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# 10 Environmental Emulsions: A Practical Approach

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## 10.1 INTRODUCTION

When oils are spilt at sea different weathering processes alter the properties of the oil as a function of time and weather conditions. Evaporation of volatiles, water-in-oil emulsification (w/o emulsions), and natural dispersion (o/w emulsions) are important weathering processes taking place when oil is spilled at sea. The emulsification of water in the oil contributes to a change in properties of the spilled oil and increases the total volume of pollutant. The natural dispersion contributes to a removal of the oil from the sea surface into the water column. The behavior of spilled crude oils and refined oil products depends on the ambient conditions (e.g., temperature, sea-state, currents) and on the chemical composition of the oil. Large variations in oil properties cause them to behave differently when spilled at sea. The Gullfaks crude spilled at the *Braer* incident in the Shetlands has a low content of waxes and asphaltenes, which are important compounds for stabilizing water-in-oil (w/o) emulsions formed on the sea surface. This, combined with heavy sea state, resulted in consequences that were much less severe than might have been expected (1). Almost all of the 84,000 tons of the spilled Gullfaks crude oil was naturally dispersed into the water column as o/w-emulsions (2). In the *Amoco Cadiz* and the *Metula* spills,

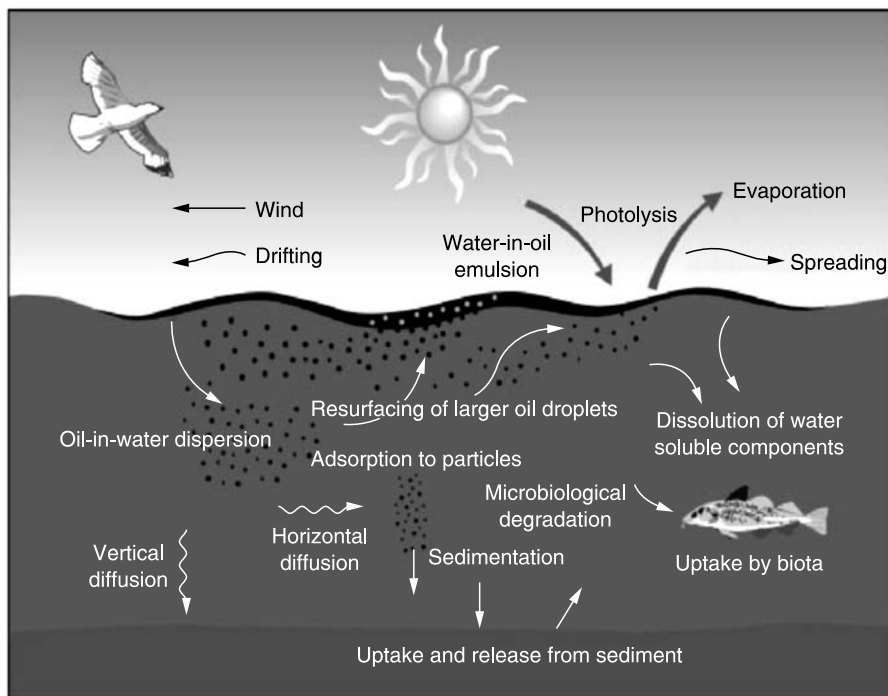
persistent “chocolate mousse” has contaminated the shorelines for years after the initial spill (3,4). Knowledge about weathering behavior of crude oils and fuel oils is therefore of importance for environmental risk assessment of a spill, for contingency planning, response analysis, net environmental benefit analysis (NEBA), and for rapid and right decision making in the case of an oil spill.

## 10.2 WEATHERING OF OIL ON THE SEA SURFACE

When a crude oil is spilt at sea a number of natural processes take place, which change the volume and the chemical properties of the oil. These natural processes are evaporation, water-in-oil (w/o) emulsification, oil-in-water (o/w) dispersion, dissolution of oil components into the water column, spreading, sedimentation, oxidation, and biodegradation. A common term for all of these natural processes is weathering. The relative contribution of each process varies during the duration of the spill. Figure 10.1 illustrates the various weathering processes taking place.

The behavior of spilled crude oils and refined oil products depends on:

- The physicochemical properties of the spilled oil and its propensity to disperse into the water column or to form stable water-in-oil (w/o) emulsions on the sea surface
- The release conditions (the rate and amount of oil spilled, surface release or underwater release, presence of gas etc.)
- The ambient conditions (e.g., temperature, sea-state, currents)



**FIGURE 10.1** The weathering processes that take place when oil is spilt on the sea surface.

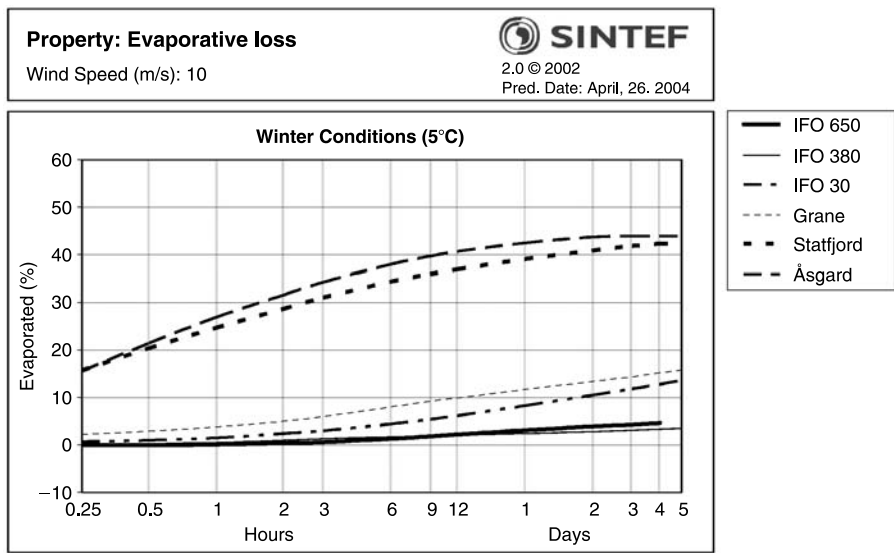
Evaporation, natural dispersion, and emulsification are the most important processes affecting the fate of the oil on the sea surface.

The weathering properties of crude oils and fuel oils are studied in the laboratory using a “stepwise” weathering procedure of the “fresh” crude oil including evaporation and water-in-oil emulsification. The laboratory data from various weathered oil samples generated in the laboratories form the basis for the input in SINTEF Oil Weathering Model (OWM) for prediction of the weathering behavior of oils at different weather conditions. A description of the SINTEF weathering methodology including small- and meso-scale laboratory testing of oils and modeling of weathering behavior of oils is given by Daling et al. (5), Johansen (6), Hokstad et al. (7), and Daling and Strøm (8).

10.2.1 EVAPORATION

Evaporation is one of the natural processes removing the volatile components from the spilled oil on the sea surface. The evaporation process starts immediately after the oil is spilled and the evaporation rate decreases throughout the duration of the oil spill. The relative amount evaporated depends on the chemical composition of the oil in addition to the prevailing weather conditions, sea temperature, and the oil slick thickness. The rate of evaporation will therefore vary for different oil types. Light refinery products (e.g., gasoline and kerosene) may evaporate completely after a few hours/days on the sea surface. Condensates and lighter crude oils can lose 50% or more of their original volume during the first days after an oil spill (9). Predicted evaporation for some residual fuel oils and Norwegian crude oils are shown in Figure 10.2.

The most significant changes caused by evaporation is that the loss of volatile and semi-volatile compounds increases the relative amount of higher molecular weight compounds (boiling point above 250 to 300°C). The chemical and physical properties of the remaining oil change



**FIGURE 10.2** Predicted evaporative loss with the SINTEF OWM on the basis of laboratory studies for some residual fuel oils and Norwegian crude oils.

due to the evaporative loss. For example the density, viscosity, pour point, and the relative wax and asphaltene contents of the oil residue will increase with the increased amount of evaporation.

10.2.2 WATER-IN-OIL EMULSIFICATION

The formation of water-in-oil emulsions significantly affects the behavior and clean-up of oil spilled at sea. As a result of emulsification, the total emulsion volume may increase to as much as six times the original spilled oil volume depending on the properties of the oil.

Formation of w/o emulsions takes place in the presence of breaking waves (i.e., wind speeds of above 5 m/s), but a slow water uptake can also occur during calmer weather or lower sea states. The maximum water uptake will vary for different crude oils. Tests performed at SINTEF have shown that the maximum water uptake is fairly independent of the prevailing weather conditions, although the emulsification rate depends highly on the weather conditions. Predicted maximum water content and emulsification rate for Grane crude oil at different wind speeds are shown in Figure 10.3.

The physical and chemical properties of the continuous phase of the emulsion (oil) govern the stability of the emulsion formed, and thus the emulsification rate and maximum water content. As different oils have different physical and chemical properties the kinetics of the emulsion formation will be highly oil dependent. Very heavy fuel oils like the oils spilled by the *Erika*, *Prestige*, and the *Baltic Carrier* form water-in-oil emulsions slowly. However, many spilled crude oils will rapidly form w/o emulsions when spilled at sea (e.g., Ref. 10). Such emulsions will initially have low viscosities, will be unstable, and will tend to revert to the oil residue and water if they are removed from the mixing action of the sea. Predicted water uptake for some residual fuel oils and Norwegian crude oils under similar conditions (10 m/s wind and 5° C) are shown in Figure 10.4.

