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Report

Oda crude oil – Weathering properties and behaviour at sea

In relation to oil spill response

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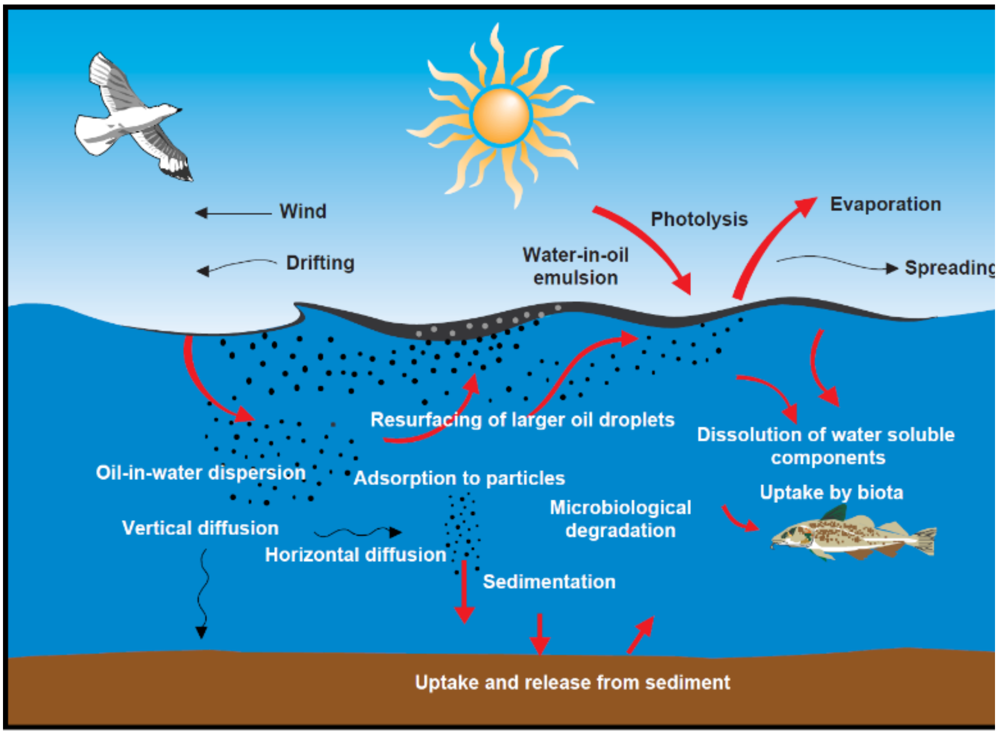

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ABSTRACT

A weathering study including dispersibility has been conducted on Oda crude oil. This study included a standardized small-scale laboratory testing and a meso-scale flume experiment at 13 °C. The SINTEF Oil Weathering Model (OWM) was used to predict the weathering properties of Oda crude oil if spilled on the sea surface reflecting summer and winter temperatures in the North Sea. The weathering properties are also discussed in relation to oil spill response by mechanical containment and recovery, and chemical dispersibility.

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1 Executive summary

Spilled oils undergo changes when weathered on the sea surface. These changes affect oil behaviour and consequently oil spill countermeasures. Oil weathering varies over time and with different environmental conditions. Based on input from the experimental weathering data of the oil, the SINTEF Oil Weathering Model (OWM) is used to predict the properties of oil as it weathered over time. The lifetime of an oil spill at sea depends on the oil's composition, the release conditions (e.g. on the surface, underwater) and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the sea surface. Evaporation of the lightest compounds increases the relative amount of wax and asphaltenes and changes the physical properties on the residual oil. This summary gives a brief overview of the main changes predicted for Oda crude oil when weathered on the sea surface.

The weathering study was conducted at 13 °C reflecting typical summer temperature in the North Sea. The OWM predictions were performed at 5 and 15 °C reflecting a span of temperatures for summer and winter conditions.

Oda is considered a light to medium paraffinic crude oil with a density of 0.820 g/mL with a relatively high content of asphaltenes (0.44 wt. %), and a medium to high wax content (5.6 wt. %), compared with Norwegian crude oils. The pour point of the fresh oil is low (-3 °C) but increases considerably by evaporation. Pour points of the evaporated residues range from +12 to + 24 °C.

The study shows that Oda can form high viscous water-in-oil (w/o) emulsions with a high-water uptake (~80 vol. %). The emulsions formed were stable but released water when adding different concentrations (500 and 2000 ppm by weight) of the emulsion breaker (Alcopol O 60 %). The highest concentration (2000 ppm) was shown to be the most effective and partly broke the emulsions and may effectively be used during an oil spill operation to remove or reduce water from the recovered oil/emulsion. Emulsion breakers are normally injected at the skimmer head prior to transferring the collected oil/water to storage tanks, which minimizes the storage volume.

The mass balances show that the Oda crude oil is broken up and removed from the sea surface within 3 days in high wind speeds (15 m/s) at winter (5 °C) and summer conditions (15 °C), due to evaporative loss and natural dispersion/entrainment. However, after 5 days in very calm weather conditions (2 m/s wind speed) as much as 60-65 % of the oil can still remain on the sea surface, but due to the emulsification the overall volumes the oil has increased with a factor of 3 times relative to the volume of oil released.

If free gas is not associated with an oil release (e.g. surface release of stabilized oil at 1 atm.), the flash point of the oil is the most important parameter when evaluating the potential for fire /explosion hazard. In such cases when the oil is spilled on the sea surface it assumes to reach the ambient water temperature within a short time period. The fire hazard, based on the volatile components from the oil, may be high if the flash point of the oil is below the sea temperature. For Oda, the flash points are predicted to exceed the sea temperature within the first hour at all wind speeds (2-15 m/s). For larger release rates, the time for the flash point to exceed the sea temperature can be extended. Moreover, some storage tanks in vessels engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C. Oda reaches this limit (60 °C) in 6 hours after a spill at very calm wind speed (2 m/s) at 15 °C and 12 hours at 5 °C, but more rapidly at higher wind speeds at both temperatures. However, this limit is not considered at relevant for oil recovery vessels with A-class certification for transport of liquids (Class I/II, flash point < 60°C).

In cases of acute oil spills involving "associated" free gas, e.g. from a subsea release, a safety zone must be established early on and downwind from the spill site based on concentrations of the free gas released into the atmosphere. In a response operation, a continuous measurement of the free gas concentration e.g. by use of an explosimeter will be important to minimize the potential risk of fire/explosion hazard and human exposure at the spill site.

The risk for boom leakage in a mechanical recovery operation is more of a concern for low viscous oils (lower than 1000 mPa.s) compared to emulsions that are more viscous. Boom leakage is also influenced by other factors such as operational speed and weather conditions. Here we show that the emulsion viscosities of Oda e.g. surpassed 1000 mPa.s about 12 hours at 2 m/s wind speed, and about 1.5-2 hours at 10 m/s wind speed both at 5 and 15 °C. Moreover, viscosities larger than 15-20 000 mPa.s are known to reduce the flowability of the oil/emulsion when using traditional weir skimmers. At the highest wind speeds (10-15 m/s), the emulsion viscosities of Oda exceeded this limit (>20 000 mPa.s.) in 6-12 hours at 5 °C, and somewhat longer time at 15 °C (9-24 hours). For lower wind speeds (2-5 m/s) flowability towards weir skimmers are expected within 1.5 - 2.5 days and > 5 days of weathering. For emulsions > 20 -50 000 mPa.s, a combination of two skimmer systems (weir - and high visc. skimmers) are recommended by NOFO. Oda could have the potential to exceed 50 000 mPa.s after several days of weathering, especially in winter temperatures, and the high visc. skimmer would likely be recommended in such conditions.

Oda is expected to have potential for chemical dispersion in both winter and summer conditions. The oil was estimated based on the dispersant testing to be easily dispersible with the dispersant Dasic NS for viscosities < 5000 mPa.s. Our study showed, however, that Oda has a potential to be reduced dispersible with Dasic NS at oil viscosities from 5000 mPa.s up to 15 000 mPa.s with a dispersant to oil ratio (DOR) 1:25. In the field, if the viscosity of Oda is between 5000 mPa.s and 15 000 mPa.s after dispersant spraying, and thus has a reduced dispersibility, additional energy (e.g. thrusters, Fire Fighting (Fi-Fi) systems or MOB (Man over board) boats) or higher DOR and/or repeated dispersant application may increase dispersant effectiveness. It is expected that Oda, particularity in calm weather conditions, requires artificial energy and high DOR to enhance the dispersibility of the oil emulsions. With viscosities higher than 15 000 mPa.s the efficacy of dispersant application is expected to be low. In addition, the meso-scale flume testing showed reduced dispersant effectiveness on Oda for oil/emulsion viscosity of 13 800 mPa.s and was therefore in good accordance with the findings from the small-scale study.

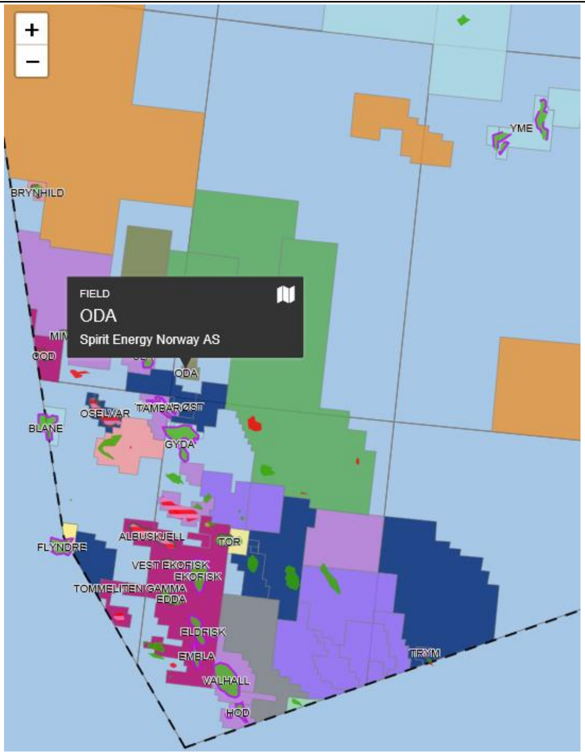
Increased weathering potentially increases the high pour points to the point of solidification (elastic properties) at the sea surface. Solidification typically arises when the pour point of the oil is 5-15°C above the seawater temperature. In such cases, if solidified (low emulsified /water free) lumps are observed on the sea surface, the use of a high-visc. skimmer may be recommended, and lower dispersant effectiveness is likely.

2 Introduction

New oil types (from heavy crude oil to light crude oils and condensates) are continuously coming into production worldwide. Due to large variations in different crude oils' physical and chemical properties, their behaviour and fate may vary greatly if spilled at sea. For example, the "Braer" accident at the Shetlands (1993) and the "Sea Empress" accident in Wales (1996) have demonstrated how different the fate and behaviour of the crude oils can be when spilled on the sea surface. For that reason, obtaining comprehensive knowledge about the expected behaviour of spilled oil at sea is of great importance. Moreover, the "Deepwater Horizon" incident in the Gulf of Mexico (2010) clearly showed how the efficacy of the different response techniques changed as the oil weathered and emulsified on the sea surface over a long period. The past experiences shape the knowledge base and the subsequent refinement of future operative strategies in terms of where, when and how the mitigation methods should operate during a response operation.

According to the Norwegian Environment Agency and the Petroleum Safety Authority Norway (Ptil) regulations for petroleum activities, section 59, the characterization of oils with respect to their weathering properties and fate in the marine environment should be performed for all oils coming into production.

SINTEF Ocean has performed a weathering study (small-scale and meso-scale flume testing) on Oda crude oil based on a request from Spirit Energy. The weathering study was conducted at 13 °C. The obtained laboratory data were used to predict the weathering properties of the oil by use of the SINTEF Oil Weathering Model (OWM) under different weathering conditions (wind speeds and temperatures). The effects of weathering properties on oil spill response options are also discussed. Appendix A describes the general physical and chemical properties and weathering processes of crude oils spilled on the sea surface. Figure 2-1 shows the location and information of the Oda field.



Oda field

Oda is a field in the southern part of the Norwegian sector in the North Sea, 13 kilometres east of the Ula field. The water depth in the area is 65 metres.

Oda was discovered in 2011, and the plan for development and operation (PDO) was approved in 2017.

Oda is developed with a subsea facility including two production wells tied-back to the Ula field and one injection well for pressure support.

The field is produced by pressure support from seawater injection. Oda produces oil from sandstone of Late Jurassic age. The main reservoir is in the Ula Formation at a depth of 2,900 metres. The reservoir is steeply dipping and has good quality

The well stream is transported by pipeline to the Ula field for processing. The oil is exported to Ekofisk and then onward in Norpipe to the Teesside terminal in the UK, while the gas is sold to Ula for injection into the reservoir to increase oil recovery from the Ula field.

Production started in March 2019.

Figure 2-1: ***https://www.norskpetroleum.no/en/facts/field/oda/***

3 Small-scale laboratory testing results

The methodology of small-scale testing is described in Appendix B. Physicochemical parameters and weathering properties of Oda crude oil were compared with similar data of other Norwegian oils as listed in Table 3-1 (Ula, Statfjord C Blend, and Vale). The oils in comparison were selected in agreement with Sprit Energy.

*Table 3-1 Oils compared with Oda crude oil**

Oil	SINTEF ID	Report no	Reference
Ula	1999-002	STF66 F99076	Resby et al. 1999
Statfjord C Blend**	2000-0043	STF66 H00138	Moldestad et al. 2001
Vale	2013-0582	A25949	Hellstrøm and Andreassen, 2014

**Oda was given the SINTEF ID 2019-4130*

*** Statfjord C Blend is hereafter in this report named as Statfjord for simplicity. The properties of Statfjord oils are fairly similar.*

3.1 Chemical composition and physical properties

The chemical composition of the hydrocarbon profile of *n*-alkanes (nC_5-nC_{36}) of Oda crude oil is shown in Figure 3-1. The wax and asphaltene contents are given in Table 3-3, and the physical properties of the crude oil are given Table 3-4. Appendix D shows the composition of OSCAR groups derived from the chemical characterization of the fresh crude oil based on GC-MS analysis and the boiling point fraction.

Gas chromatographic flame ionization detector (GC-FID) characterization

The hydrocarbon profile of the Oda crude oil was analysed by use of gas chromatography (GC) coupled with Flame Ionization detector (FID). Figure 3-1 illustrates the GC-FID output (i.e. gas chromatogram) of the fresh oil of Oda and its corresponding evaporated residues at three different degree of evaporative loss of volatiles at 150, 200 and 200°C+ (see Appendix B.2). The loss of low molecular weight compounds (shown towards the left of the chromatogram) at the three temperatures mimics that of natural weathering (evaporative loss at sea) and provides support for the artificial evaporation of the crude oil by use of distillation (topping) in the laboratory.

The gas chromatograms show the *n*-alkanes as systematic narrow peaks. The first peaks in the chromatogram represent components with the lowest boiling points. Some of the more complex components, such as resins and naphthenes, are shown as a broad and poorly defined bump below the sharp peaks and are often described as the "Unresolved Complex Mixture" (UCM). Heavier compounds such as asphaltenes ($> nC_{40}$) are not possible to analyze with this technique. The GC characterization shows that Oda crude oil is a paraffinic crude oil with a high content of light components (alkanes, aromatics and naphthalenes).

Oda has a high degree of paraffins in the range (nC_5-nC_{36}) that reflects high content of light components, and a moderate wax content in the area higher $> nC_{20}$. For comparison (see Figure 3-2), the chromatograms for Ula, Statfjord and Vale also show that these oils are light to medium paraffinic crude oils. Oda and the other oils for comparison also have low UCM hump, which indicating low resins and naphthenes content.

GC-FID is also a tool in oil spill identification, where common screening parameters are the nC_{17}/pristane and nC_{18}/phytane ratios. These ratios relate the more biodegradable *n*-alkanes to the more recalcitrant isoprenoids (pristane and phytane). Thus, the ratios of nC_{17}/pristane and nC_{18}/phytane are reduced as biodegradation proceeds. These ratios for Oda and the other oils for comparison are shown in Table 3-2 and indicate low degree of biodegradation.

Table 3-2: nC_{17}/Pristane and nC_{18}/Phytane ratios

Oil	nC_{17}/Pristane	nC_{18}/Phytane
Oda	2.0	2.4
Ula	2.2	2.3
Statfjord C Blend	2.0	2.4
Vale	1.7	3.0

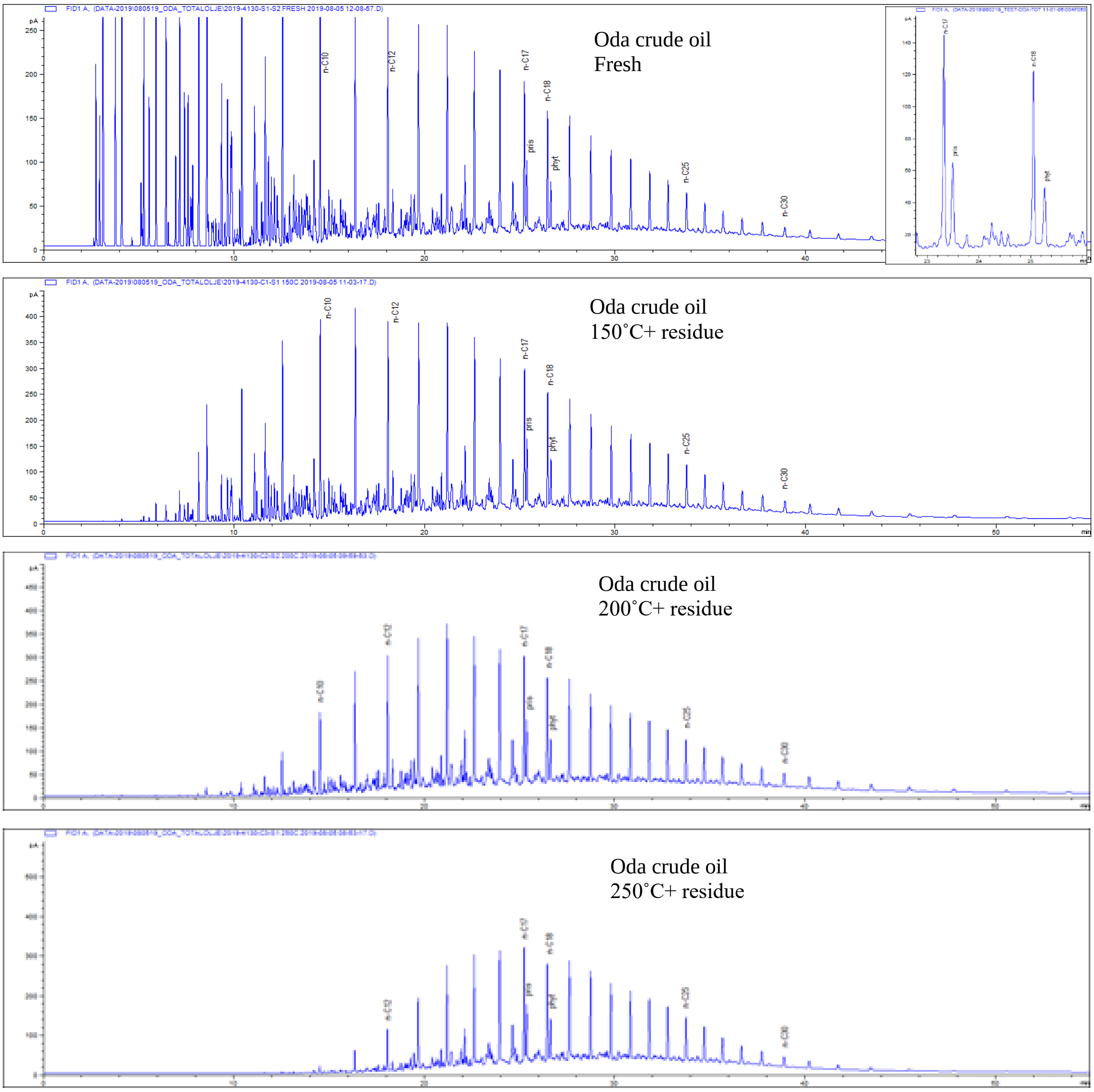


Figure 3-1: GC-FID chromatograms of fresh sample and evaporated residues of Oda crude oil

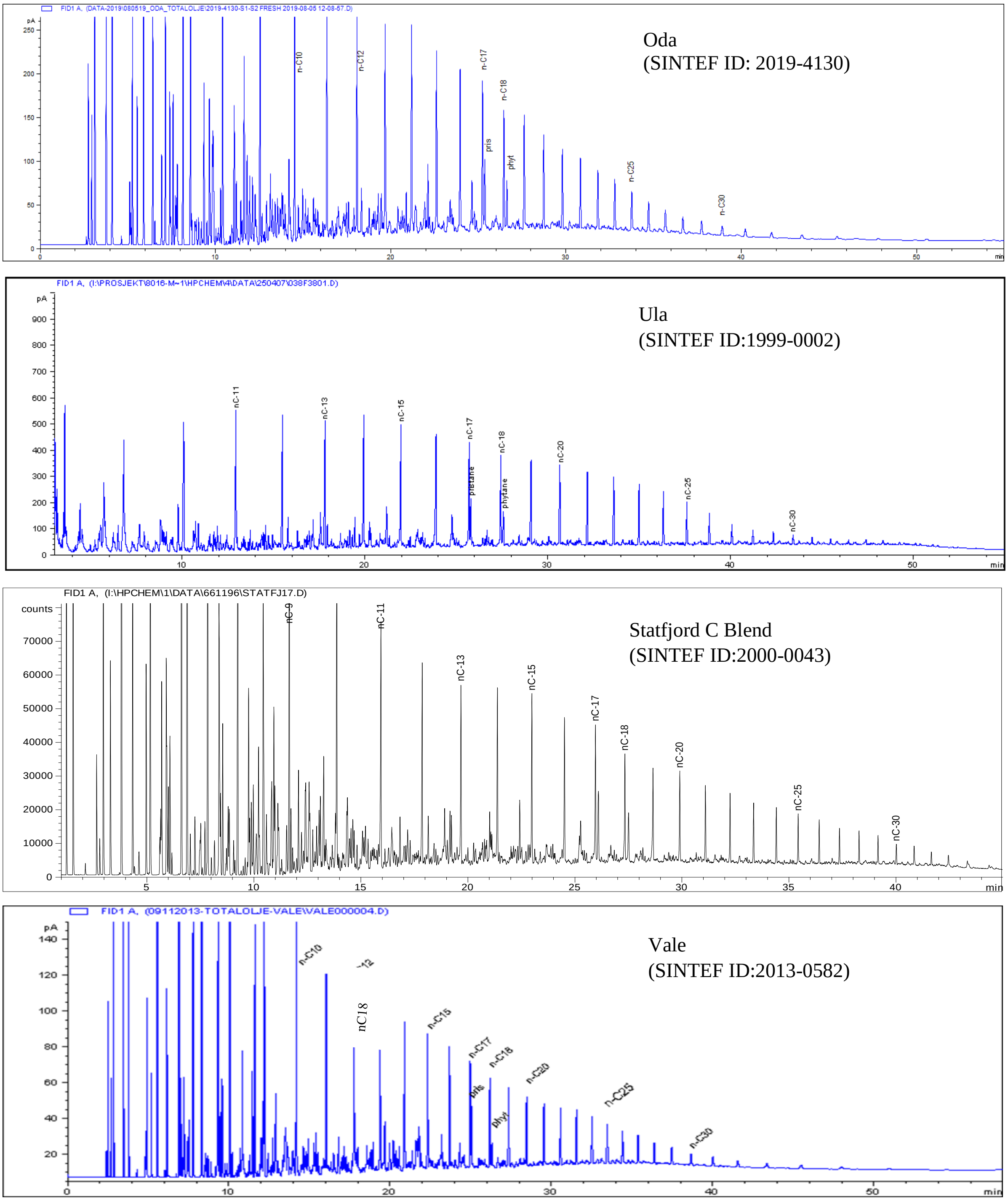


Figure 3-2: GC-FID chromatograms for fresh oils of Oda, Statfjord, Ula and Vale. The retention time may differ between the chromatograms due to different temperature programs and may also differ in resolution (relative comparison)

Asphaltene and wax content for the fresh and weathered residues

The contents of asphaltene and wax for the fresh oil and weathered residues of Oda and the other oils for comparison are given in Table 3-3. The fresh oil of Oda has a medium to high content of wax (5.6 wt.%), and a relatively high content of asphaltenes (0.44 wt. %), compared with other Norwegian crude oils. Oda and Ula exhibit similarities in the wax and asphaltene content, whilst Statfjord and Vale (light crude oil) have lower content of wax and asphaltenes.

Table 3-3: Asphaltene ("hard") and wax content for Oda crude oil, and other oils for comparison

Oil type	Residue	Asph.* (wt. %)	Wax (wt. %)
Oda	Fresh	0.44	5.6
	150°C+	0.56	7.1
	200°C+	0.63	8.1
	250°C+	0.75	9.6
Ula	Fresh	0.42	5.8
	150°C+	0.52	7.1
	200°C+	0.59	8.1
	250°C+	0.67	9.2
Statfjord	Fresh	<0.1	4.2
	150°C+	0.10	5.2
	200°C+	0.10	5.9
	250°C+	0.15	6.8
Vale	Fresh	0.03	3.3
	150°C+	0.04	4.3
	200°C+	0.05	5.1
	250°C+	0.06	6.4

**n-heptane (nC$_7$) precipitation*

Physical properties for the fresh and weathered residues

The physical properties of the fresh and the weathered residues of Oda crude oil are listed in Table 3-4, in comparison of the other oils (Ula, Statfjord and Vale). Oda has a slightly higher evaporative loss than Ula and Statfjord, that reflects the lower density. Oda has density of 0.820 g/mL, whilst Ula and Statfjord have densities of 0.832 and 0.833 g/mL, respectively. The light crude oil Vale has a higher evaporative loss and hence even lower density (0.816 g/mL). Oda exhibits low pour point of the fresh oil (-3 °C) that increases rapidly with the evaporative loss (range +12 to + 24 °C for the residues). The pour points of Ula, Statfjord and Vale also show similarities (same ranges) as for Oda. The viscosity of the fresh oil of Oda increases significantly with increasing evaporation, and here Statfjord and Vale show same degree of increasing viscosities as for Oda. Ula on the other hand has relatively low viscosities for the weathered residues.

The initial interfacial tension IFT values are quite high for Oda fresh crude oil and its residues. In general, the wax reduces the surface-active components of the oil to migrate to the oil/water interface, and the high molecular weight surface activities components (as asphaltenes) migrate slowly to the oil /water interface.

Table 3-4: Physical parameters of Oda, Ula, Statfjord and Vale

Oil type	**Residue**	**Evap. (vol. %)**	**Residue (wt. %)**	**Density (g/mL)**	**Flash point (°C)**	**Pour point (°C)**	**Visc. (mPa.s) 13 °C (10 s^{-1})**	**Visc. (mPa.s) 13 °C (100 s^{-1})**	**IFT (mN/m) ini / eq.**
Oda	Fresh	0	100	0.820	-	-3	13	10	36/22
	150°C+	26	78	0.862	41	12	264	125	35/20
	200°C+	36	69	0.876	77	18	1565	423	34/17
	250°C+	46	58	0.890	117	24	6070	1146	33/19*
Ula	Fresh	0	100	0.832	-	-9	6	7	-
	150°C+	20	83	0.861	45	15	42	49	-
	200°C+	31	73	0.874	84	18	168	142	-
	250°C+	41	63	0.886	118	21	188	175	-
Statfjord	Fresh	0	100	0.833	-	-3	21	11	-
	150°C+	20	81	0.870	-	9	310	123	-
	200°C+	31	71	0.884	-	18	1320	309	-
	250°C+	40	62	0.896	-	24	4179	636	-
Vale	Fresh	0	100	0.816	-	-9	32	14	29**
	150°C+	27	77	0.851	33	6	189	50	29**
	200°C+	40	64	0.866	69	18	1169	244	24**
	250°C+	53	51	0.879	108	27	5098	1024	-

- *No data *Measured at 30°C ** Measured as IFT ini.*

3.2 Emulsifying properties

Emulsification

In general, emulsification is the mixing of seawater droplets into spilled oil at the water's surface (water-in-oil emulsion), forming a weathered oil residue that often tends to be relatively resistant to other weathering processes such as evaporation, and increases the total volume of oil due to the uptake of water into the oil.

The emulsifying properties of Oda crude oil were studied by use of rotating cylinders as described in Hokstad et al., 1993 (Appendix B). Experiments containing residues of 150°C+, 200°C+ and 250°C+ were made to produce data for stability, viscosity, maximum water uptake, kinetics, and the effectiveness of the emulsion breaker application. The emulsion containing the maximum water content after 24 hours rotation is shown in Figure 3-3, below. The figure shows from left to right emulsions prepared from the residues of 150°C+, 200°C+ and 250°C+, respectively.

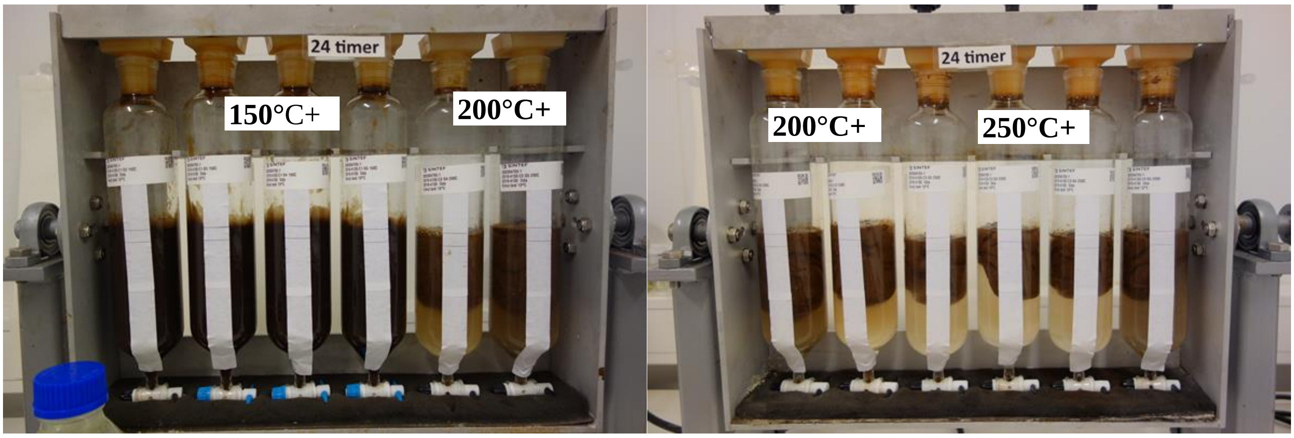


Figure 3-3: Rotating cylinders of water-in-oil (w/o) emulsions of Oda crude oil after 24 hours at 13 °C

Water uptake and maximum water content

The rate of water uptake (kinetics) was studied by use of the rotating cylinders. The water content in the water-in-oil (w/o) emulsions as a function of time is tabulated in Table 3-5. The $t_{1/2}$ value is defined as the time (hours) it takes to incorporate half of the maximum water uptake (vol. %) in 24 hours (rotating time).

