

**Methodology for Assessing Oil Weathering in a Dedicated Hydraulic Canal:
Evolution of the Physical-Chemical Properties and
Dispersibility of Various Crudes**

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Abstract

When spilled at sea, crude oil is subjected to weathering processes such as evaporation, emulsification, dispersion, and photo-oxidation. These processes occur under natural conditions due to sea surface agitation by wind, waves, and currents and exposure of the oil to solar light. The chemical composition and physical properties of the oil are constantly changing according to its weathering stage. Understanding these changes is a key element in evaluating the potential impacts, optimizing the response options, and implementing the emergency response plan to an oil spill.

The objective of this study was to obtain experimental data on the behaviour of crude oils from different oil fields. The various weathering processes were realistically simulated in Cedre's hydraulic canal, in which different marine water conditions can be recreated: wind, waves, and UV light. All the experiments were carried out with a similar agitation level and at two temperatures. The parameters measured or assessed were: density, viscosity, water content and kinetics of emulsification, chemical composition and kinetics of evaporation, flash point, emulsion stability, oil adhesion, and chemical dispersibility.

1.0 Introduction

Various weathering processes (evaporation, emulsification, dispersion and photo-oxidation) occur under natural conditions and affect the whole of the oil spilled at sea. The chemical composition and physical properties of the oil are constantly changing according to its weathering stage. The light fractions of the oil evaporate gradually, its density increases, and part of the oil can disperse naturally in the water column, while the oil remaining on the water surface is emulsified with sea water and oxidized by solar UV. Oil can get increasingly viscous and become a new persistent pollutant in the environment. The behaviour of the weathered oil is often different from that of the original oil.

Understanding these changes is a key element in evaluating the potential impacts and optimizing the emergency response to an oil spill. Each spill entails a series of questions.

- What is the fate of the pollutant and what is the rate and extent of its weathering?
- Is natural dispersion possible?
- Does the oil emulsify? What is the emulsification rate? How stable is the emulsion?
- Is the oil chemically dispersible? How long would it remain dispersible? Which dispersant would be the most suitable?
- Is the oil likely to be mechanically recovered?

- Can the recovered emulsion be broken using demulsifiers? Which demulsifiers are suitable?
- What is the potential for bioremediation?

During a response situation, there is no time for investigating these questions. Therefore, they must be addressed during the emergency response planning process, in order to allow responders to make quick and appropriate decisions.

The objective of this study was to obtain experimental data on the behaviour of crudes from different oil fields. People in charge of preparing and implementing the emergency response plan to an oil spill will use these data. The goal is to help them choose the most appropriate response options according to the weathering stage of the oil.

In addition, when a large panel of products has been weathered in the flume with similar energy conditions and at a minimum of two temperatures, the resulting data will provide a useful basis for predicting the behaviour of an oil according to its initial chemical composition and physical parameters.

2.0 Experimental Weathering

The weathering of crude oils is complex, as different processes (evaporation, dispersion, emulsification, photo-oxidation) take place simultaneously. Laboratory methodologies exist to simulate each of these different processes. For example, evaporation can be simulated by a simple topping (distillation), pan evaporation or rotary evaporation. Concerning the oil emulsification, the modified Mackay-Zagorsky method using rotary funnels (Hokstad *et al.*, 1993) can be used. An alternative method consists in adding progressively sea water to the oil; in this case, the mixing energy is provided by a rotating stirrer.

However, no laboratory method exists to consider all the parameters simultaneously and to simulate the whole weathering process. In order to simulate these various phenomena realistically, Cedre has equipped its facilities with a hydraulic canal in which different marine (as well as inland) water conditions can be recreated, such as wind, waves, UV light and, if necessary, dilution. This canal consists of a loop, in which the water can be circulated. Large windows located along the canal allow observations at the surface, in the water column, and at the bottom. The canal is set in an air-conditioned room and is equipped with a wave generator (adjustable period), a current generator, and a UV light. When necessary, natural dilution processes can be re-created through tidal movements using a pumping system that pumps water from an additional water storage tank.

With this equipment, it is possible to weather samples of a specific oil under a variety of climatic conditions. In this study, all the experiments were carried out with the same agitation level and at two temperatures (10 and 20°C). In addition, for one oil, the temperature was the average annual temperature of the oil field from which it was extracted as it was an offshore oil.

3.0 Methodology

Cedre has studied the weathering of samples from different oil fields in its hydraulic canal for 7 days in order to determine the fate and behaviour of this oil in the first hours and days after an oil spill. During the test, the following parameters were assessed:

Evaporation and chemical composition

- modification of the oil composition
- kinetics of evaporation
- maximum evaporation rate

Flash point

- evolution of flash point

Emulsification

- kinetics of emulsification
- maximum water content
- assessment of the possibilities of using demulsifiers
- changes in the stability of the emulsion

Density

- evolution of the surface oil density

Viscosity

- changes in the oil viscosity

Dispersibility

- natural dispersibility of the oil
- chemical dispersibility of the oil
- window of opportunity for the use of dispersants

Oil adhesion

- adhesion of the oil on oleophilic surfaces

Treating agents

- selection of appropriate dispersants

Oil biodegradation

- assessment of the possibility of the oil degrading

4.0 Materials and Methods

Tests were performed at two temperatures (10 and 20°C) and at a moderate surface energy (waves and wind, e.g. about sea state 3). The test lasted 7 days in the canal; surface oil samples were taken periodically to determine the characteristics of the oil. At the end of the experiment, when the oil had reached its final state, a dispersibility test was performed directly in the flume.

4.1 Cedre's Hydraulic Canal (the *Polludrome*) and Sampling Procedure**4.1.1 Cedre's Hydraulic Canal**

For this study, dealing with open sea conditions, the *Polludrome*, shown in Figure 1, was used in the loop configuration with the water constantly being circulated.

The general characteristics of the canal are:

- Canal dimension: width : 0.6m; wall height : 1.6 m ; average water depth : 1 m.
- Tides: tidal range : up to 0.6 m (± 0.3 m); period : from 4 to 12 hours.
- Climate room : 0 to 30 °C.