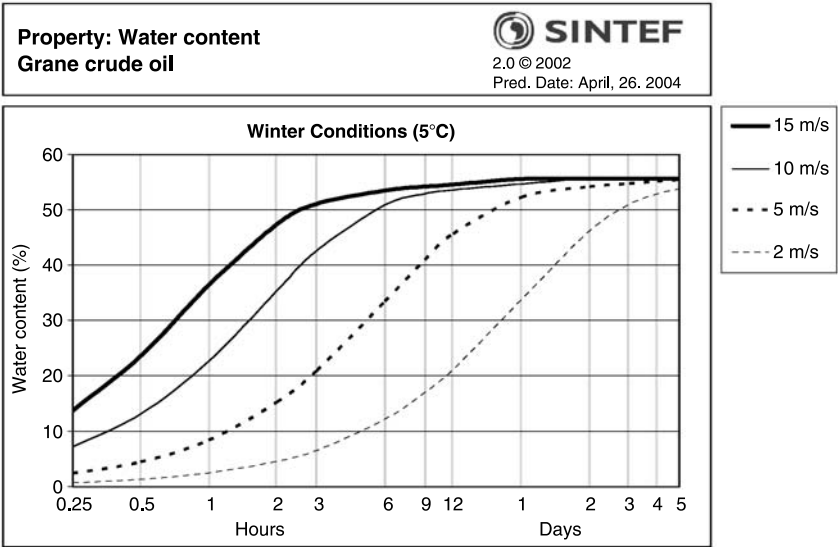
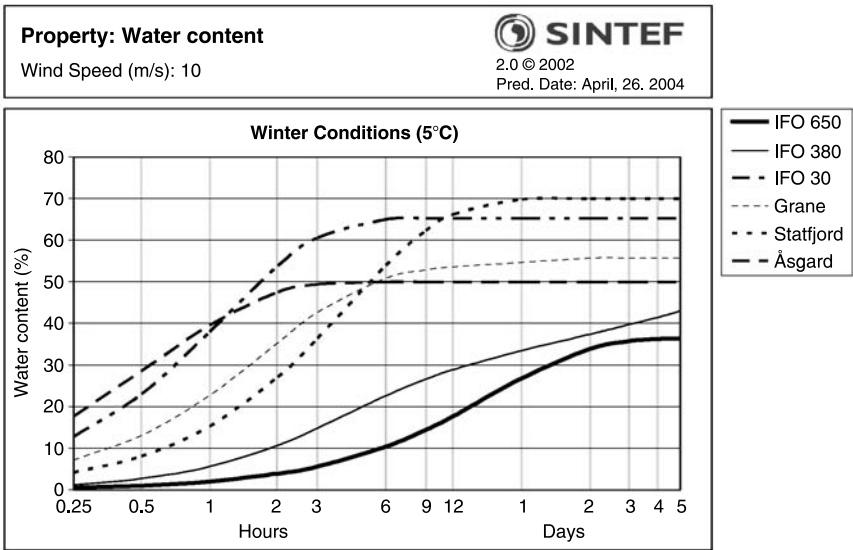
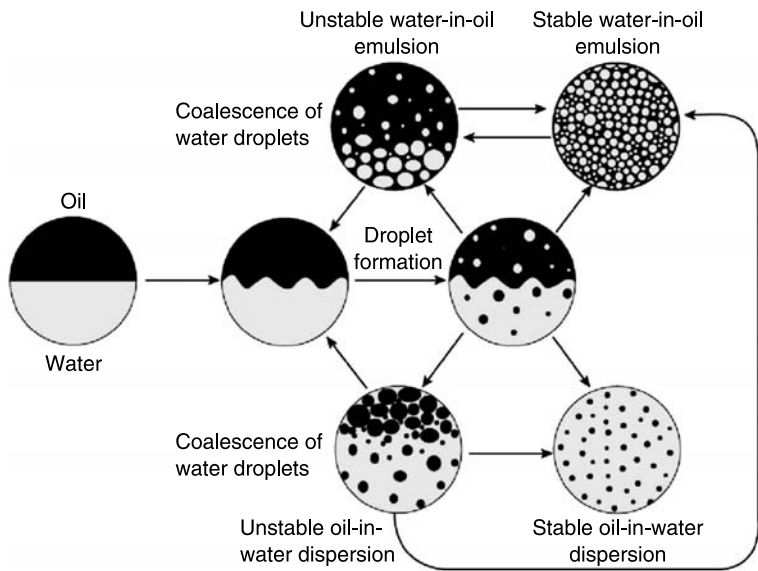


FIGURE 10.3 Predicted emulsification of Grane crude oil with SINTEF OWM on the basis of laboratory data at different wind speeds.



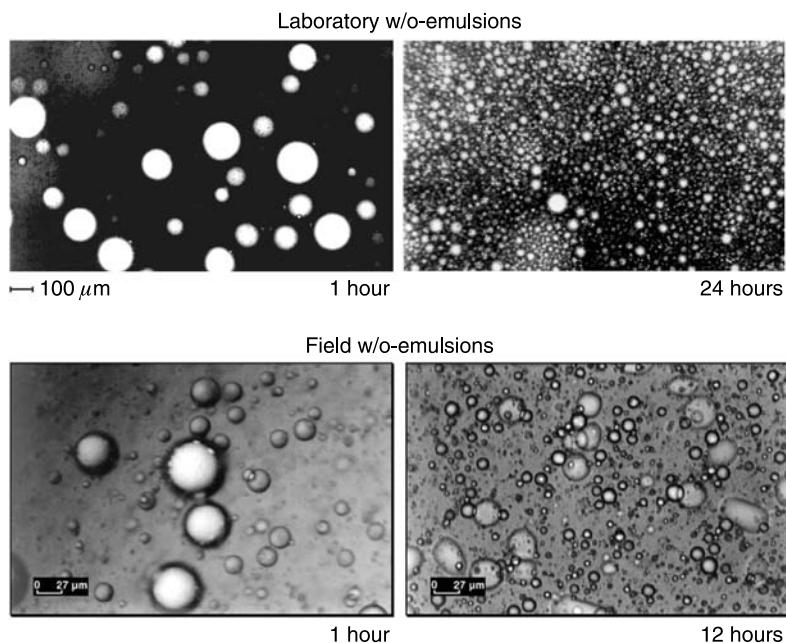
**FIGURE 10.4** Predicted water uptake with SINTEF OWM on basis of laboratory data for some oils.



**FIGURE 10.5** Mixing of oil and water at sea.

Unstable emulsions are simply mixtures of water droplets in oil and the w/o emulsion present on the surface will be the result of the dynamic equilibrium of emulsion formation and emulsion breakdown (see Figure 10.5).

The stability of the w/o emulsion depends on the water droplet size in the emulsion. Not all of the water droplets in the emulsion are stable. The largest droplets may coalesce and settle



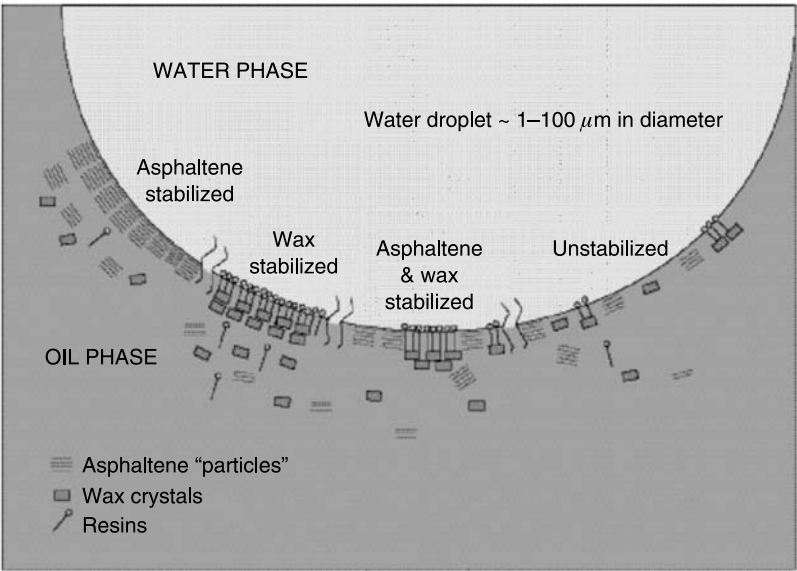
**FIGURE 10.6** Microscope pictures of w/o emulsions produced using the rotating flask method showing the influence of mixing time.

out of the w/o emulsion. Large water droplets may be reduced in size by the flexing, stretching, and compressing motion of a slick due to wave action. After a period of time the droplet size distribution in the emulsion are shifted towards the 1 to 10  $\mu\text{m}$  area, yielding a more stable emulsion. Microscope pictures of emulsion formed in the rotating flasks (emulsification method described by Mackay and Zagorski (11)) are shown in Figure 10.6.

Another factor that influences the stability of the w/o emulsion is the amount of surface-active components present in the parent oil. As the viscosity of the oil residue increases due to the evaporative loss of volatile components and the precipitation of stabilizing agents (asphaltenes, photo-oxidized compounds (resins), and in some crude oils precipitated waxes) the emulsion becomes more stable. Resins and asphaltenes have hydrophobic and hydrophilic properties and will concentrate at the oil/water interface. The precipitated asphaltenes create an elastic “skin” between the water droplets and the oil (see Figure 10.7). The stability of the emulsion will then increase because the water droplets cannot coalesce and drain so easily from the emulsion due to this “skin” formation and the equilibrium will tend to favor emulsion formation.

The asphaltene content of the oil is important to enable the formation of stable emulsions, and the presence of wax will contribute further to the stabilization of the emulsion formed. Oils low in asphaltenes but high on wax form emulsions that are stabilized by the rheological strength of the continuous phase (oil) due to precipitated wax rather than the chemical stabilization of asphaltenes and resins. Emulsions from such waxy oils are constituted by larger droplets and are generally less stable than asphaltene stabilized emulsions. Stability and stability classes of w/o emulsions formed during oil spills are also discussed by others (12,13).

The Gullfaks crude spilled at the *Braer* incident in the Shetlands is a biodegraded crude oil with a very low content of waxes and asphaltenes. As the oil lacked stabilizing compounds



**FIGURE 10.7** Stabilization of the interfacial layer between the water and oil in a w/o emulsion by wax and asphaltenes.

**TABLE 10.1**  
**Wax and Asphaltene Content in Some Selected Crude Oils from The North Sea**

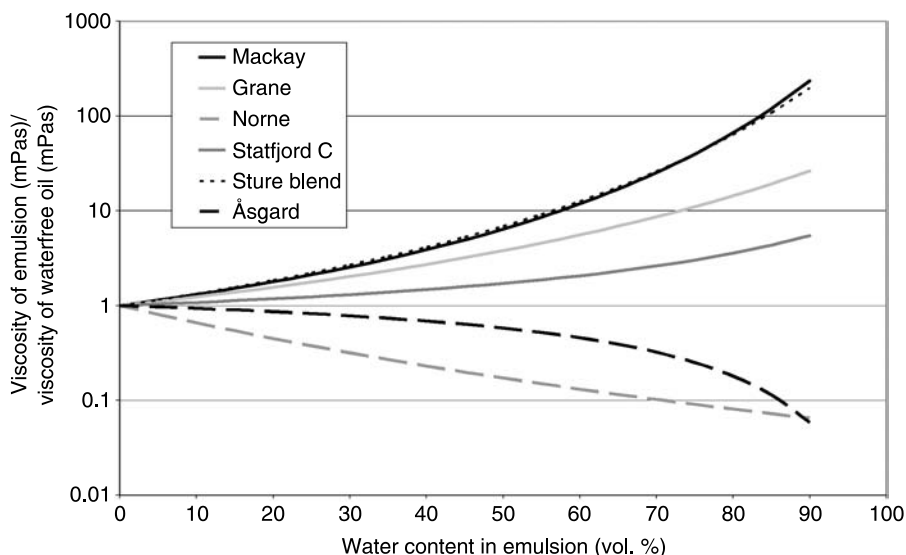
Crude Oil	Wax (wt%)	Asphaltenes* (wt%)	SARA Analysis**			
			Asphaltenes (wt%)	Resins (wt%)	Aromatics (wt%)	Saturated (wt%)
Forties		0.2				
Grane	3.2	1.4	3	37	38	22
Gullfaks	1.6	<0.1	0.8	7	53	39
Statfjord	4.2	0.1	1.5	11	29	59
Åsgard	4.6	0.05				

\*The asphaltenes are those that are insoluble in hexane (IP 143).