After 24 hours rotating time, Oda expressed rapid and a high-water uptake for all the residues 150°C+, 200°C+ and 250°C+, which ranged from 91 to 76 vol. % (Table 3-5). Supersaturation of the maximum water uptake for the 150°C+ emulsion was observed. This means that all the water was totally emulsified into the oil. However, a maximum water of 91 vol. % is not likely to be observed on the sea surface.

Table 3-5: Water uptake for the evaporated residues of Oda crude oil at 13 °C

Mixing time	**150°C+ * (vol. % water)**	**200°C+ * (vol. % water)**	**250°C+ * (vol. % water)**
Start	0	0	0
5 min	47	24	21
10 min	61	38	17
15 min	67	46	35
30 min	91	59	71
1 hour	91	85	75
2 hours	91	84	77
4 hours	91	83	77
6 hours	91	83	78
24 hours	91**	84	76
$t_{½}$	**0.07**	**0.14**	**0.60**

** Depending on weather situation and release rate, the residues are corresponding to approximately 0.5-1-hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface*
***Supersaturation, not likely to happen in a spill situation*

Efficiency of emulsion breaker and stability of emulsion

In mechanical recovery operations, separating oil from water enables optimal use of available storage (i.e. facilities/tankers), and the efficiency of this separation can be enhanced by applying emulsion breakers. The effectiveness of the emulsion breaker Alcopol O 60% was evaluated on different residues of emulsified Oda crude oil. Our results shown that the emulsified oil volume decreased after treatment with the emulsion breaker in all residues, as water was released from the emulsion (Table 3-6). The emulsions were partly broken when adding the emulsion breaker (Alcopol O 60%). A concentration of 2000 ppm (0.2 wt. %), relative to the oil, was shown to be most effective to break the emulsions, and therefore recommended.

The emulsion stability was studied by quantifying the amount of water released from the emulsion after 24 hours settling time. The Oda crude oil formed stable w/o-emulsions of the 150, 200 and 250°C+ residues, as shown in the first row of Table 3-6. Figure 3-4 shows emulsions from stability testing of the 150, 200 and 250°C+ residues after 24 standstills followed by rotation, and the effect on emulsions (release water) after adding emulsion breaker.

Table 3-6: Stability of emulsion and the effectiveness of emulsion breaker at 13 °C of Oda crude oil

Residue	Emulsion breaker	Water-in-oil emulsion (vol. %) at 13 °C		Stability ratio**
		Reference	24 hours *	
150ºC+	None	91	91	1.00
200ºC+	None	84	84	1.00
250ºC+	None	76	77	1.00
150ºC+	Alc. O 60 % 2000 ppm	91	6	0.01
200ºC+	Alc. O 60 % 2000 ppm	84	27	0.07
250ºC+	Alc. O 60 % 2000 ppm	76	53	0.35
150ºC+	Alc. O 60 % 500 ppm	91	46	0.09
200ºC+	Alc. O 60 % 500 ppm	84	80	0.77
250ºC+	Alc. O 60 % 500 ppm	76	76	1.00

ppm: parts per million

**: w/o-emulsion after 24 hours rotation and 24 hours settling*

*** Stability ratio of 0 implies a totally unstable emulsion after 24 hours settling; all the water is settled out for 24 hours settling. Stability ratio of 1 implies a totally stable emulsion*

Figure 3-4: Stability of Oda emulsions of 150, 200 and 250°C+ residues (left) and effect of emulsion breaker (right)

Viscosities of water-free and emulsified residues

The viscosity describes the oils ability to resist gradual deformation by increasing shear, where viscosities of so-called *Newtonian* oils remains constant independent on the applied shear rate (s^{-1}) at a given temperature. When shear is applied on so-called *non-Newtonian* oils, the viscosity of such oils decreases.

The viscosities of the fresh oil, water-free residues and emulsified residues of Oda crude oil at 13 °C are given in Table 3-7. The fresh oil behaves as a *Newtonian* fluid with shear rates of 10, 100 and 1000 s^{-1}. The water-free residues and emulsions behave as *non-Newtonian* fluids due to the increasing degree of weathering (evaporation and water uptake), with higher viscosities at a lower shear rate (10 s^{-1}) compared to the viscosities measured at higher shear rates (100 and 1000 s^{-1}). The yield stress, the force that must be applied to make the oil to begin to flow, is tabulated in Appendix E.

Table 3-7: Viscosities of fresh oil, residues and emulsions of Oda crude oil at 13 °C

Residue	**Water content (vol. %)**	**Viscosity (mPa.s) Oda crude oil 13 °C**		
		10 s^{-1}	**100 s^{-1}**	**1000 s^{-1}**
Fresh	0	13	10	10
150°C+	0	264	125	52
200°C+	0	1565	423	115
250°C+	0	6070	1146	291
150°C+	50	538	327	n.a
200°C+	50	992	591	n.a
250°C+	50	8610	2196	n.a
150°C+	75	2487	837	n.a
200°C+	75	6548	1844	n.a
250°C+	65*	33242*	8089*	n.a
150°C+	91	6312	1284	n.a
200°C+	84	17805	3563	n.a
250°C+	76	31081	3056	n.a

*n.a: not applicable *Water uptake reached 65 vol. %*

3.3 Chemical dispersibility

The dispersibility testing of Oda crude oil included:

- Screening of dispersant effectiveness
- Dosage testing of a relevant dispersant
- Systematic testing on weathered /emulsified samples as a basis to predict the time-window for effective application of dispersant

Screening testing of dispersants

The screening testing on was performed using the low-energy IFP test (Institute Francais du Petrole), reflecting non-breaking waves (< 5 m/s wind speed), in combinate with the high-energy MNS test (Mackay-Nadeau-Szeto). Dispersants tested were Dasic NS, Corexit 9500, Finasol OSR-52, Radiagreen OSD and Gamlen OD 4000. The screening testing was performed at a standard temperature of 13 °C, using a 200°C+ residue emulsified with 50 vol. % seawater. The results are presented in Table 3-8 and illustrated in Figure 3-5. Corexit 9500 and Dasic NS expressed the highest dispersibility effectiveness on IFP with effectiveness of 67 and 63 %. The MNS test showed 100 % effectiveness when applied on the same emulsion with Dasic NS, Corexit 9500 and Finasol OSR-52. Radiagreen OSD is European Maritime Safety Agency (EMSA) product and is not included as a part of the dispersant stockpile in Norway.

Table 3-8: Screening testing on Oda using the IFP-test and MNS-test at standard temperature of 13 °C

Dispersant (DOR/DER =1:25)	Efficiency dispersant (200°C+ /50 vol. % emulsion)* IFP	Efficiency dispersant (200°C+ /50 vol. % emulsion)** MNS
Dasic NS	63	100
Corexit 9500	67	100
Finasol OSR 52	42	100
Gamlen OD 4000	26	-
Radiagreen OSD	26	-

** Emulsion viscosity: 922 mPa.s (10s^{-1})*
-: Not analysed

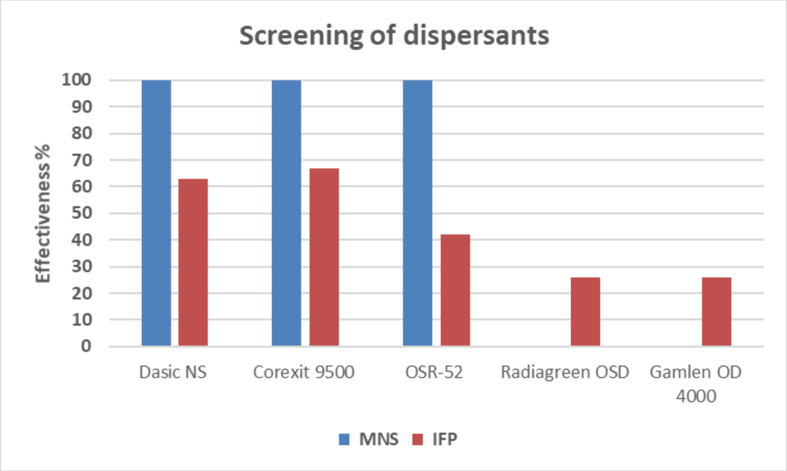


Figure 3-5: Results from screening of dispersants on Oda 200°C+/50 vol. emulsion

Dosage testing of dispersants

Dosage testing at 13 °C was performed using Dasic NS on the Oda emulsion (200°C+ / 50 vol. %). The dosage test helps to identify optimal design conditions for dispersant use and was performed with dispersant-to-oil/emulsion ratios (DOR /DER) of 1:25, 1:50, 1:100 and 1:200, and with no dispersant added. The results are presented in Table 3-9 and Figure 3-6. The results show a clear dosage dependant effect for the low-energy test (IFP), where DOR 1:25 showed the highest effect (63%). For the MNS-test, the results indicated that emulsions of Oda were easily dispersible in breaking waves conditions (> 5 m/s wind speed), with results ranging from 91-100 % for the different dosages. However, no dispersion effectiveness (< 5 %) was observed and measured with no dispersant added neither with using the IFP-test nor the MNS-test. This means that application of dispersants is found to be necessary for Oda to be dispersible, even in breaking waves conditions.

Table 3-9: Dosage testing on Oda emulsions with Dasic NS at 13 °C

Dispersant (dosage rate)	**Effectiveness of dispersant on 200°C+/50 vol. % emulsion***	
	IFP	**MNS**
Dasic NS (1:25)	63	100
Dasic NS (1:50)	48	99
Dasic NS (1:100)	18	100
Dasic NS (1:200)	7	91
No disp.	<5	<5

** Emulsion viscosity: 1259 mPa.s (10s^{-1})*

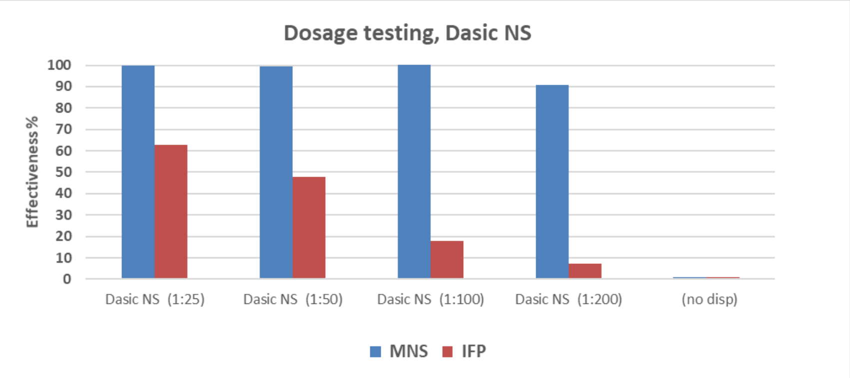


Figure 3-6: Results from dosage testing on Oda 200°C+/50 vol. emulsion (Dasic NS)

Systematic dispersant testing of the oil dispersibility at varying weathering

In agreement with Spirit Energy, Dasic NS was also chosen for the continued systematic testing of the oil/emulsion dispersibility at varying weathering degrees to determine the time window for dispersant use. Dasic NS is the dispersant agent in NOFO's stockpile, and a dosage rate of 1:25 (4 wt.%) is commonly used as the standard procedure to establish the time window for dispersant application and was also shown to be a good representative among the dispersants tested from this study.

Table 3-10 shows the tabulated results from the systematic dispersant testing as basis to estimate the dispersibility limits expressed as a function of effectiveness and viscosities (Figure 3-7). The dispersibility limits (viscosities) are further used as input to the SINTEF Oil Weathering Model (OWM) to predict the time-window for dispersant use.

Table 3-10: Effectiveness of Dasic NS on Oda residues and emulsions at 13 °C

Residue	Water content (vol. %)	Viscosity (mPa.s) 10 s^{-1}	Effectiveness (%) IFP	Effectiveness (%) MNS
150°C+	0	264	65	100
200°C+	0	1565	21	94
250°C+	0	6070	<5	12
150°C+	50	538	79	100
200°C+	50	992	63	100
250°C+	50	8610	7	83
150°C+	75	2487	72	81
200°C+	75	6548	<5	8
250°C+	65	33242	<5	<5
150°C+	86	6312	53	94
200°C+	81	17805	<5	8
250°C+	75	31081	<5	<5

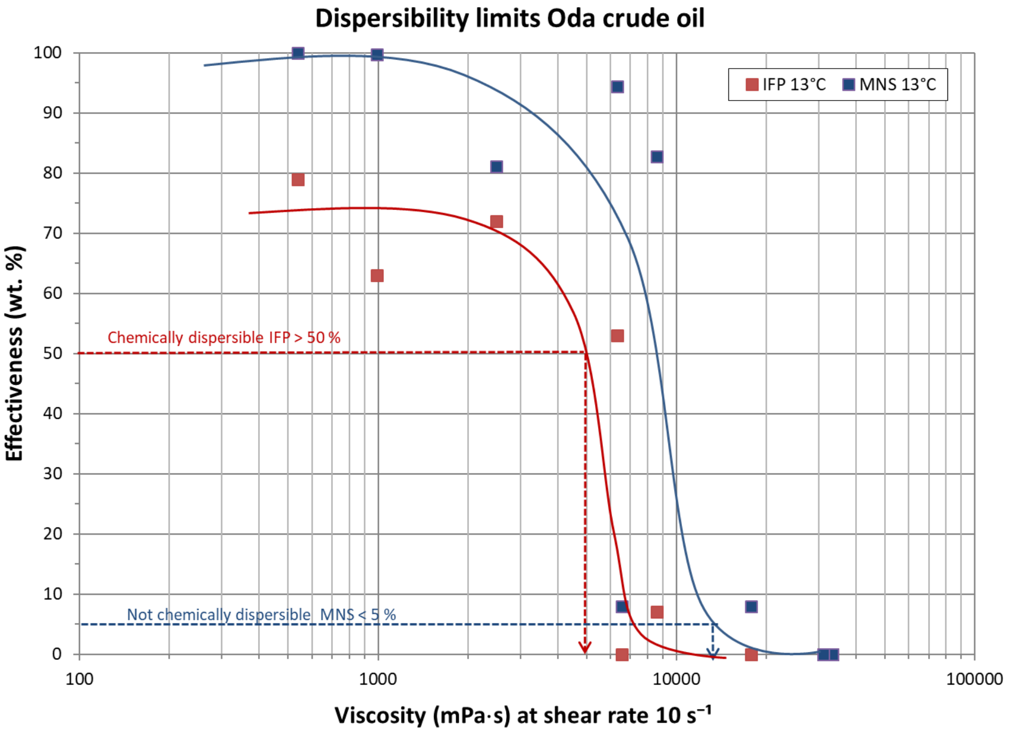


Figure 3-7: Estimated dispersant effectiveness on Oda crude oil at 13 °C

Oda was found to be dispersible for viscosities lower than 5000 mPa.s, reflecting > 50 % effectiveness by use of the IFP-test. Moreover, reduced dispersibility is expected with viscosities above 5000 mPa.s and up to 15 000 mPa.s. It should be emphasized that reduced dispersibility means that the oil is still dispersible but may require additional energy and/or higher dispersant dosage to enhance effective dispersion. The viscosity limit where Oda is not dispersible, expressed with effectiveness lower than 5 % using the MNS-test, was estimated to 15 000 mPa.s. The dispersibility limits are also summarised in Table 3-11.

Table 3-11: Estimated viscosity limit for Oda for use of dispersant and criteria for definition of time window

Dispersibility	Criteria for effectiveness (wt. %)	Dispersibility limits based on emulsion viscosity (mPa.s)
Chemically dispersible	IFP > 50 %	5000
Not chemically dispersible	MNS < 5 %	15 000

4 Meso-scale flume testing

The weathering behaviour of Oda crude oil was studied in a meso-scale flume. A total of 9 litres of the fresh Oda crude oil were applied carefully and evenly to the flume surface water using a watering can. The water and air-temperature for this experiment was 13 °C (±2 °C) due to sequence of the climate system. After application of the crude oil the wind and wave energy were switched on. The oil was weathered for 72 hours (3 days) before application of dispersant after a standard procedure. Further description of the meso-scale flume is given in Appendix B.3. This section provides an overview of the results from the flume testing, including the weathering properties, estimated mass balance and visual observations of the Oda crude oil. The results obtained give valuable operational information about the oil's behaviour. The weathering behaviour of the oil in the flume basin is a supplement to the small-scale laboratory testing.

The experimental results obtained for Oda in the meso-scale flume are presented below. Table 4-1 shows the water content, evaporative loss, viscosity, and concentration of dispersed oil in the water column (naturally and chemically dispersed) at 13 °C at different time points throughout the test.

Table 4-1: Results from the meso-scale flume laboratory testing of Oda crude oil at 13 ºC

Sample no	Time (hours)	Water content (vol%)	Evaporative loss (wt%)	Viscosity (mPas), 10 s^{-1}	Oil-in-water ppm*	Oil-in-water % of orig. amount
1	0.5	60	24	76	26	1.5
2	1	66	25	707	-	
3	2	77	27	626	-	
4	4	77	34	1399	-	
5	6	78	36	1902	-	
6	24	65	36	5892	-	
7	48	62	37	10609	-	
8	72	65	39	13860	26	1.5
1st application of dispersants: 71.1.2 g Dasic NS (DOR = 1.6 wt. %)						
3 min. disp 1	-	-	-	-		-
10 min. disp 1	-	-	-	-	-	-
30 min. disp 1	-	67	39	8900	31	1.8
2nd Application of dispersants: 66.4 g Dasic NS (DOR= 1.5 wt. %)						
3 min. disp 2	-	-	-	-	48	2.7
10 min. disp 2	-	-	-	-	69	3.8
30 min. disp 2	-	33	39	6028	90	5.4
3rd Application of dispersants: 64.7 g Dasic NS (DOR= 1.4 wt. %)						
3 min. disp 3	-	-	-	-	125	7
10 min. disp 3	-	-	-	-	238	14
30 min. disp 3	-	-	-	-	540	33
60 min. disp 3	-	32	39	6015	388	23

-: no measured data. **:ppm=parts per million*

The oil weathering from the meso-scale flume basin (maximum water uptake, evaporative loss and emulsion viscosity) were compared with weathering predictions using the SINTEF Oil Weathering Model (OWM) with input data from the small-scale study.

The evaporative loss (Figure 4-1) shows that the predicted and experimental flume data harmonized well. For the water uptake, Oda reached a maximum water content of approx. 80 vol. % within 2 hours weathering (Figure 4-2), as predicted by the OWM. However, the reduction of the water content from the flume experiments after one day of weathering could be caused by the sampling and pre-handling of the emulsion but could not be directly explained. The emulsion viscosities from the flume experiment did also support the OWM predictions (Figure 4-3).

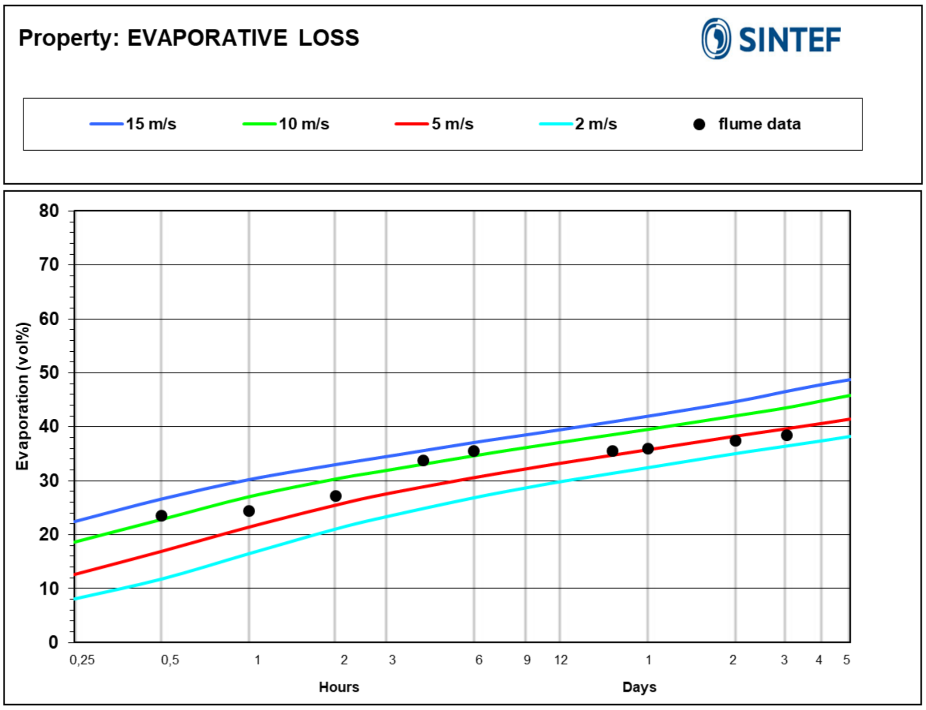


Figure 4-1: Predicted evaporative loss for Oda crude oil. The dots represent the experimental data from the meso-scale flume testing

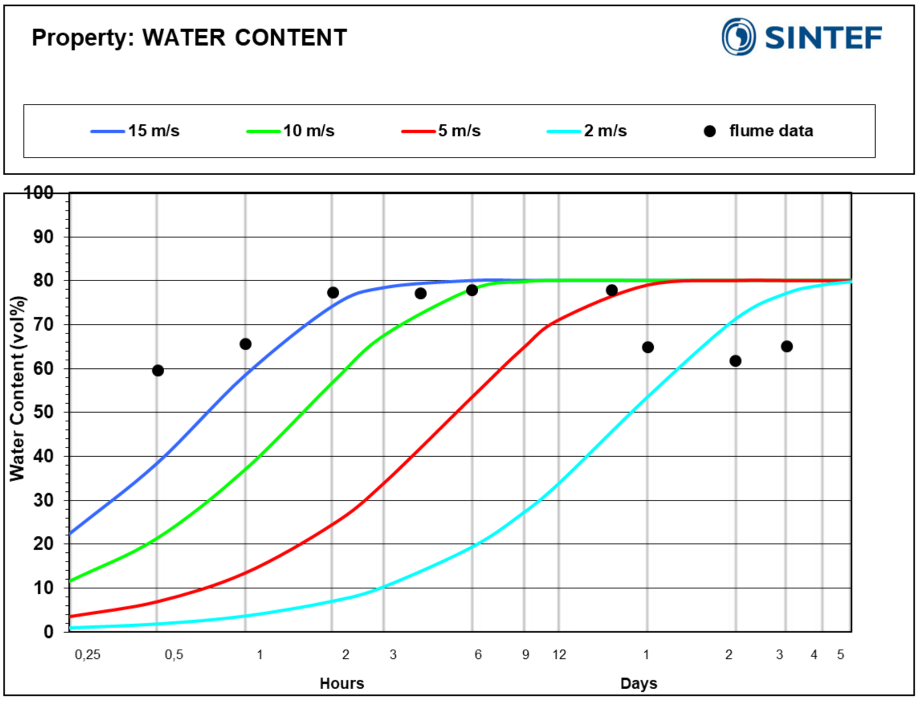


Figure 4-2: Predicted water uptake for Oda crude oil. The dots represent the experimental data from the meso-scale flume testing

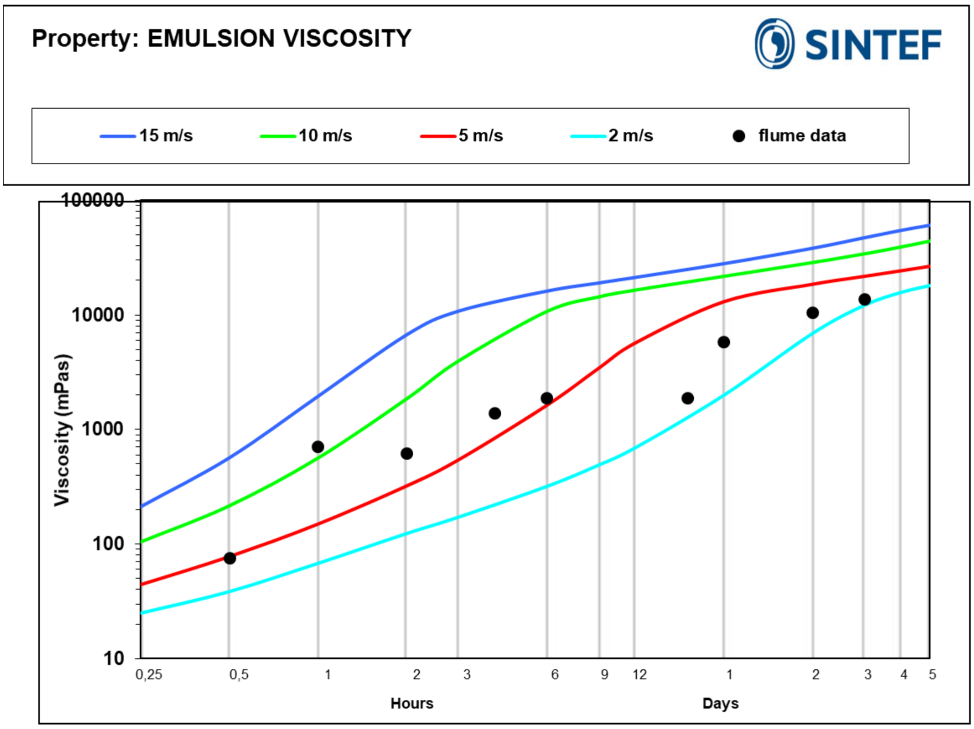


Figure 4-3: Predicted emulsion viscosity for Oda. The dots represent the experimental data from the meso-scale flume testing

Mass balance

The main elements in the mass balance for a crude oil spilled at sea are evaporative loss, the amount of oil on the surface, and the amount of oil dispersed. In order to conduct a mass balance, all oil must be accounted for. Therefore, in addition to the main elements, it was also necessary to consider each individual oil sample removed from the flume, the subsequent reduction in water volume, and the amount of oil absorbed to the flume wall.

The amount of oil evaporated, oil on surface, naturally dispersed and sampled oil was calculated, and the oil adsorbed to the flume walls was estimated by weight. Table 4-2 shows the estimated results (by weight) of the mass balance after 24 hours of weathering time, whilst Figure 4-4 shows the mass balance before applying dispersant agent into the flume.

Table 4-2: Tabulated values of the estimated mass balance of Oda by weight.
Example after 24 hours weathering time.

Properties	**Mass balance (% of initial oil)**
Evaporated	36
Oil on water surface	54
Dispersed oil	0
Sampled amount of oil	1.6
Oil adsorbed to the flume walls*	5

**Estimated value from observations*

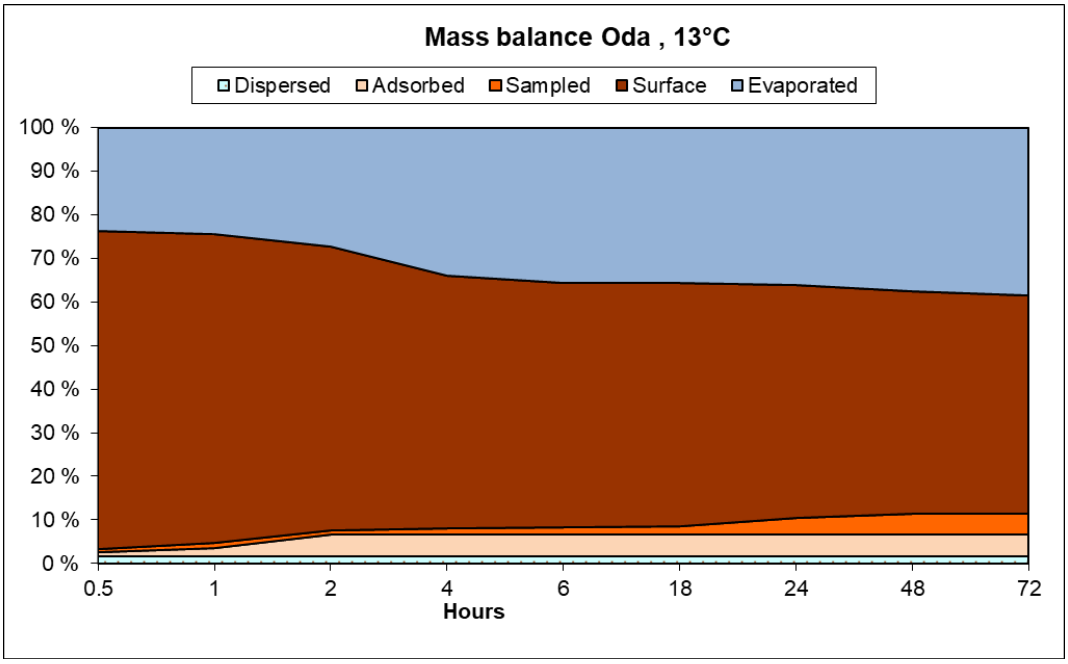


***Figure 4-4*: Mass balance for Oda crude oil in the meso-scale flume basin at 13 °C, before dispersant application**

In-situ chemical dispersion after 72 hours of weathering

After 72 hours of weathering, the dispersant Dasic NS was sprayed successively 3 times on the remaining surface oil emulsion (*in-situ* application). The amount of application and dosage rates are summarized in Table 4-3. In addition, dispersed oil was sampled and quantified as followed:

- 30 minutes; after first dispersant application
- 3, 10 and 30 minutes; after second dispersant application
- 3,10, 30 and 60 minutes; after third dispersant application

Figure 4-5 shows the mass balance of dispersed oil after application of dispersant (Dasic NS). After the third round of dispersant the percent of available oil dispersed in the water phase was in the range of 50-70 %.