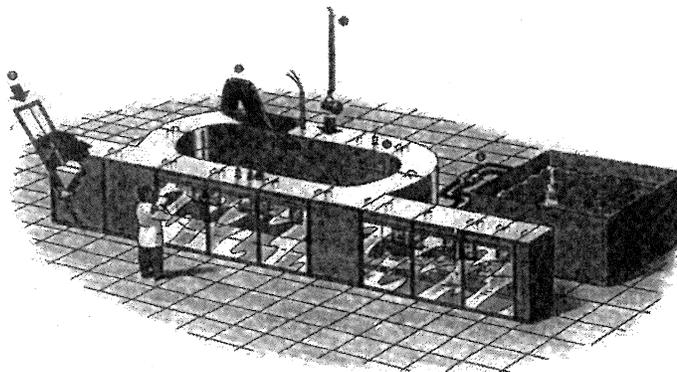


Figure 1 The Polludrome

4.1.2 Environmental Conditions

All tests were run assuming a moderate situation (sea state 3, which corresponds to wave heights between 0.5 and 1.25 m). The corresponding parameters for the Polludrome were:

- wave height: 25 cm
- mean period: 6 s
- current speed (water): 20 cm/s
- wind velocity: 3 m/s
- volume of seawater : 9.5 m³

The air temperature was set at 10 and 20°C, but it was also possible to recreate the average annual temperature of the oil field if necessary (from 0 to 30°C). The solar energy was recreated by four UV lights (up to 40 W/m²). Full salinity seawater (33 ppt) was used in tests.

4.1.3 Sampling Procedure

The oil volume poured onto the water surface at the beginning of the test was set at 20 L to ensure an extensive sampling even in case of high evaporation rates and to account for oil that sticks on the tank walls. During the first 12 hours, one sample was collected at least every 2 hours; after that period, the intervals could be increased to 4 to 6 hours and, finally, remaining oil was sampled twice a day until the weathering time reached one week. (Table 1).

Table 1 Sampling Times

Sample #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Time (hrs)	1	2	4	6	8	10	14	20	24	30	48	54	72	120	140

Samples were collected by using a large funnel equipped with a tap after the oil had been gathered with a little boom set in the canal in order to form temporarily a thick slick. Natural dispersion could be observed only during the first hours of weathering for the tested oils and was assessed by collecting samples at a depth of 30 cm after 1 hour.

4.2 Measurements

4.2.1 Evaporation and Chemical Composition

The evolution of the oil composition was assessed by fractionation into 4 chemical families (saturates, aromatics, resins, and asphaltenes). Resins and

asphaltenes do not evaporate and their relative proportions increase with the evaporation rate.

The saturate and aromatic fractions were analyzed using gas chromatography and High Performance Liquid Chromatography (Budzinski *et al.*, 1993). Chromatograms of these volatile compounds at different weathering times show the evolution of their distribution. The lighter molecules disappear progressively and the quantitative analysis of samples compared to the initial oil gives the evaporation rate. These analyses performed at various weathering times provide an assessment of the kinetics of evaporation. Considering the low rate of dissolution and natural dispersion compared to evaporation, water soluble fractions were not taken into account to assess the proportion of oil that evaporated.

The calculation of the maximum evaporation rate was checked by comparing the oil density at its final weathering state with samples obtained in the laboratory and characterized by their evaporation rate (measured by gravimetry). It was also possible to calculate a Weathering Index as proposed by Wang and Fingas (1994).

The fractionation into 4 chemical families was also necessary to assess the oil biodegradability. The biodegradability rate for resins and asphaltenes is low. For aromatics and saturates, further analyses by Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) must be performed as these families are divided into two series of compounds of high and low biodegradability, as discussed in section 4.2.9.

4.2.2 Flash Point

The flash point was measured according to the ASTM method D93-99c Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester (ASTM, 1999) on oil samples free from water or with low water content. This parameter was assessed until it reached 100°C, which is considered a reasonable limit in terms of risk of ignition for an oil slick during response operations. This limit was imposed by the emulsion formation: for temperatures greater than 100°C, the water ebullition was observed and could not allow a measurement of the flash point.

4.2.3 Emulsification

Emulsification was assessed, using three different methods, by measuring the following water contents in the oil samples:

- the water that settles naturally from the oil;
- the water that settles after 0.1% of demulsifier (*Demulsip*) has been added to the oil sample; and
- the water that is distilled using the Dean & Stark method, ASTM D95-99 Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation (ASTM, 1999).

From the Dean & Stark measurements, it was possible to determine the kinetics of emulsification as well as the maximum water uptake.

The assessment of the stability of the emulsion resulted from the comparison of the water content measured by the three different methods. The Dean & Stark method gives the real water content whereas the two other measurements characterize the water that settles due to the instability of the emulsions ('natural' instability or that caused by the added demulsifier).

4.2.4 Density

The density of the samples of surface oil was determined according to the ASTM method D70-97 Standard Test Method for Specific Gravity and Density of Semi-Solid Bituminous Materials (Pycnometer Method) (ASTM, 1999). This measurement gives the real density of the emulsion that would remain on the sea surface.

4.2.5 Viscosity

The viscosity of the oil samples was measured by establishing the rheological curve using a Haake VT 550 viscosimeter at the test temperature, to get the evolution of the viscosity at dedicated shear rates (e.g. 1, 10, 100 s⁻¹) as well as the thixotropic behaviour of the formed emulsion.

4.2.6 Dispersion

Natural dispersion (combined with the possible dissolution) was measured from water column samples. Oil was extracted using dichloromethane and the concentration was measured by UV spectrophotometry at 390 nm. For low natural dispersion rate, dissolution was assessed by analysing the extract by Gas Chromatography without sample preparation.

The chemical dispersibility of the surface oil was measured by using the Labofina-WSL test method (Martinelli, 1984) with modified mixing times (1, 5, and 15 minutes instead of 2 minutes), modified settling time (30 seconds instead of 1 minute) at test temperature, and with a reference dispersant (Inipol IP 90). Tests were performed using samples collected during the oil weathering. The different modifications of the WSL test are justified in the interests of assessing the influence of the mixing energy characterized by the test duration. Low values for long mixing times are correlated with a poor dispersibility. On the contrary, high efficiencies for short mixing time characterized a high dispersibility.