\*\*Iatroscan.

the emulsion formed were unstable and had a low viscosity. This, combined with the weather conditions that prevailed at the time of the spill, resulted in almost all of the 84,000 tons of the spilled Gullfaks crude oil being naturally dispersed (14). During the *Sea Empress* spill of Forties Blend crude oil (another North Sea crude oil) a significant amount of the surface oil was converted into w/o emulsions (2). Forties crude oil is a paraffinic crude oil with a relative high wax content and a low content of asphaltenes.

Wax and asphaltene content and SARA-analysis (Saturated, Aromatics, Resins, Asphaltines) for some crude oils are shown in Table 10.1. As seen in Table 10.1 from the SARA analysis, the relative composition of the crude oils is very different. Gullfaks has low content of stabilizing



**FIGURE 10.8** The Mackay curve and experimental curves as input to models for predicting emulsion viscosities for emulsions formed at sea.

compounds and a higher aromatic content. The paraffinic Statfjord, which has similarities to Forties crude oils, has a higher content of stabilizing agents and saturates.

As oil emulsifies on the sea surface, the viscosity will increase with increasing water content. A widely used approach for predicting w/o emulsion viscosity is the Mooney equation which gives the viscosity ratio as a function of water content. The viscosity ratio is defined as the w/o emulsion viscosity divided by the parent oil viscosity. Mackay (15) has studied viscosity of w/o emulsions and determined the typical values for the constants in the equation for emulsions formed when oil is spilt at sea. Figure 10.8 shows the “general correlation equation” based on the Mackay relationships between dispersed water phase volume and viscosity used in many models to predict the viscosity of emulsion based on the viscosity of parent oil and water content. Specific laboratory measurements of the viscosity of oil residues and the emulsions generated from them in the rotating flask method are used to “tune” this correlation equation for specific oil being considered. This will lead to more reliable predictions of the emulsion viscosity for individual oils, compared to using only a “general” correlation equation, because the variation in water droplet size distribution is considered.

The maximum water content of w/o emulsions is different (Figure 10.9) due to various chemical and physical properties of oils. Weathering studies of oils have shown that the maximum water content decreases as the viscosity of the residue increases.

Predicted emulsion viscosities are shown for some crude oils and fuel oils in Figure 10.10 and shows very high viscosity for the heavy fuel oils (100,000 to 300,000 mPas after some days at sea). The viscosity of the crude oils after some days at sea varies from 10,000 to 70,000 mPas. This shows that crude oils and fuels may behave very differently when spilt at sea and that various crude oils behave differently at sea due to differences in chemical and physical properties of the oils.

The weathering processes change the appearance of the oils as seen in Figure 10.11. The pictures are taken after 3 days’ weathering in a meso-scale flume. The colors of the emulsified



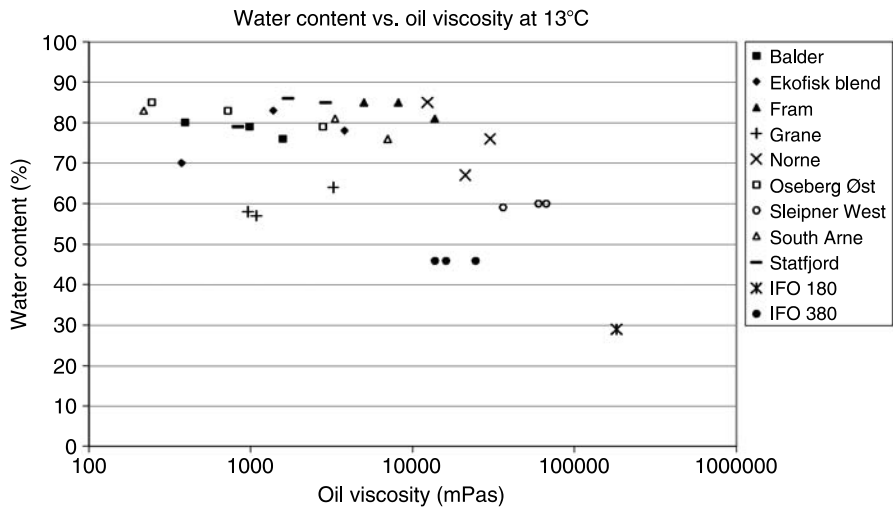


FIGURE 10.9 Water content in emulsion versus oil residue viscosity.

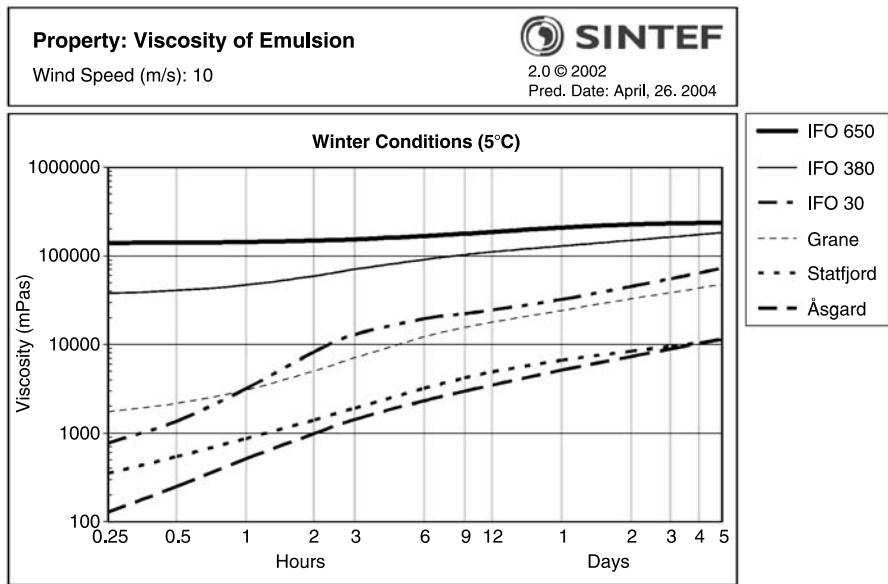
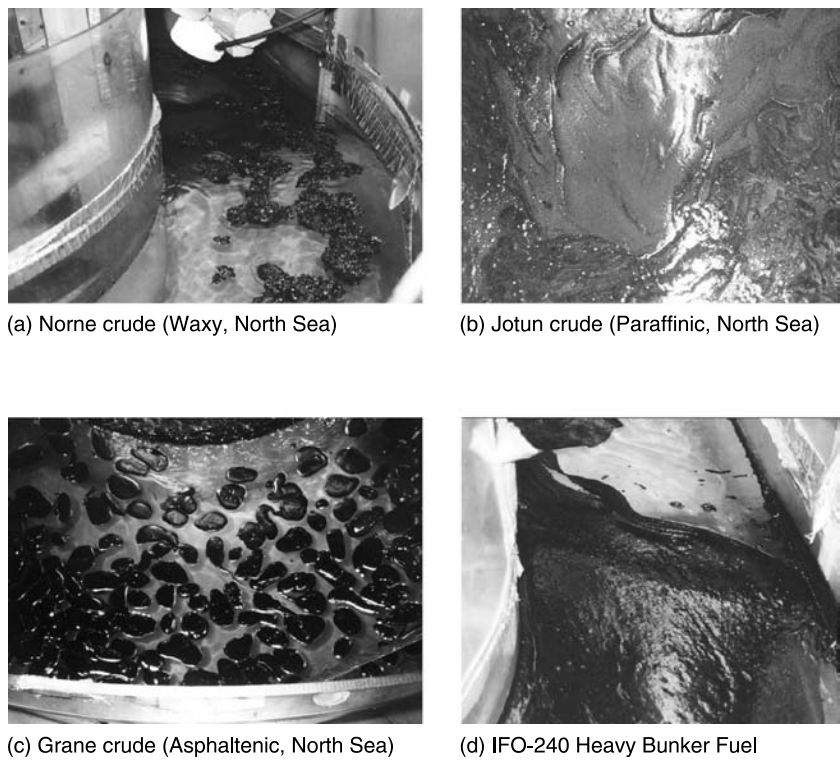


FIGURE 10.10 Predicted viscosities of a selection of crude oils and fuel oils.

oils vary from the yellow/brown, paraffinic Jotun to the dark brown, solidified waxy Norne and the black lumps of the asphaltenic Grane. Some oils form continuous slick while others form lumps. Table 10.2 shows the water content and viscosity of these emulsions. The viscosity varies from approximately 2400 to 23,000 mPas for these oils, and the water content from 35 to 70%.



**FIGURE 10.11** Difference in w/o emulsion properties and appearance after 3 days’ weathering in the SINTEF meso-scale weathering basin.

**TABLE 10.2**  
**Example of Emulsion Properties and Appearance After Weathering in the SINTEF Meso-Scale Flume**

Oil	Water Content (%)	Dynamic Viscosity at 10 sec <sup>-1</sup> (mPa sec)	Appearance of the Emulsion Formed
Norne crude oil (waxy, Norwegian Sea)	35	3000 (5 °C)	Solidified oil lumps, turn slowly into brown color
Jotun crude oil (paraffinic, North Sea)	58	2430 (13 °C)	Yellow/light brown
Grane crude oil (asphaltenic, North Sea)	70	11,000 (13 °C)	Dark, viscous, sticky lumps
IFO-240 Heavy Fuel Oil (Esso refinery)	50	23,000 (13 °C)	Dark emulsion

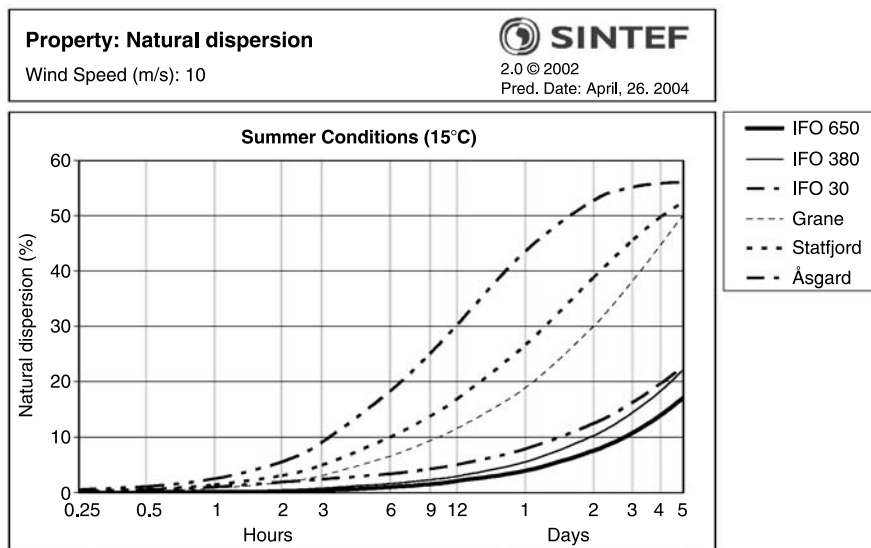
### 10.2.3 NATURAL DISPERSION

Natural dispersion is caused by the action of breaking waves. As a breaking wave collapses on an oil slick, oil droplets of various sizes are detached from the principal slick and entrained into the water masses (16). The oil droplets can remain dispersed, resurface, and coalesce with the principal slick, or resurface and form a thin film trailing behind the principal slick. This depends on the size of the droplets, the submergence depth, and the height (or energy) of the breaking wave. If the droplets coalesce with the principal slick, water may become trapped within the reformed slick and a stable water-in-oil emulsion may be formed by successive breaking events. Oil slick dispersion (o/w emulsification) and w/o emulsification comprises therefore a series of batch process, the outcome of each determined by a combination of oil properties (oil chemistry, density, interfacial tension, and viscosity) and hydrodynamics (breaking wave frequency, submergence depth, and intensity of mixing associated with each breaking wave). The intermittent nature of the breaking events may also be important, especially for viscous oils, as the duration of the event may be too short to form stable droplet size distributions corresponding to the prevailing intensity of mixing.