Table 4-3: Dispersant dosage on* Oda *in the meso-scale flume basin (in-situ application)

Dispersant application (#)	Dasic NS application (g)	Dispersant -to -Oil Ratio (DOR /DER)	Dispersant (wt. %)
1	71.1	1:63	1.6
2	66.4	1:68	1.5
3	64.7	1:70	1.4
1+2+3	202.2	1:22*	4.5

**Dispersant-to-emulsion Ratio (DER) 1:64*

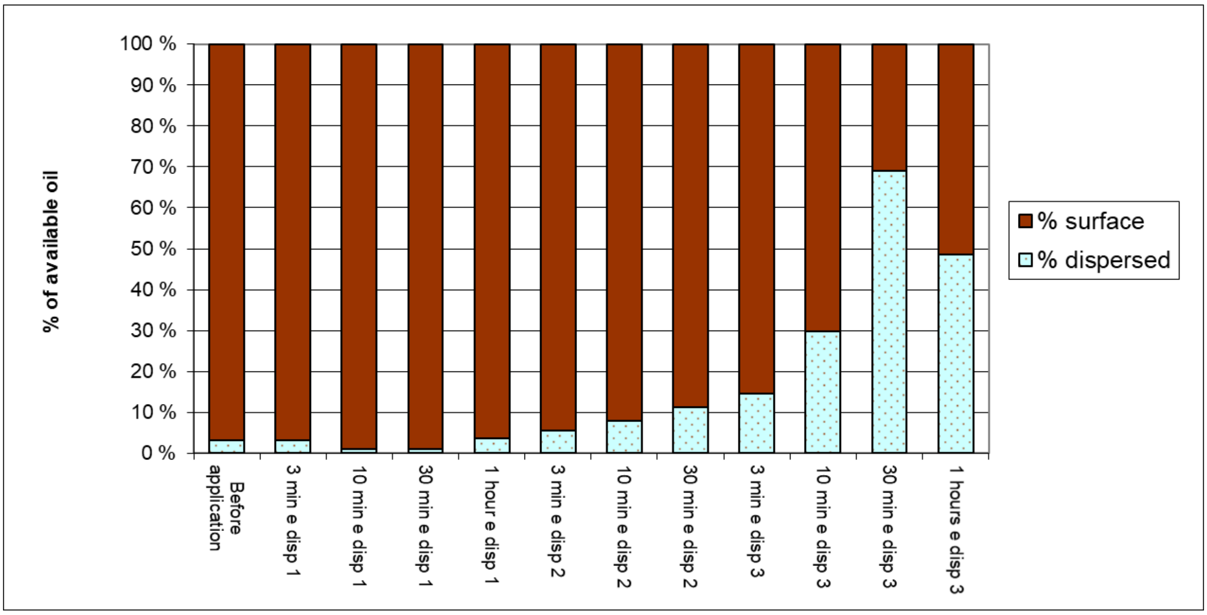


Figure 4-5: Mass balance of Oda after application of Dasic NS as percentage of available surface oil

Observations from the flume basin experiments of Oda

A selection of pictures taken during the flume experiment is presented below. The apparent difference in colour among the pictures is due to the changing colour of the oil as evaporation and emulsification takes place. Artificial sunlight simulated using a solar simulator was turned on during the experiments simulating photo-oxidation and will also influence on the photos (colours).

The oil was spread thinly when poured onto the water surface and covered the entire surface. The oil started to emulsify within the first hours, but the initial formed emulsions were unstable with large pockets of water that broke easily. During the first half hour some of the oil was submerged into the water phase, but within the first hours most of these large droplets in mm-size had resurfaced.

For 48-72 hours of weathering the emulsification continued and produced a more viscous and stable emulsion with time, still with an insignificant amount of dispersed oil (droplets) in the water phase. After 72 hours the viscosity had increased significantly from 76 mPa.s (0.5 hours) to 13 860 mPa.s. Figure 4-6 shows the appearance from 30 minutes to 72 hours of weathering.

Figure 4-6: Weathering of Oda crude oil from upper left: 30 min., 4 hours, 6 hours, 24 hours, 48 hours and 72 hours weathering time.

After 72 hours weathering in the flume, the dispersant Dasic NS was sprayed on the remaining surface oil (in-*situ* application) using a Wagner paint sprayer. About 50 % of the total volume of oil (9 litres) was available for chemical dispersion. The dispersant was applied 3 times on the surface oil/emulsion giving a cumulative dispersant-to-oil ratio (DOR) of 1:22, reflecting a dosage-to-emulsion ratio (DER) of 1:64. A short summary from the dispersant application is given as followed:

Dispersant application 1: The first round with application of Dasic NS gave not any visually and measurable dispersion of the surface oil (emulsion) into the water phase (Figure 4-7). However, the continuous "slick" appeared to lose some structure and viscosity reduced from 13 860 to 8900 mPa.s. The water content was not reduced, and most of the emulsified oil remained on the surface.

Figure 4-7 Left: The surface emulsion before application (visc. 13 860 mPa.s). Middle and Right: After 1. round of dispersant application, the structure of emulsion is broken to large patches. Viscosity reduced to 8900 mPa.s.

Dispersant application 2: In the second round, the emulsion viscosity was reduced to 6028 mPa.s and the water content was reduced from 65 to 30 vol. %. The emulsion was broken into smaller patches, and the amount of oil droplet dispersed into the water phase slightly increased. Figure 4-8 and Figure 4-9 show the effect of dispersant after 3 and 10 minutes.

Figure 4-8: Left: Emulsion before 2.round of dispersant application. Middle: The emulsion was broken into patches (3 min. after 2. round). Right: Slightly increased amount of oil droplets in the water phase

Figure 4-9: 10 minutes after the second application. The emulsion appears a continuous slick (left). Some dispersed oil observed in the water phase (right)

Dispersant application 3: After the third round, the emulsion continued to be more dispersed into the water phase (Figure 4-10). The viscosity of surface oil (emulsion) was only slightly reduced to 6015 mPa.s, and the water content was 32 vol. %. The water samples from the third application round are shown in Figure 4-11.

Figure 4-10: Left: The 3. application once again breaks the emulsion. Middle: More dispersed oil observed in the water phase (3 min. after application). Right: Surface oil (emulsion) 60 minutes after the third application – the colour of the water indicates that more oil is even more dispersed (visc. 6015 mPa.s, water content 32 vol.%)

Figure 4-11: Water samples from 3. Round of dispersion application. From Left to Right: 60, 30, 10 and 3 min. after third application.

The flume testing showed reduced dispersant effectiveness on Oda when the weathered and emulsified oil had reached a viscosity of 13 800 mPa.s (72 hours of weathering). The flume testing indicated that the oil/emulsion required 3 times application round of dispersant (cumulative DOR 1:22) to break up the "slick" into patches and disperse the oil (i.e.50-70 % of available oil). Oda crude oil may need replicative application and/or higher dosage to disperse the emulsion when it has reached such high viscosities with time. The third round of dispersant application also showed that the dispersant needed time, in combination of waves, to give an effect on the high viscous and stable emulsions of Oda. However, it is expected that Oda could be good dispersible within 24 hours of weathering for viscosities lower than 5000 mPa.s, as the estimated limit from the small-scale study. The upper limit for dispersant use was estimated to 15 000 mPa.s from the small-scale study. This is therefore in a good accordance to the observation from the meso-scale testing.

5 Predictions with SINTEF Oil Weathering Model (OWM)

5.1 Description of SINTEF OWM

A systematic stepwise laboratory procedure developed at SINTEF (e.g. Daling et al., 1990) was used to isolate and map the various weathering processes that take place when oil is spilled on the sea surface. Laboratory study of the weathering properties of Oda crude oil was conducted at 13 °C, and the analytical data were further used as input to the SINTEF Oil Weathering Model (OWM) (version 11.0.0). The experimental design for the study is described in Appendix B. The input data to the SINTEF OWM is given in Appendix C.

The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, wind speeds and sea temperature) and predicts the change rate of the oil's properties on the sea surface with time. The SINTEF OWM is schematically shown in Figure 5-1. The predictions obtained from the SINTEF OWM are useful tools in the oil spill contingency planning related to the expected behaviour of oil on the sea surface, and to evaluate the time window for operational response strategies in a spill operation. In this report, the presented predictions span a period from 15 minutes to 5 days after an oil spill has occurred. The SINTEF OWM is described in more detail in Johansen (1991), and in the user's guide for the model.

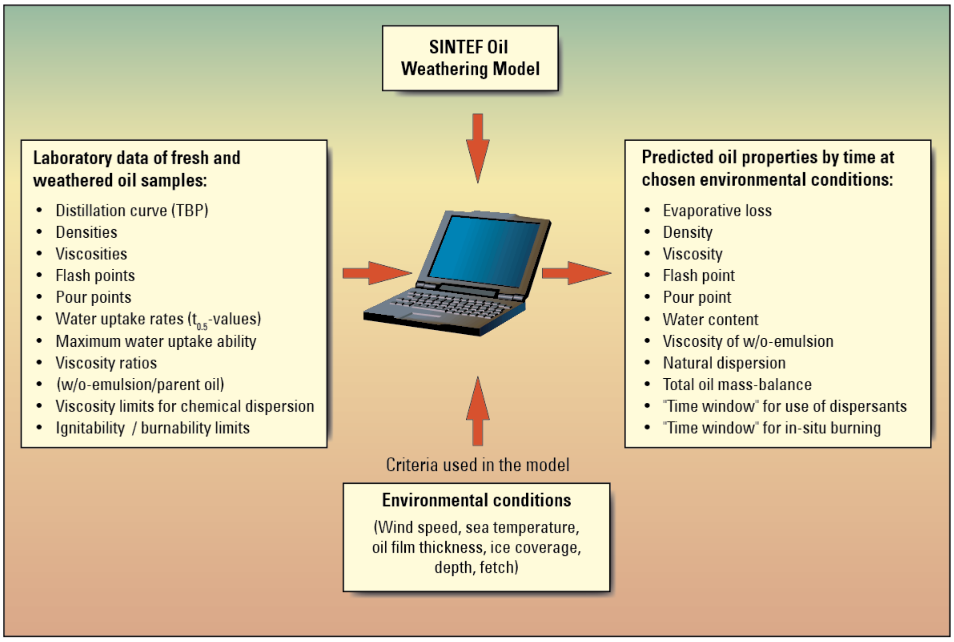


Figure 5-1: Schematic input data to the SINTEF OWM and the predicted output oil properties

Spill scenario

A standard surface release from the OWM was used as the spill scenario (see section 5.2). The scenario chosen is not oil field specific but selected to give predictions of the expected weathering properties of the oil based on the experimental data and specified terminal oil film thickness. A standardized scenario will also more easily compare results of weathering properties with other oils.

Oil film thickness

The oils are categorized as condensate, emulsifying crude, low emulsifying crude, heavy bunker fuel or refined distillate. The categorization of oil is also based on the experimental results obtained in the laboratory. The terminal film thicknesses vary among these categories based on experimental (field) experience. Oda is categorized as an emulsifying (crude) oil with terminal oil film thicknesses of 1 mm.

Sea temperature

The prevailing weather conditions greatly influence the weathering rate of oil on the sea surface. Due to the location of the oil field, the prediction temperature chosen for Oda crude oil was 5 and 15 °C.

Wind speed

The relationship between the wind speed and significant wave heights used in the prediction charts obtained from the SINTEF OWM are shown in Table 5-1.

Table 5-1: Relationship between wind speed and significant wave height used in the SINTEF OWM

Wind speed [m/s]	**Beaufort wind**	**Wind type**	**Wave height [m]**
2	2	Light breeze	0.1 - 0.3
5	3	Gentle to moderate breeze	0.5 - 0.8
10	5	Fresh breeze	1.5 - 2.5
15	6 – 7	Strong breeze	3 - 4

5.2 Predictions of Oda crude oil weathering properties

Input to the OWM

Oil type:	Emulsifying crude oil
Geographical area:	North Sea
Terminal oil film thickness:	1 mm
Release rate:	80 m^3/hour or 1900 m^3/day
Seawater temperature:	5 and 15 °C
Wind speed:	2 m/s, 5 m/s, 10 m/s and 15 m/s

How to use the prediction charts: an example

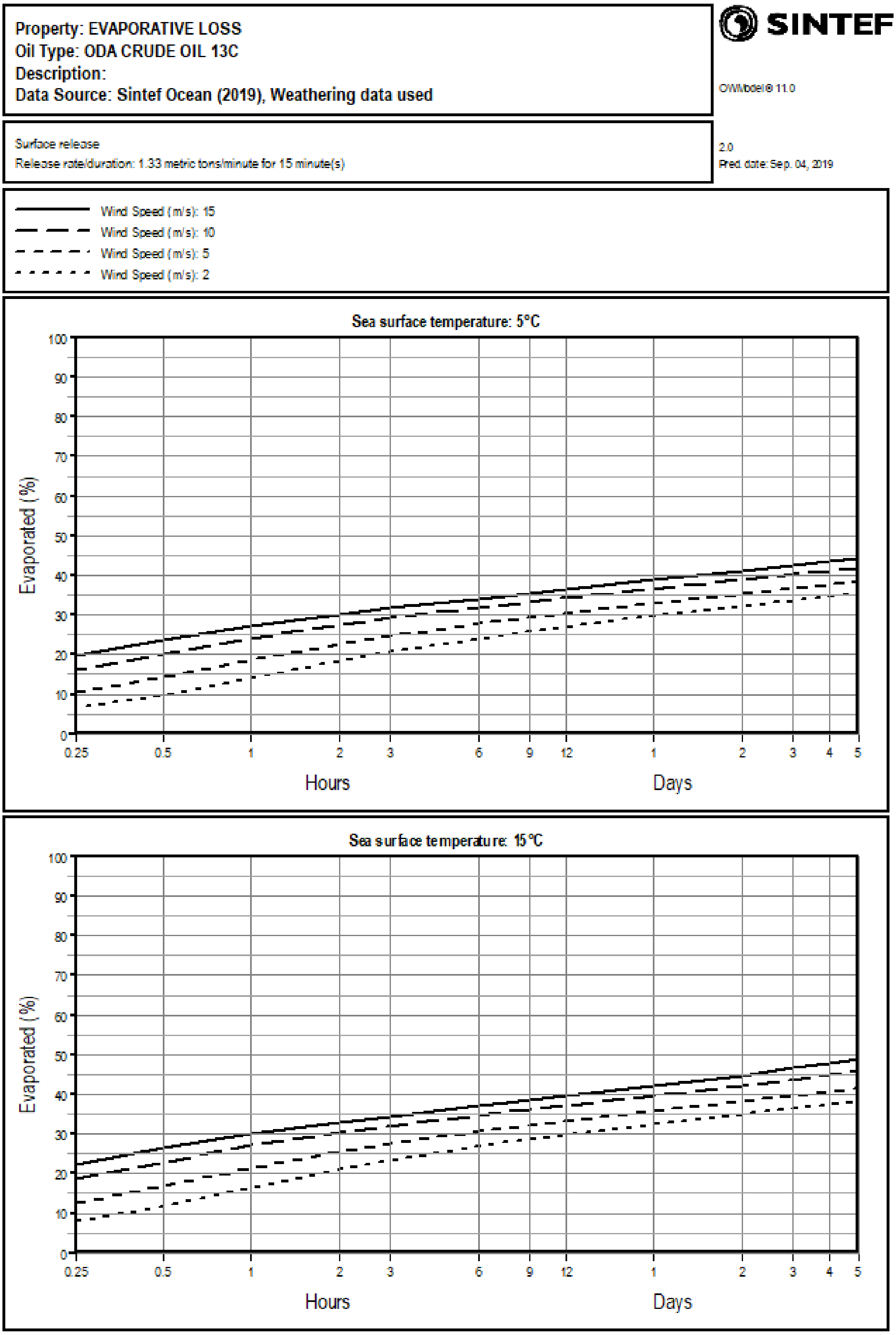
If the oil has drifted on the sea surface, the following prediction charts could be used to determine the weathering properties of the oil/emulsion. Table 5-2 gives examples for the following scenario:

- Drifting time: 2, 12 and 24 hours
- Seawater temperature: 5 and 15 °C
- Wind speed: 10 m/s

Table 5-2: Example of weathering properties for Oda crude oil obtained from the OWM predictions after 2, 24 and 24 hours of weathering at 10 m/s wind speed

Weathering property	**2 hours 15 °C 10 m/s**	**12 hours 15 °C 10 m/s**	**24 hours 15 °C 10 m/s**	**2 hours 5 °C 10 m/s**	**12 hours 5 °C 10 m/s**	**24 hours 5 °C 10 m/s**
Evaporation, wt. %	30	37	40	28	34	37
Water content, vol. %	57	80	80	57	79	79
Flash point, °C	72	99	108	62	87	96
Pour Point, °C	17	22	23	15	20	21
Viscosity, mPa.s *	1850	16400	21600	2400	20800	28000

**mPa.s = cP (mPa.s: SI-standard / cP: Industrial denotation*



Property: EVAPORATIVE LOSS
Oil Type: ODA CRUDE OIL 13C
Description:
Data Source: Sintef Ocean (2019), Weathering data used

OWModel® 11.0

Surface release
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

2.0
Pred. date: Sep. 04, 2019

Figure 5-2: Evaporative loss of Oda crude oil predicted at sea temperatures of 5 and 15 °C

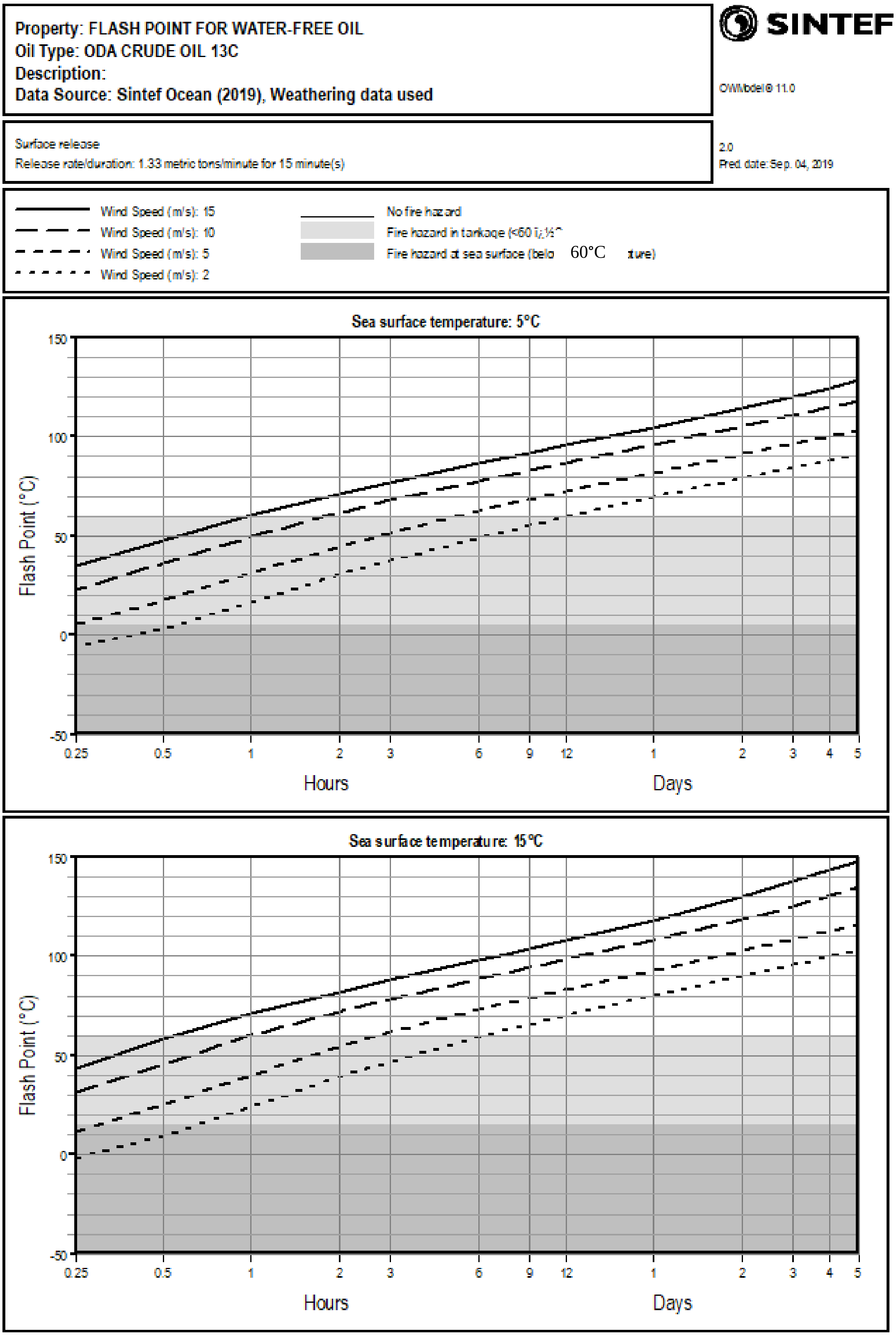


Figure 5-3: Flash point of Oda crude oil predicted at sea temperatures of 5 and 15 °C

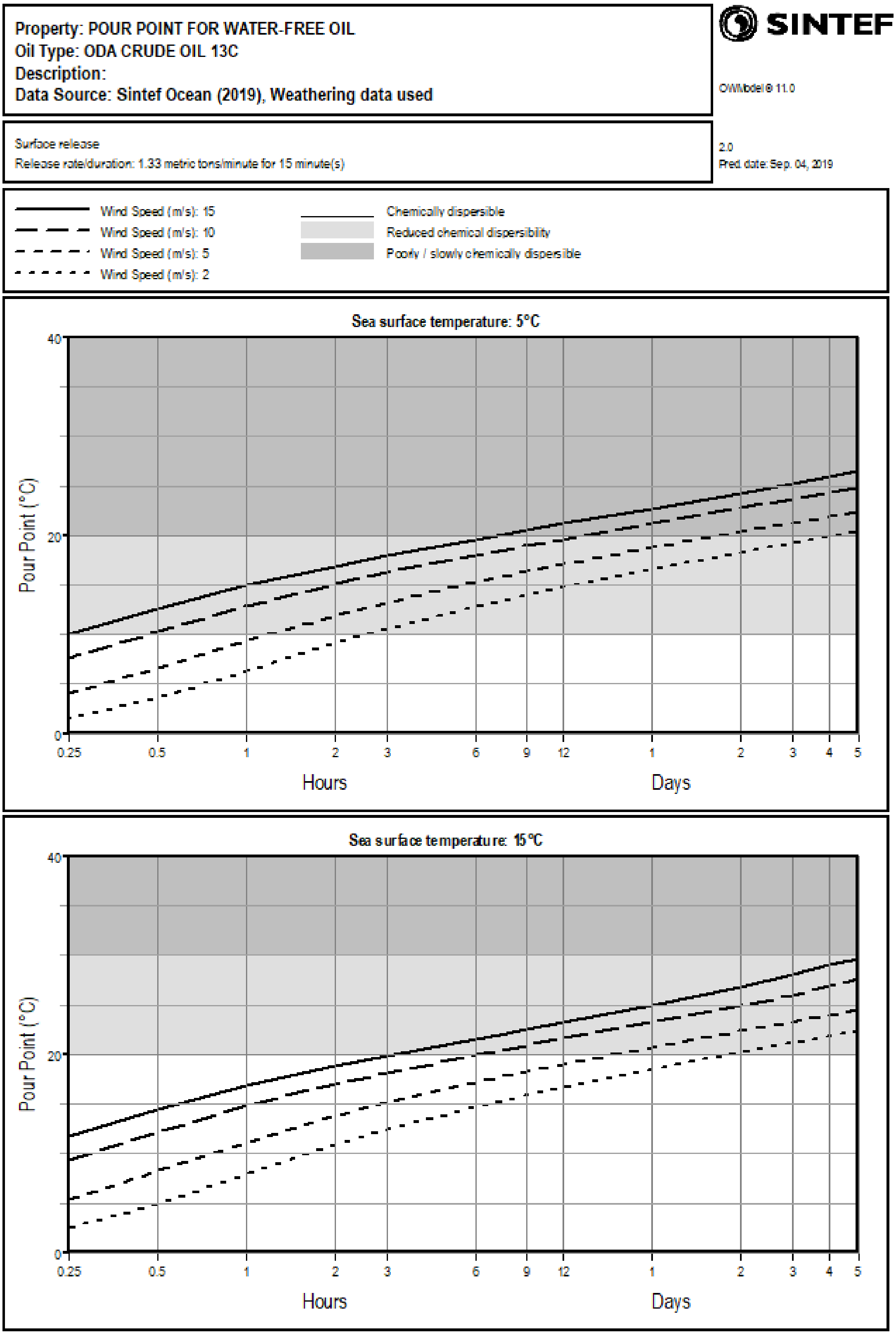


Figure 5-4: Pour point of Oda crude oil predicted at sea temperatures of 5 and 15 °C

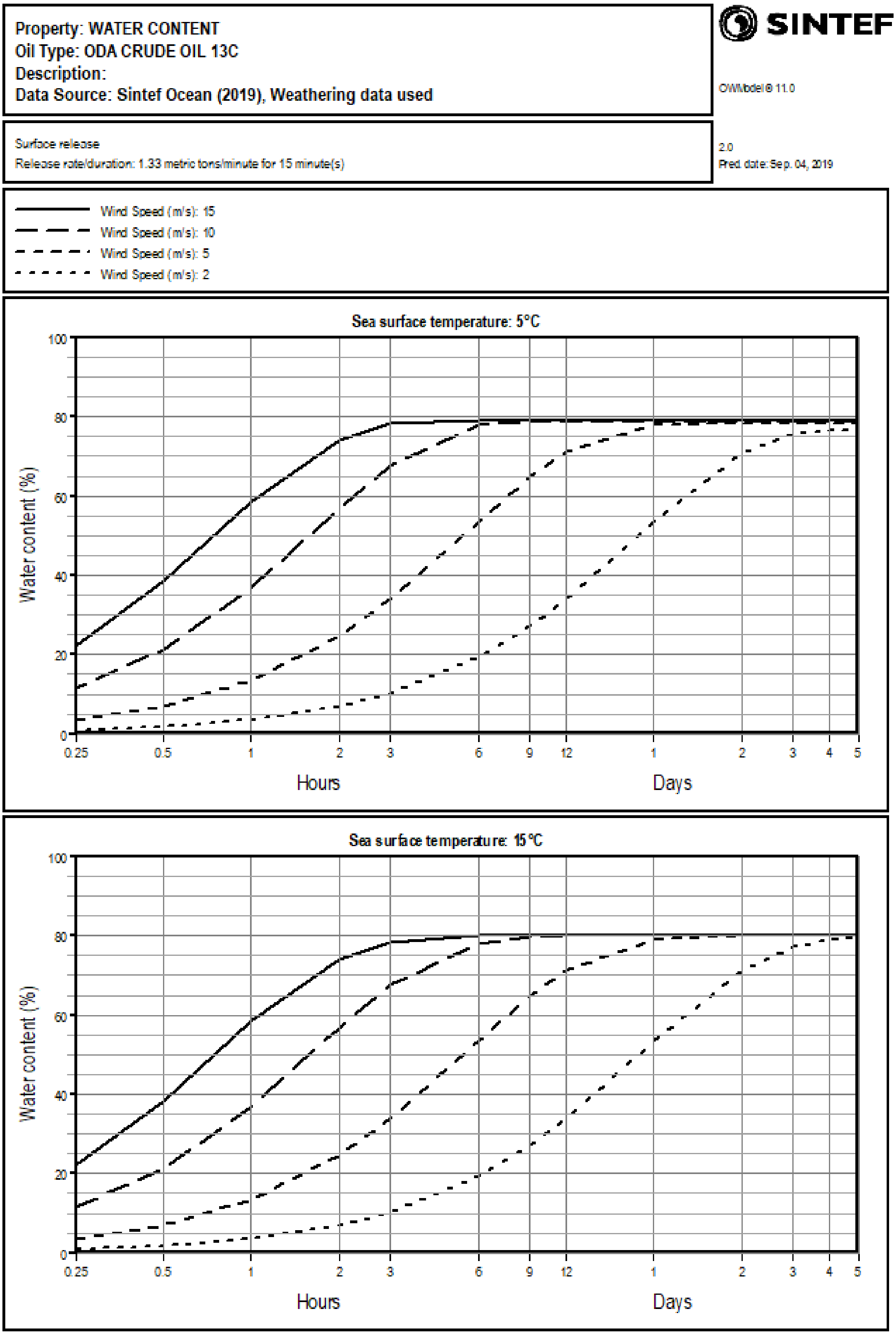


Figure 5-5: Water content of Oda crude oil predicted at sea temperatures of 5 and 15 °C