At the end of this weathering experiment, one dispersant was applied on the slick in its final state (high viscosity and high water content) directly in the Polludrome to obtain a more representative value of the dispersant efficiency in real conditions. When it is difficult to conclude (case different from those mentioned previously), a dispersion test directly in the Polludrome represents a useful tool as it seems to provide efficiencies closer to real conditions (Guyomarch *et al.*, 1999a).

4.2.7 Oil Adhesion

The evolution of the oil adhesion was measured by weighing the amount of oil that sticks to a given oleophilic plate (plate made of PVC, 10 x 10 cm). These data will help to document the efficiency of oleophilic skimmers over time.

4.2.8 Treating Agents

A series of dispersants (4 products) were tested on an oil sample in its final weathering state using the Labofina WSL test method in order to recommend the most appropriate dispersants. The 4 products were: Inipol IP 90, Corexit 9500, Dasic NS, and Finasol OSR 52. In addition, Inipol IP 90, Corexit 9500, and Dasic NS have been previously selected for their high efficacy on viscous oils (Guyomarch *et al.*, 1999b).

4.2.9 Oil Biodegradation

The biodegradability of the oil was assessed by determining its final composition (fractionation into 4 chemical families) and by analyzing the various compounds in the aromatic (by using High Performance Liquid Chromatography) and saturate fractions (by using gas chromatography). The biodegradability rates according to the kind of compounds were considered as:

Saturates

- Unresolved Complex Mixture (UCM) 60%
- Resolved peaks 100%

Aromatics

- 2 to 3 rings 50%
- more than 4 rings 30%

Resins

Asphaltenes

} 15%

The different rates were assessed according to values proposed by Oudot (1984). This information will document on the possibility of carrying out bioremediation operations.

4.3 Crude Oils

Crude oils were supplied by TOTALFINA-ELF from different oil fields located around the world. Density and viscosity of these tested oils are shown in Table 2.

Table 2 Density and Viscosity of the Oils

Oil Origin	Angola	Arabia	Argentina	North Sea
Density at 20°C	0.864	0.847	0.822	0.864
Viscosity at 10°C (mPa.s)	35	13	14	28
Viscosity at 20°C (mPa.s)	18	7	7	20

5.0 Examples of Characterizations

The various parameters were plotted versus the weathering time and, when possible, a curve was applied. This fit was the result of a statistical analysis using the Sigmaplot 4.0 software (SPSS Inc.). The data presented below come from different products and provide examples of evolutions that characterize oils.

5.1 Emulsification

5.1.1 Kinetics of Emulsification and Maximum Water Content

The kinetics of emulsification (A , the maximum water content, and k , the first order rate constant) were calculated by linear regression in the following way considering an 'Exponential Rise to a Maximum' model:

$$\%H_2O = A(1 - e^{-k \times t})$$

where A = maximum water content
(% volume)
 k = rate constant (hours⁻¹)
 t = weathering time (hours)

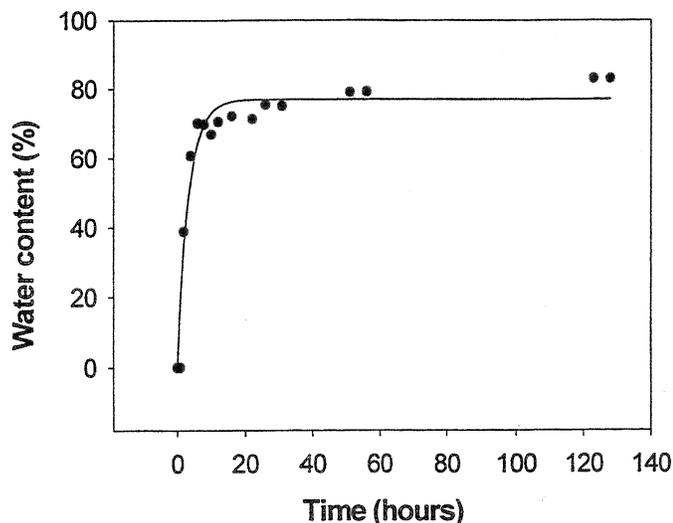


Figure 2 Example of Water Content Evolution

In the example presented in Figure 2, an increase of the water content very close to its maximum was observed after a few hours. According to the model, 90% of the maximum water content was obtained after 8 hours. The rate constant was 0.296 h^{-1} , but proved to be lower in other cases, and less than 0.04 h^{-1} for one oil.

The model provides a general view of the water content evolution, however, and cannot account for slight increases, as it was observed after 40 hours in this case. The maximum water content measured was 83% whereas this value was 77% according to the model.

5.1.2 Stability of Emulsions

The emulsions proved to be very sensitive to demulsifier treatments at each stage of the weathering period. To assess the stability, it was necessary to measure the amount of water that settled after 30 minutes. The stabilization assessment was possible when the water content had reached its maximum and had stabilized. An emulsion characterized by an 80% water content (80 ± 2) is shown in Figure 3. For this oil, it was possible to point out a significant stabilization according to the weathering time.

It was also possible to obtain similar curves considering 'natural settling' after 24 hours. These observations are in agreement with several studies that demonstrated the influence of the photo-oxidation process on the stability of emulsions (Aomari-Badri, 1999) and the transformation of polyaromatic compounds into polar molecules (Ducieux *et al.*, 1986; Barbas *et al.*, 1996).