According to Shaw (16), the key variables that determine the size distribution of the detached oil droplets are oil–water interfacial tension, oil or emulsion density (relative to the density of sea water), oil or emulsion viscosity, and the prevailing forces in the environment (shear stress). Others (17) maintain that turbulent dissipation rate is a more relevant measure of the splitting force, but none of these parameters are easy to relate to the actual sea state. It may thus be more practical to use wave energy as a measure of the splitting force, as in the empirical correlations derived by Delvigne and Sweeney (17). The same authors neglected oil–water interfacial tension in their experimental study, assuming that oil viscosity was the most representative property of the oil in this context. This may be justified since the variation in the interfacial tension is limited among fresh crude oil, and the relative importance of the interfacial tension seems to diminish with increasing oil viscosity (16). However, addition of surfactants to the oil–water will reduce the interfacial tension significantly, an effect that is exploited in oil spill countermeasures based on chemical dispersion.

Delvigne and Sweeney found that breaking waves entrain oil droplets to a depth corresponding to the height of the breaking wave. They also found that the number distribution of the droplets that were formed by breaking waves could be described by the same power law relationship,  $N(d) \sim d^{-2.3}$ , independent of the applied wave energy and the oil properties. The oil mass entrained per unit area in droplets of a given size range was independent of the surface oil film thickness, but increased almost in proportion to the height of the breaking wave. Experiments with oil weathered to various degrees showed that the entrained oil mass decreased with increasing oil viscosity of the oil. In a later study, Delvigne and Hulsén (18) found that the entrained oil mass was practically independent of oil viscosity for viscosities up to 100 cSt, but started to decrease considerably as viscosities increased above this range. The reduction in oil droplet entrainment with increasing viscosity implies that the natural dissipation rate will diminish as the oil remaining in the surface slick is subjected to weathering and emulsification.

These findings have been used to derive algorithms that are used in SINTEF's Oil Weathering Model for prediction of the dissipation rate of surface oil depending on oil type, degree of weathering, and sea state (19). The main assumption in that context is that droplets smaller than a certain size will stay submerged in the water masses, while larger droplets will resurface and rejoin the primary slick within a short time span. The entrainment rate of droplets smaller than the size limit is calculated from sea state and oil/emulsion viscosity with relations derived from Delvigne's studies. Examples of predictions are shown in [Figure 10.12](#).



**FIGURE 10.12** Predictions of natural dispersion for different crude oils and oil products.

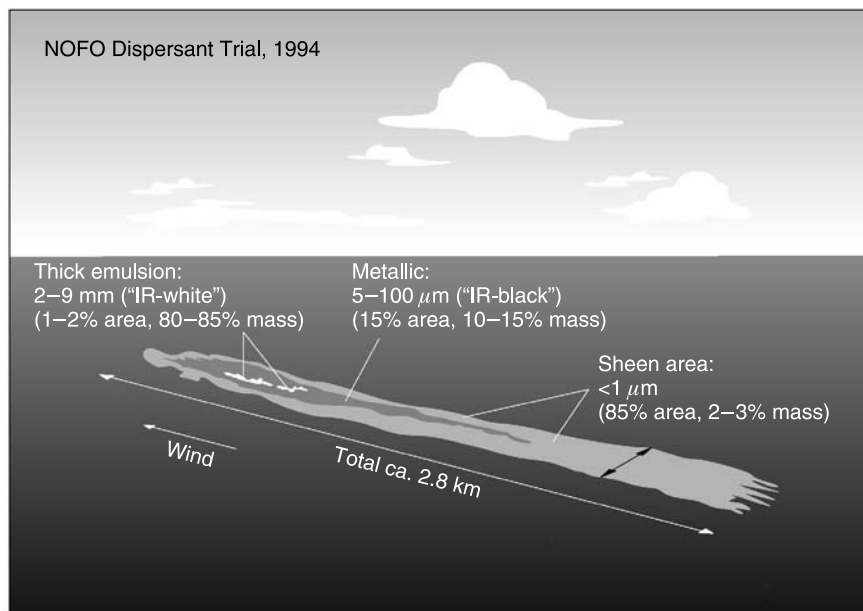
### 10.3 FULL-SCALE FIELD TRIALS IN NORWAY

Emulsification and behavior of spilled oils have been studied during series of experimental releases with various oils simulating various release conditions. These studies involved both surface releases (1994, 1995, and 1996), simulated sub-sea pipeline leaks (release of oil and no gas, 1994), and simulated sub-sea blowouts (oil with gas) released both from 100 m depth (1996) and 850 m depth (DeepSpill June 2000). Three of the field series were carried out in the Frigg area in the North Sea, while the DeepSpill experiment was performed in the Helland Hansen area in the Norwegian Sea. The field trials have been performed in cooperation between spill response organizations (NOFO), individual oil companies, and governmental pollution control agencies (SFT and MMS). A summary report of the field trials in Norway has been prepared (20).

#### 10.3.1 THE NOFO 1994 FIELD TRIAL: SURFACE RELEASE

One of the main objectives of the 1994 field trials was to verify the results from laboratory studies and model predictions of oil weathering (evaporation, natural dispersion, and emulsification) up to 2 days at sea. Two oil slicks ( $2 \times 20 \text{ m}^3$  of Sture Blend North Sea crude) were released on the surface. The sea state was quite rough with wind speed varying between 8 and 12 m/s and about 2.5 m significant wave heights. A control slick ("Charlie") was followed with extensive surface monitoring for 32 h before dispersants treatment. The other slick ("Tango") was treated twice with dispersant after 3 and 7 h weathering at sea.

As soon as the oil was released on the surface, the slicks rapidly formed an elongated shape as some of the oil was temporarily dispersed and then re-surfaced away from the thicker areas (in front of the slick) and spread out again as sheen. Measurements showed a very wide variation



**FIGURE 10.13** Schematic drawing of the distribution of oil slick thickness after 3 h at sea.

in the slick thickness, with three main categories observed:

- Thick w/o-emulsion (2 to 9 mm) in the front part of the slick
- Metallic (up to about 0.1 mm, also called IR-black)
- Sheen (up to about 1 to 5  $\mu\text{m}$ )

This correlation between visual appearance and ground truth film thickness measurements was in good agreement with the Bonn Agreement Oil Appearance Code (BAOAC), OTSOPA (21).

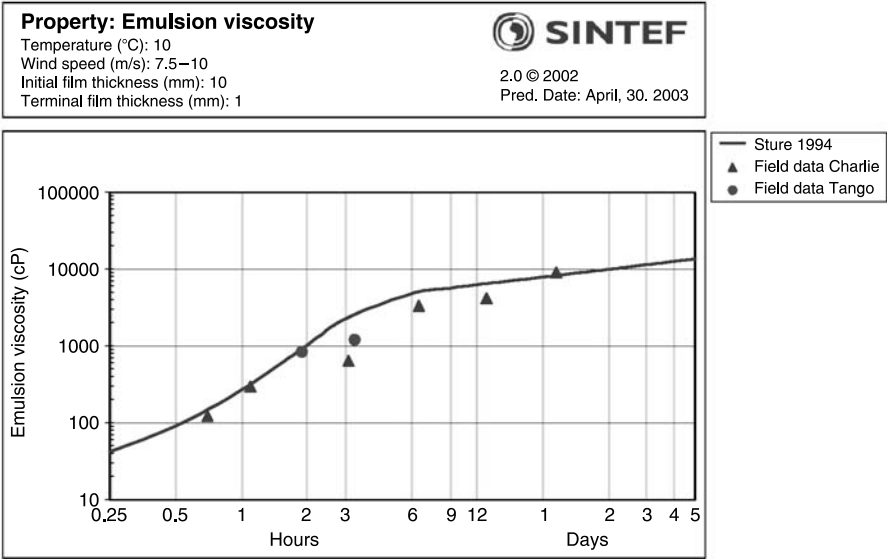
An estimate of the distribution in area and mass of these categories based on remote sensing and film thickness measurement is presented schematically in Figure 10.13. The weathering behavior and physical properties of the thick emulsion that formed on the surface were in accordance with results from previous laboratory studies.

The weathering data were used to calibrate and verify the SINTEF Oil Weathering Model (8). Figure 10.14 shows the measured viscosity of the emulsions sampled from the sea surface, at different times during the field trial. The viscosity of the fresh crude oil is approximately 10 mPas increasing to 9000 mPas after 28 h of weathering on the sea surface.

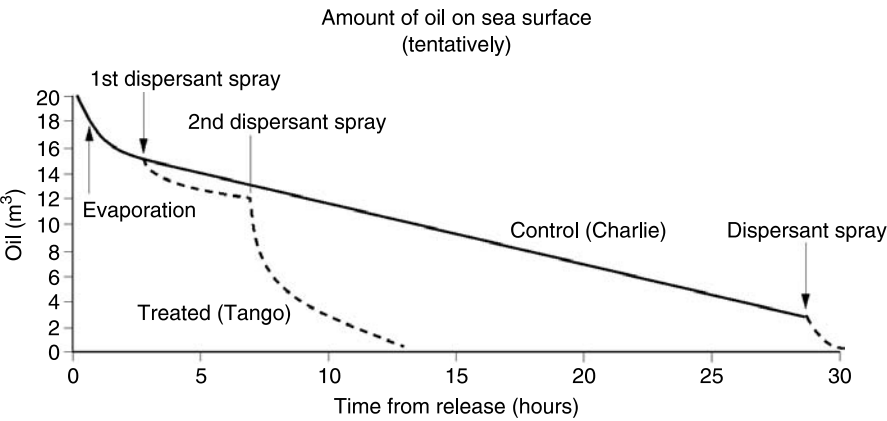
Figure 10.15 gives an estimate of amount of oil on the surface and the lifetime of the two slicks based on aerial surface monitoring. Further details concerning operational aspects, monitoring, analytical methods, and conclusions from this sea trial have been published in several reports, e.g., Lewis et al. (10).