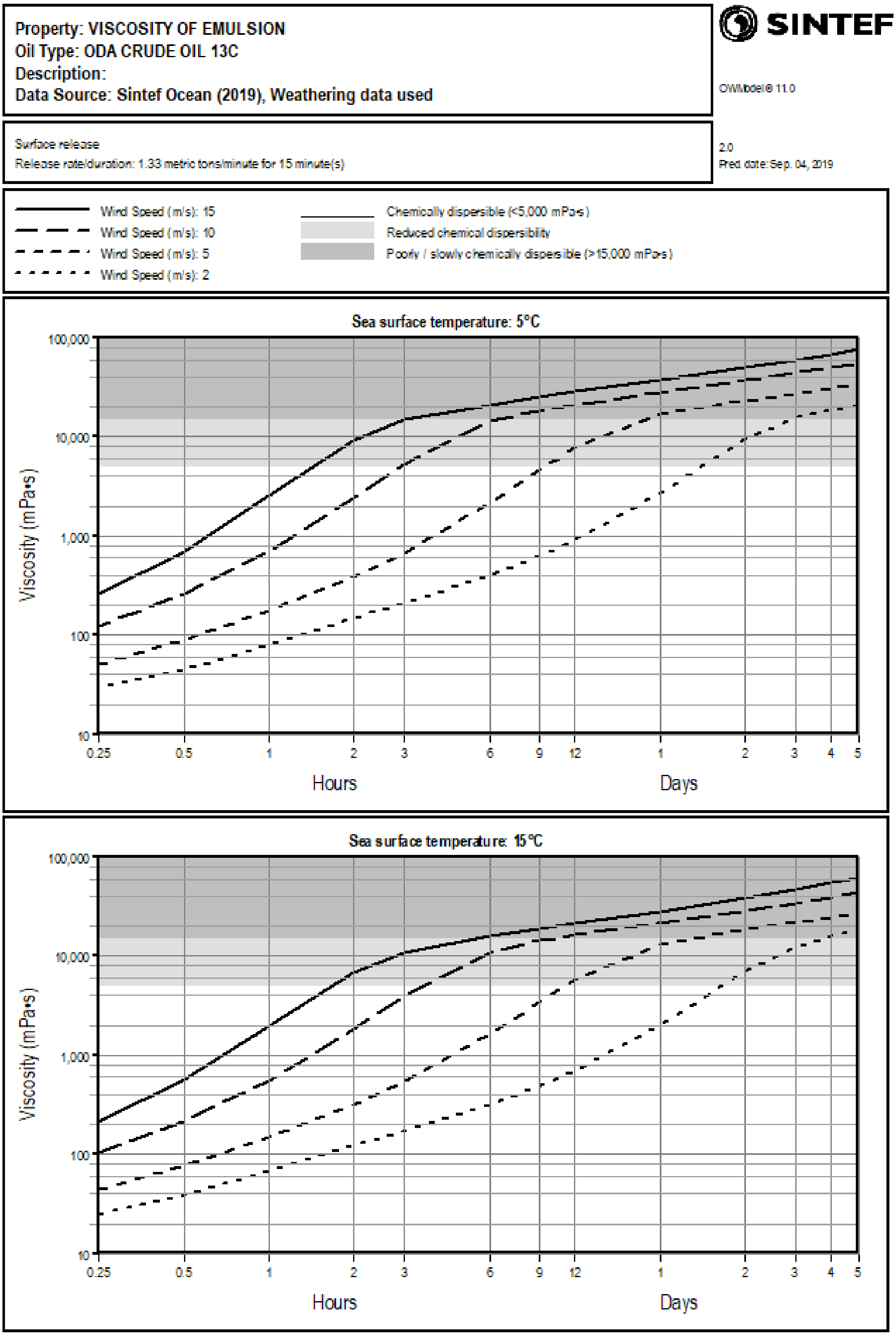


Figure 5-6: Viscosities of Oda crude oil emulsions predicted at sea temperatures of 5 and °C. Predictions are based on measurements of emulsions performed at a shear rate of 10 s^{-1}

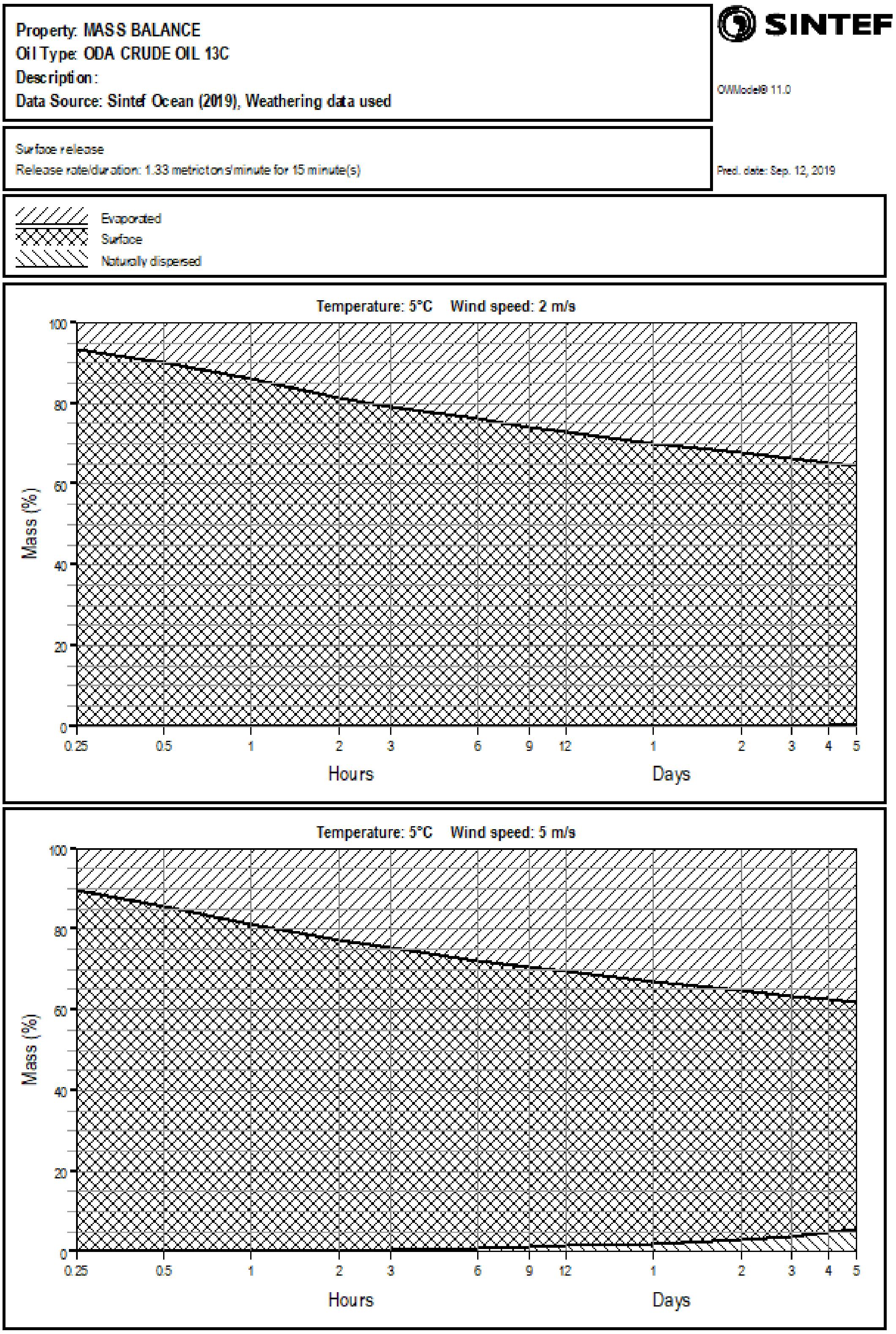


Figure 5-7: Predicted mass balance for Oda crude oil at 5 °C and wind speeds of 2 and 5 m/s

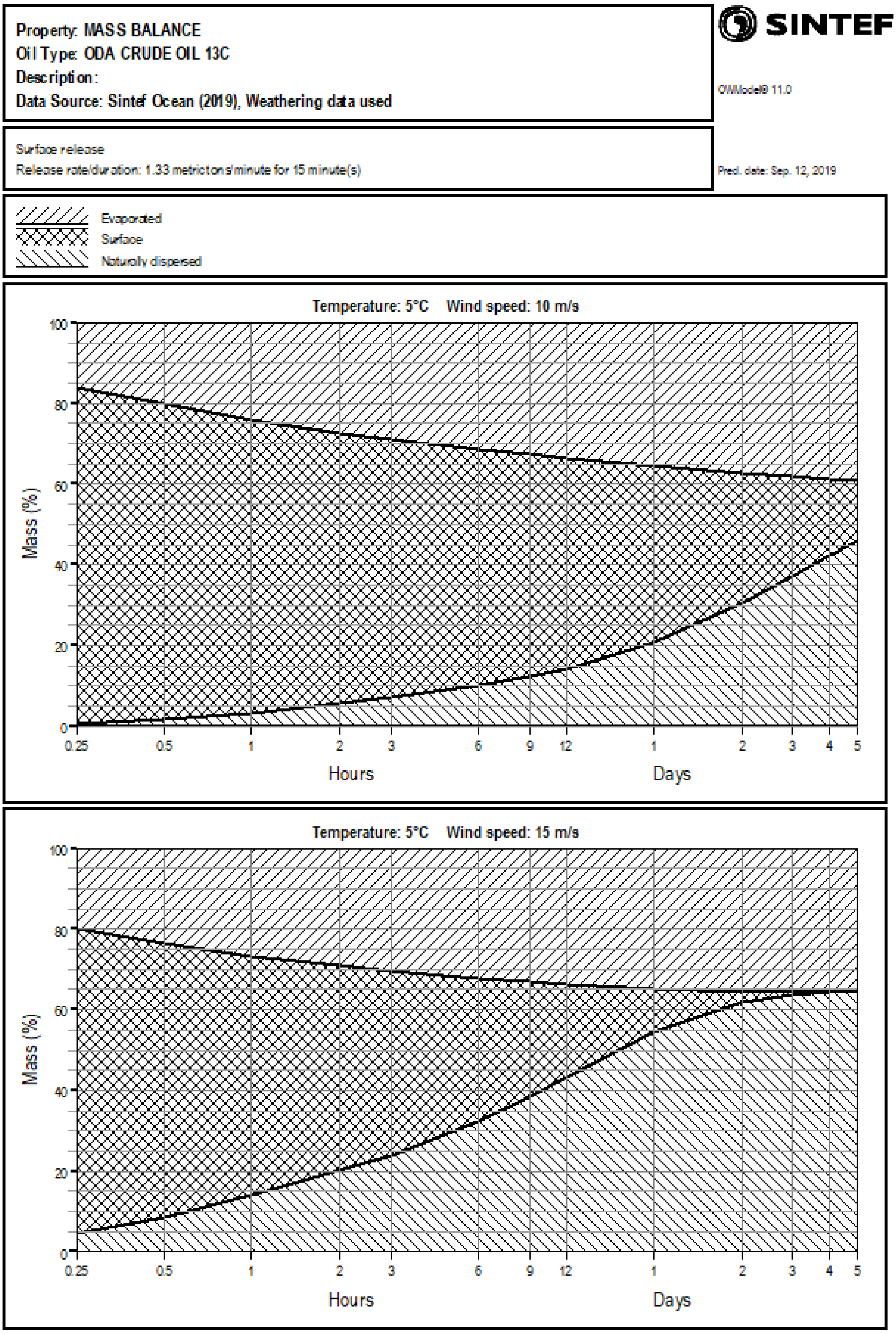
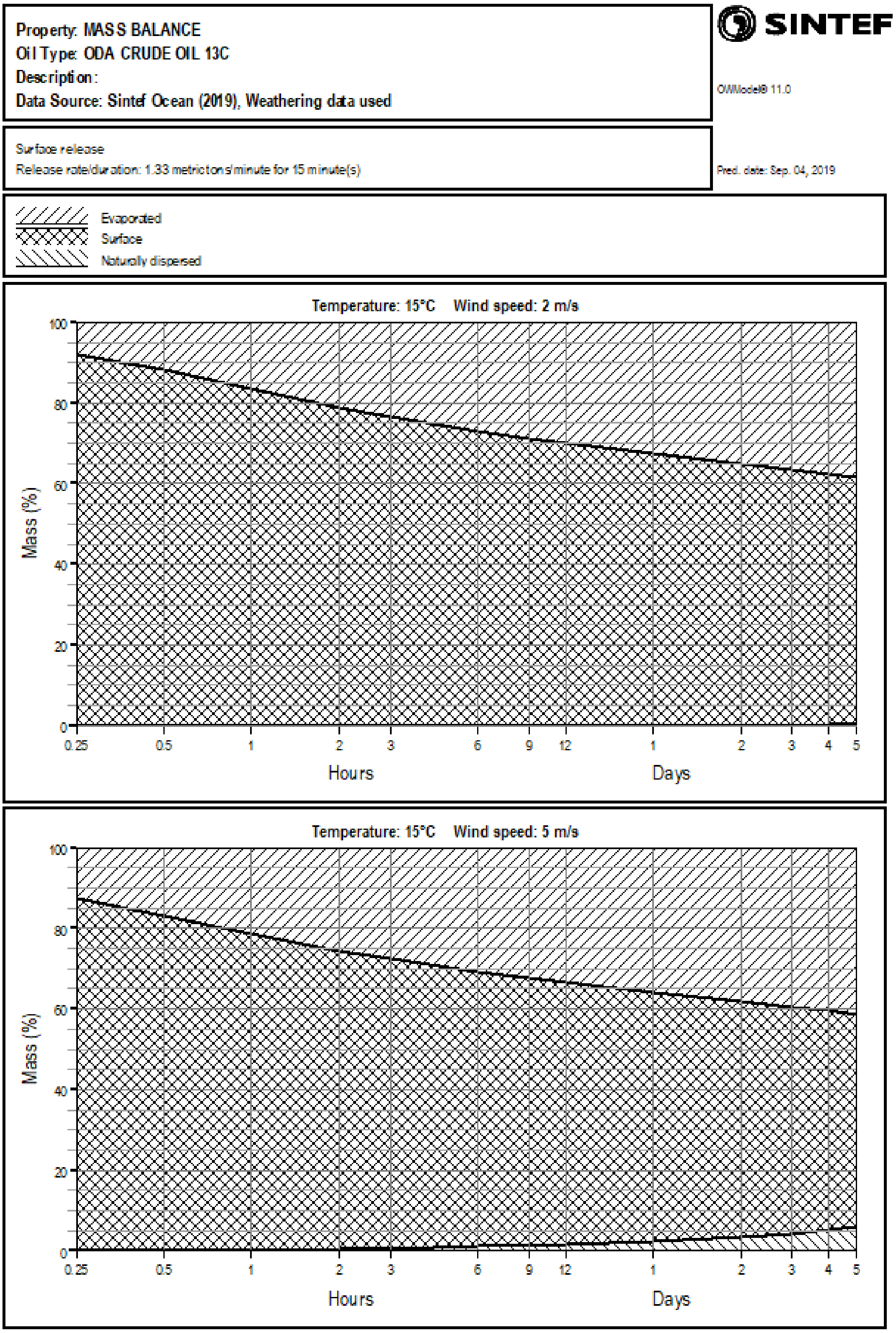


Figure 5-8: Predicted mass balance for Oda crude oil at 5 °C and wind speeds of 2 and 5 m/s



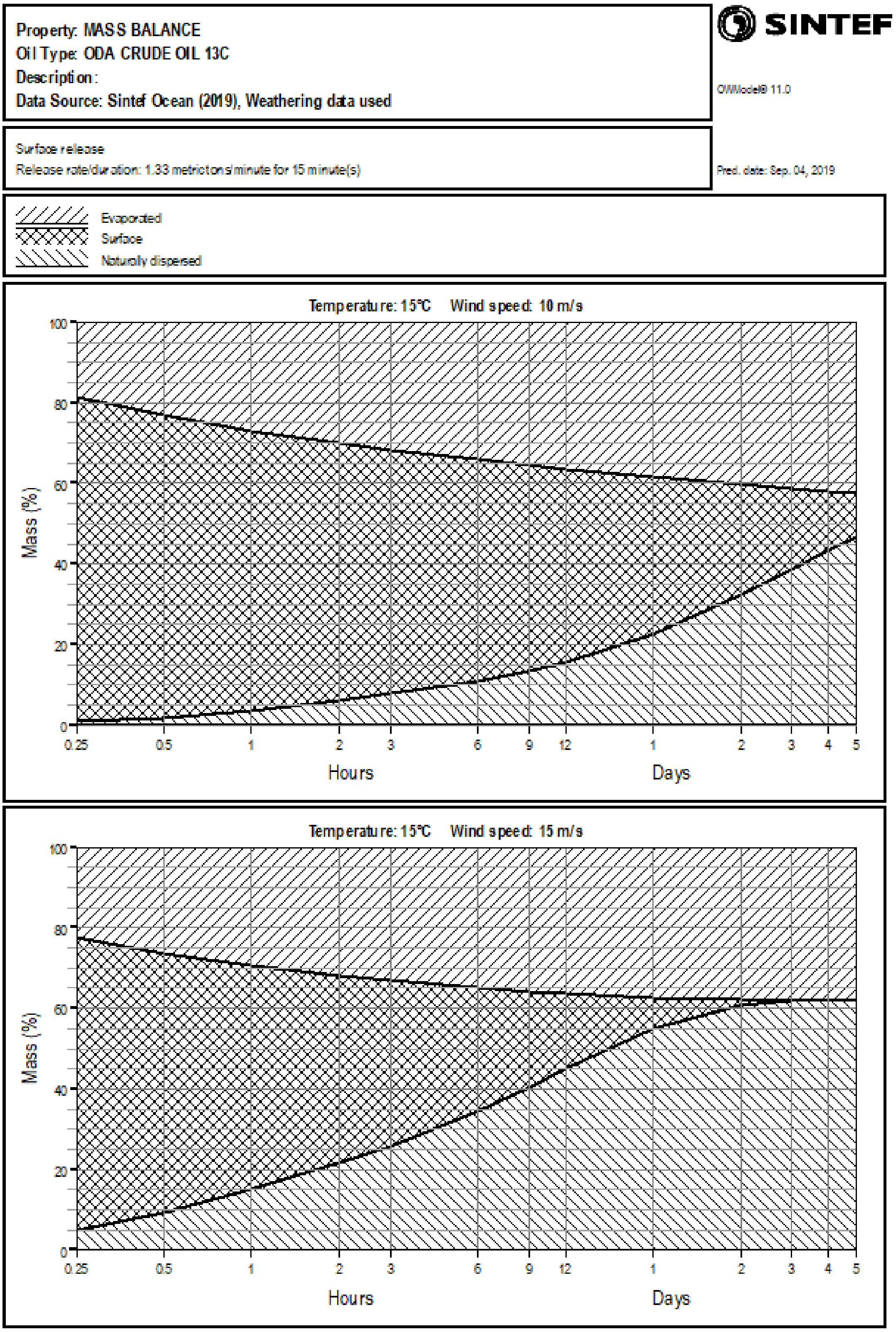
Property: MASS BALANCE
Oil Type: ODA CRUDE OIL 13C
Description:
Data Source: Sintef Ocean (2019), Weathering data used

Surface release
Release rate/duration: 1.33 metrictons/minute for 15 minute(s)

OWModel® 11.0

Pred. date: Sep. 04, 2019

Figure 5-9: Predicted mass balance for Oda crude oil at 15 °C and wind speeds of 2 and 5 m/s



Property: MASS BALANCE
Oil Type: ODA CRUDE OIL 13C
Description:
Data Source: Sintef Ocean (2019), Weathering data used

Surface release
Release rate/duration: 1.33 metrictons/minute for 15 minute(s)

Figure 5-10: Predicted mass balance for Oda crude oil at 15 °C and wind speeds of 10 and 15 m/s

6 Comparison of Oda OWM predictions with other crude oils

Weathering predictions of Oda crude oil were compared with predictions of the paraffinic crude oils of Ula, Statfjord and Vale. The presented comparisons given in the figures below are based on predictions at a sea temperature of 15 °C and a wind speed of 10 m/s.

6.1 Evaporative loss

Evaporation is one of the natural process that promotes removing spilled oil from the sea surface. Carcará shows similar evaporative loss compared with Statfjord (Figure 6-1). Ula has a slightly lower evaporative loss, whilst the light crude oil of Vale has much higher evaporation due to higher fraction of the lightest hydrocarbons compared with the other crude oils.

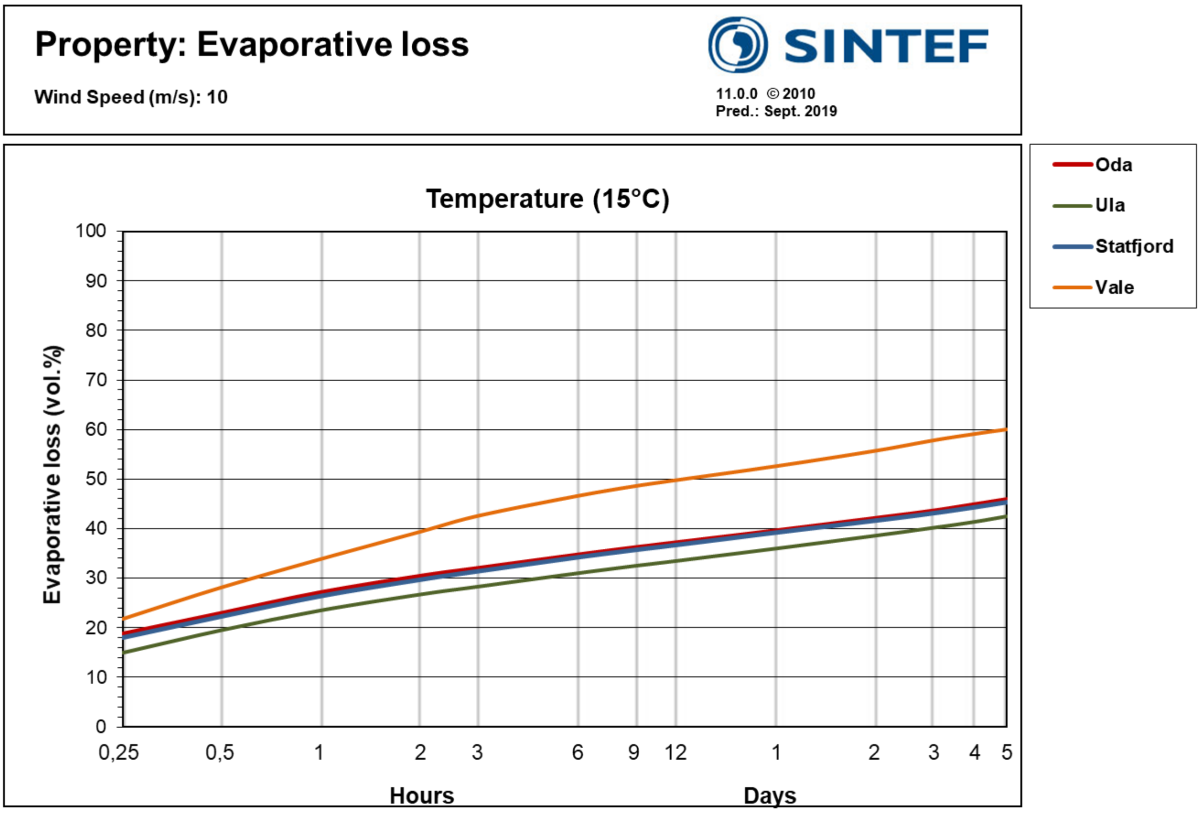


Figure 6-1: Predicted evaporative loss at 15 °C and 10 m/s for Oda compared with other crude oils

6.2 Flash point

In general, oils spilled on the sea surface will be cooled to the ambient water temperature within a short period. The probability of fire hazard will be high if the flash point of the oil is below the sea temperature. Moreover, fire hazard is dependent upon the concentration of volatile components in the oil, and the potential for fire is usually surpassed within the first few minutes of a spill due to the rapid evaporation of those components.

The flash points of Oda compared with Ula and Vale is shown in Figure 6-2. The crude oils exhibts great similarities in the flash points during 5 days of weatheirng, and indicate no fire or explosion hazard 15 minutes after release at 10 m/s wind speed for this scenario, where flash points are above the sea temperature of 15 °C.

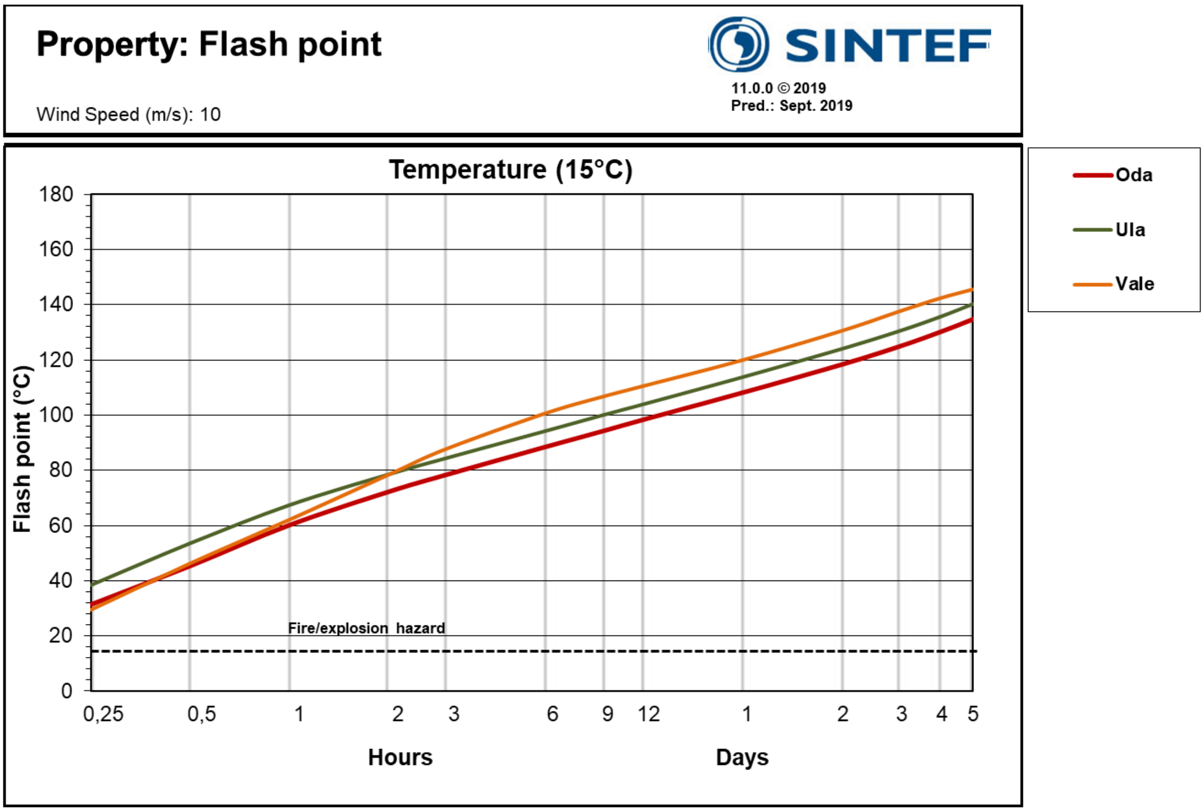


Figure 6-2: Predicted flash point at 15 °C and 10 m/s for Oda compared with other crude oils

6.3 Pour point

Pour point depends on the oil's wax content and the amounts of light components that can keep the wax components dissolved in the oil phase. In addition, contents of asphaltenes prevent or reduce precipitation and lattice formation and hence lowers the pour point. High pour points may prevent the dispersant to soak into the oil slick and influence the dispersant effectiveness and may also reduce the potential for flowability towards weir skimmers.

In cases when high viscosities are not a limiting factor, high pour points may cause solidification (elastic properties) when oil is spilled on the sea surface. High pour point may therefore imply solidification on the sea surface immediately after the release, and this is pronounced when the pour point is typically 5-15 °C above sea temperature and in cold temperatures.

The predicted pour points of Oda in comparison with Ula, Statfjord and Vale are given in Figure 6-3. Oda, Ula and Statfjord show very similar points of their residues during 5 days of weathering, whilst Vale has the highest pour points.

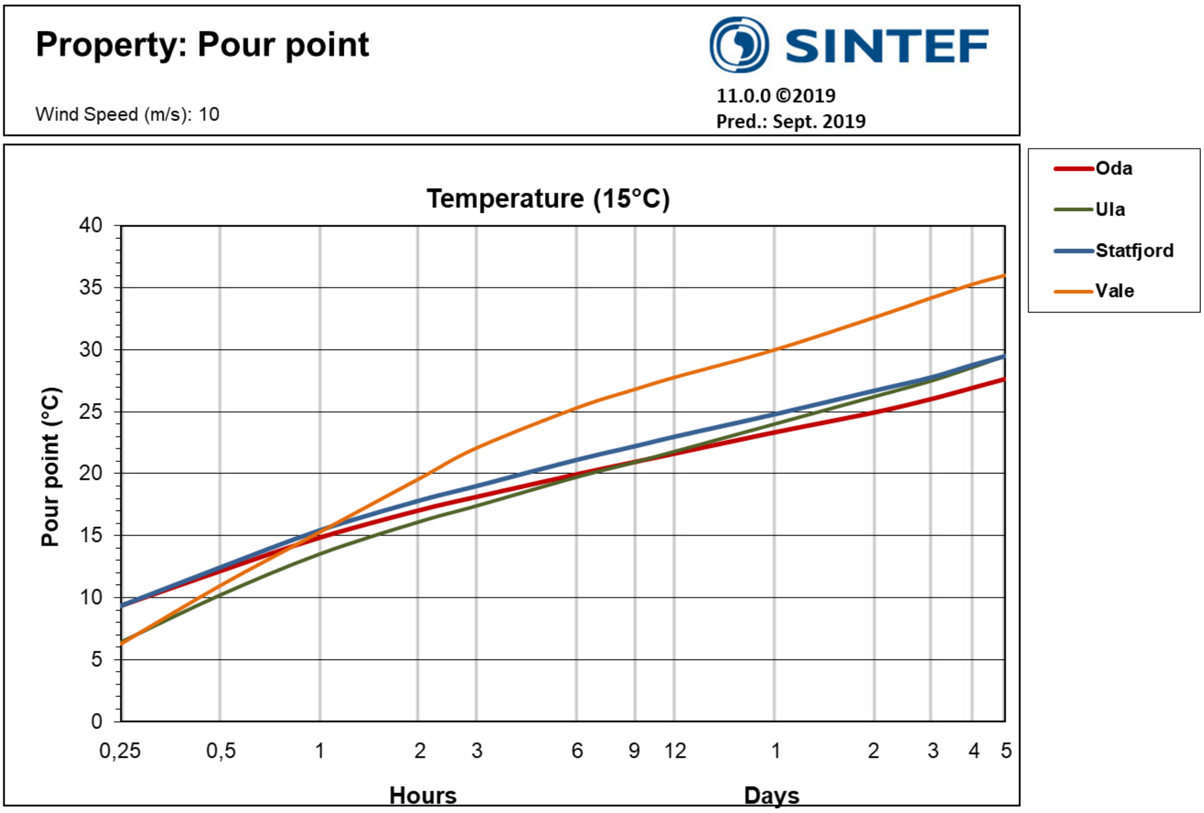


Figure 6-3: Predicted pour point at 15 °C and 10 m/s for Oda compared with other crude oils

6.4 Water content

The water uptake and content for Oda in comparison with Ula, Statfjord and Vale is shown in Figure 6-4. The predictions show that Oda and Vale follow quite similar predictions and reach a maximum water uptake of 75-80 vol. %. Ula shows the most rapid emulsification rate among these crude oils and reaches a water uptake of 80 vol.% within short time (1 hour). Statfjord emulsifies slower with a slightly lower maximum water uptake of 70 vol. %.

