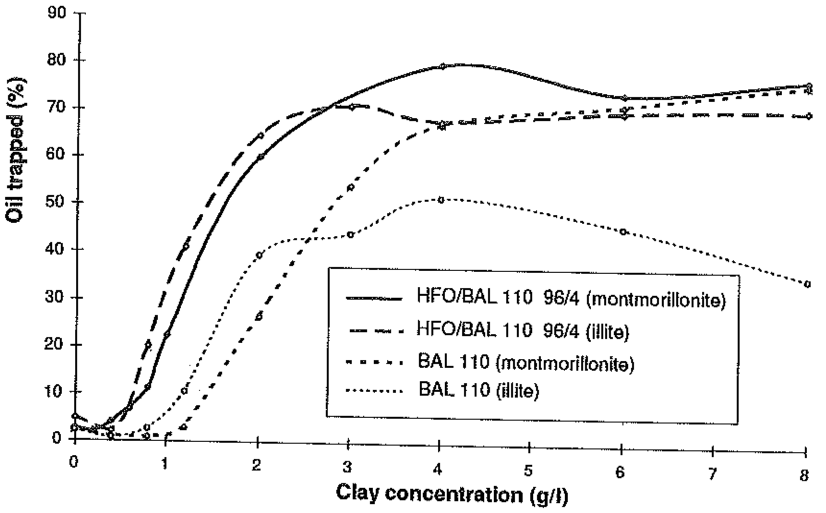

Figure 8. Influence of the Clay Nature. Salinity : 35‰.

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2.4 Results of the IFP Tests

Figure 9 confirms the results obtained with the WSL test method (influence of the polar compounds content on the 40% flocculation). In addition, the aggregates formation process occurred at lower clay concentrations and the relative amounts of oil and clay which induced a 40% flocculation for the FOREF was the same (oil/clay ratio equal to 5 as in the WSL test). The maximum amount of oil trapped was linked with the dispersant efficiency (Table 2) : all the dispersed oil was trapped on the mineral fines.

Table 2. Efficiency of Slickgone NS according to the WSL Test Method

OIL	WSL Dispersibility Efficiency (Dasic Slickgone NS)
FORTIES BLEND crude	22 [a]
HFO / BAL 110 (96/4)	32 [b]
FOREF	98 [b]

[a] Lunel *et al.*, 1997

[b] Guyomarch *et al.*, 1999

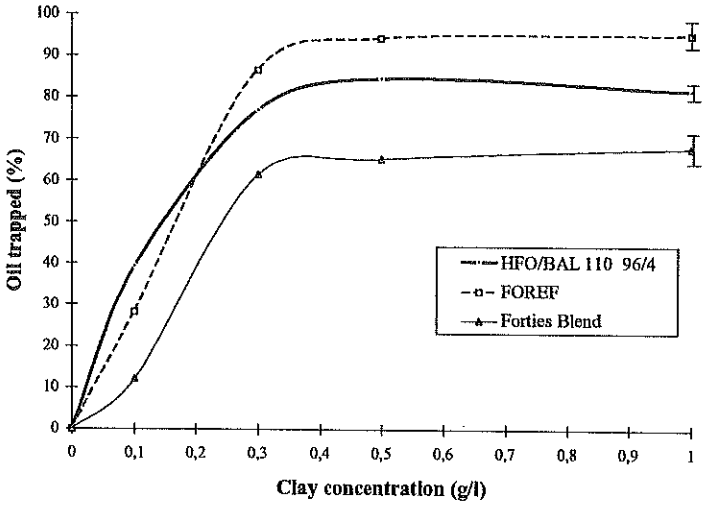

Figure 9. % of Oil Trapped with the Mineral Fines in the IFP Tests (Error Bars represent 95% Confidence Limit). Salinity: 35‰, Clay: Montmorillonite.

Guyomarch, J., F.-X. Merlin and P. Bernanose, Oil Interaction with Mineral Fines and Chemical Dispersion: Behaviour of the Dispersed Oil in Coastal or Estuarine Conditions, Proceedings of the Twenty-second AMOP Technical Seminar, Environment Canada, Ottawa, ON, pp. 137-149, 1999.

3.0 Polludrome Test

3.1 Experimental

One flume test (Polludrome) was performed to confirm the laboratory observations and to determine the oil distribution in the water column for a dynamic system. Temperature was set at 15°C and water height at 90 cm (corresponding to a 8 m^3 volume; salinity : 35‰). 4 liters of a mixture HFO/BAL 110 (70/30) (1700 cP at 20°C) were poured onto the water surface and treated with 5% dispersant (w/w). The maximum oil concentration was 200 mg/l. In these conditions, it was assumed that a 750 mg/l clay concentration (Montmorillonite) was sufficient to induce aggregates formation (oil/clay ratio : 0.3).

The energy needed to disperse the oil was provided by waves. After 30 minutes, the dispersion was achieved (the relative progress of the rate of the oil dispersion was followed using a turbidimeter).

3.2 Sedimentation and Dispersant Efficiency

When the dispersion was completed, the wave beater was stopped and samples were collected after 20 minutes at 4 heights from the bottom of the flume : 10 cm, 30 cm, 50 cm and 80 cm. Figure 10 shows that 80% of the oil was located in the lower section of the flume due to sedimentation. The efficiency of the dispersion was 60% without taking into account oil losses on the walls.