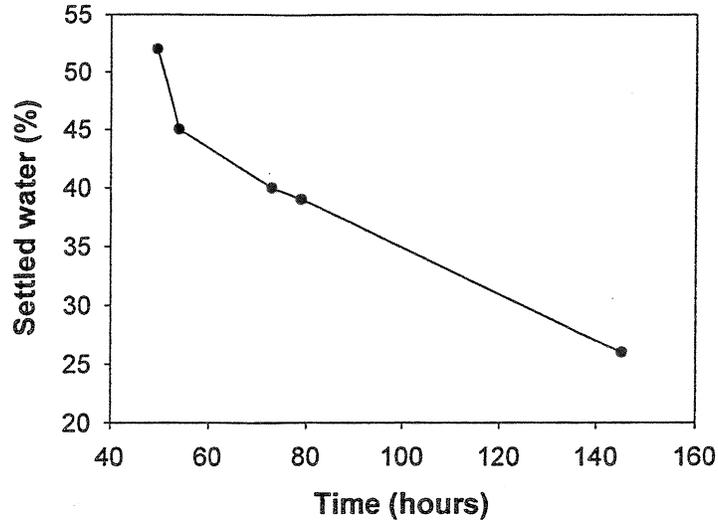


Figure 3 Example of Settled Water according to the Weathering Time

5.2 Density

The density was modelled by a function 'Exponential rise to a maximum':

$$\text{Density} = d_0 + A_1(1 - e^{-k_1 \times t})$$

where A_1 = maximum increase of density
 d_0 = initial density
 k_1 = rate constant (hours⁻¹)
 t = weathering time (hours)

In the example shown in Figure 4, the maximum density was close to 0.93 but increased to 1.0 in other cases, whereas the initial densities and viscosities were very similar. These differences were due mainly to the water content of the samples and slightly to the evaporation rate.

The viscosity evolution was due to evaporation of the lighter fractions of the oil and incorporation of water. According to their water content, the density of water-in-oil emulsions was described as follows:

$$d_{emulsion} = d_{HC} \times \%_{HC} + d_{water} \times \%_{water}$$

where d_{HC} = oil density
 d_{water} = sea water density
 $\%_{HC}$ = oil fraction
 $\%_{water}$ = water fraction

This relationship could be transformed into:

$$d_{emulsion} = d_{HC} + \%_{water} (d_{water} - d_{HC})$$

The emulsion density was plotted versus $\%_{water}$ for weathering times great enough to consider d_{HC} as a constant. By linear regression, d_{HC} was calculated at the end of its increase and had reached the value 0.937 for the oil presented in Figure 5 ($R = 0.99$).

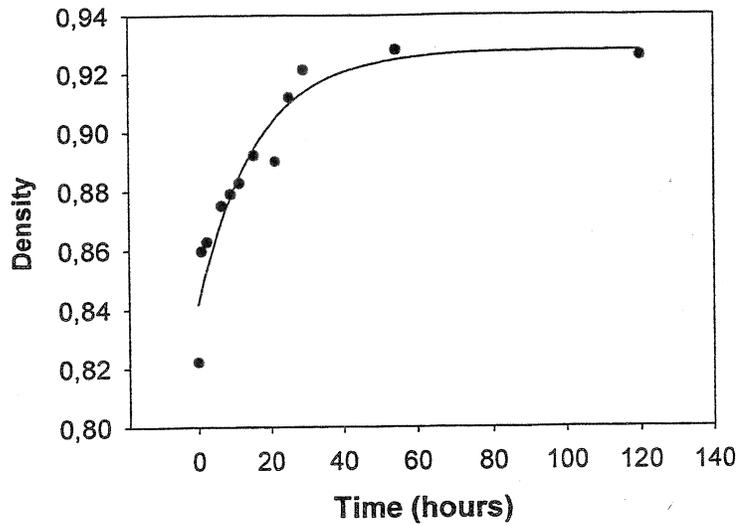


Figure 4 Example of Density Evolution versus Weathering Time

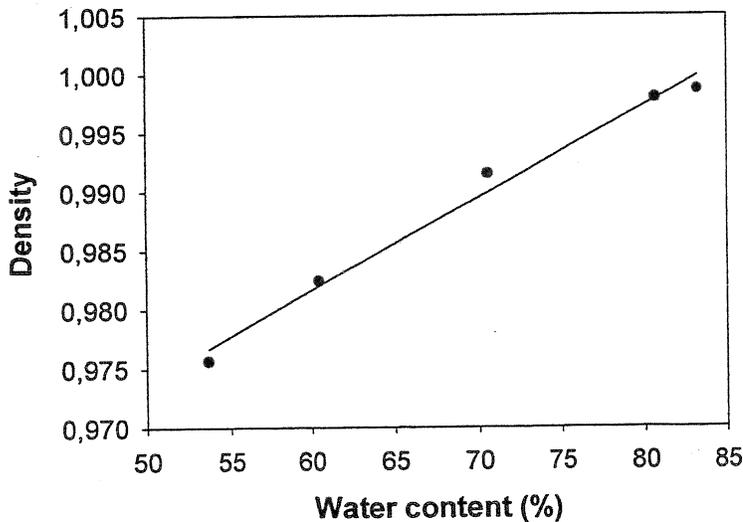


Figure 5 Example of Density Evolution versus Water Content

5.3 Viscosity

The viscosity was modelled in the same way as the water content (except that an additional parameter was introduced to account for the initial viscosity) and the same trend was observed.

$$\text{Viscosity} = \eta_0 + A_2(1 - e^{-k_1 t})$$

where A_1 = maximum increase of viscosity
 η_0 = initial viscosity
 k_1 = rate constant (hours⁻¹)
 t = weathering time (hours)

The low rate constant (compared to the water content evolution for the same oil) revealed a moderate initial increase in viscosity and the 90% value was obtained only after 70 hours. Viscosity is normally linked to the water content and the evolutions should have followed the same kinetic. This could be explained by evaporation, which was still occurring after more than 70 hours for most of the oils, hence the progressive increase of viscosity during the same period. The photo-oxidation process could also be responsible for this evolution, as well as the slight additional amount of water that can be incorporated between 40 and 120 hours. The viscosity evolution was the result of the combination of these three weathering processes, but it was difficult to determine the real effect of each of them. For one oil, viscosity increased from a stabilized viscosity of 1200 to 4800 mPa.s a few hours after the activation of UV lights.