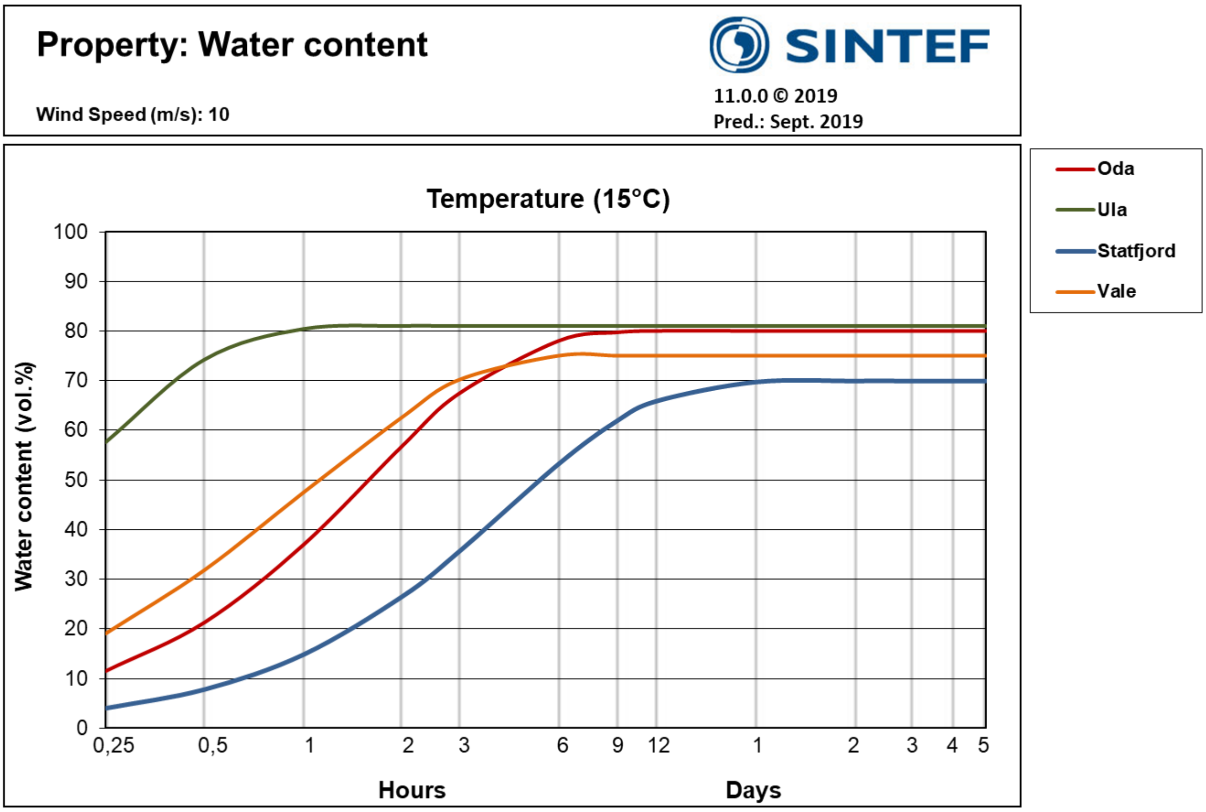


Figure 6-4: Predicted water content at 15 °C and 10 m/s for Oda compared with other crude oils

6.5 Emulsion viscosity

Figure 6-5 shows the predicted emulsion viscosities of Oda in comparison with Ula, Statfjord and Vale. Oda has low emulsion viscosities of 100-1000 mPa.s during the first hours and increases significantly from 6 hours (10 000 mPa.s), and then increases even more with time to around 44 000 mPa.s after 5 days of weathering. Ula and Statfjord d have slightly higher initial emulsion viscosity compared with Oda and reach viscosities to around 20-40 000 mPa.s. Vale is a light crude oil that forms more loose emulsions and ends up with the lowest emulsion viscosity around 5000 mPa.s.

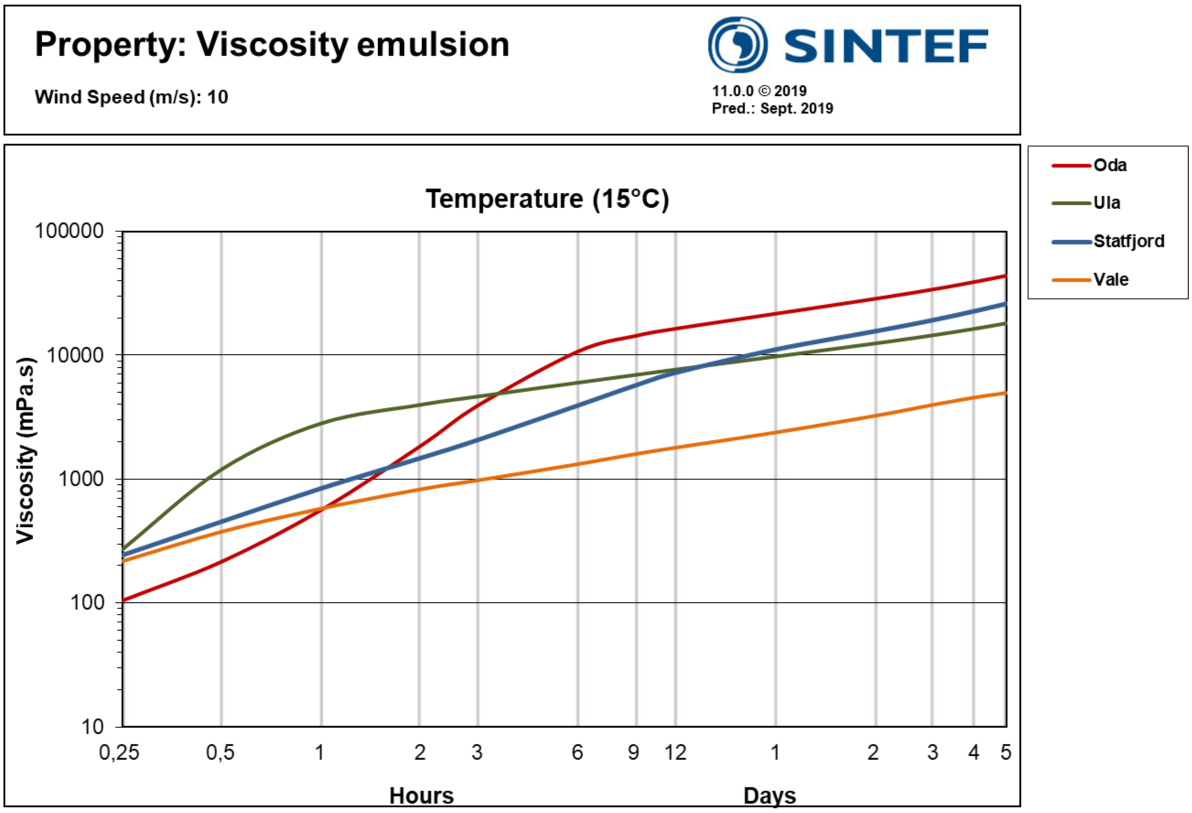
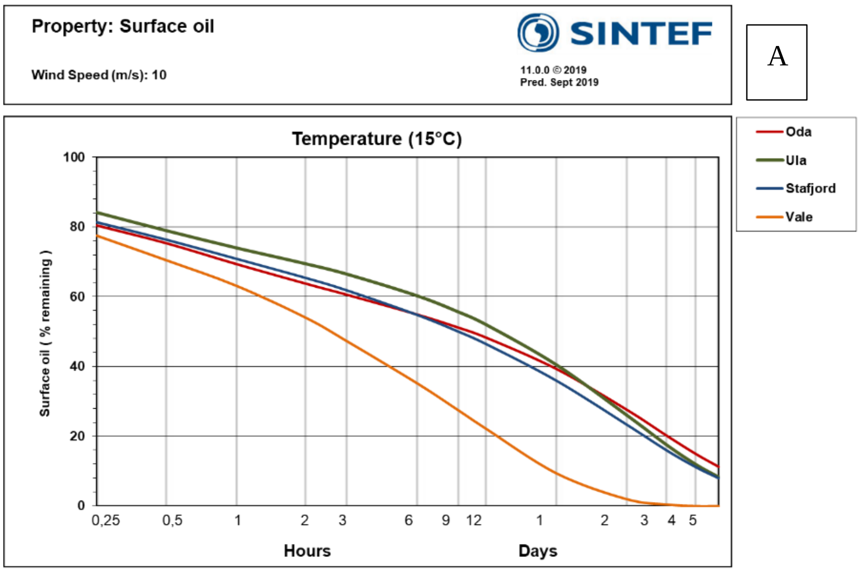


Figure 6-5: Predicted emulsion viscosity at 15 °C and 10 m/s for Oda compared with other crude oils

6.6 Surface oil and surface emulsion

Due to evaporative loss and natural dispersion/entrainment, the amount oil (assumed no emulsification) on the sea surface will gradually be reduced. Figure 6-6 A illustrates the predicted mass balance of Oda remaining surface oil as a function of weathering compared to Ula, Statfjord and Vale. The crude oils except from Vale exhibit very similar predictions of the surface oil showing approximately 8-10 % of remaining oil after 5 days of weathering. Vale light crude oil has no predicted remaining surface oil after 3 days.

Predicted volumes of surface oil emulsion (relative to the amount of oil released) are shown in Figure 6-6 B. The total surface reduces with time due to evaporation and natural dispersion in the initial stages of weathering. However, the volume of water mixed into the oil increases the total volume of the surface emulsion considerably. Increasing surface emulsions should be considered in a spill operation, for example, when evaluating skimmer capacity based on the total volume of emulsified oil. In the example below (10 m/s wind speed), Oda has increased its total volume about 5 times after 6 hours weathering relative to the amount of oil released.



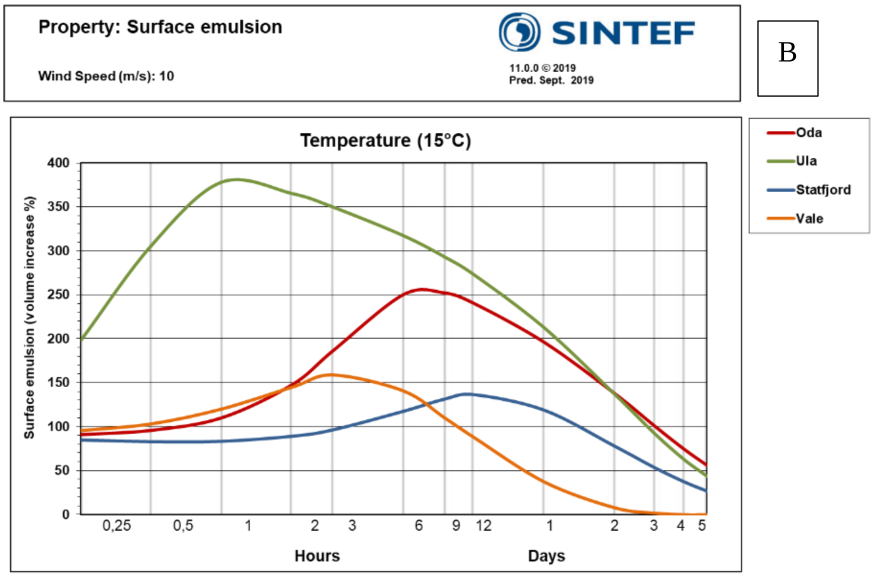


Figure 6-6:

A: Predicted remaining surface oil (no emulsification) at 15 °C and 10 m/s for Oda compared with other oils

B: Predicted surface emulsion (emulsification) at 15 °C and 10 m/s for Oda compared with other oils

7 Weathering properties of Oda crude oil when spilled at sea

The relative concentration of heavy oil components within a spilled oil increases due to weathering, and the physical and chemical properties of the oil will change over time. Knowledge about how the oil's properties change during weathering is therefore important in the management of oil spill response.

7.1 Oil properties

Oda is a light to medium density crude oil (0.820 g/mL), with medium content of wax (5.6 wt. %), and a relatively high content of asphaltene (0.44 wt. %), compared with other Norwegian crude oils. The fresh oil exhibits low viscosity of 10 mPa.s at shear rate 100s^{-1} (13 °C). Oda is categorized as a paraffinic crude oil, and the chromatographic characterization shows the hydrocarbon profile as systematic peaks of *n*-alkanes (paraffins). The fresh crude oil has a low pour point of -3 °C that increases from +12 to +24 °C for the residues after evaporation of the lightest compounds. Oda forms stable water-in-oil (w/o) emulsions that may reach a maximum water uptake of about 80 vol. % and has the potential to produce high emulsion viscosities by time.

7.2 Flash point – Fire/explosion hazard

Flash point refers to the lowest temperature at which a fuel or oil can vaporize to form an ignitable mixture in the air. In case of an oil spill on the sea surface, the (heated) oil rapidly will be cooled to the ambient seawater temperature within a short period of time. The fire/explosion hazard will be at its greatest if the flash point of the spilled oil is below the seawater temperature. The prediction of flash point (Figure 7-1) are based on the evaporation of volatiles when free gas associated with the oil release is not the case (e.g. stabilized oil at 1 atm.). In such cases, the flash point is the most important parameter when evaluating potential for fire/explosion hazard.

The predictions show that the flash points for Oda are above the sea temperature within a few minutes at 5 and 15 °C for wind speeds 5-15 m/s. At calmer weather conditions (2 m/s wind speed) care should be taken during the first hour (Figure 7-1).

Moreover, some vessels/storage tanks engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C, e.g. towing vessels, smaller cargo or other vessels available in the emergency. This means that fuels or oils with the flash point less than 60 °C, are for those type of vessels not permitted as cargo. However, this limit is not considered as relevant for oil recovery vessels with A-class certification for transport of liquids (Class I/II, flashpoints < 60 °C), according to NFPA classification of Flammable and Combustible Liquids (http://www.thetankshop.ca). At low wind speed (2 m/s) this limit is reached within 6 hours at 15 °C and 12 hours at 5 °C, and shorter time for the higher wind speeds as shown in Figure 7-1.

Acute oil spills from e.g. a subsea release may lead to high volumes of associated free gas that release into the atmosphere when the gas plume reaches the sea surface. In such cases, a safety zone must be established early on and downwind. A safety zone (distance) could for instance be 1-hour drifting time of the slick (from the source), however the distance is highly depending on the concentration of the free gas (mainly methane) released. Measurement of free gas concentrations is therefore important to minimize the potential risk of human exposure and fire/explosion hazard at the spill site. The following precautions should therefore be taken:

- Prior to the initiation of spill response operations, an evaluation of the potential risk of fire/explosion hazard and human exposure must always be conducted at the site
- Explosimeters should be utilized continuously and one should be aware of the possibility for varying release rates if free gas is involved

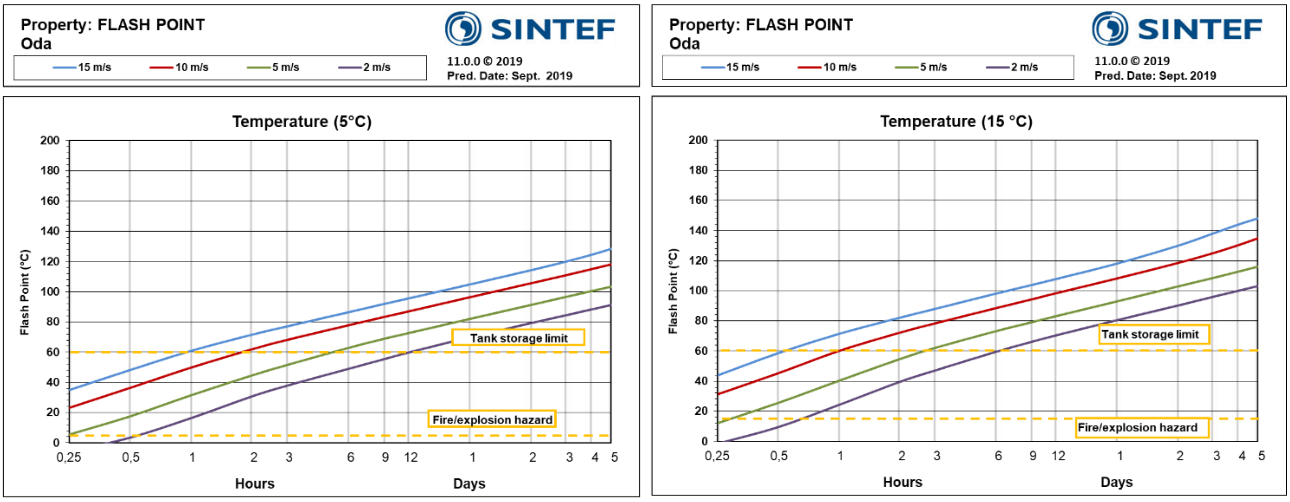


Figure 7-1: A (Above): Predicted flash points at different wind speeds for Oda crude oil at 15 °C
B (Below): Predicted flash points at different wind speeds for Oda crude oil at 5 °C

7.3 Natural dispersion and evaporation

The lifetime of an oil spill at sea depends on the oil's composition, the release conditions (e.g. on the surface, underwater) and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the surface. Figure 7-2 shows the remaining surface oil over time for different wind speeds and temperatures. At high wind speed of 15 m/s, no oil remained on the sea surface after 3 days of weathering, but at calmer weather conditions 2-5 m/s wind speeds (no-breaking waves), the remaining surface oil is in the range of 50-65 %. The variation of remaining surface oil after a release is strongly dependent on the wind speeds and typically oils are more persistent on the sea surface with lower wind.

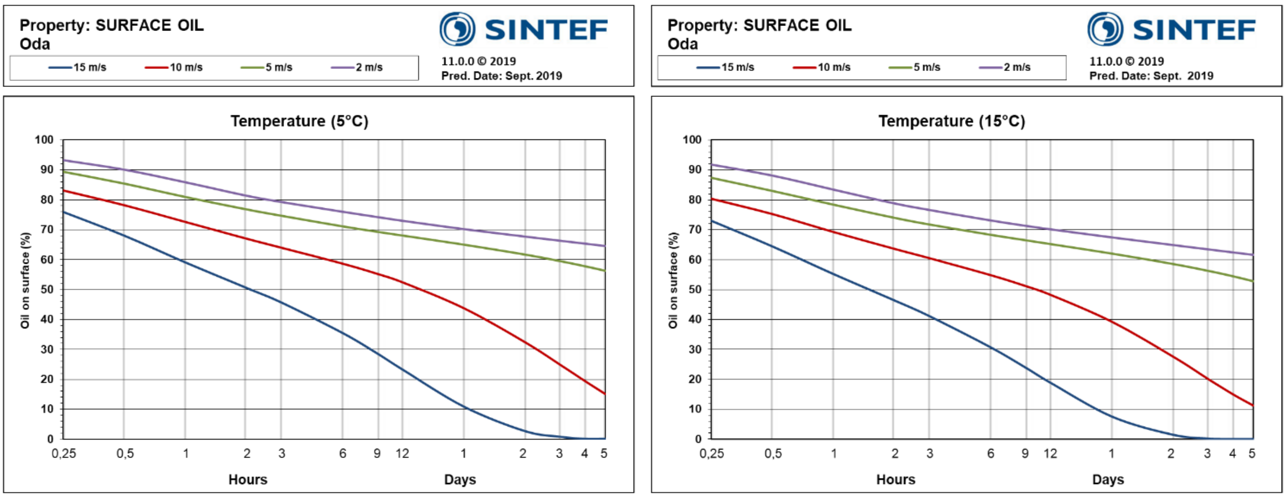


Figure 7-2: Remaining surface oil for Oda crude oil at 5 and 15 °C

7.4 Emulsion formation

The total amount of oil on the sea surface is normally reduced due to evaporation and natural dispersion or entrainment in the early stage of weathering. However, as emulsions are formed by seawater mixed into the oil phase, the total volume of the spilled oil at sea subsequently increases. Figure 7-3 illustrates this increase of volume relative to the volume of the remaining surface oil at different wind speeds at 5 and 15 °C. The volume of Oda has the potential to increase 5 times due to the high-water uptake.

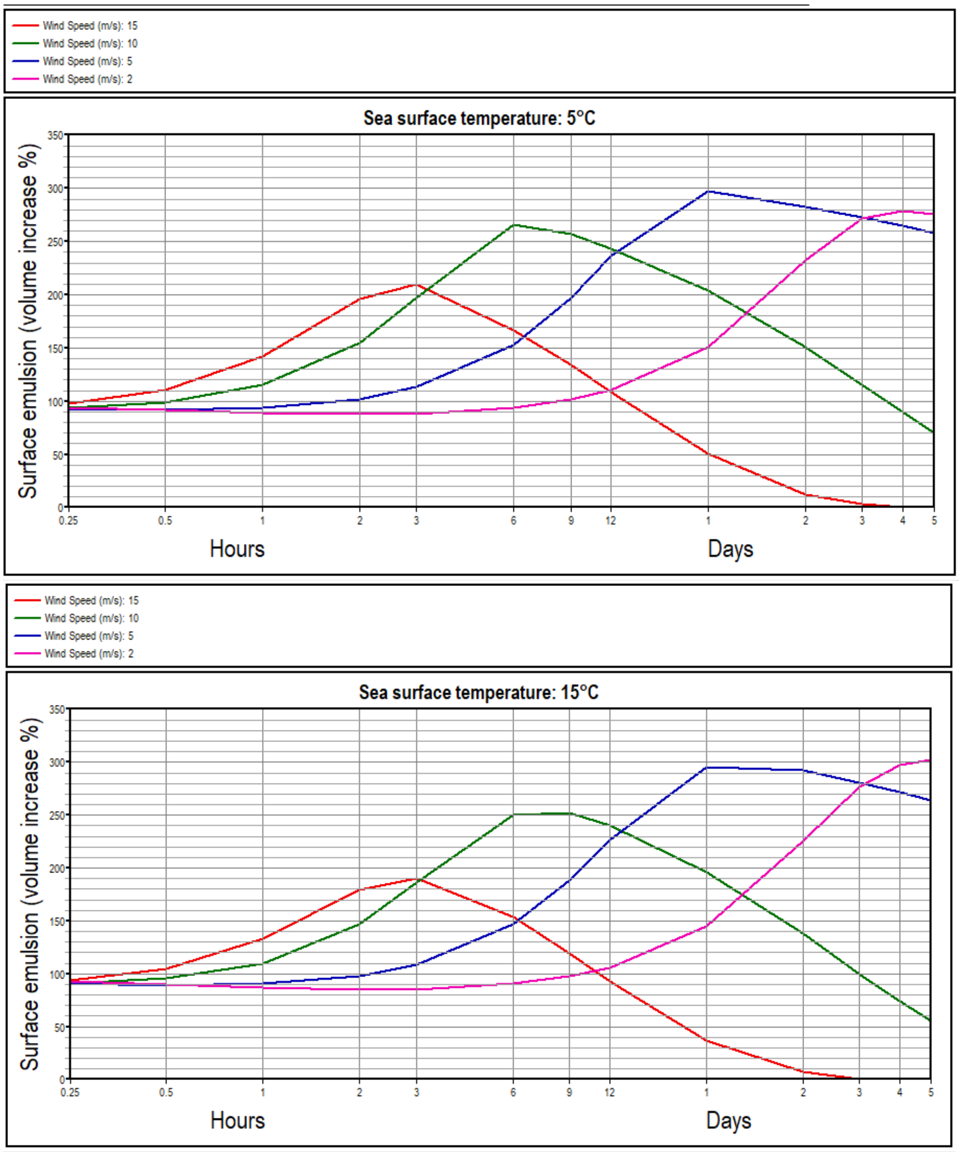


Figure 7-3: Difference in the total volume of Oda crude oil due to emulsification at different wind speeds (2, 5, 10 and 15 m/s) . The decrease in total volume is due to evaporation and natural dispersion is shown in Figure 7-2.

7.5 Effect of adding emulsion breaker

Emulsion breaker can be used during an oil spill operation to enhance the release of water from an emulsion. Emulsion breakers are normally injected at the skimmer head prior the entering to storage tank and are not added directly on the oil spill at open sea.

Figure 7-4 illustrates the relative volumetric composition of emulsion and free water for the 200 and 250°C+ residue, reflecting approx. 0.5-1 day and 0.5-1-week weathering with and without addition of emulsion breaker (Alcopol O 60 %; 500 and 2000 ppm by weight). The effectiveness of the emulsion breaker was found to be most efficient with increasing concentration relative to the oil. The concentration of 2000 ppm (emulsion breaker) was found to be considerably more efficient than a concentration of 500 ppm. The use of emulsion breaker could be considered for Oda to increase the storage capacity when recovered.

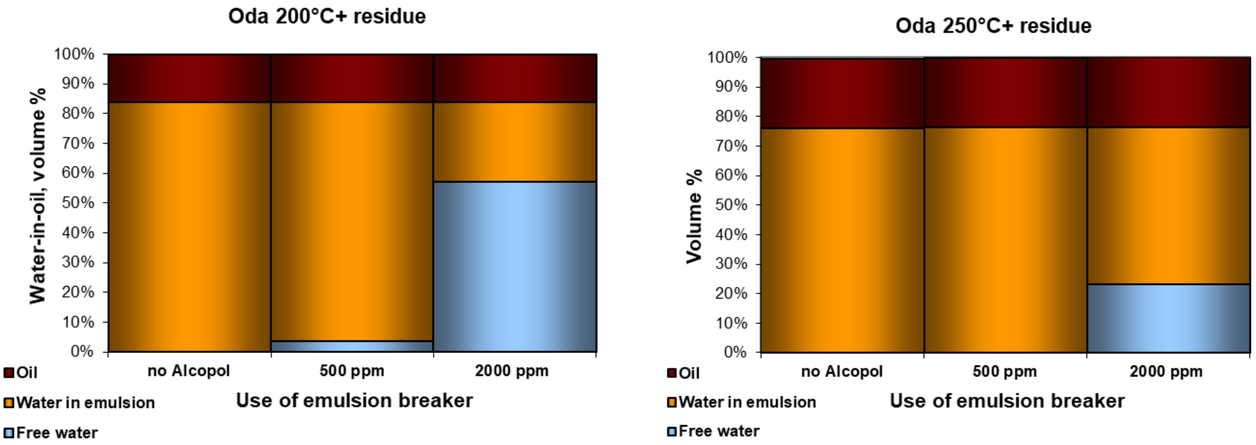


Figure 7-4: Relative volumetric composition of emulsion and free-water after approximately 1 day (left) and 1 week (right) of weathering. The x-axis shows the dosage of emulsion breaker Alcopol O60% (500 ppm and 2000 ppm by weight) and no emulsion breaker

7.6 Emulsion film thickness

Mechanical recovery and requires normal oil film thicknesses > 0.1-0.2 mm and effective dispersant application > 0.05 0.1 mm. Lower film thicknesses are likely to disperse naturally. The emulsion film thicknesses of Oda are illustrated in Figure 7-5. The increase in film thickness is due to emulsification.

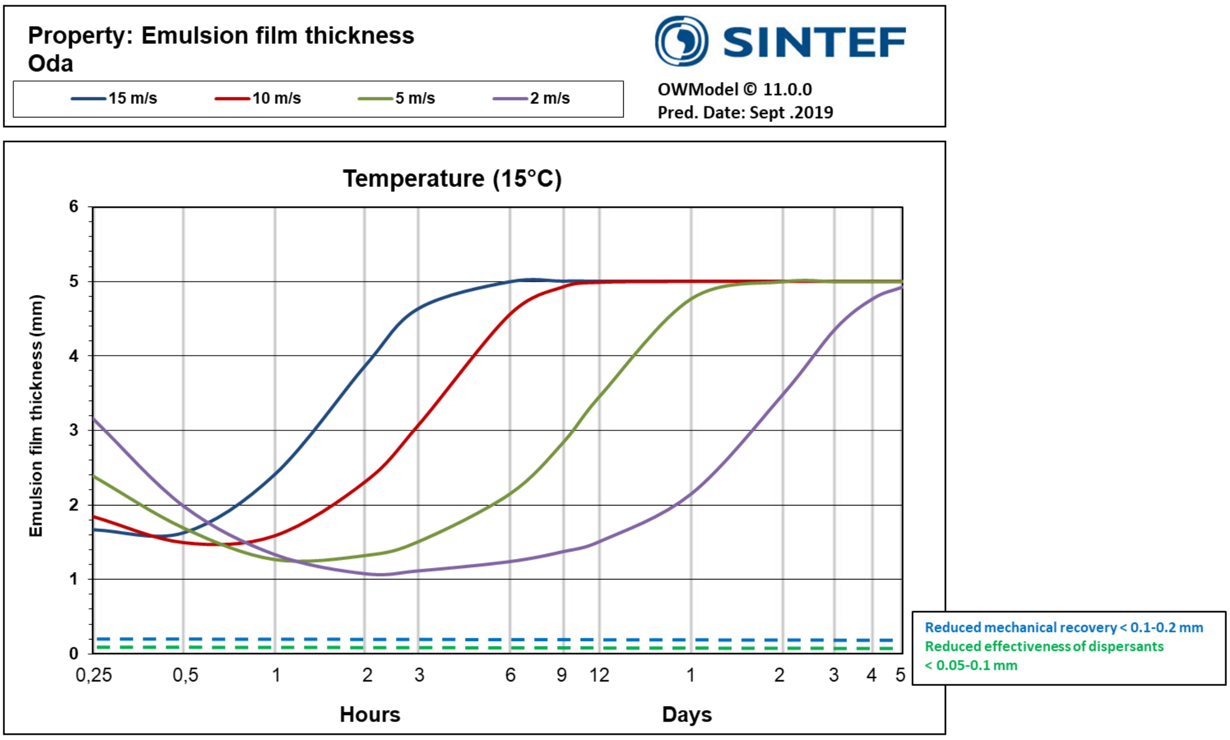


Figure 7-5: Predicted emulsion film thickness of Oda after 5 days of weathering from a surface release

7.7 Mechanical recovery by boom and skimmer

Experiences from Norwegian field trials with oil spill booms have demonstrated that the effectiveness of various mechanical clean-up operations may be reduced due to the high degree of leakage of the confined oil or emulsion from the oil spill boom.

Boom leakage is particularly pronounced if the viscosity of the oil or the w/o-emulsion is lower than 1000 mPa.s (Nordvik et al., 1992). The lower viscosity limit for an optimal mechanical clean-up operation has therefore been estimated to 1000 mPa.s (Figure 7-6). However, other factors like the operational speed of recovery vessel and current weather conditions will also influence on the risk of boom leakage. Therefore, it may be possible to recover surface oil (emulsion) in calm weather conditions with viscosities lower than this limit (1000 mPa.s). Previously studies at SINTEF have shown that weir skimmers may reduce recovery rates (m^3/h) when skimming oils with viscosities in the range 15-20 000 mPa.s (Leirvik et al., 2001). Moreover, NOFO is operating with viscosity limits for skimmer efficiency as followed: primary use of weir skimmers (< 20 000 mPa.s), combination of weir and high-visc. skimmer (20-50 000 mPa.s), and primary high visc. skimmer (> 50 000 mPa.s).