### 10.3.2 THE NOFO 1995 FIELD TRIAL: SURFACE AND UNDERWATER “PIPELINE” RELEASES

One of the aims of the NOFO field trial in 1995 (22) was to study the behavior of oil released from sub-sea pipeline leaks. A total of 25 m<sup>3</sup> of Troll Crude was released over a period of 20 min

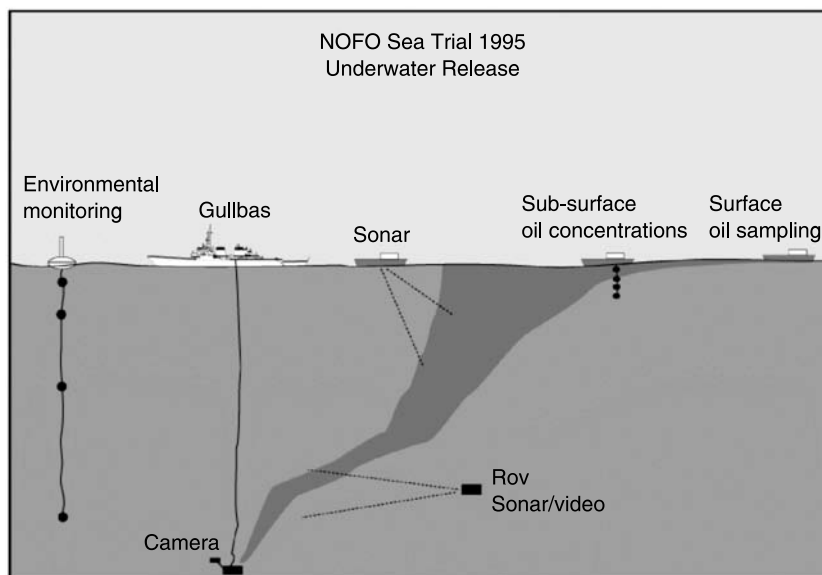


**FIGURE 10.14** Measured viscosity of emulsions on the sea surface at different times during the field trial. The line shows predicted emulsion viscosity from the SINTEF OWM.



**FIGURE 10.15** Lifetime of surface oil slick; slick treated with dispersant (“Tango”) versus control slick (“Charlie”).

from 100 m depth (slick called “Uniform”). A reference spill (surface slick “Sierra”) was released using the same conditions as in the 1994 trials. The release and monitoring arrangement of the sub-sea release is illustrated in Figure 10.16. Due to relatively low exit velocities (about 2 m/s), relative large oil droplets were formed (typically 2 to 6 mm in diameter) when released from the sub-sea installation. An oil slick started to form at the surface about 10 min after the start of the release. Oil samples taken as the oil appeared on the surface indicated that no w/o emulsion



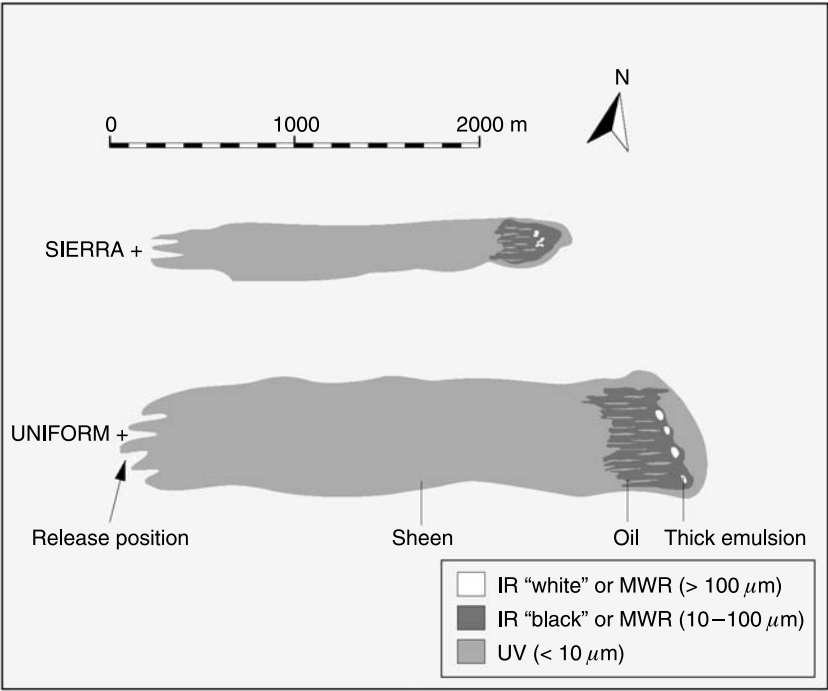
**FIGURE 10.16** Schematic illustration of the sub-sea release arrangement, the plume created and monitoring strategy.

was formed in the plume, but that the emulsion was subsequently formed after the oil appeared on the sea surface. The weathering properties of the thick emulsion formed on the surface were similar to the properties of the emulsion generated in the surface release (“Sierra”). Subsequent analysis of oil samples from both slicks showed good agreement with model predictions based on laboratory input data of Troll crude oil (8).

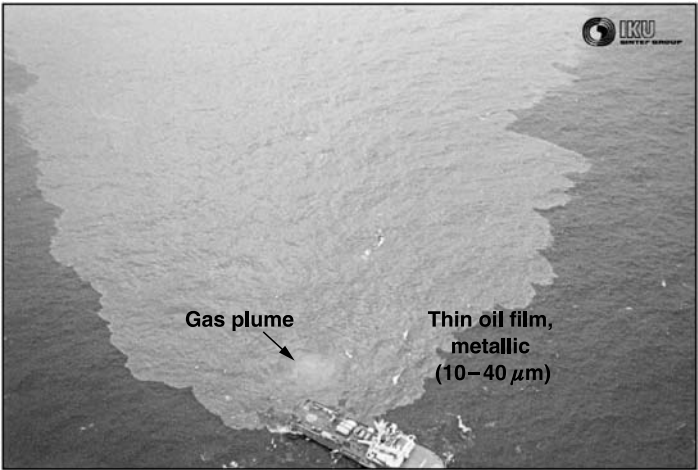
Observations of the two oil slicks 4 h after the releases indicated that the slick formed from the sub-sea release was slightly larger due to the larger spreading at the start of the release (Figure 10.17). Further details both concerning operational aspects, monitoring, analytical methods, and conclusions from this sea trial are described in several reports including Brandvik et al. (22).

### 10.3.3 THE NOFO 1996 FIELD TRIAL: SIMULATED SUB-SEA BLOWOUT FROM MODERATE DEPTHS

One of the aims of the NOFO field trial in 1996 (23) was to increase the knowledge of the behavior of the oil in sub-sea blowouts. This was done by simulating a blowout released from 100 m depth with a realistic gas-to-oil ratio ( $GOR = 65$ ) and a release rate of  $1 \text{ m}^3$  Troll crude oil per minute, with a total of  $45 \text{ m}^3$ . For safety reasons, pressurized air was used in place of natural gas. The release method and monitoring arrangement were similar to the 1995 sub-sea release (see Figure 10.16). However, due to a much higher exit velocity (about 20 m/s), very small oil droplets were formed that were carried to the surface by the gas bubble plume. The first oil appeared on the surface about 2 min after the start of the release. The high initial spreading of the oil on the surface (see picture in Figure 10.18) was in accordance with calculations using the blowout model developed by Fanneløp and Sjøen (24). The horizontal spreading of the plume near the surface resulted in a very thin and homogenous oil film on the surface. Some small tendency



**FIGURE 10.17** Composite sketch of remote sensing imagery showing the slick dimensions of the surface release (Sierra) and the underwater release (Uniform) after 4 hours of weathering at sea.



**FIGURE 10.18** Photo of the surface slick taken during the simulated sub-sea blowout (NOFO-1996 trial).



to Langmuir cells could also be observed by IR images, in a thickness range of 10 to 40  $\mu\text{m}$ . This thickness appeared, however, to be too thin for any emulsion to form on the surface, and the oil slick dissipated naturally within a few hours. Further details concerning operational aspects, monitoring, analytical methods, and conclusions from this sea trial are described in several reports (e.g., Refs. 23 and 25).