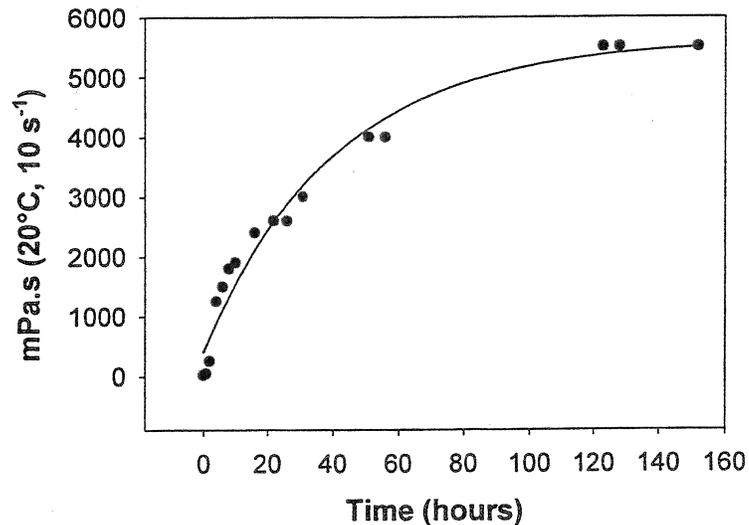


Figure 6 Example of Viscosity Evolution

5.4 Flash Point

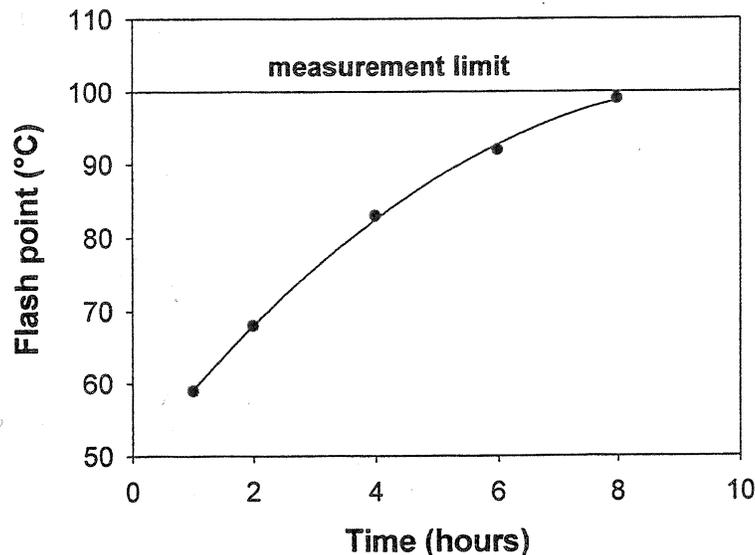


Figure 7 Example of Flash Point Evolution

From less than 18°C (ambient temperature), the flash point increased rapidly and reached the measurement limit of 100°C after 8 hours. This phenomenon was observed in most of the cases at the test temperature of 20°C.

5.5 Evaporation and Chemical Composition

Weathering induced a change in the chemical composition (Figure 8). The saturates and aromatics evaporated whereas the resins and asphaltenes could be considered as non-volatile compounds. The evolution of the chemical composition led to the calculation of the evaporation rate. The increase in the proportions of polar compounds (resins + asphaltenes) was a result of the evaporation of a part of the aromatics and saturates. The calculation showed that 25% of the initial oil evaporated throughout the entire weathering process.

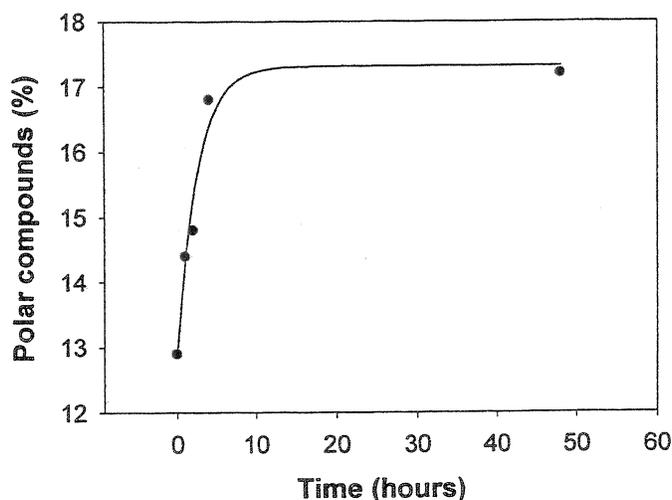


Figure 8 Example of Evolution of Polar Compounds Content

The kinetics of evaporation could be assessed by analyzing the n-alkanes distribution as illustrated in Figure 9. For this oil, the corresponding kinetic of evaporation is presented in Figure 10 ($\%Evaporation = A (1 - e^{-k \cdot t})$).