The emulsion viscosities of Oda are shown in Figure 7-6 at 5 and 15 °C. For example, the emulsion viscosity exceeds 1000 mPa.s after 1-1.5 hours at 10 m/s wind speed but low viscosities may be stretched to 12 hours in calm wind conditions (2 m/s), at both temperatures. The time-window for use of weir skimmer (low visc. skimmer) at 10 m/s wind speed is estimated to 12 hours at 5°C and 1 day at 15 °C. However, a combination of systems (low - and high visc. skimmer) increase the time window to 2 to 3 days (10 m/s wind speed) at 5 and 15 °C, respectively. Overall, mechanical recovery has a wide window of opportunity both for traditional weir-skimmer head and even longer in combination with a high visc. skimmer system. The use of high-visc. skimmer only can be beneficial for emulsions above 50 000 mPa.s, but this system has reduced capacity compared to e.g. weir skimmers that needs to be considered for lower emulsion viscosities.

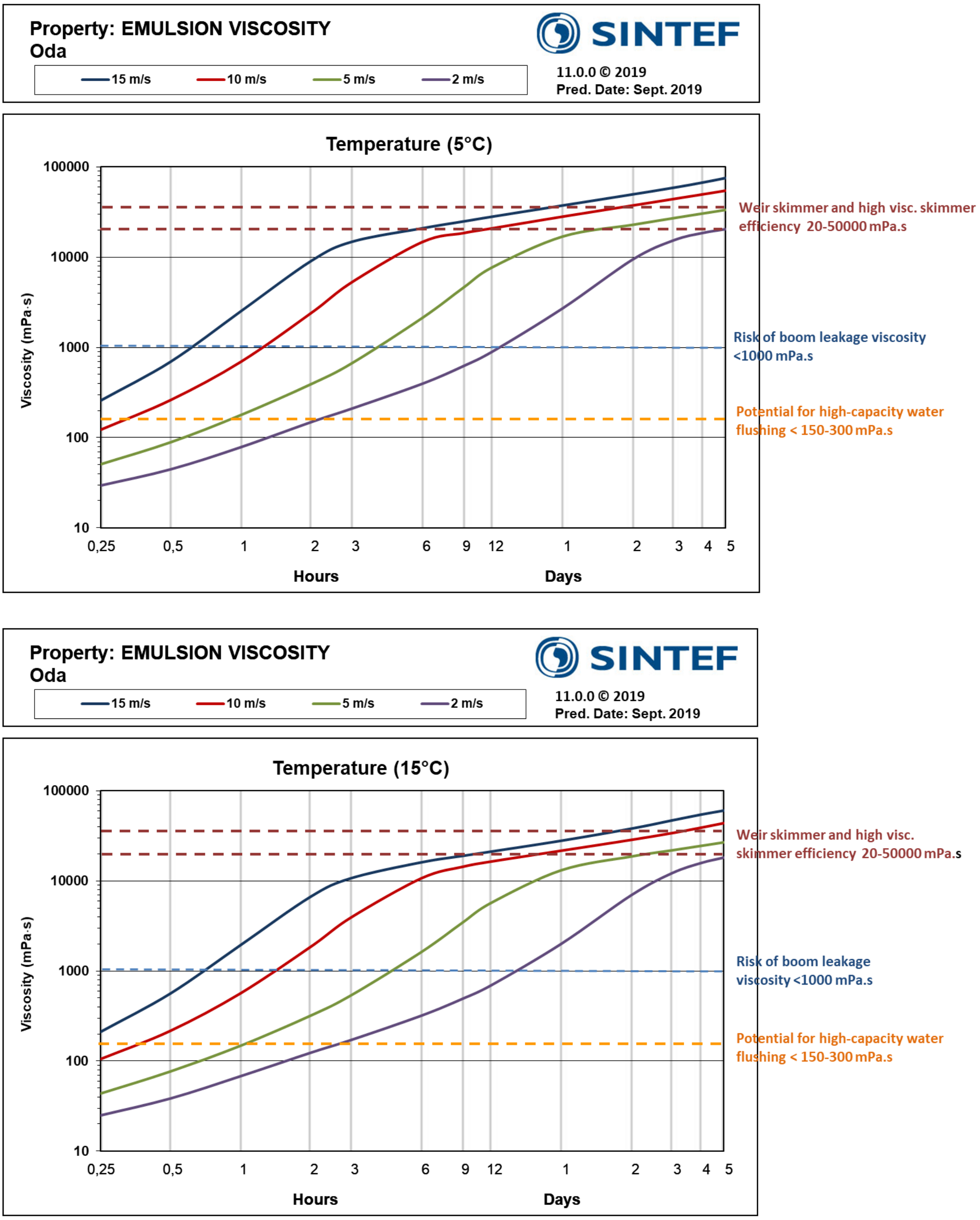


Figure 7-6: Expected time window for effective use of booms and skimmers (combination of weir and high visc.), and high-capacity water flushing (see chapter 5.9) as a function of emulsion viscosity of Oda, at 5 and 15 ºC

7.8 Mechanical dispersion by high-capacity water flushing

In general, mechanical dispersion by high-capacity water flushing could have a potential for viscosities < 150 - 300 mPa.s with initial film thickness up to 0.2 - 0.3 mm. In such cases, water flushing from high-capacity water flush boom or firefighting (Fi-Fi) systems may break up the film into smaller droplets e.g. in an early phase of a spill. However, for Oda crude oil mechanical dispersion by water flushing is not considered as a main strategy for the oil spill response due to the formation of high emulsion film thicknesses (Figure 7-5) by emulsification, even the oil has low emulsion viscosities in the very early stage after an oil spill, as shown in Figure 7-6. The rapidly emulsification of Oda is the limiting factor for this strategy in a surface oil spill.

7.9 Use of oil spill dispersant

Oda has a potential for use of oil spill dispersant from aircraft and /or vessel . The window of opportunity for use of the dispersant Dasic NS is presented in Figure 7-7. The viscosity limit for effective dispersant use was estimated to 5000 mPa.s in the laboratory (low energy IFP-test). The viscosity limit for when the emulsified oil is not considered to be dispersible was estimated to 15 000 mPa.s by use of the high energy MNS-test.

Figure 7-7 shows that the oil/emulsion of Oda has reduced dispersibility for viscosities between 5000-15 000 mPa.s after 9-12 hours at 5 m/s wind speed at 5 and 15 °C. In cases were the oil (emulsion) is expected to be reduced dispersible, an additional energy or use of a higher dispersant dosage and/or repeated dispersant application is recommended to possible enhance the dispersant efficiency. Providing additional energy through use of Fi-Fi systems, thrusters or MOB boats after dispersant application may increase the dispersion rate in calm weather conditions. Moreover, the oil /emulsion is poorly dispersible after 3-6 hours at 15 m/s but has a considerably longer time window in lower wind speeds, as shown in Figure 7-7.

In cases when high viscosity of the spilled oil is not a limiting factor, high pour point may cause solidification (elastic properties) at sea. Solidification typically arises at 5-15 °C above the sea temperature. High pour points could reduce the dispersant effectiveness, where the dispersant droplets have a reduced ability to diffuse into the oil and may appear as droplets on the surface of the solidified wax and be washed of by wave activity. In certain weather conditions, e.g. in very calm wind, the low emulsification rate may enhance formation of solidified lumps, particularly at 5 °C. In a spill situation, the use of a simplified dispersibility testing kit is therefore recommended to assess the potential for chemical dispersion.

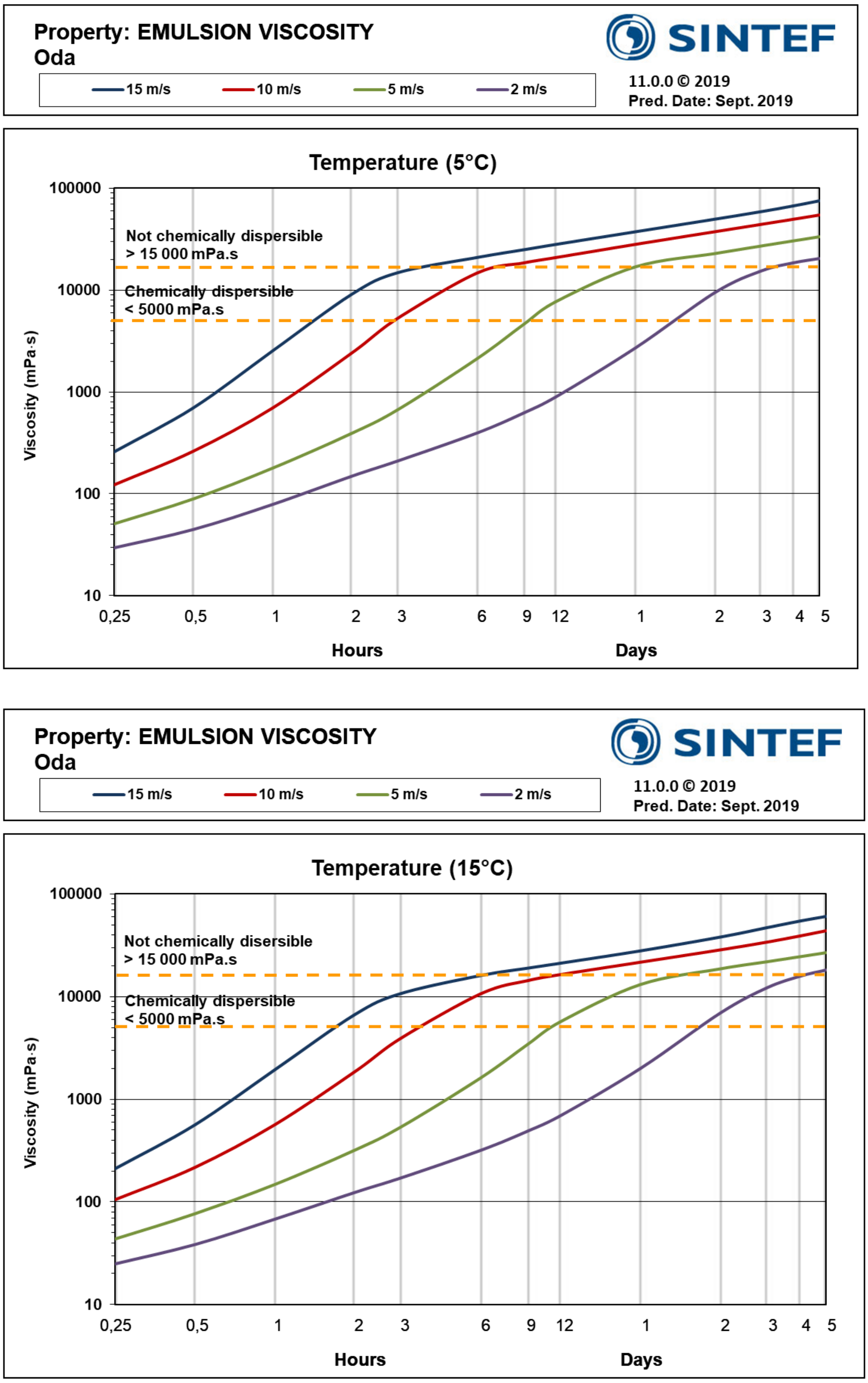


Figure 7-7: Expected time window for effective use of dispersants as a function of emulsion viscosity of Oda at 5 and 15 ºC

8 Categorization of crude oils

A semi-quantitative categorization has been developed by SINTEF to map crude oils into four main groups: *Paraffinic, waxy, naphthenic*, and *asphaltenic* oils, based on their typically physiochemical properties, as described below.

Naphthenic oils typically exhibit disrupted *n*-alkane (paraffins) patterns due to high degree of biodegradation of the oil in the reservoir. The content of paraffins are therefore normally low in for these oils and have low pour points (typically <-10 °C) with corresponding low wax content. Such biodegraded crude oils may have high densities and a high degree of UCM (Unresolved Complex Mixture) consisting of a wide range of complex components, such as resins and naphthenes, but this is not true for all naphthenic oils.

Paraffinic oils are often characterized by low to medium density, which reflects high content of light and saturated components, such as paraffins (*n*-alkanes). Paraffinic crudes differ mainly from the waxy crudes with a lower wax content (typically < 6 wt. %), hence the pour point of the fresh crude is often lower compared with waxy crude oils. Paraffinic crudes exhibit medium to high evaporation loss, with rapid and high-water uptake, and normally form stable emulsions.

Asphaltenic oils have high content of heavier components reflected by high densities (> 0.9 g/mL) and low evaporation loss. The asphaltenic crudes often exhibit low pour points (typically >-4 °C) due to the high asphaltene content (> 1 wt. %) preventing wax precipitation and formation of a wax lattice structure. Compared with paraffinic and waxy crudes the asphaltenic crude oils usually have both a slower and a lower maximum water uptake. The asphaltenic crude oils form very stable, highly viscous and persistent blackish emulsions with long expected lifetime on the sea surface. The high stability is caused by the stabilization by the polar components in the oil.

Waxy oils often exhibit high pour points due to large content of wax components (> 6 wt. %). These oils tend to solidify producing elastic properties on the sea surface, particularly observed at low seawater temperatures. Solidification is typically pronounced if the seawater temperature is 5-15 ºC below the pour point. Waxy crude oils typically exhibit a light to medium evaporative loss. The water uptake can vary extensively, whereas the emulsions can be very stable or even highly unstable depending on the content of stabilizing and polar surface-active components like the asphaltenes and resins.

The categorization of a selection of Norwegian crude oil including Oda is presented in Figure 8-1, below. Oda is categorized as a paraffinic crude oil.

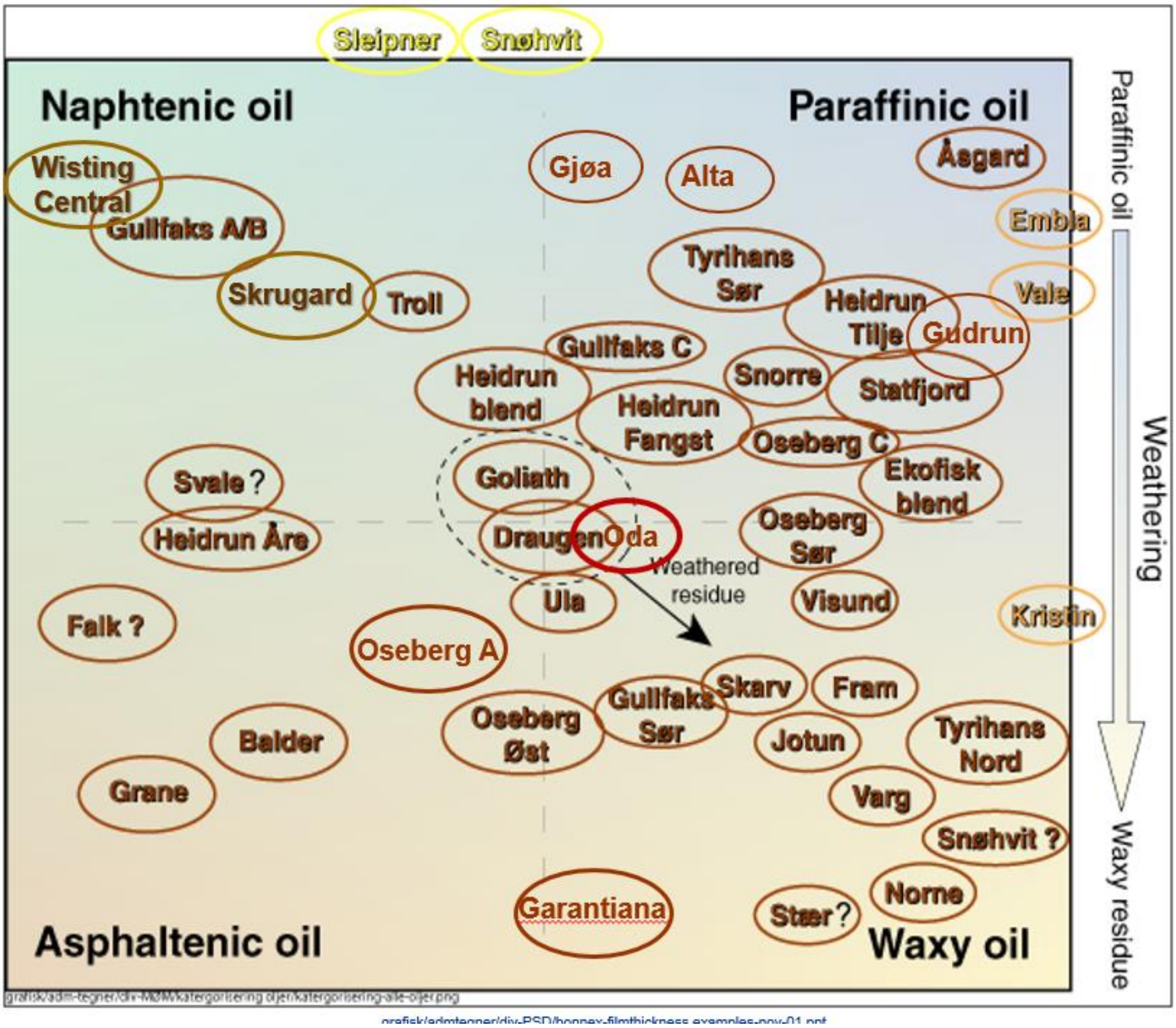


Figure 8-1 Categorization of a selection of Norwegian crude oils

9 Conclusion - short summary

Short summary of the main findings from this project

- Compared with other Norwegian crude oils, Oda is a low to medium density crude oil (0.820 g/mL) with a moderate wax (< 6 wt. %), and a relatively high content of asphaltene (0.44 wt. %)
- The flash points of Oda will be above the sea temperature within the first hour at winter and summer temperature at 2 m/s, and earlier at higher wind speeds
- Oda forms high viscous water-in-oil (w/o) emulsions with a maximum water uptake of 80 vol. %
- The emulsions formed were found to be very stable but released water when adding emulsion breaker (Alcopol O 60 %). The use of emulsion breaker (2000 ppm) could be considered for Oda to increase the storage capacity when recovered
- A combined response of chemical dispersion and mechanical recovery could be applied to an oil spill, both under summer and winter conditions. The emulsion film thicknesses are not considered as limiting factor for either mechanical recovery and / or chemical dispersion from a surface release
- Wide window of opportunity for mechanical recovery with use of skimmers, such as the Transrec equipped with traditional weir-skimmer head and in combination with the high.visc skimmer
- The oil has a potential for solidification due to high pour points of the residues. In such cases, use of high-viscosity skimmer could be recommended, and lower dispersant effectiveness is likely
- Oda is found to be easily dispersible adding the dispersant Dasic NS for viscosities < 5000 mPa.s and was found not/poorly dispersible for viscosities >15 000 mPa.s.
- The meso-scale flume testing showed reduced dispersant effectiveness on Oda when the weathered and emulsified oil had reached a viscosity of 13 800 mPa.s (during 72 hours of weathering). The flume testing indicated that the oil/emulsion required 3 times application round of dispersant (cumulative DOR 1:22) to break up the "slick" into patches and disperse the oil (i.e.50-70 % of available oil).
- In the field, additional energy or higher DOR and/or repeated dispersant application may increase dispersant effectiveness if viscosities are between 5000 mPa.s and 15 000 mPa.s

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A The behaviour of crude oil on the sea surface

A.1 The chemical composition of crude oils and condensates

Crude oil is a complex mixture of thousands of chemical components. The relative compositions vary, giving rise to crude oils with different chemical and physical properties. The components found in crude oil are classified into two main chemical groups: hydrocarbons and non-hydrocarbons see Figure A-1.

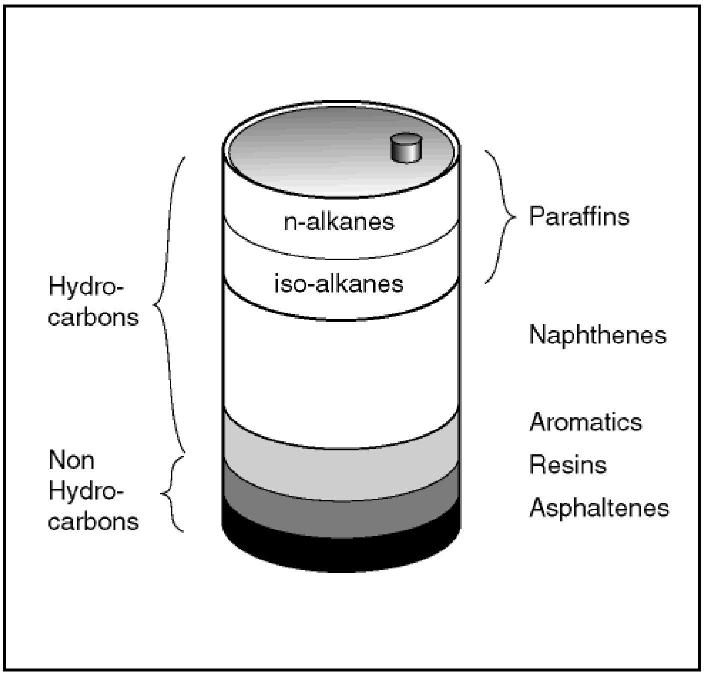


Figure A-1: The chemical composition of crude oils

A.1.1 Hydrocarbons

Most compounds in crude oils are hydrocarbons, which are composed of hydrogen (10-15 wt. %) and carbon (85-90 wt. %). These range from simple, volatile gases, such as methane with only one carbon atom to large, complex molecules with more than 100 carbon atoms. The hydrocarbons in crude oils include saturated and unsaturated molecules in linear, branched and cyclic configurations.

Hydrocarbons are further classified into aliphatic and aromatic compounds. The two main groups of aliphatic compounds are paraffins and naphthenes.

Paraffins

Paraffins include *n*-alkane and *iso*-alkane aliphatic compounds. Waxes are an important subgroup of paraffins, containing more than 20 carbon atoms. The wax components of a crude oil will be present in a solution at elevated temperatures. At low temperatures, they may precipitate from the solution. These are principally n-alkanes. The wax content of crude oils can vary from 0.5 wt.% up to 40 or 50 wt.% in extreme cases, although the majority of the world's crude oils have a wax content of 2-15 wt.%.

Naphthenes

This group includes cycloalkanes containing one or more saturated rings. Each ring may have one or more paraffinic side chains, which are chiefly five- and six-membered rings.

Aromatics

Aromatics are a specific type of unsaturated cyclic hydrocarbons. Benzene, toluene and xylenes are examples of mono-ring aromatics, naphthalenes are di-ring aromatics and polycyclic aromatic hydrocarbons (PAH) contain three or more aromatic rings.

A.1.2 Non-hydrocarbons

In addition, hydrogen and carbon, some organic compounds in crude oils also contain small amounts of oxygen, nitrogen or sulphur, as well as some trace metals such as vanadium and nickel. These compounds are referred to as heteroatom organic compounds because they contain a heteroatom, which is any atom that is not carbon or hydrogen. The two most important groups of heteroatom organic compounds are resins and asphaltenes.

Resins

Compared to the hydrocarbons, resins are relatively polar and often have surface-active properties. Resins have molecular weights ranging from 700-1000. Carboxylic acids (naphthenic acids), sulphoxides and phenol-like compounds can be found in this group as well.

Asphaltenes

Asphaltenes are is a complex group of poorly characterized chemical compounds that consist of condensed polycyclic aromatic compounds. They are large molecules with 6-20 aromatic rings and side chains (molecular weight 1,000-10,000). Asphaltenes may be classified as "hard" or "soft" based on the method of determination. Crude oils may contain up to 6 wt. % "hard" and 10 wt. % "soft" asphaltenes (Peregrino:13.4 wt.%)

A.2 Main oil categories – Related to weathering

Different oil types can have extremely different compositions, which impact their physical properties and effect their behaviour after a spill at sea.

Oils that are subject to weathering can roughly be divided into 3 main categories:

- Crude oils
- Light oils
- Condensates

Crude oils contain relatively more of the heavier components than light oils or condensates. Crude oils can be weathered in the laboratory to mimic natural weathering that occurs on the sea surface. The laboratory weathered crude oil identified as 250˚C+ residue, corresponds to 0.5 to 1 week after a spill at sea, and contains less than 50% of its original volume due to evaporation. The heavier components allow the formation of stable water-in-oil (w/o) emulsions, which reduces oil spreading at the sea surface. The final (terminal) film thickness of a crude oil depends on the emulsion’s physical properties, and will be in the order of 1 mm.

Light oils and crude oils are not specifically differentiated in reservoir terminology. However, it is suitable to deal with the light oils as a separate category when referencing weathering properties. Light oils have a high content of low molecular weight hydrocarbons. When subjected to laboratory weathering, the 250˚C+ residue of light oils may lose 50-70% of their total volume due to evaporation. In contrast to condensates, which only contain light components, light oils contain a mixture of light and heavy components. These heavy components may cause light crudes to emulsify in water, but these w/o emulsions are, however, very unstable. A light oil will spread less than a condensate, with a final film thickness of approximately 0.5 mm.

Condensates only contain low molecular weight hydrocarbons and are considered extremely volatile. Laboratory weathered condensates, such as the 250˚C+ residue, typically lose more than 70% of their initial volume. Condensates do not contain components such as asphaltenes or heavier waxes and will not emulsify significant amounts of water. The spreading of condensates is relatively fast, and can result in a final film thickness of approximately 0.05 mm.

A.3 Physical properties of crude oils

The physical properties of specific oils are a result of their chemical composition. The most important physical properties in oil spill scenarios are discussed below.

Density

The density of a crude oil is dependent on the density of all of its components. The density of hydrocarbons increases with increasing molecular weight. Furthermore, paraffinic oils have lower density than those containing larger amounts of high molecular weight aromatics, such as naphthenic and asphaltenic oils.

Specific gravity is defined as the oil density at 60°F (15.5°C) divided by water density at 60°F. In American literature, the density of the oil is often expressed as °API, where:

$$\boxed{^\circ\text{API} = \frac{141.5}{\text{Secific gravity}} - 131.5}$$

In the present study, the density of the oil is presented as specific gravity.

The density of fresh crude oils normally lies in the range 0.78 to 0.95 g/mL (50 to 10 °API).

A.3.1 Rheological properties

The viscosity of crude oils expresses its resistance to flow and is of special interest when pumping oil.

Absolute viscosity also known as dynamic viscosity) is a measure of internal resistance. In the SI system, absolute viscosity has units of N s/m^2, Pa s or kg/(m s), where 1 Pa s = 1 N s/m^2 = 1 kg/(m s). Absolute viscosity can also be expressed in the metric CGS (centimeter-gram-second) system as g/ (cm s), dyne s/cm^2 or Poise, where 1 Poise = 1 dyne s/cm^2 = 1 g/(cm s) = 1/10 Pa s = 1/10 N s/m^2. https://www.engineeringtoolbox.com/dynamic-absolute-kinematic-viscosity-d_412.html

The industry often uses centipoise, as the *Poise* is normally too large, 1 Poise = 100 cP and 1 cP = 0.001 N s/m^2. The viscosity of fresh crude oils can vary from less than 1 to more than 2000 mPa.s (cP) at ambient sea temperature. In comparison, water has an “absolute” viscosity of 1 cP and syrup's is 120 000 cP at 20°C.

Kinematic viscosity is absolute viscosity divided by density. 1 centistoke (cSt) = 1 cP / density. Because the density of weathered oils and emulsion are typically 0.9 – 1 g/mL, the units cSt and cP will often have similar values.

Viscosity is temperature dependent. For liquids, the viscosity decreases with increasing temperatures. Viscous and waxy crude oils can exhibit non-Newtonian behaviour (viscosity varies with shear rate), especially close to, or below, their pour point. Water-in-oil (w/o) emulsions exhibits this non-Newtonian behaviour with shear thinning. In an oil spill situation, an emulsion may be liquid under turbulent conditions at sea, but can become much more viscous, or even semi-solid in calmer water conditions, or on beaches. Thus, the measurements of the viscosity of w/o-emulsions must be carried out under strictly controlled conditions (defined shear rates and thermal and mechanical history of the sample). At SINTEF, a shear rate of 10 s^{-1} is routinely used for expressing viscosity data on w/o-emulsions.

The viscosity of an oil increases with evaporation since the heavier, more viscous components remain in the residue (Mackay et al., 1982). The difference in viscosity for crude oils is approximately 3 to 2000 mPa.s for fresh crude oils and several hundred/thousand mPa.s for their residues.

Water-in-oil (w/o) emulsions are generally more viscous than the parent crude oil; this is illustrated in Figure A-2.

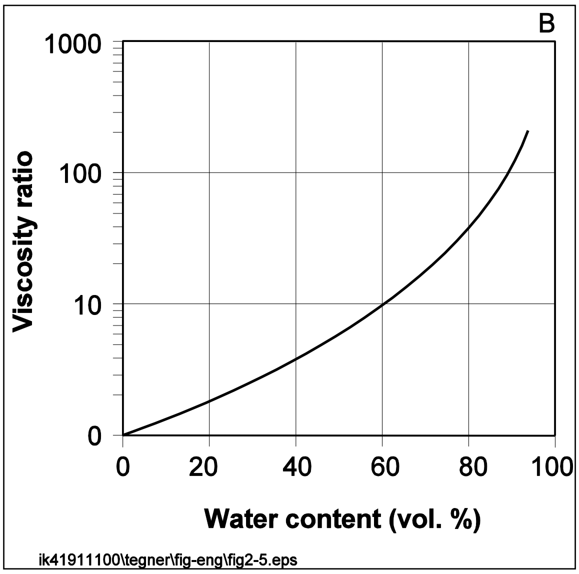


Figure A-2: Example of viscosity ratio as a function of water content

A.3.2 Pour point

The temperature at which oil ceases to flow when cooled without disturbance under standardized conditions in the laboratory is defined as the oil's pour point (ASTM-D97). The method accurately determines the temperature at which the oil become semi-solid under the specified laboratory conditions. Due to the movement at the sea surface, the oil may remain a liquid at sea at temperatures as low as *5 to 15°C lower* than the pour point of the oil. The pour point of oil with high wax content will increase dramatically with evaporation as the lower weight molecules, which contribute to keeping the wax in solution, evaporate. The pour point for oils with high wax contents can reach 30°C, while low viscous naphthenic oils may have pour-points as low as - 40°C.