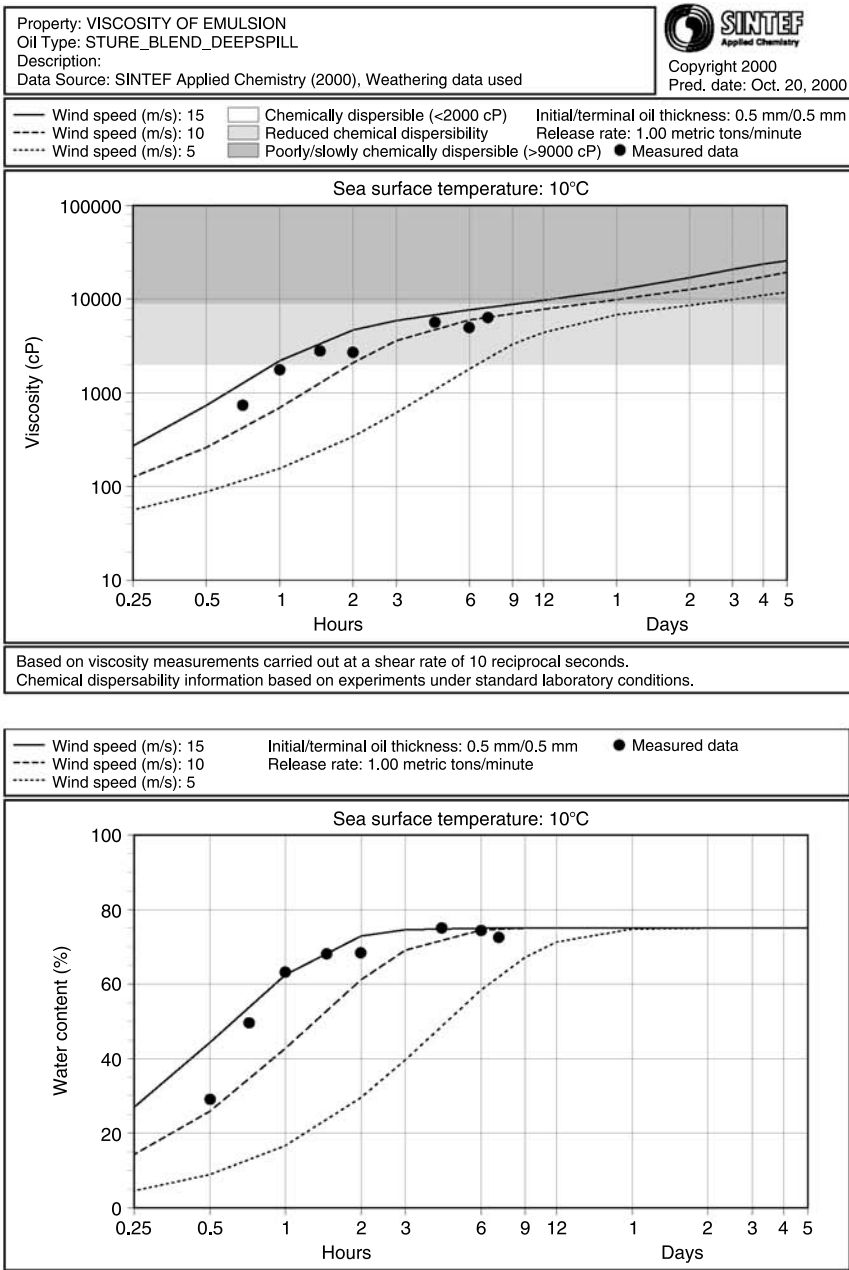
#### 10.3.4 THE DEEPSpill EXPERIMENT

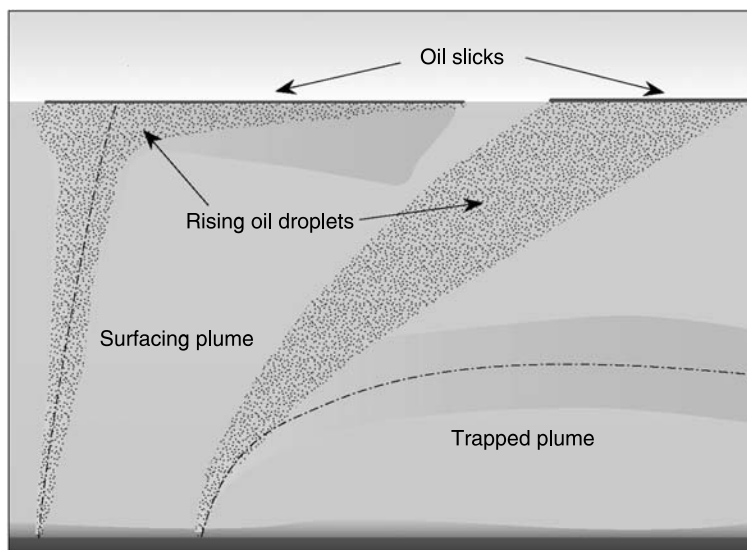
The DeepSpill experiment was conducted in the Norwegian Sea in June 2000, and included releases of oil and natural gas from 850 m depth. The main objective was to provide data for verification of numerical models for simulating accidental releases in deep water. Three experiments were performed, one with gas only, one with gas and marine diesel (simulating a non-emulsifying oil), and one with gas and crude oil (Sture Blend). Each release lasted for 1 h, with gas rates of 1  $\text{Sm}^3/\text{sec}$  and oil rates of 1  $\text{m}^3/\text{min}$ . The oil and gas was pumped from the discharge vessel through separate coiled steel tubing lines down to a discharge platform deployed on the seabed. The gas was transported to the site in liquefied state (LNG), and was transformed into gas in a seawater-heated evaporator during the release (26).

Met-ocean data were measured continuously during the field trial with wind sensors and a downward facing acoustic Doppler current profiler (ADCP) mounted under the research vessel, supplemented with an upward facing ADCP mounted on the seabed. The wind speed during the experiments varied between 9 and 14 m/sec. Ocean currents that were measured in the range of 10 to 20 cm/sec showed a significant variation with depth. Video cameras mounted on remote operated vehicles (ROVs) provided close-up pictures of gas bubbles and oil droplets, and ship mounted echo-sounders provided images of the plumes of water, gas bubbles, and oil droplets that were rising through the water column.

In both experiments with oil, the first oil appeared on the surface 1 h after the start of the release, while the main surfacing took place around 2 to 4 h after release. The water in the plume was trapped below the perennial thermocline (below 500 m depth), while gas bubbles and oil droplets were then separated from the trapped water and continued towards the surface with the rise velocity of individual bubbles and droplets (see [Figure 10.19](#)). Observations during the pure gas release (without oil) showed no presence of the gas bubbles above 150 m depth, indicating that the gas bubbles had been dissolved completely in seawater at this level. However, the oil droplets continued to the surface and formed a surface slick that developed gradually over time. In the crude oil experiment, the oil film thickness in the surface slick was measured in the range from 200 to 400  $\mu\text{m}$  of non-emulsified oil (see [Figure 10.20\(a\)](#)). This thickness was sufficient for the formation of patches of emulsified oil during the coming hours on the sea surface (see [Figure 10.20\(b\)](#)). The water uptake rate and the time development of the viscosity of the thick emulsion was in good agreement with model predictions using the SINTEF OWM based on laboratory input data of the Sture Blend crude oil (see [Figure 10.21](#)). The emulsion became stable after about 5 h weathering on the sea surface. The viscosity of the fresh crude oil is approximately 10 mPas increasing to 8000 mPas after 8 h of weathering on the sea surface.

The last aerial survey that was made about 8 h after the start of the crude oil release depicted a slick about 8 km in length and 1 km in width. In the marine diesel experiment, where no emulsion was formed, the maximum slick size was observed about 5 h after the start of the release, with a length in the order of 1.5 km and a width of 500 m. No remains of the slick could be detected during the last surveillance flight about 3 h later. The difference in behavior between emulsifying and non-emulsifying oils is illustrated schematically in [Figure 10.22](#).





**FIGURE 10.20** Schematic drawing of sub-sea blow-outs from medium depths (top) and deep waters (bottom).

Further details both concerning operational aspects, monitoring, analytical methods, and conclusions from this sea trial are described by Johansen et al. (26).

## 10.4 EFFECTS OF EMULSION PROPERTIES ON OIL SPILL COUNTERMEASURES

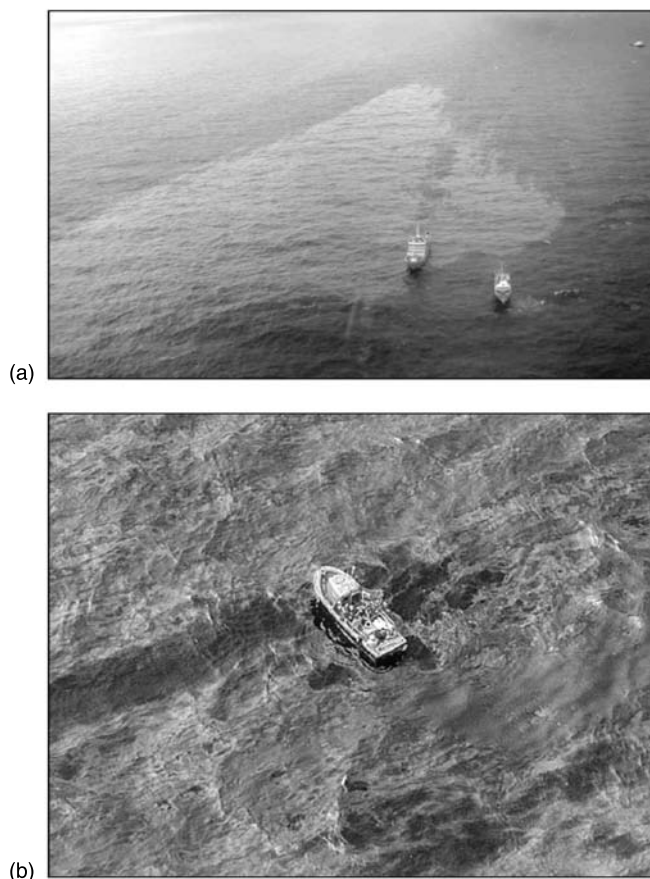
One of the main reasons for studying the properties of emulsions formed on the sea surface is its effect on oil spill countermeasures. Good knowledge about the specific oil properties is crucial in connection with net environmental benefit analysis (NEBA), contingency planning, and decision making in spill situations. Some examples of the direct impact of emulsion properties in oil spill response operations are described below.

### 10.4.1 SLICK LIFETIME

One of the first tasks in an oil spill response operation is to assess the lifetime of the slick on the sea surface. If the oil's estimated lifetime is short, mobilization of oil spill countermeasures may not be needed.

The two processes contributing to the removal of oil from the sea surface are evaporation and natural dispersion. For most crude oils natural dispersion is the main contributor to removing oil from the sea surface. Figure 10.23 shows predictions of the lifetime of slicks of different oils on the sea surface. A slick's lifetime on the sea surface is very dependent on the release conditions and weather conditions. The example below is only representative to one specific set of release conditions (i.e., thick enough to form emulsion on the surface), temperature, and wind speed.

The relatively light Åsgard crude has a limited lifetime on the sea surface while the heavy bunker fuel oils are persistent to natural dispersion and can survive for weeks and months on the sea surface.

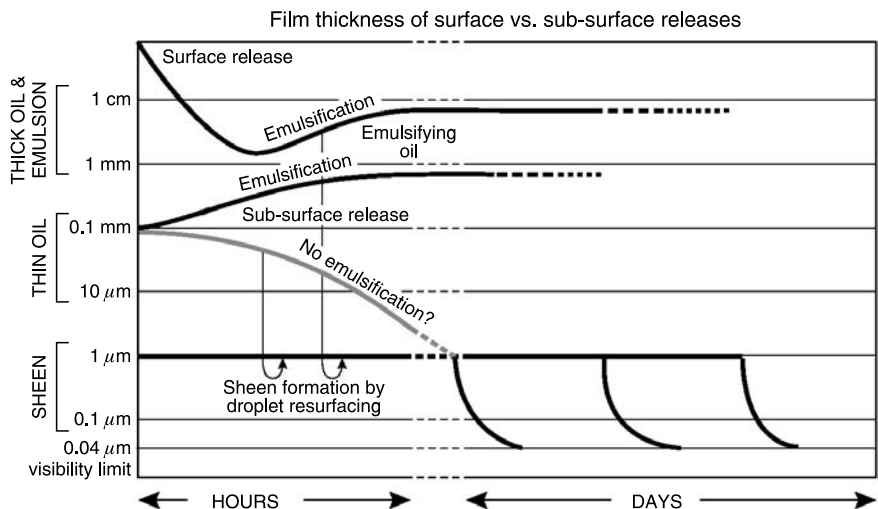


**FIGURE 10.21** (a) Aerial photo of the surface slick taken after the crude oil release. (b) Photo taken during surface sampling from emulsified patches (1 to 1.5 mm thick) generated during 3 h weathering on the surface (DeepSpill 2000).