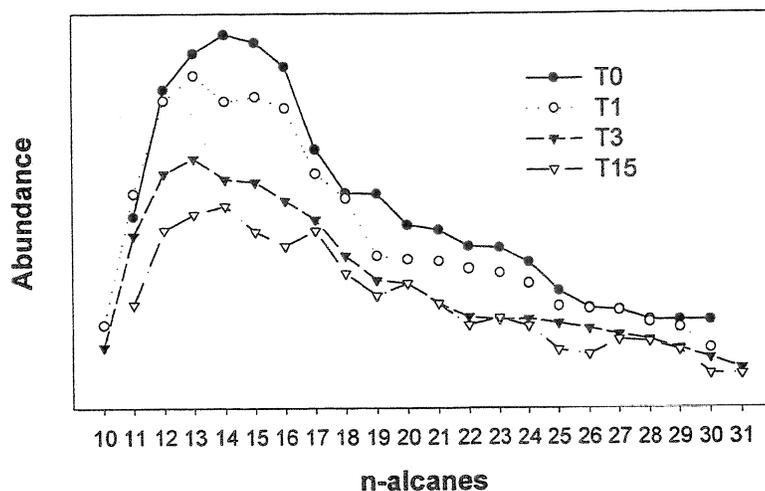


Figure 9 Example of n-alkanes Distribution Evolution

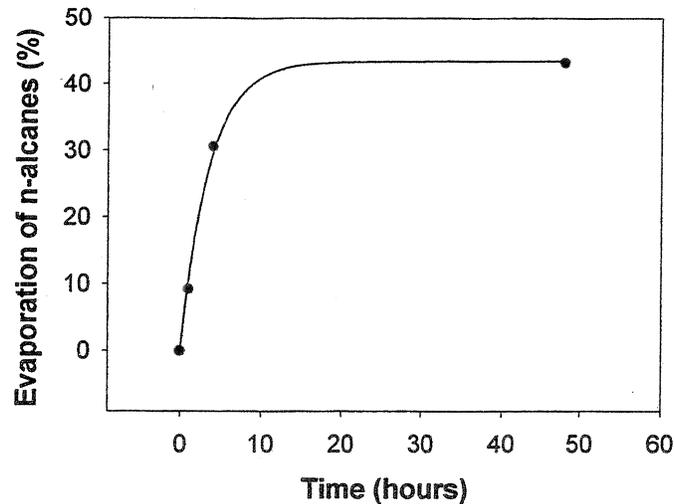


Figure 10 Example of Evaporation of n-alkanes Kinetics

After 8 hours, some chromatograms showed that less than 50% of the final evaporation was completed. This demonstrates that the increase of viscosity was mainly due to progressive evaporation; this process was 90% completed after about 24 hours but was still occurring at up to 70 or 80 hours in some cases.

The analysis of the saturates using gas chromatography and aromatics using HPLC of the initial oil compared to the oil at its final weathering stage led to another way of calculating the evaporation of the whole oil.

Finally, a third method was investigated, using the Weathering Index. It was calculated according to:

$$WI = \frac{nC15 + nC16 + nC17 + nC18}{nC24 + nC25 + nC26 + nC27}$$

Samples of the given oil were weathered in the laboratory and characterized by their evaporation rate and Weathering Index. The calibration curve (shown in Figure 11) that resulted from these data could be used to determine the evaporation rate of the same oil by analyzing by GC the remaining oil at the water surface.

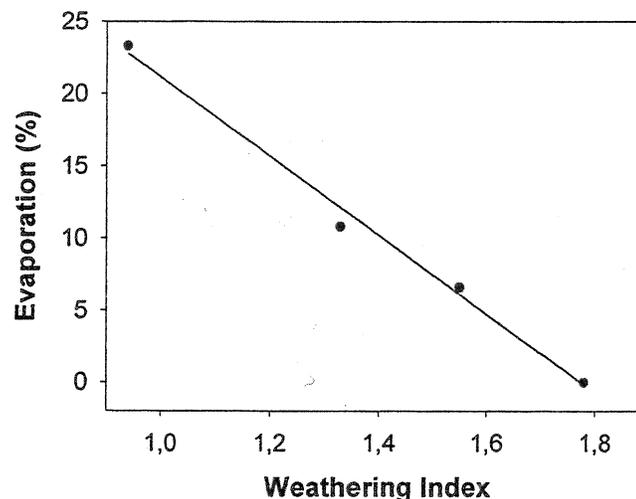


Figure 11 Example of Calibration Curve: Evaporation versus Weathering Index

For the oil presented as an example in this section, the evaporation rates assessed according to the three methods mentioned previously were:

- 30% by analysing saturate and aromatic fractions;
- 32% by using the calibration curve; and
- 25% according to the increase of polar compounds content.

It must be noticed that the polar compounds content depends on the chromatographic fractionation. This method can give variable results for the same sample and therefore, the evaporation rate calculation is not always reliable.

Concerning the use of the Weathering Index, it has been assumed that the linearity was conserved up to 35% evaporation rate as laboratory studies suggest (Brown, 1999).

5.6 Oil Biodegradability

The biodegradability of one oil was assessed at its final weathering stage. It was found that some aromatic compounds cannot be totally biodegraded whereas they can completely evaporate. This is shown in Table 3.

Table 3 Oil Biodegradability

	Weathered Oil Composition (%)	Biodegradability Rates (%)	Oil Biodegradability (%)
Saturates	resolved 26.6	100	26.6
	unresolved 41.5	50	20.8
Aromatics	2-3 rings 7.5	50	3.8
	> 4 rings 7.5	30	2.2
Resins	} 16.9	15	2.6
Asphaltenes			
Total			56.0

The high proportion of saturates, which are considered the most biodegradable compounds, provides a relatively high biodegradation rate of around 56%.

6.0 Treatment Possibilities

6.1 Oil Adhesion

Oil adhesion on an oleophilic plate was assumed to represent a reliable parameter to assess the possibility of using oleophilic skimmers. As expected, the oil adhesion increased with weathering time, provided that it is linked with the oil viscosity.

$$Adhesion = Ad_0 + A_3 \langle 1 - e^{-k_3 t} \rangle \quad \text{where } A_3 = \text{maximum increase of adhesion}$$

$Ad_0 = \text{initial adhesion (g/m}^2\text{)}$
 $k_3 = \text{rate constant (hours}^{-1}\text{)}$
 $t = \text{weathering time (hours)}$

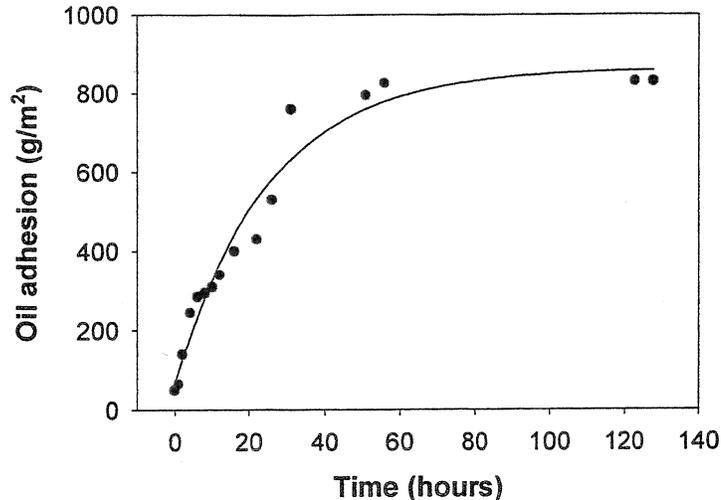


Figure 12 Example of Oil Adhesion Evolution

6.2 Chemical Dispersibility

6.2.1 Dispersibility According to the WSL Test

Figure 13 gives an example of the oil dispersibility versus viscosity (modified WSL test: 1,5, and 15 minutes mixing time and 30 seconds settling time). It shows that the dispersibility was reduced when the oil becomes emulsified. However, the efficiencies seemed to reach their minimum value rapidly for viscosity lower than 4000 mPa.s. These values could underestimate the real efficacy of a dispersion at sea, particularly in the range of viscosities (from 1000 up to 10,000 cSt) that were measured in these experiments. These values must therefore be calibrated with more realistic tests.