In an oil spill clean-up situation, the pour point provides essential information for when determining the efficiency of various skimmers, pumping rates and the use of dispersing agents.

A.3.3 Distillation curve (True Boiling Point curve)

The distillation curve, which is obtained by measuring the vapour temperature as a function of the amount of oil distilled, shows the relative distribution of volatile and heavier components in the oil. The boiling point of a chemical component depends on its vapour pressure, which is a function of its molecular weight and chemical structure. Low molecular weight oil components have a higher vapour pressure, thus lower boiling points than higher molecular weight components of a similar type. Aromatic compounds boil at a higher temperature than paraffinic compounds of the same molecular weight, and *iso*-alkanes boil at a lower temperature than the equivalent *n*-alkanes. Hence, the distillation curve is an indicator of the relative amount of different chemical components, principally as a function of molecular weight, but also as determined by the chemical composition.

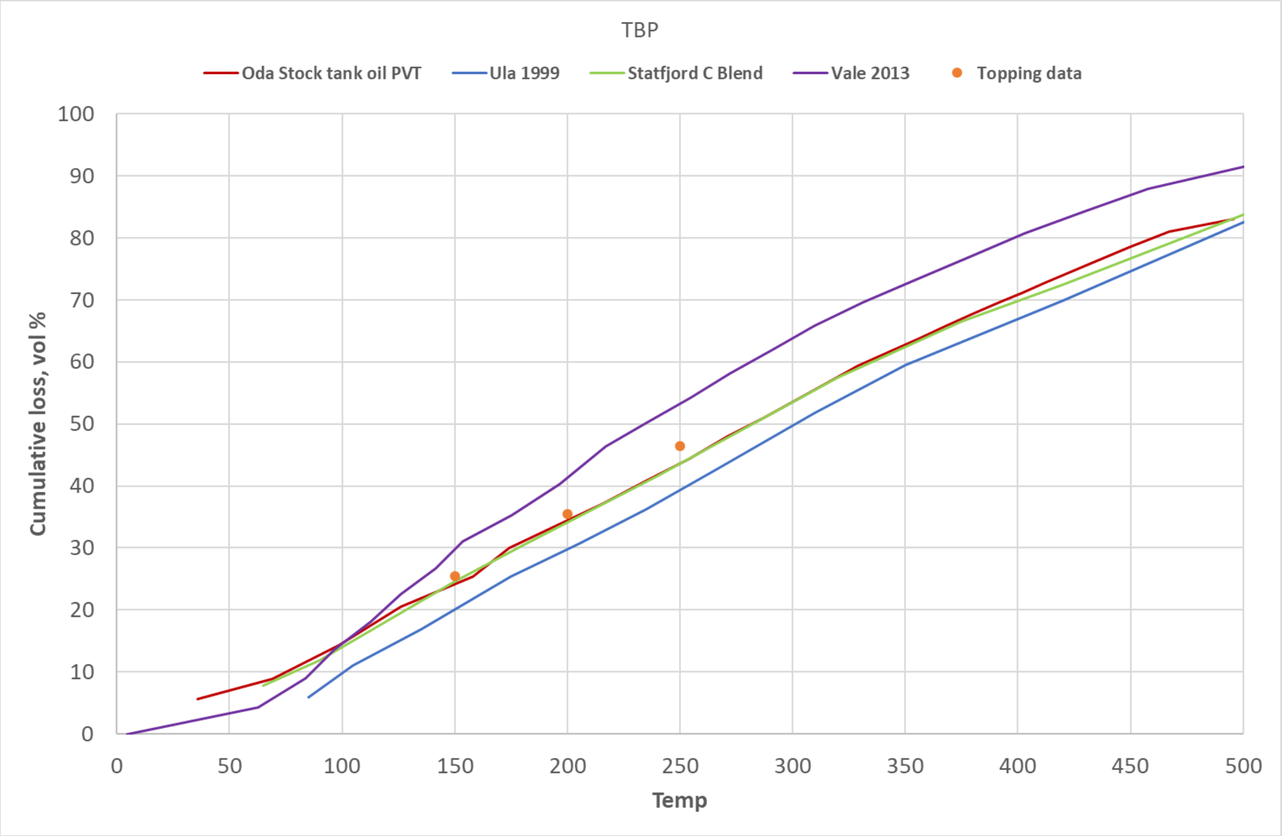


Figure A-3: Distillation curves from SINTEF OWM for Oda crude oil in comparison with Ula 1999, Statfjord C Blend and Vale

A.3.4 Flash point

The flash point is the lowest temperature at which the gas or vapour generated by the heating of oil will form an ignitable mixture in air. The flash point depends on the proportion of low molecular weight components. Fresh crude oils normally have a low flash point (from -40°C to 30°C).

From a safety point of view, flash points are most significant at, or slightly above, the maximum temperature that may be encountered in storage or transport. The flash point is an approximate indicator of the relative fire and explosion hazard of oil.

Rule of thumb:

In the presence of an oil slick at sea, a fire and/or explosion hazard exists when the oil's flash point is close to or lower than the sea temperature.

Natural weathering processes such as evaporation and emulsion formation contribute to reducing the potential hazard by increasing the flash point. Thus, it will be a relatively short fire and/or explosion danger in the initial stages of oil spill.

In the laboratory, the flash point is measured in a closed system with the components in the oil and gas equilibrated. In the field, however, the weather situation will influence the flammability of the air above the slick. The gas concentration will be high just above the oil film in calm weather and high temperatures, whereas the concentration will be low in cold and windy weather due to dilution and transport and a lower degree of evaporation.

A.4 The behaviour of crude oil spilled at sea

This chapter gives a general description of the main weathering processes when oil is spilled at sea. There are many natural processes take place that change the volume and chemical properties of the oil. These natural processes are evaporation, water-in-oil (w/o) emulsification, oil-in-water (o/w) dispersion, spreading, sedimentation, oxidation and biodegradation. A common term for all these natural processes is weathering. The relative contribution of each process varies during the duration of the spill. The weathering of oil depends on the oil type (chemical and physical properties), the weather conditions (wind, waves, temperature and sunlight) and the properties of the seawater (salinity, temperature, bacterial flora, etc.).

Figure A-4 illustrates the various weathering processes, and Figure A-5 shows their relative importance over time.

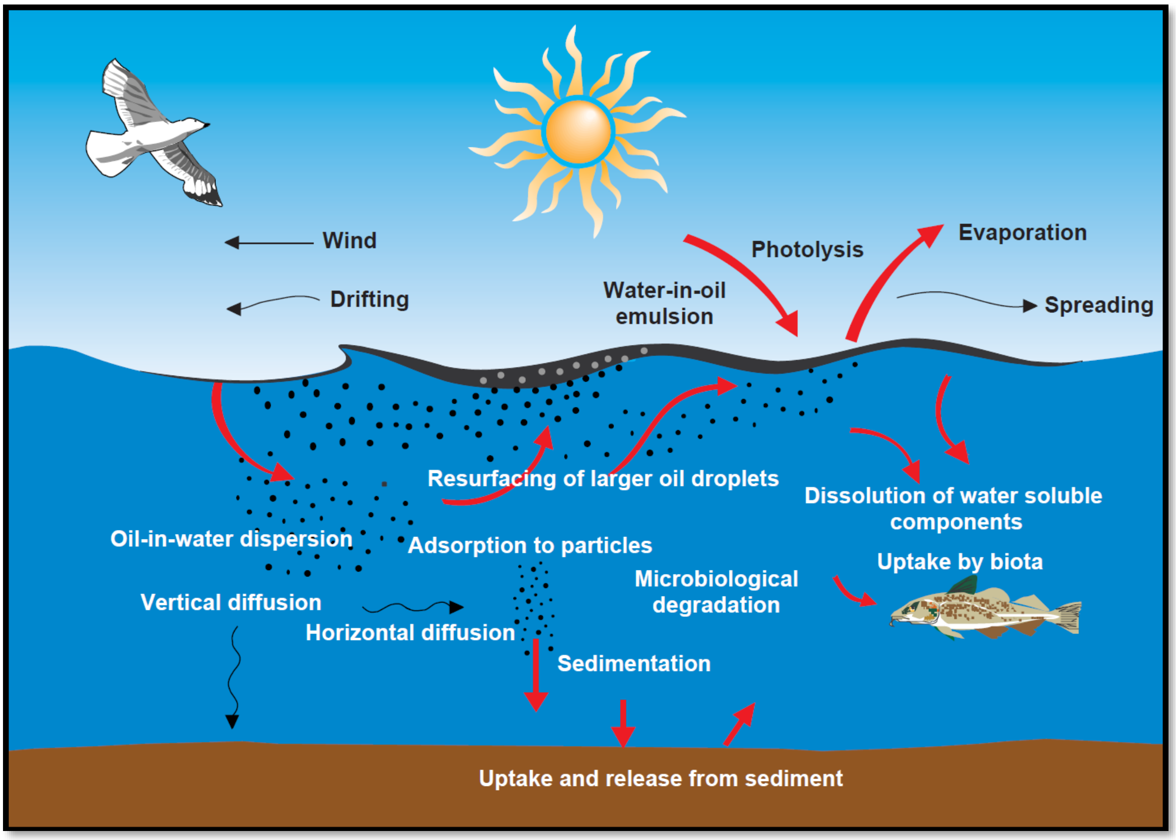


Figure A-4: Illustrating the weathering processes that take place when oil is spilled on the sea surface

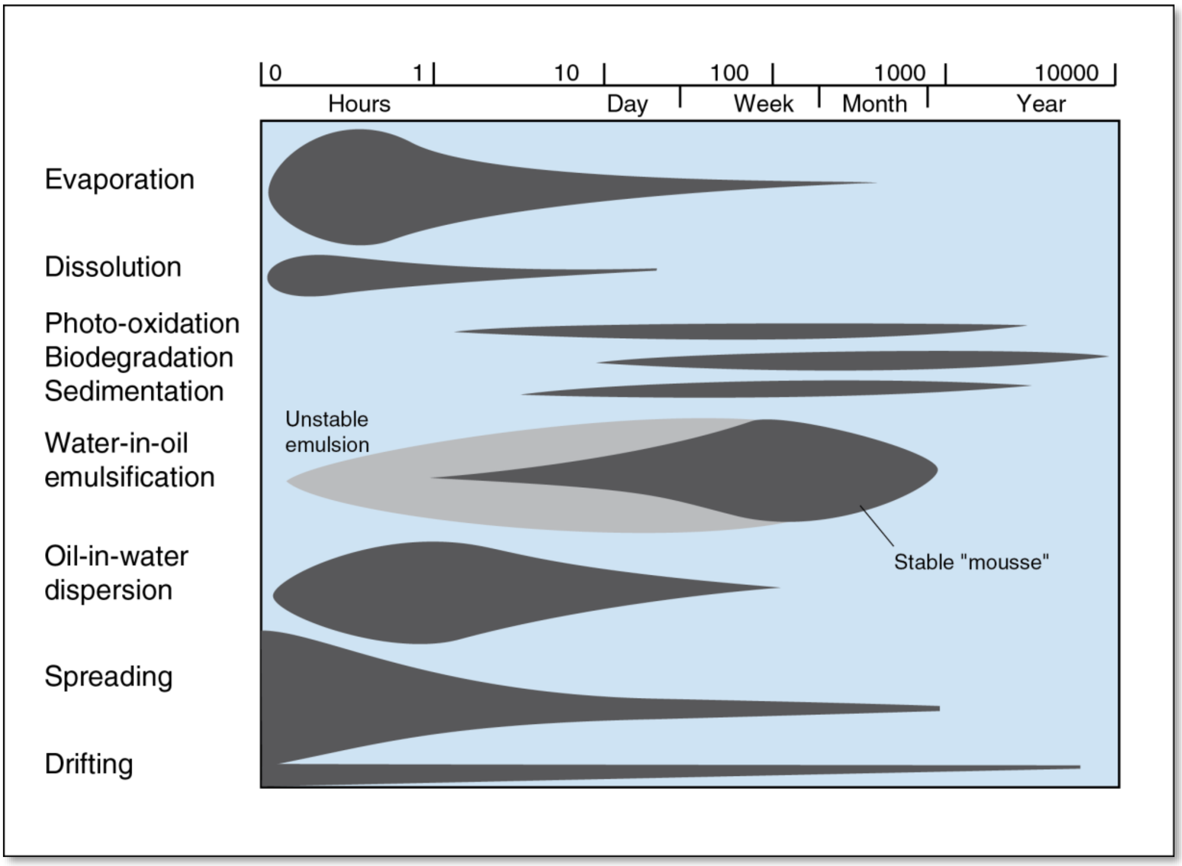


Figure A-5: Weathering processes' relative importance over time. Note: logarithmic scale

A.4.1 Evaporation

Evaporation is one of the natural processes that support the removal of spilled oil from the sea surface. The evaporation process starts immediately after the oil is spilled, and the evaporation rate decreases exponentially throughout the duration of the oil spill.

The evaporated amount depends on the chemical composition of the oil in addition to the prevailing weather conditions, sea temperature and oil film thickness.

The rate of evaporation varies for different oil types. Light refinery products (e.g. gasoline and kerosene) may completely evaporate 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.

The most significant difference caused by evaporation is the loss of volatile and semi-volatile compounds, which increases the relative amounts of higher molecular weight compounds.

With evaporations, the chemical and physical properties of the remaining oil will change. The density, viscosity, pour point and wax and asphaltene content, will all increase with increased evaporation.

A.4.2 Spreading

Oil spilled at sea will spread on the sea surface. Spreading is often the dominant process in the initial stages of an oil spill and decreases as the viscosity and density of the remaining oil increases. The spreading process is also reduced if the oil's pour point is 5-15°C below the sea temperature.

Oceanographic conditions (e.g. wind, waves and currents) affect the spreading process. The oil slick will be broken into "wind rows" aligned in the direction of the wind, see Figure A-6. The thickness of the oil slick varies, often differing by a factor of several thousand. Experience has shown that most of the total oil slick area consists of a thin film (<1 µm oil thickness) that only contains 10% of the oil volume. Most of the oil volume (~90%) is located in small patches of w/o emulsions with a film thickness of 1 to 5 mm, which often constitutes less than 10% of the total oil slick area.

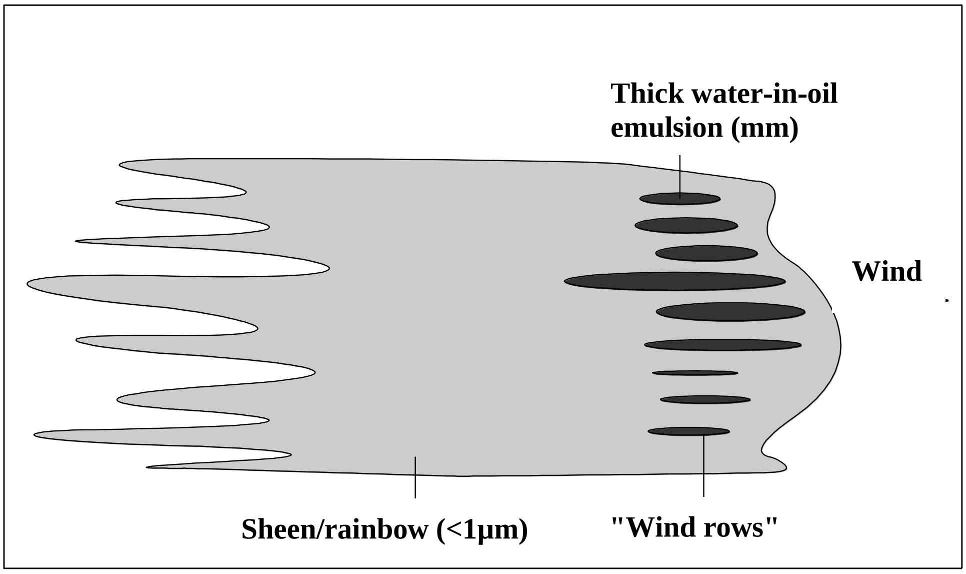


Figure A-6: The spreading of oil spilled on the sea surface and the distribution within the oil slick

A.4.3 Drift of an oil slick

The oil slick will drift as the weathering processes continue. The wind and current conditions cause the oil slick to drift, as illustrated in Figure A-7. Waves and wind create a current in the mass of water which amounts to approximately 3% of the wind speed at the sea surface. The influence of the wind decreases rapidly with the depth of the water below the surface. At 1 to 2 meters the current reduces to approximately 1% of the wind speed. This means that oil on the surface of the open sea, will move faster than the water below (e.g. Reed and Turner, 1991; Reed et al., 1994). In the absence of wind, the oil drift is governed by the prevailing (background) current.

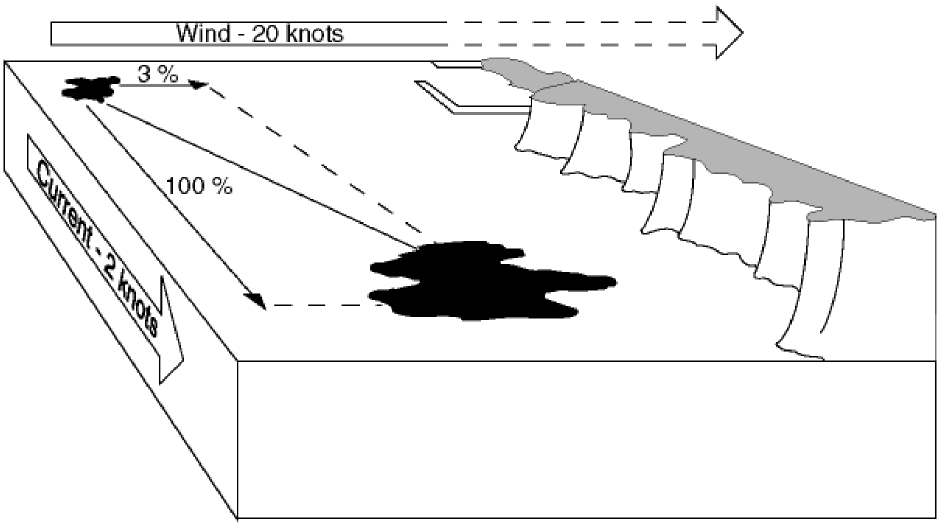


Figure A-7: An illustration showing how wind and current can influence the drifting of an oil slick

A.4.4 Water-in-oil (w/o) emulsion

The formation of water-in-oil emulsions significantly affects the behaviour and clean-up of oil spilled at sea. Because 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. The formation of w/o emulsions also contributes to keeping oil on the sea surface. A w/o emulsion normally has a higher viscosity than the parent crude oil, so the emulsification process will therefore retard/delay evaporation and the natural dispersion process.

The minimum criterion for the formation of w/o emulsions is the presence of breaking waves (i.e. a wind speed of >5 m/s). Nonetheless, a slow water uptake can also take place during calmer weather. Figure A-8 shows how wind speed influences the w/o formation rate.

Surface active compounds present in crude oil will promote the formation of w/o emulsions and contribute to stabilizing the emulsion. These components contain both hydrophilic and hydrophobic groups.

The maximum water uptake will vary for different crude oils. Tests performed at SINTEF have revealed that the maximum water uptake is independent of the prevailing weather conditions if the lower energy barrier for the formation of w/o emulsions is exceeded. The rate, however, depends highly on the weather conditions. In the laboratory, the $t_{1/2}$-value is determined, which is the time in hours it takes before the oil has emulsified half of its maximum water content.

The w/o emulsion formation rate depends on the oil's chemical composition, which varies for different oil types.

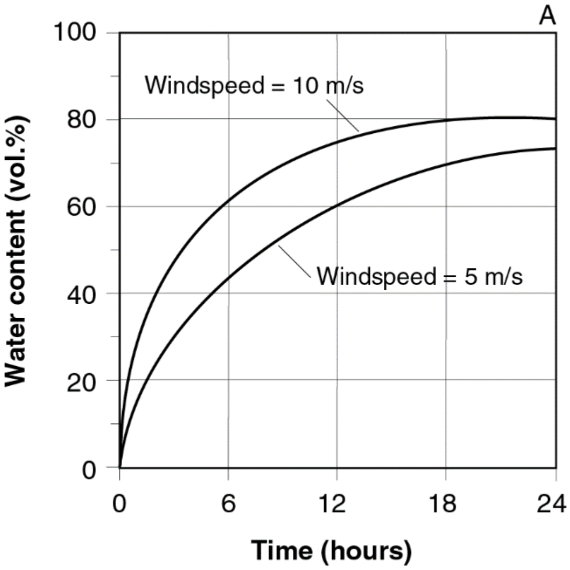


Figure A-8: Example of how weather conditions influence the w/o emulsion formation for typical oils

The stability of the w/o emulsion depends on the water droplet size, since not all water droplets in the emulsion are stable. Larger water droplets may be reduced in size by the flexing, stretching and compressing motion of the slick due to wave action, whereas the largest droplets may coalesce and be squeezed out of the w/o emulsion. After a certain period, the emulsion may only contain small water droplets with diameters of 1 to 10 µm, yielding a more stable emulsion.

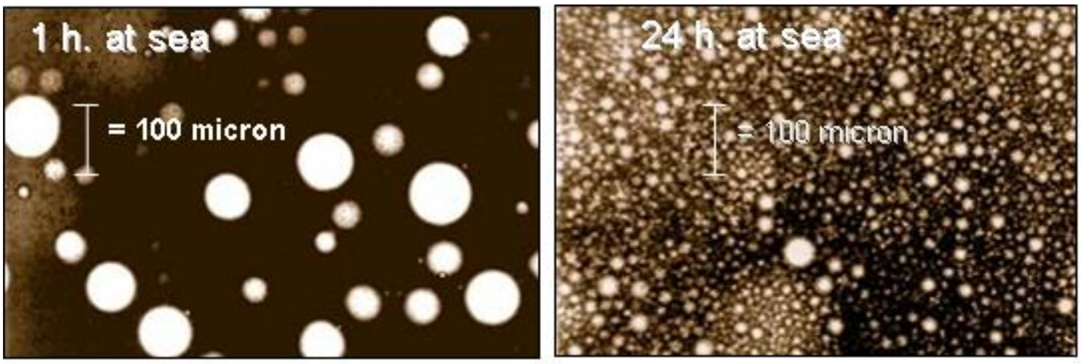


Figure A-9: Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder

Thus, the formation of emulsions is the result of water retention by oil as an effect of both viscous and interfacial forces. The interfacial forces are the most important, and asphaltenes are largely responsible for this. Resins are similar compounds to asphaltenes and can stabilize an emulsion, but not to the same extent.

Resins and asphaltenes have both hydrophobic and hydrophilic properties and will concentrate at the interface between the water and oil, thereby forming a layer that stabilizes the water droplets. The hydrophobic properties can lead to the concentration of wax along the water droplets, which further stabilizes the interfacial "skin" layer. The interfacial layer between the oil and water forms a physical barrier that hinders the coalescence of the water droplets and will stabilize the w/o emulsion. The stabilization of the water droplets by asphaltenes and wax is shown in Figure A-10.

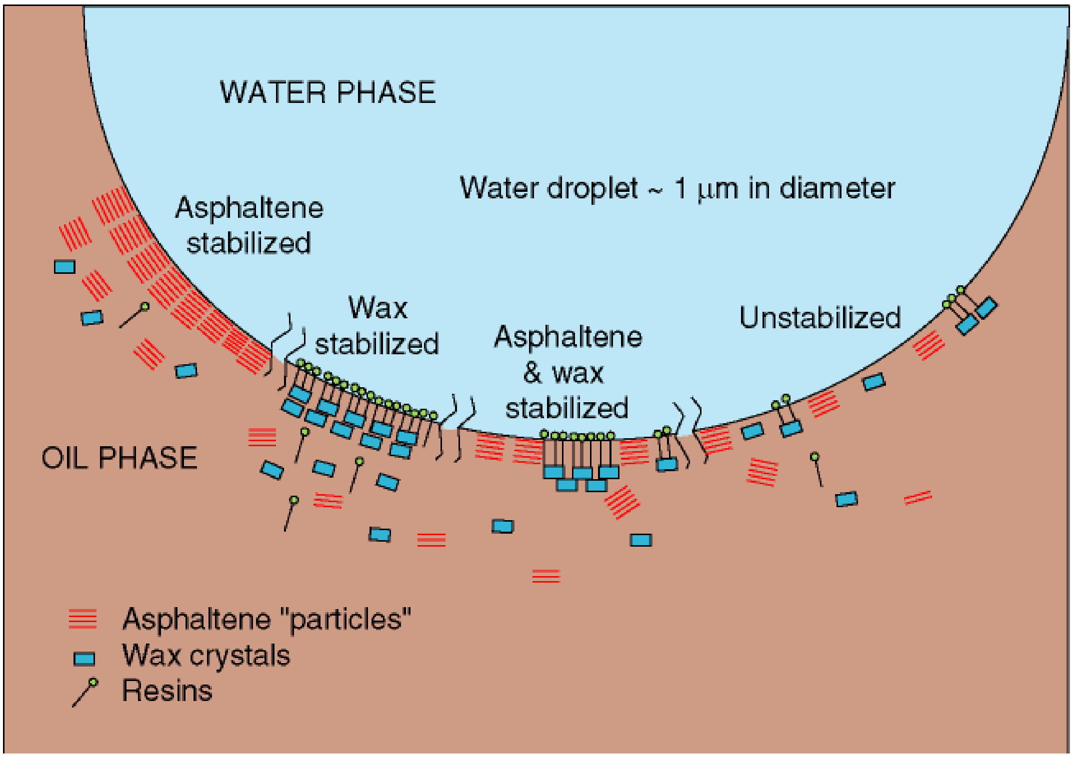


Figure A-10: Interfacial layer stabilized by wax and asphaltenes in w/o emulsion

Oils that contain large amounts of wax and small amounts of asphaltenes can form w/o emulsions stabilized by a continuous phase's rheological strength (viscosity and elasticity) due to wax structure formed by precipitated wax. Wax stabilized emulsions are characterized by large water droplets and are fairly stable when stored, although they may break down when stress is applied and/or when the emulsion is heated to, e.g. 40-50°C.

Crude oil and sea water interfacial tension (IFT) plays a key role in the process of oil droplet formation. The need to understand and control droplet formation in dispersant system is extremely important. Addition of dispersants reduces the interfacial tension between oil and water that subsequently promotes the formation of a larger number of small oil droplets when surface waves entrain oil into the water column. These small submerged oil droplets are then subject to transport by subsurface currents and other natural removal processes, such as dissolution, volatilization from the water surface, biodegradation, and sedimentation resulting from interactions with suspended particulate material.

A.4.5 Oil-in-water (o/w) dispersion

Natural oil-in-water (o/w) dispersion will take place if there is sufficient energy on the sea surface, i.e. if there are breaking waves present. The waves will break the slick into small oil droplets (~1 µm - 1 mm in diameter), which are then mixed into the upper water column. The largest oil droplets will resurface and form a thin oil film (typically <50 µm). This thin oil film will be rapidly dispersed again by breaking waves as smaller droplets into the water column and will be available for rapid biodegradation.

The natural dispersion rate depends highly on oil type and can be one of the main processes that determine the lifetime of an oil slick on the sea surface. Natural o/w dispersion will gradually decrease with time since the evaporation of the lighter compounds will increase the viscosity of the remaining oil.

The purpose of applying chemical dispersing agents is to increase, or enhance, the natural dispersion rate. Dispersants reduces the interfacial tension between water and oil and thus promote natural o/w dispersion. When effective chemical dispersion is achieved, small oil droplets are formed, with typical diameters ranging from 5 to 100 μm. These are retained in the upper layers of the water column by the prevailing turbulence of wave action.

A.4.6 Water solubility

The water solubility of saturated hydrocarbons is generally very low, while lower molecular weight aromatic compounds are water-soluble to some extent; particularly aromatics, such as BTEX, 2-ring PAH and paraffin's up to C_7) have a potential to be dissolved in the water column (McAuliffe, 1987). Within the various types of hydrocarbons, the water solubility decreases from aromatics to naphthenes and from *iso*-alkanes to *n*-alkanes. In each series, the water solubility decreases with *increasing* molecular weight.

Evaporation and the release of oil components into the water mass are competitive processes since most of the water-soluble components are also volatile. The evaporation process is approximately 10 to 100 times faster than the release in the water column. The concentration of soluble oil components into the water column during an oil spill is quite low (< 1 mg/L), while the dissolution of oil components into the water column does not contribute to removing the oil from the sea surface. However, the water-soluble fraction is of great interest since it has a high bioavailability and thus the potential to cause acute toxic effects on marine organisms.

A.4.7 Photo-oxidation

Under the influence of sunlight, some of the oil components will slowly oxidize to resins and finally asphaltenes. The photo-oxidized components will stabilize the w/o emulsions and influence the oil's persistence on the sea surface. After a long period of weathering at sea, tar balls (mainly consisting of asphaltenes) may be formed. These tar balls break down very slowly, both at sea and on beaches.

A.4.8 Biodegradation

Seawater contains an abundance of microorganisms that can break down all types of oil components. Various microorganisms prefer specific oil components as their energy source. Bacteria prefer to degrade oil in contact with water and the rate of biodegradation depends on the water/oil interface area. The interface area increases as the oil is spread over the sea surface in a thin layer or by chemical or natural dispersion of oil into the water column.

Important factors influencing the biodegradation rate are temperature, the concentration of available nutrients (i.e. nitrogen and phosphorus), oxygen, oil type and the degree of weathering. Low molecular compounds are degraded more rapidly than the high molecular weight/heavier compounds in the oil, thus giving the following order for biodegradation: straight-chain *n*-alkanes > branched *iso*-alkanes > cyclic alkanes > cyclic naphthenes > aromatics> resins > asphaltenes (Perry, 1984).

At sea, the formation of oil droplets by natural or chemical enhanced dispersion will increase the biodegradation rate in the water mass by 10 to >100 times compared to surface oil due to increased water/oil interfacial area. When immobilised on hydrophobic synthetic fabrics, n-alkanes biodegraded within 2-4 weeks at North Sea conditions (13°C; Brakstad and Lødeng, 2005). Some small PAHs dissolved in water can be degraded within a few days (Brakstad and Faksness, 2000), but high molecular-weight oil compounds associated with particulate oil biodegrade more slowly and some very high molecular-weight compounds (equivalent to the heavy residues in crude oil that are used to make bitumen) may not biodegrade to any significant degree.