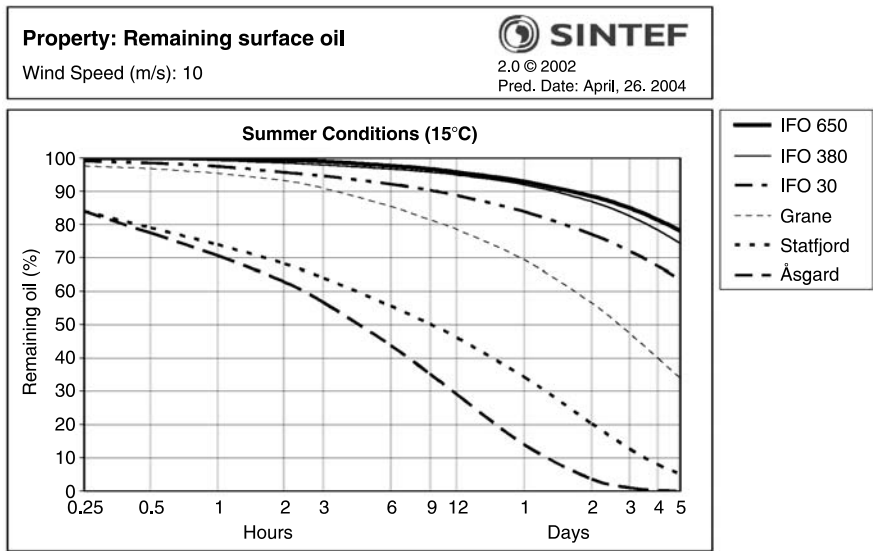
As illustrated in [Figure 10.13](#), the thickness within an oil slick varies greatly in a surface release spill. [Figure 10.24](#) shows the predicted lifetime of a Norwegian crude oil as a function of oil film thickness and wind conditions. The predictions show how important it is to give priority to the thick w/o emulsion within the slick during a response operation.

#### 10.4.2 MECHANICAL RECOVERY

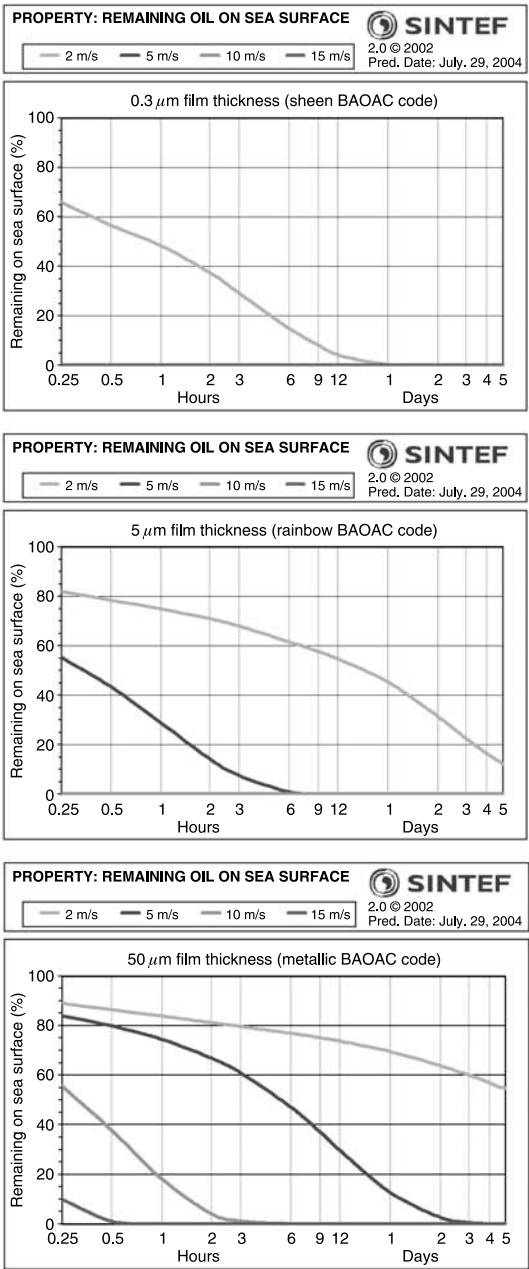
Past experiences from Norwegian field trials have shown that the effectiveness of many mechanical clean-up operations is reduced due to a high degree of leakage of the confined oil or w/o emulsion from the boom systems (especially in high current). This leakage is especially pronounced if the viscosity of the oil or the w/o emulsion is lower than 1000 mPas (at a shear rate of  $10 \text{ s}^{-1}$ ) (27). It is therefore often recommended to let the oil weather to a viscosity of minimum 1000 mPas before recovery in order to optimize the recovery operation.



**FIGURE 10.22** Schematic illustration of the development in film thickness, breakdown, and relative lifetime on the sea surface of an emulsifying surface release, versus emulsifying and non-emulsifying underwater releases.

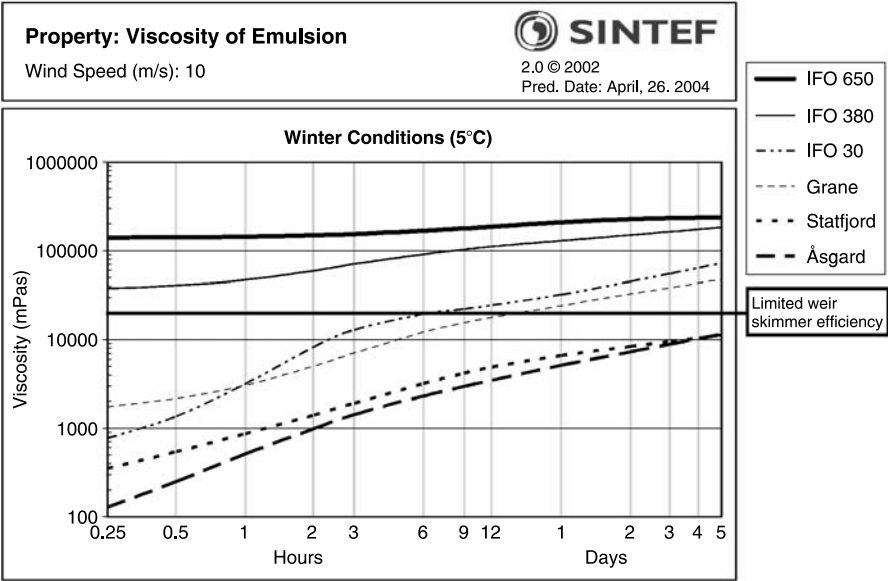


**FIGURE 10.23** Predicted lifetime of different oils at the sea surface. The oil is removed from the surface by evaporation and natural dispersion.



**FIGURE 10.24** Lifetime of a Norwegian crude oil at different oil film thickness.

When using skimmers to recover oils both too high a viscosity and too high pour point may reduce the efficiency of the skimmer. Recent tests performed by SINTEF using a weir skimmer showed that the efficiency may be reduced for semi-solid and solidified oils (i.e., oils with a high wax content and pour point values higher than 10 to 15° C above ambient sea temperature) and for oils with viscosities above approximately 20,000 mPas (28). For oils with viscosities



**FIGURE 10.25** Predicted viscosities of a selection of crude oils and fuel oils.

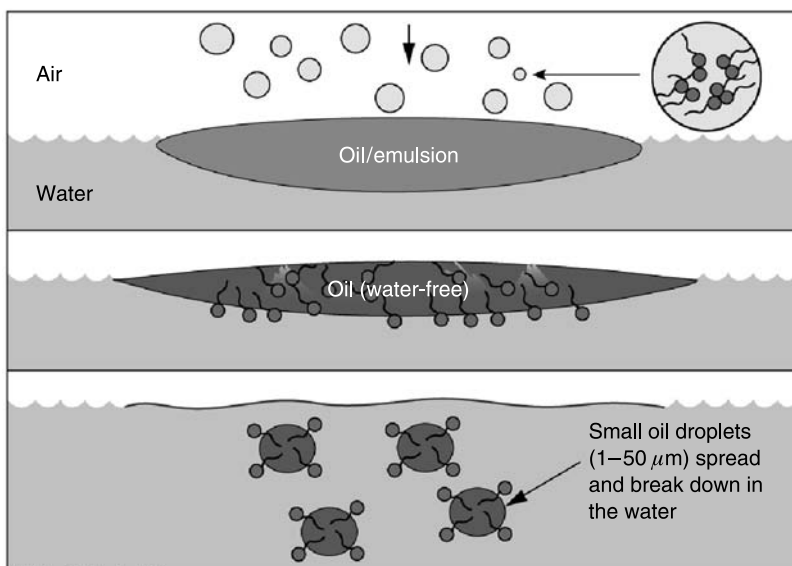
above these values, or with high yield stress values, skimmer equipment requiring the oil to passively spread towards the skimmer may render useless, and special equipment for high viscous oil recovery may be needed.

Figure 10.25 shows variations in emulsion viscosities between different oils with weathering on the sea surface. As for limitations in skimmer efficiency some of the oils will always have viscosities above the critical limit, some will obtain critical viscosities with time on the sea surface, and some will never cause problems in a mechanical recovery operation even after days of weathering on the sea surface. Knowledge about the viscosity of the emulsions formed is crucial when choosing skimmer equipment both in contingency planning and in the case of a spill situation.

### 10.4.3 USE OF CHEMICAL DISPERSANTS

One of the means in Norwegian oil-spill contingency for combating oil slicks is the application of oil spill dispersants. Dispersants work in the same way as a household soap, stabilizing the formation of small oil droplets, enhancing the mixing of oil into the water. The purpose of using oil spill dispersants is to remove spilled oil from the surface and dilute it into the bulk of the water column as droplets at a faster rate than occurs naturally. The appropriate use of dispersants could prevent subsequent shoreline pollution or damage to other sensitive areas/resources. A schematic picture of how dispersants work is shown in [Figure 10.26](#).

Effective use of dispersants depends on chemical interactions between the added chemicals and naturally occurring components within the oil (e.g., wax, asphaltenes, resins). Oils have different chemical composition, causing variations in their ability to interact with the dispersants. This gives a great variation in the potential for use of dispersants between different oils. Viscosity and pour point will also be important to the effectiveness of chemical dispersants. A high viscosity or high pour point of the oil will give poor mixing between oil and chemical dispersant, and will also cause the oil to resist being mixed into the water by wave energy.



**FIGURE 10.26** Dispersion of oil into water.

The methodology for defining the “window of opportunity” for use of dispersants is described in detail by Daling and Strøm (8). Laboratory data on weathering properties and dispersibility is used as input to the OWM for prediction of the “window of opportunity.” Figure 10.27 shows the “window of opportunity” divided into categories (easily, reduced, and poorly dispersible) for a selection of Norwegian crude oils with weathering on the sea surface.