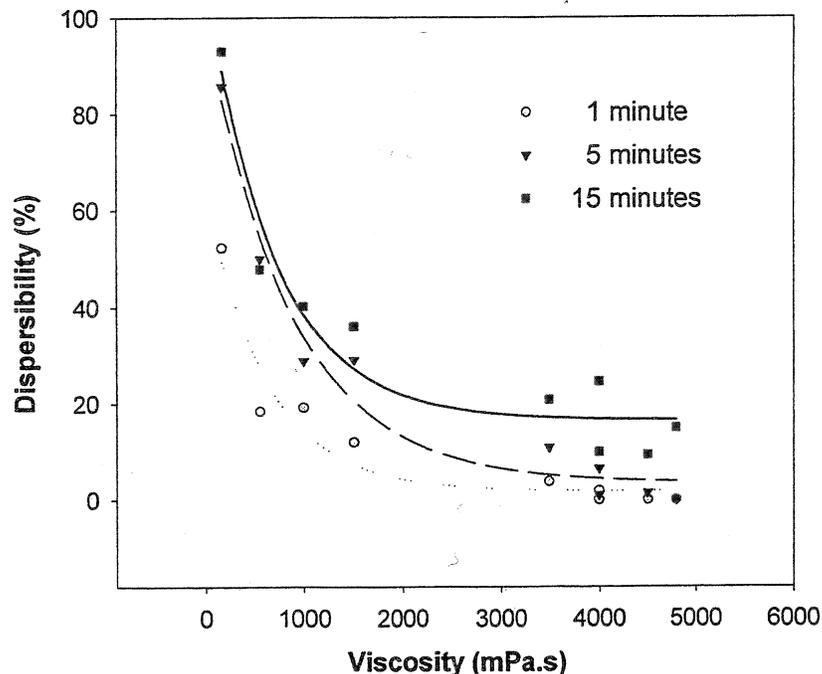


Figure 13 Example of Oil Dispersibility for Various Mixing Times

It must be noticed that for most of oils, natural dispersibility in the Polludrome was very low and not significant after a few hours.

6.2.2 Treating Agents

Table 4 shows the efficiency obtained with various dispersants on the oil at its final weathering stage (5500 mPa.s, 83% water content) according to the WSL test method (2.5 and 15 minutes mixing time, 1 minute settling time) at the test temperature of 20°C.

Table 4 Efficiency of Various Dispersants for 2.5 and 15 Minutes Mixing Time

Dispersant	Efficiency 2.5m (%)	Efficiency 15m (%)
Inipol IP 90	11	24
Corexit 9500	13	20
Finasol OSR 52	4	13
Slickgone NS	10	23

6.2.3 Dispersibility in the Flume Test

The 20% efficiency obtained according to the WSL test could underestimate the efficiency of a real dispersion. As a matter of fact, one dispersant (INIPOL IP 90) was applied directly on the slick in the Polludrome at the end of the weathering time [Dispersant Emulsion Ratio (DER) =1:50]. A second treatment was then applied [Dispersant Oil Ratio (DOR) =1:20] and the dispersion was completed within 30 minutes. Very little oil was remaining on the water surface (Table 5).

At this stage of the experiment, it was also possible to assess different treatment strategies such as combinations of demulsifier and dispersant or other double dispersant treatments using different products.

Table 5 Dispersibility in the Flume

	Viscosity (mPa.s)	Water content (%)	Dispersibility (%)
Initial Oil	20	0	-
Weathered	4800	80	≈ 0
1 st application	600	40	61
2 nd application	-	-	98

The 'two treatments strategy' was used as it seems to provide higher efficiencies. The first treatment at a low dosage acts as a demulsifier as the water content evolution shows. The second treatment is then improved, as the resulting oil is less viscous. These results demonstrate that the WSL test can underestimate dispersibility of emulsions; this is in agreement with previous studies conducted at Cedre (Guyomarch *et al.*, 1999a).

7.0 Differences of Evolutions

7.1 Nature of the Oil

The initial increase in viscosity was the result of either emulsification or evaporation, or both. For some oils, no water uptake was observed at the beginning of

the experiment as illustrated in Figure 14. The water incorporation occurred only after a few hours and required a partial evaporation of the oil. In this case, the model applied to the curve for the emulsification part was the same as mentioned previously. For the evaporation part, it seemed that an 'exponential growth' model fitted this kind of evolution (dash line for the example in Figure 15).

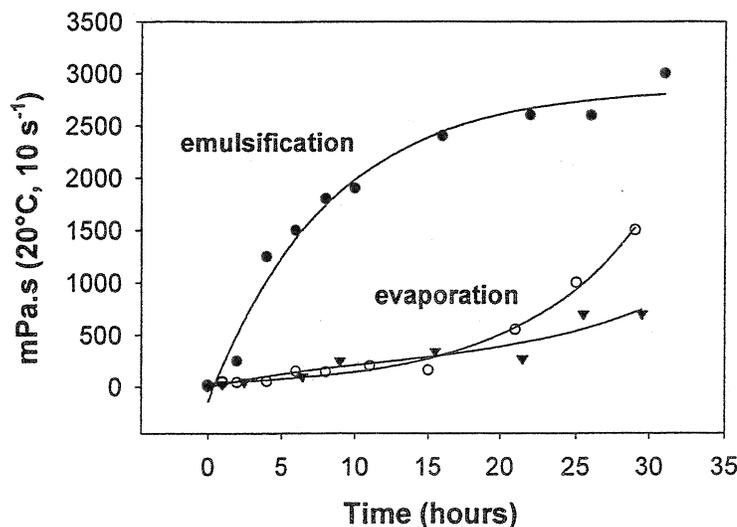


Figure 14 Initial Increase of Viscosity for Various Oils

7.2 Temperature

The same oil was weathered under the same conditions at two different temperatures. Surprisingly, after 48 hours in the flume, viscosity at 20°C was higher than at 10°C. Considering the type of evolution presented in Figure 15, it seemed that evaporation constituted a key factor. At 10°C, the oil incorporated some water at the beginning of the experiment and the following increase of viscosity was mainly due to evaporation. However, the emulsion was unfavourable to this process, which was considerably slowed down. At 20°C, the oil initially evaporated and then, incorporated some water: the resulting emulsion was more viscous. The comparison of the flash point evolution shown in Figure 16 seemed to be in agreement with this explanation.