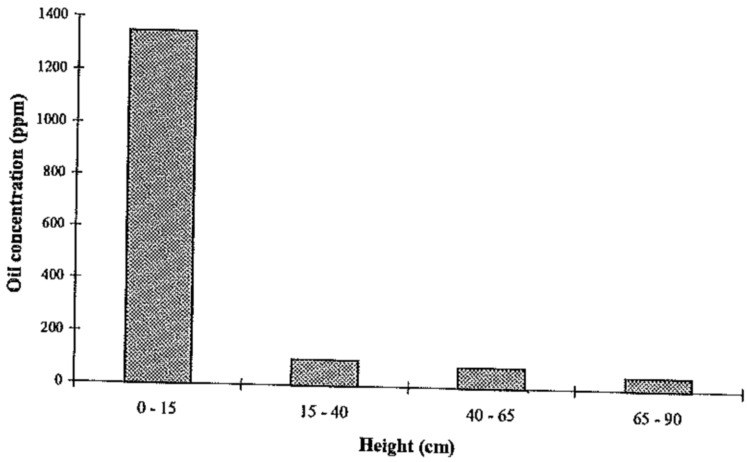

Figure 10. Oil Repartition in the Water Column

3.3 Oil in the Water Column and Current Speed

After 24 hours, the sedimentation was completed and there was no more oil in the water column. The current generator was switched on and gradually speeded up (3 speeds - 15, 45 and 75 cm/s - maintained for 30 minutes); samples were collected at a 60cm height to quantify the amount of pollutant removed from the bottom of the flume by the flow. Figure 11 gives the average oil concentration in the water column versus the current speed : the oil is totally resuspended in the water column for

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current as slow as 15 cm/s.

It should be noted that the bottom of the flume is smooth aluminium which is likely to result in less adherence of settled aggregates. In addition, the size and the configuration of the flume induce high turbulences of the flow. In other words, the remobilization of the aggregates might require a stronger current in a real environment.

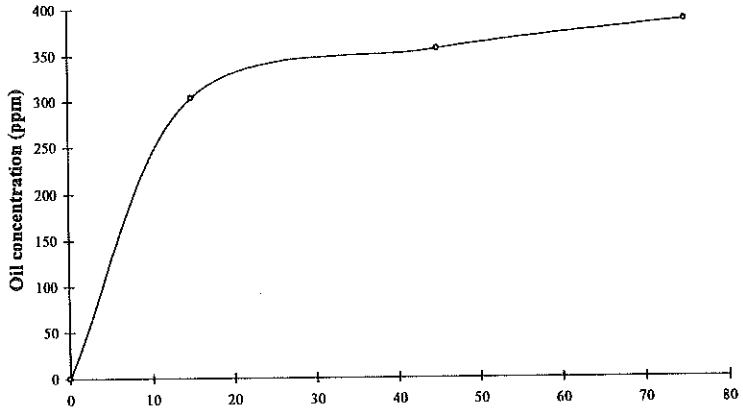

Figure 11. Oil Concentration at 60 cm versus Current Speed

4.0 Conclusion

4.1 Laboratory Studies

A simple test procedure (WSL test method : closed system, high oil concentrations, high energies) showed that :

- a small clay concentration hindered the chemical dispersion,
- a mineral load of at least several g/l (from 1.3 to 3.6 g/l according to the oil) was beneficial to remove oil from the water surface due to aggregates formation followed by sedimentation,
- this threshold mineral concentration value depends on the oil and clay types, their relative concentrations and the water salinity.

The IFP tests confirmed the results of the previous tests, particularly :

- the relative proportions of oil and clay required for oil-mineral aggregates formation (L_f40),
- the influence of the polar compound content on the L_f40,

and showed also that the maximum amount of oil trapped on the mineral particles depended on the dispersant efficiency (the aggregates formation concerned the totality of the dispersed oil).

4.2 Polludrome Test

These laboratory observations were confirmed at a larger scale, especially the associations of all the dispersed oil with clay for high mineral load (750 mg/l). In

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addition, most of the oil associated with clay minerals sedimentated in the absence of water current. After sedimentation was complete, a current speed of 15 cm/s was sufficient to resuspend the pollutant from the bottom of the flume (data obtained with an aluminium bottom).

The first experiments were run at high clay and oil concentrations. However, in the Polludrome test, the oil concentration was 120 ppm, comparable with the highest concentrations measured during the Protecmar sea trials program conducted in France between 1979 and 1986. The clay concentration (750 mg/l) was also representative of mineral loads found in estuaries (Gallenne, 1974). Consequently, the aggregation process is likely to occur in estuaries in case of chemical dispersion.

Finally, the laboratory studies should be carried on at lower concentrations commonly encountered during the last oil spill dispersion operations (Lunel and Davies, 1995) and for different environmental conditions such as external estuaries or other coastal systems.

The aggregates size and density seemed also variable (visual observations during the experiments) which implies different behaviours and fates according to hydrodynamic conditions : sedimentation, neutrally buoyant in the water column or presence at the water surface. The transport path of oil-mineral aggregates must be studied further to determine if it is beneficial to apply an oil dispersant in estuaries or coastal zone. This decision will depend on the hydrographical characteristics of the affected area.

5.0 Aknowledgements

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