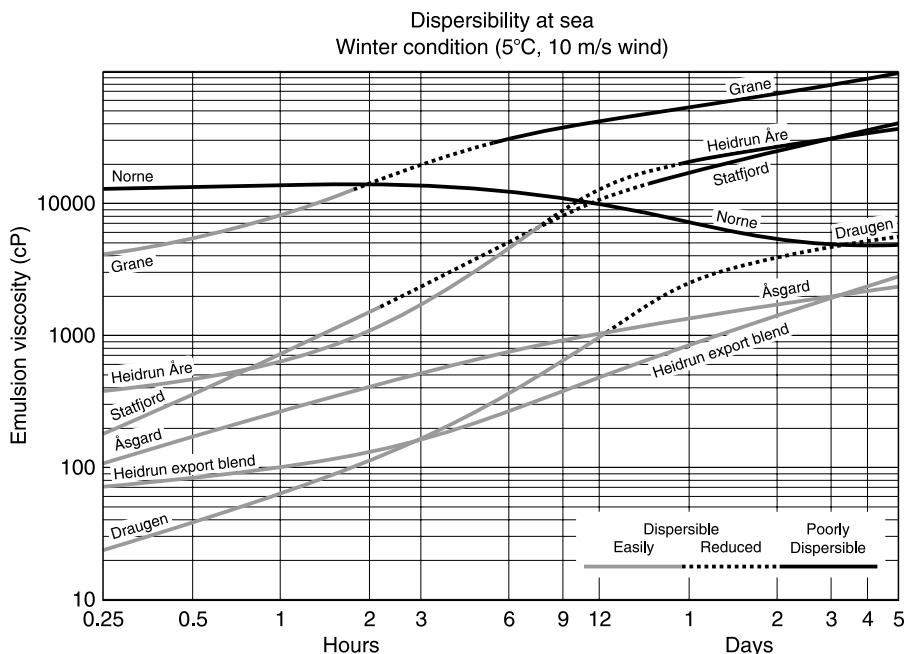
Figure 10.27 shows examples of how the dispersibility varies with time on the sea surface for different Norwegian crude oils. As the oils hold different chemical properties, the potential for use of dispersants is not directly correlating with the viscosity of the emulsion. It is important that the predicted “window of opportunity” for use of dispersants is taken into account in oil-spill contingency planning and operational decision making in spill situations.

## 10.5 CONCLUSIONS

Laboratory experiments and full scale field experiments have been performed during the last decades in order to obtain more knowledge about the w/o emulsification and o/w dispersion of oils at sea. A broad range of oils has been investigated in the laboratory both in bench- and meso-scale. Field trials have been performed to verify laboratory results, for calibration of models, and to study the influence of different release conditions. The major findings from these studies are:

- When oils are spilt at sea different weathering processes alter the properties of the oil as a function of time and weather conditions. Water-in-oil emulsification (w/o) and natural dispersion (o/w) are two important weathering processes taking place when oil is spilt at sea.
- Laboratory studies of a wide spectrum of oils have revealed that both the physicochemical properties of the oils and the release conditions that control the initial film thickness are fundamental parameters for the rate of emulsion formation and for the rheological properties of the emulsion formed.





**FIGURE 10.27** Window of opportunity for the use of chemical dispersants for a selection of Norwegian crude oils.

- Knowledge about weathering behavior of crude oils and fuel oils is of importance for contingency planning, response analysis, net environmental benefit analysis (NEBA), and for rapid and appropriate decision making in the case of an oil spill.
- The appearance and rheology of oil slicks at the sea surface can be very different for different oils and degrees of weathering. Continuous oil slicks may be observed at an early stage after release, but weathering processes will soon transform the slicks into a patchy appearance consisting of broken fragments of highly emulsified oil.
- There is a generally good agreement between analysis of oil samples taken during experimental field trials and model prediction using the SINTEF Oil Weathering Model based on oil specific laboratory data.
- None of the three underwater releases (1995, 1996, and 2000) showed any emulsion formation in the rising plumes of oil droplets. The emulsification took place on the sea surface (when the initial oil film thickness was sufficient).
- Simulated underwater blowouts from moderate depths (<300 m) showed that the gas-bubble plume will come to the surface, bringing entrained water with it. The rapid surface spreading of this entrained water will cause the surfacing oil to spread into a thin oil film. This film may be too thin for emulsification to take place unless further concentration of the oil into thicker narrow bands (windrows) occurs with the development of wind-driven Langmuir circulation cells.
- With blowouts in deep waters (>500 m), the plume may be trapped in the water column, and the rising oil droplets will surface within a more limited area. This may lead to initial oil film thicknesses that are sufficient for emulsion formation.

## REFERENCES

1. Harris, C. The Braer incident – Shetland Island, January. In *Proceedings of the 1995 Oil Spill Conference*, API Washington, DC, 1995, pp. 813–820, 1995.
2. Lunel, T.; Rusin, J.; Bailey, N.; Halliwell, C.; Duvis, L. A successful at sea response to the Sea Empress spill. In *Proceedings of the 19th AMOP Seminar*, June 12–14, 1996, Canada, pp. 1499–1520.
3. Grundach, E.R.; Neff, J.M.; Little, D.I.; Aurand, D.A. Evaluation of historic spill sites for long-term recovery studies. In *Proceedings of the 1995 Oil Spill Conference*, API, Washington, DC, 1995, p. 974.
4. Baker, J.M. Net environmental benefit analysis for oil spill response. In *Proceedings of the 1995 Oil Spill Conference*, API, Washington, DC, 1995, pp. 611–614.
5. Daling, P.S.; Brandvik, P.J.; Mackay, D.; Johansen, Ø. “Characterization of Crude Oils for Environmental Purposes”. *Oil & Chemical Pollution* 7, 1990/91, pp. 199–224.
6. Johansen, Ø. Numerical modeling of physical properties of weathered North Sea crude oils. DIWO-report no. 15. IKU-report 02.0786.00/15/91. Open. 1991.
7. Hokstad, J.N.; Daling, P.S.; Lewis, A.; Strøm-Kristiansen, T. Methodology for testing water-in-oil emulsions and demulsifiers: Description of laboratory procedures. In *Proceedings Workshop on Formation and Breaking of W/O Emulsions. MSRC*, Alberta, June 14–15, 1993, p. 24.
8. Daling, P.S.; Strøm, T. “Weathering of oil at sea; model/field data comparisons”. *Spill Science & Technology Bulletin*, 1999, Vol. 5, No. 1, pp. 63–74.
9. Stiver, W.; Mackay, D. “Evaporation rate of spills of hydrocarbons and petroleum mixtures.” *Environ. Sci. Technol.*, 1984, Vol. 18, No. 11, pp. 834–840.
10. Lewis, A.; Daling, P.S.; Strøm-Kristiansen, T.; Brandvik, P.J. The behaviour of Sture Blend crude oil spilled at sea and treated with dispersants. In *Proceedings from the 18th AMOP Technical Seminar*, June 14–15, 1995, Edmonton, Canada, pp. 453–469.
11. Mackay, D.; Zagorski, W. Studies of water-in-oil emulsions. Report EE-34: Environment Canada, Ottawa, Ontario, 1982.
12. Fingas, M.F.; Fieldhouse, B.F.; Lane, J.; Mullin, J.V. 2000. Studies of water-in-oil emulsions: Long-term stability, oil properties, and emulsions formed at sea. In *Proceedings of the 1997 AMOP Technical Seminar*, Environment Canada No. 23a, pp. 145–160.
13. *Encyclopedic Handbook of Emulsion Technology*. Johan Sjöblom (editor). Marcel Dekker Inc., New York, 2001, pp. 1–736.
14. Ritchie, W.; et al. (Ecological Steering Group on the oil spill in Shetland). An interim report on survey and monitoring, May 1993, Edinburgh, The Scottish Office.
15. Mackay, D.; Buist, I.; Mascarenhas, R.; Paterson, S. Oil spill processes and models. Department of Chemical Engineering, University of Toronto, Toronto, Ontario, Publ. No. EE-8.
16. Shaw, J.M. “A microscopic view of oil slick break-up and emulsion formation in breaking waves”. *Spill Science & Technology Bulletin*, 2003, Vol. 8, pp. 491–501.
17. Delvigne, G.A.L.; Sweeney, C.E. “Natural dispersion of oil”. *Oil and Chemical Pollution*, 1988, Vol 4, pp. 281–310.
18. Delvigne, G.A.L.; Hulslen, L.J.M. Simplified laboratory measurement of oil dispersion coefficient – application in computations of natural oil dispersion. In *Proceedings of the 17th Arctic and Marine Oil Spill Program (AMOP) Technical Seminar*, Vol. 1, pp. 173–187. Environment Canada, 1994.
19. Daling, P.S.; Aamo, O.M.; Lewis, A.; Strøm-Kristiansen, T. SINTEF Oil Weathering Model – predicting oil’s properties at sea. In *Proceedings from 1997 International Oil Spill Conference*, Fort Lauderdale, Florida, April 2–10, pp. 297–307.
20. Moldestad, M.Ø.; Brandvik, P.J.; Daling, P.S. Development of data sets from experimental oil spills for OWM algorithm and model testing and validation. SINTEF report: STF66 A04025, 2004.
21. OTSOPA. Bonn Agreement Aerial Surveillance Handbook. OTSOPA, 2004.
22. Brandvik, P.J.; Lewis, A.; Strøm-Kristiansen, T.; Hokstad, J.N.; Daling, P.S. 1996. NOFO 1996. Oil on water exercise – Operational testing of Response 3000D Helibucket. IKU report no. 41.5164.00/01/96. p. 53.
23. Rye, H.; Brandvik, P.J.; Strøm, T. “Subsurface Blowouts: results from field experiments”. *Spill Science and Technology Bulletin*, 1996, Vol. 4, No. 4, pp. 239–256.

24. Fanneløp, T.K. and Sjøen, K. "Hydrodynamics of underwater blowouts". Norwegian Maritime Research, 1980, No. 4, pp. 17–33.
25. Rye, H.; Brandvik, P.J.; Strøm-Kristiansen, T.; Lewis, A; Daling, P.S. NOFO 1996 Oil on water exercise – Simulated blow-out, releasing oil and gas at 106 meters depth, 1996.
26. Johansen, Ø.; Rye, H; Melbye, A.G; Jensen, H.V.; Serigstad, B.; Knutsen, T. DeepSpill JIP – Experimental Discharges of Gas and Oil at Helland Hansen – June 2000, Technical Report. SINTEF Report STF66 F01082, SINTEF Applied Chemistry, Trondheim, Norway, 2001, p. 159.
27. Nordvik, A.B.; Daling, P; Engelhardt, F.R. Problems in the interpretation of spill response technology studies. In: *Proceedings of the 15th AMOP Technical Seminar*, June 10–12, Edmonton, Alberta, Canada, pp. 211–217.
28. Leirvik, F.; Moldestad, M.; Johansen, Ø. Kartlegging av voksrike råoljers tilflytsevne til skimmere. SINTEF Report. 2001.