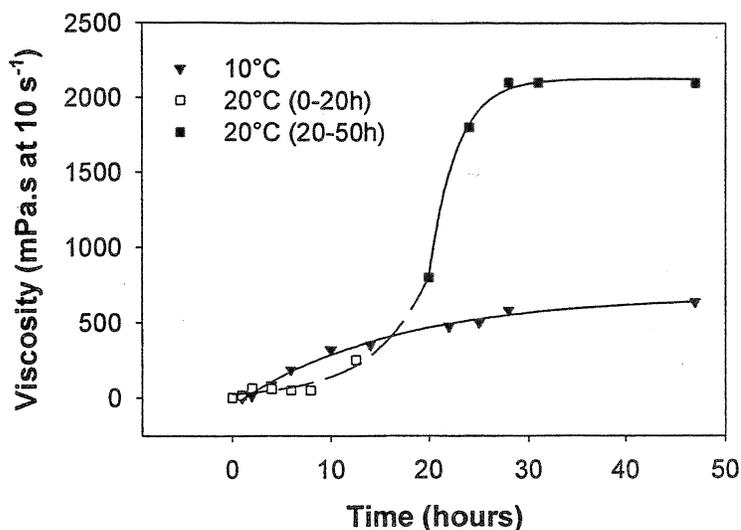


Figure 15 Example of Viscosity Evolution at 10 and 20°C

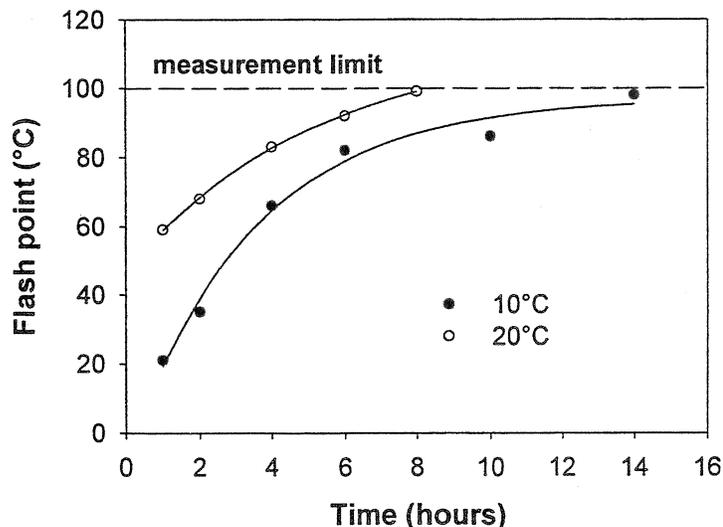


Figure 16 Example of Flash Point Evolution at 10 and 20°C

For this example, the other parameters presented the same trend in comparison with viscosity and flash point illustrated above.

7.3 Summary of Results

Table 6 summarizes the evolutions of 5 crude oils tested in the Polludrome. These results show the variety of behaviours with maximum water contents varying from 33 up to 83% and also great variations of maximum emulsion densities. Kinetics is also characterized by constant rates, which point out great differences of speeds of evolution.

Table 6 Evolution of the Physical-Chemical Properties of the Oils

Oil Origin	Angola	United Arab Emirates	Argentina	North Sea
Test temperature (°C)	26	20	20	20
Test duration (hours)	145	145	107	40
Maximum viscosity (mPa.s at 20°C, 10 s ⁻¹)	5500	4800	2500	2100
90% max. viscosity (hours)	70	65	93	25
Maximum emulsion density	0.997	1.001	0.926	0.972
Maximum oil density	0.937	0.929	0.868	0.922
Maximum water content (%)	83	83	33	78
90% max. water content (hours)	8	45	30	18
Evaporation rate (%)	30	30	10	25
Oil adhesion (g/m ²)	800	3150	650	1550
Time for Flash Point > 100°C (hours)	6	5	6	10

8.0 Conclusion

All the experiments were carried out according to a rigorous methodology: environmental parameters were identical, which induced waves and currents very similar from one experiment to another. Measurements were also planned (same order of measurements that must be performed immediately) and settling times imposed between the sampling and the analysis. This methodology proposed for the oil weathering characterization seems to provide coherent results as illustrated by the density, which could be correlated with the water content. In addition, the general evolution of all the parameters was in agreement with previous studies and/or models. Curves obtained could also be modelled using a function according to the parameter assessed, which allows further comparisons between the different experiments and test temperatures. It must be noted that this study has just begun and the objective is to constitute a database regularly enriched with different oils.

This set of data also provides several elements on the oil behaviour and evolution in specific environmental conditions in order to more realistically simulate the oil weathering process. It will be used by oil companies to implement the response plan in case of oil spills.

The next step of this study is to calibrate the flume test with real conditions at sea, particularly concerning the emulsification and evaporation kinetics. In a first stage, this calibration will be devoted to the evaporation process through experiments carried out in a large open pool. Concerning the different kinetics illustrated in this study, the fact remains that the mass phenomenon cannot be simulated and therefore experiments must be conducted at sea. This year, a study will be conducted and devoted to the assessment of remote sensing responses of different oils. This study will include a monitoring of the physical-chemical parameters, which characterize these oils.

9.0 Acknowledgements

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