A.4.9 Sedimentation

Crude oil and oil residues rarely sink into the water mass since there are few oils that have a density higher than water, even after extreme weathering. Oil can sink by sticking to materials present in the water mass. W/o emulsions that have a higher density value (e.g. emulsified bunker fuel oils) can more easily stick to a material, particularly if coming to the shore, and can sink to the bottom if washed out again from the shore. In connection to sub-sea blowout at the sea bottom, it is assumed that some of the oil droplets generated in the plume may adsorb to suspended particles or encounter with the seabed sediment. This can cause some sedimentation of oil droplets to the seabed near the release. It is assumed that sub-sea dispersant treatment will reduce the potential for such sedimentation, due to lower adsorption /stickiness to sediment particles.

A.4.10Deep water releases

Size distribution of the oil droplets formed during a subsurface release strongly influences the subsequent fate of the oil in the environment. Large droplets (typically larger than 5 mm) reach the surface after a couple of hours rise time from a depth of approximately 1000 m, while smaller droplets (down to 0.5 mm) may rise for up to a day before they will come to the surface. Fine droplets (below 100 microns) may stay in the water for weeks or even month before they eventually reach the surface. However, factors like vertical turbulence mixing in the water column, density stratification and cross flows will contribute to keep such fine small droplets submerged for even prolonged periods (Johansen et al., 2003). In case of deep-water releases, large droplets (mm range) will usually rise to the surface and form an oil layer with sufficient thickness to emulsify (form water-in-oil emulsions). This is usually caused by loss of buoyancy and more horizontal entrainment of the gas/oil/water plume due to dissolution of gas, possible hydrate formation, cross currents and density layers. However, large droplets (mm range) will leave the entrained plume and rise to the surface, illustrated in Figure A-11. This was observed both during the "DeepSpill" experiments in 2000 (Figure A-12) and the DWH oil spill in 2010 (Figure A-13). This emulsification will be dependent on oil properties and environmental conditions, such as temperature and sea state.

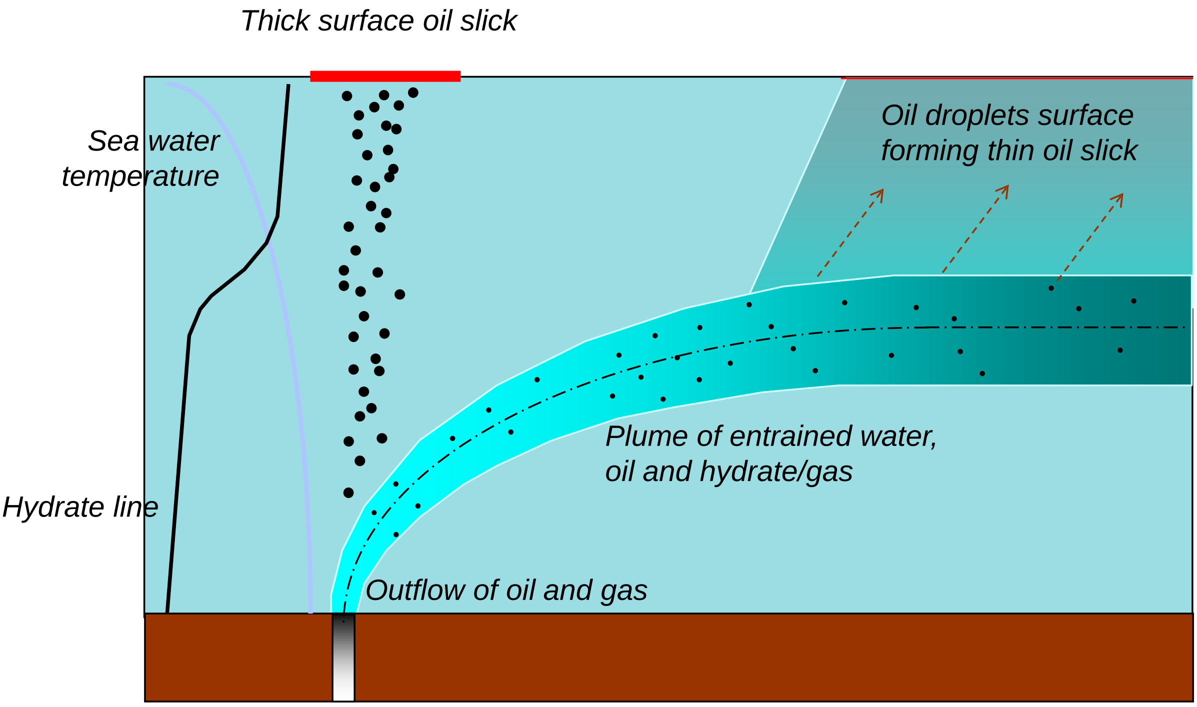


Figure A-11: Illustration of possible creation of thick surface oil slick (> 200 µm) from deep-water release of oil

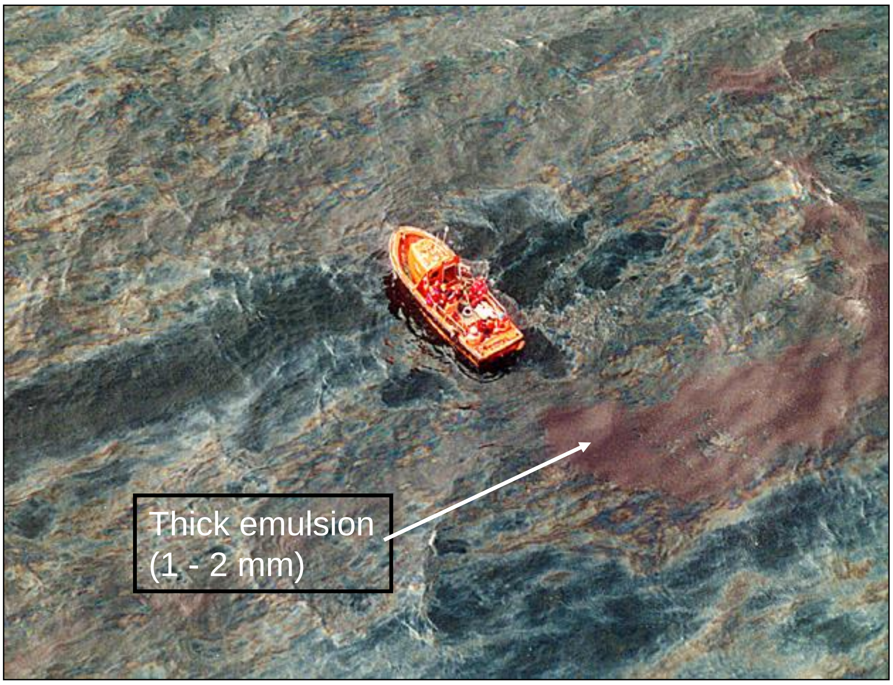


Figure A-12: Surface oil slick (initial thickness > 200 µm) from the experimental deep-water release "DeepSpill" in 2000. Surface oil is emulsifying similar to an oil slick from a surface batch release (from Leirvik et al., 2011)

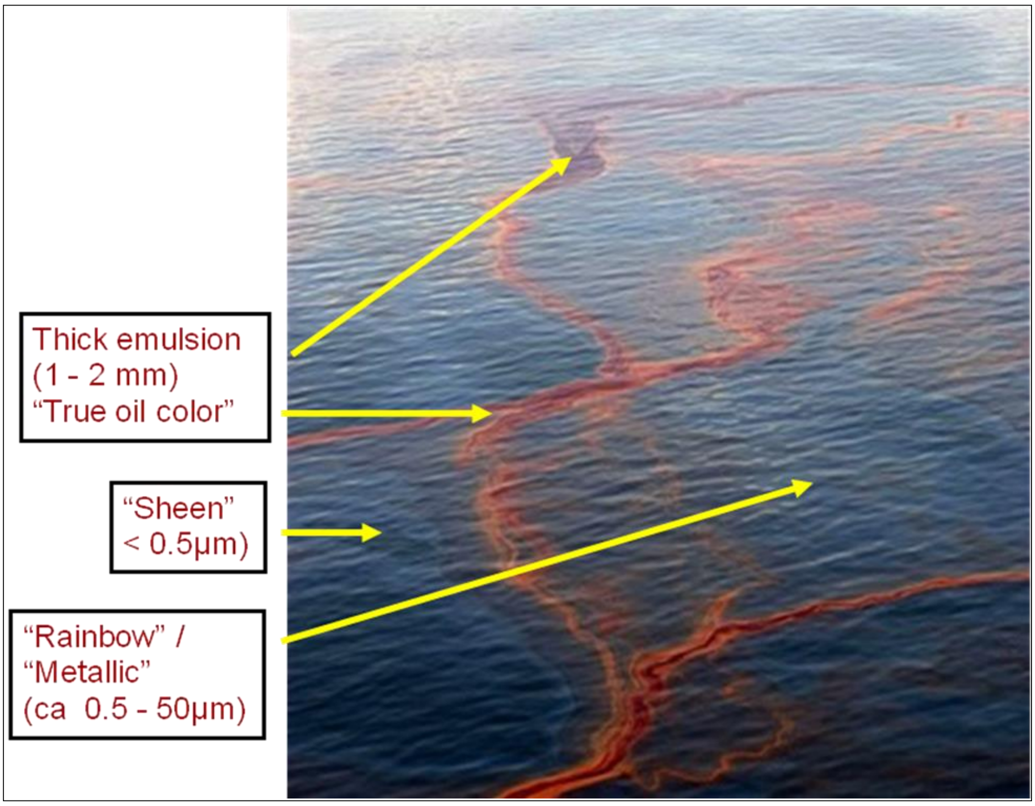


Figure A-13: Surface oil slick (initial thickness > 200 µm) from the DWH deep-water release. Surface oil is emulsifying similar to an oil slick from a surface batch release

A.4.11Shallow releases

In case of a sub-surface release of oil and gas in shallower water (<500 meter) the buoyancy of the rising water/gas/oil plume is usually sufficient to reach the surface. The gas will be released to the atmosphere, while the large volumes of water will set up a horizontal current that will create a wide and thin surface oil slick (see Figure A-14, Figure A-15 and Rye et al., 1997). This surface oil slick could be too thin to emulsify (< 200 microns) and evaporation and natural dispersion will be the predominant weathering processes.

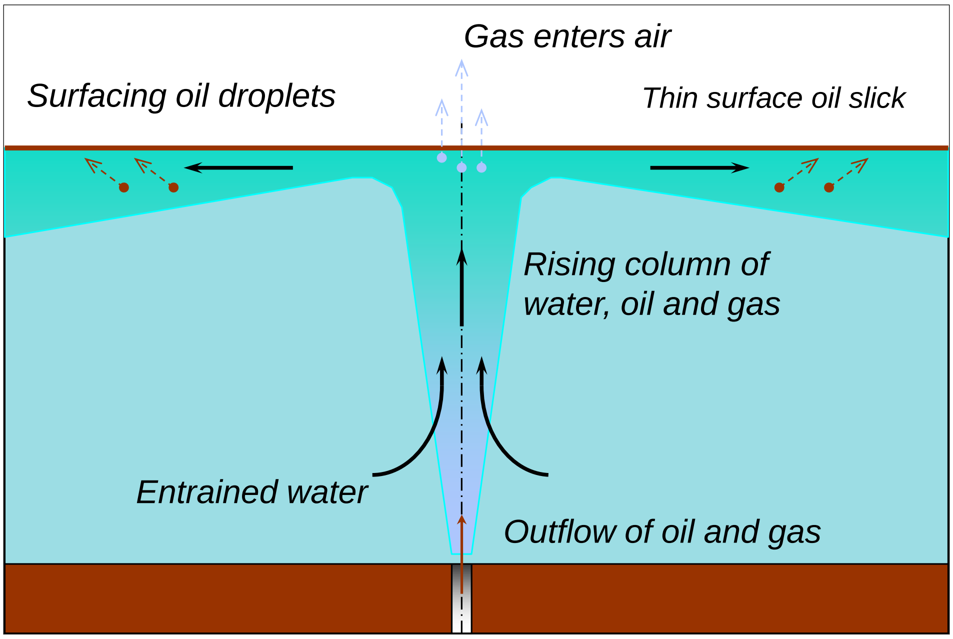


Figure A-14 Illustration of possible creation of thin surface oil slick (< 200 µm) from a shallow subsurface release (<500 m)

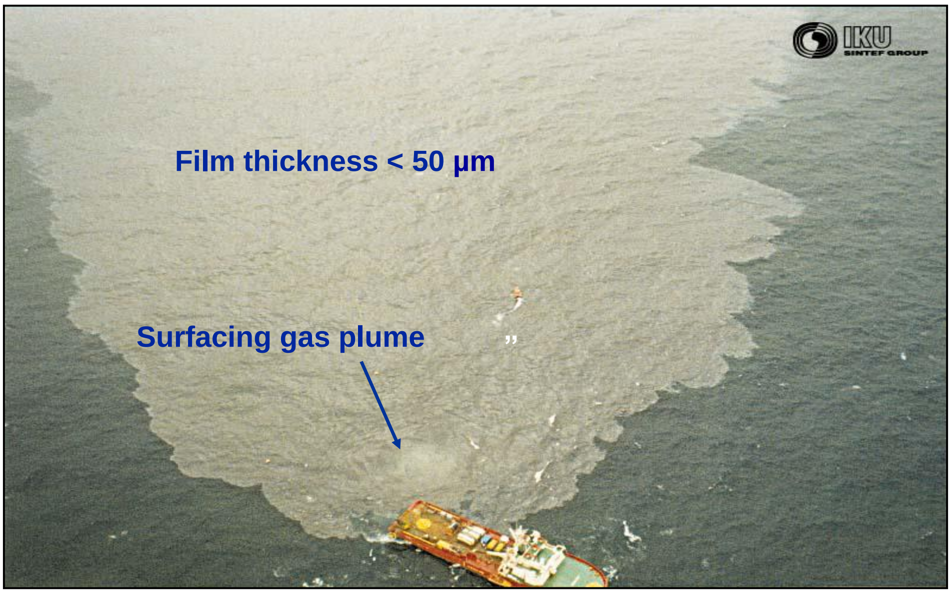


Figure A-15: Surface oil slick (< 50 µm) from experimental subsurface release at 106 m in 1996. The surface oil didn't emulsify and had a very limited life time (hours) due to the low film thickness and high rate of natural dispersion (even at < 10 m/s wind)

B Experimental setup

B.1 Oil sample, pre-handling and test temperature

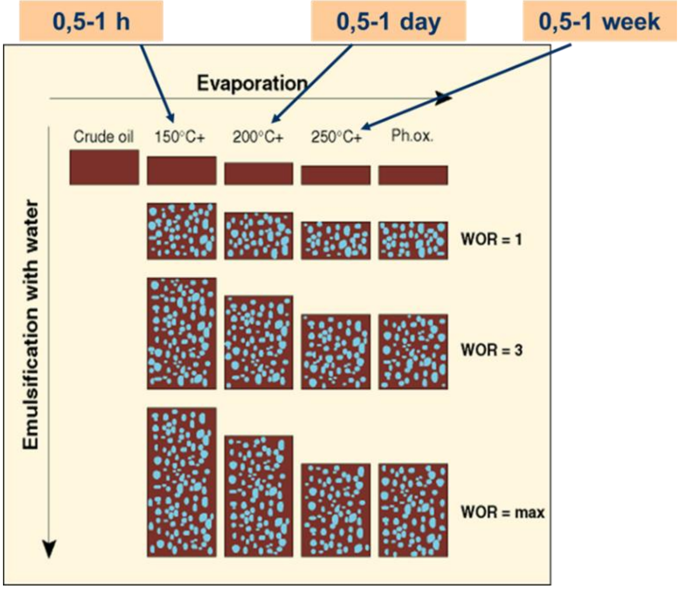
2x25 Litres of Oda crude oil arrived at SINTEF Ocean AS 12.04.2019 (Figure B-1). The crude oil was registered in LIMS (Laboratry information management system) for workflow and data tracking support, given the unique SINTEF ID 2019-4130. The weathering study were performed at 13 °C in agreement with Spirit Energy.

The crude oil was measured for water content by Karl Fisher titration and homogenized prior to topping /distillation. The water content was < 1 vol. %. Low water content in oil is important for HSE during the distillation step. Some "free gas" in the oil was observed. Flushing of excess gas was overnight before homogenization and topping, as described in the chapter below.

Figure B-1: 2 x 25 litres barrels of Oda crude oil arrived at SINTEF Ocean 12th April, 2019

B.2 Small-scale laboratory testing

To isolate and map the various weathering processes at sea, the crude oil was exposed to a systematic, stepwise procedure developed at SINTEF (Daling et al., 1990). The general procedure is illustrated in Figure B-2.



WOR: Water to Oil Ratio

WOR=1: 50 vol.% water

WOR=3: 75 vol.% water

WOR=max: the maximum water content

Figure B-2: Small-scale laboratory weathering flow chart of oil

B.2.1 Evaporation

The density of the oil was monitored during the degassing. This was performed before evaporation by standard procedure. The evaporation procedure used is described in Stiver and Mackay (1984). Evaporation of the lighter compounds from the fresh oil was carried out as a simple one-step distillation to vapour temperatures of 150 °C, 200 °C and 250 °C, which resulted in oil residues with an evaporation loss corresponding to approximately 0.5-1-hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface. These residues are referred to as 150°C+, 200°C+ and 250°C+, respectively.

B.2.2 Physical and chemical analysis

The viscosity, density, pour point and flashpoint of the fresh and water-free residues was analysed. In addition, wax content and "hard" asphaltenes was measured for the 250°C+ residue. Viscosity for all the w/o emulsions was determined. The analytical methods used are given in Table B-1 and Table B-2.

Table B-1: Analytical methods used to determine the physical properties

Physical property	Analytical method	Instrument
Viscosity	McDonagh et al, 1995	Physica MCR 300
Density	ASTM method D4052-81	Anton Paar, DMA 4500
Pour point	ASTM method D97	-
Flash point	ASTM D 56-82	Pensky-Martens, PMP1, SUR
Interfacial tension (IFT)	Pendant drop method	Krüss DSA100 Drop Shape Analyser

Table B-2: Analytical methods used to determine the chemical properties

Chemical property	Analytical method
Wax content	Bridiè et al, 1980
“Hard” asphaltene	IP 143/90

Chemical characterization by GC-FID and GC-MS

- The distribution of hydrocarbons (nC_5-nC_{40}) was analysed using a Gas Chromatograph coupled with a Flame Ionisation Detector (GC-FID). The Gas Chromatograph used was an Agilent 6890N with a 30m DB1 column.
- The analysis and quantification of PAHs, phenols and alkylated phenols (C_0-C_4) were completed using an Agilent 6890 Gas Chromatograph coupled with a, 5973 MSD detector (GC-MS) operating in SIM mode (Selected Ion Monitoring)

The volatile components were in the range of nC_5-nC_{10} and were quantified by use of PT-GC-MS (Purge and Trap Gas chromatograph Mass Spectrometer operating in full-scan mode and using a modified version of the EPA 8260 analysis method).

B.2.3 Emulsification properties

The w/o emulsification studies were performed by the rotating cylinders method developed by Mackay and Zagorski (1982), which is described in detail by Hokstad et al.,1993. The method includes the measuring of the following parameters:

- Relative water uptake (kinetics)
- Maximum water uptake
- Stability of the emulsion
- Effectiveness of emulsion breaker (Alcopol 60%)

The principle of the rotating cylinders method is illustrated in Figure B-3. Oil (30 mL) and seawater (300 mL) are mixed and rotated with a rotation speed of 30 rpm in separating funnels (0.5 L). The emulsification kinetics is mapped by measuring the water content at fixed rotation times. The maximum water content is determined after 24 hours of rotation.

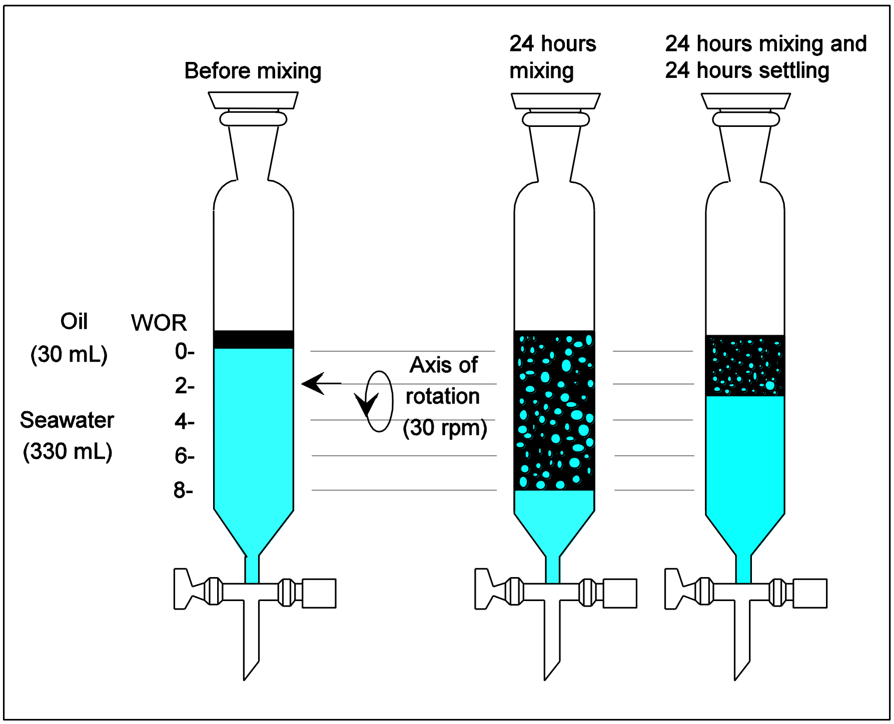


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Figure B-3: Principle of the rotating cylinder method

B.2.4 Chemical dispersibility testing

As a screening test, the oils dispersibility properties were tested using five different dispersants at a dosage of 1:25 (4 wt. %). The dispersants tested were; Dasic Slickgone NS, Corexit 9500A, Gamlen OD 4000, OSR-52 and Radiagreen OSD. For the dispersant showing greatest dispersibility, different dosages were studied. The screening was performed using the IFP method (discussed below) on the 200°C+ residue. For the dosage testing, both the IFP and the MNS tests were used. The viscosity of all the weathered samples was determined.

There are several different tests for evaluating the effect of chemical dispersants. The energy input will differ in the different tests, and the obtained efficiency will be representative of different wave energies. At SINTEF the IFP and MNS test is used in dispersibility testing.

IFP (Institute Francais du Petrole test, Bocard *et al.*, 1984) is a low energy test estimated to represent low wave energies (2-5 m/s wind speed). A surge beating up and down in the test vessel at a given frequency, gives energy input to the seawater column. The water column is continuously diluted, which gives a more realistic approach to field conditions, compared to other tests.

MNS (Mackay-Nadeau-Szeto test, Mackay and Szeto, 1980) is estimated to correspond to a medium to high sea-state condition. The energy input in this system, applied by streaming air across the oil/water surface, produces a circular wave motion. The sample of the oily water is taken under dynamic conditions after a mixing period of 5 min.

Both IFP and MNS test apparatus is shown in ***Figure B-4***.

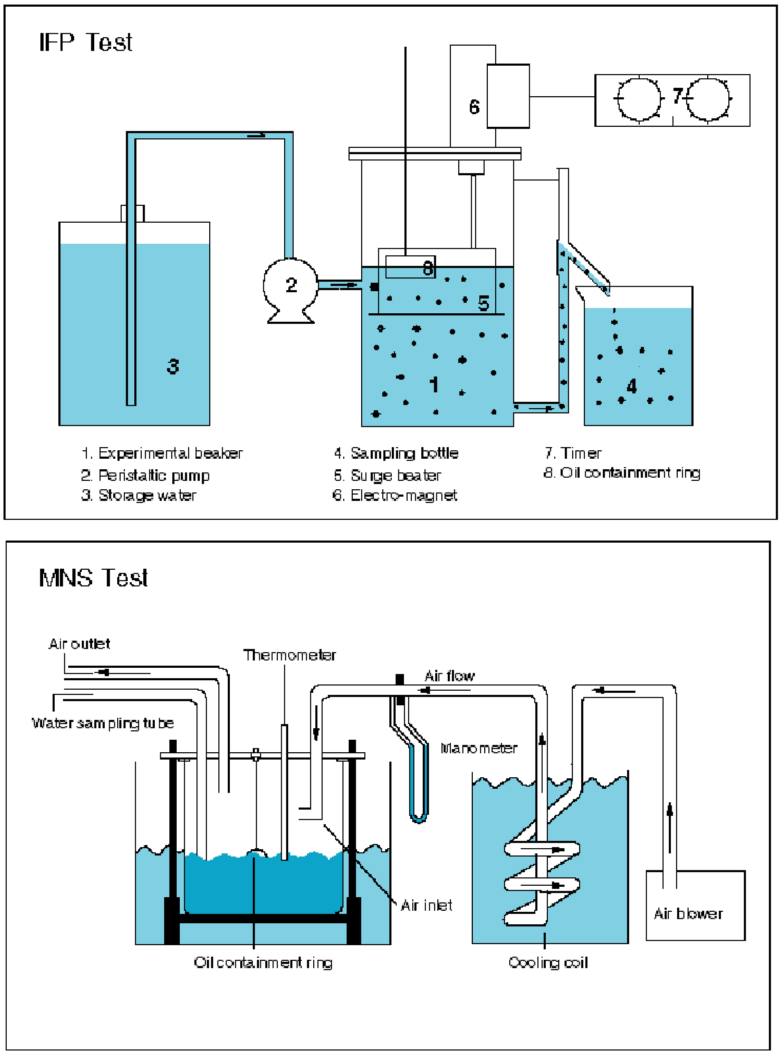

Figure B-4: IFP and MNS test apparatus.

B.3 Meso-scale laboratory testing

In an oil spill situation at sea, the weathering processes will occur simultaneously and affect each other. In the small-scale laboratory testing, these processes are studied individually. By using the meso-scale flume, the weathering and effect of dispersants can be studied under more realistic conditions, having the weathering processes to occur at the same time, giving a better image of the behaviour of the oil at sea.

B.3.1 Description of the flume basin

A meso-scale flume basin (Singsaas et al., 1993), located at SINTEF's Sealab, is routinely used to simultaneously study the weathering processes under controlled conditions. The meso-scale flume basin was rebuilt in 2006, having state of the art instrumentation. A schematic drawing of the flume is given in Figure B-5.

Approximately 5 m^3 seawater circulates in the 10 metres long flume. The flume basin is stored in a temperature-controlled room (0°C-20°C). Two fans are placed in a covered wind tunnel, controlling the wind speed. The fans are calibrated to simulate an evaporation rate corresponding to a wind speed of 5-10 m/s on the sea surface.

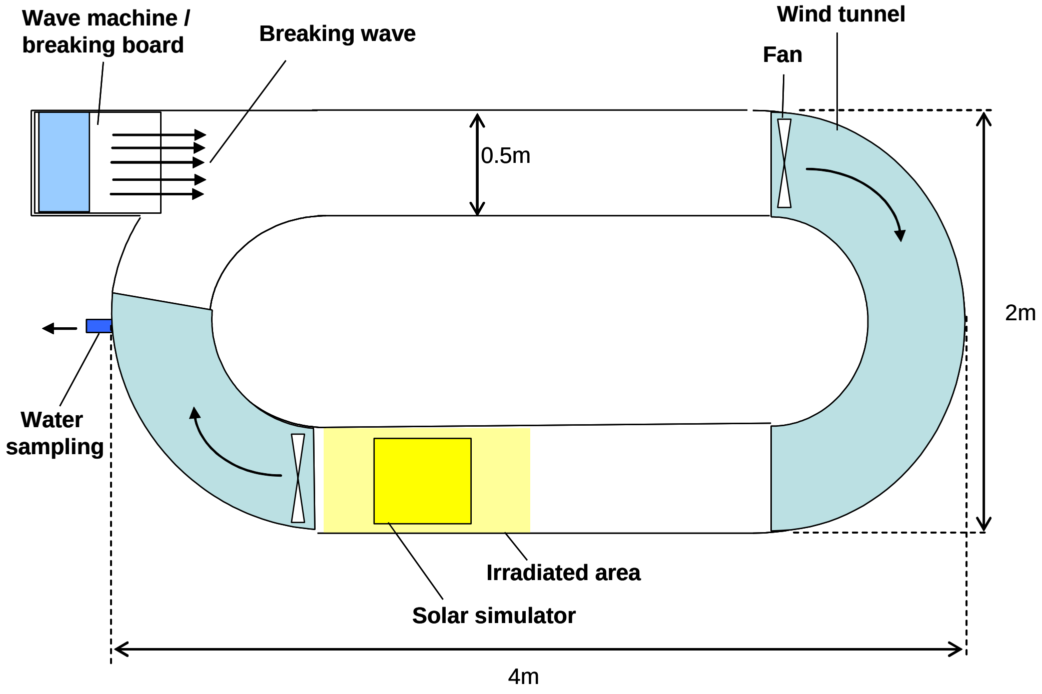

Figure B-5: Schematic drawing of the meso-scale flume

B.3.2 Oil weathering in the flume basin

In a meso-scale flume study, a standard volume sample (9 L) of the relevant oil is carefully released on the seawater surface under calm conditions. The wave machine and fans are then started, and the experiment begins. A reference water sample is collected before the beginning of the experiment. Both surface oil/emulsion and water column are sampled frequently the first 6 hours, then after 12 hours and subsequently every day.

After three days (72 hour) dispersant is applied to the surface emulsion. Water samples are then collected more frequently. The addition of dispersant may be repeated once or twice, in which case water samples are also collected.

Analysis of surface oil/emulsion

Samples of the surface oil/emulsion are collected using an aluminum tray and transferred to a 0.5 L separating funnel. The free water is removed after settling for 10 minutes in the climate room. The oil phase is further handled for an analysis of its physical properties.

The physical properties determined for all surface oil samples during the experiments are:

- Viscosity
- Water content
- Density
- Evaporative loss
- Emulsion stability

Analysis of water samples

Water samples are analysed for oil concentration in the water column (droplets and dissolved components). The samples are taken at a depth of 50 cm through a tap in the basin wall into a Pyrex glass bottle (1 L). The sampled water is acidified with some droplets of 10% HCl (pH < 2). The sampling position is shown in Figure B-5. Samples are then extracted by liquid-liquid extraction with dichloromethane (DCM) and quantified by Ultraviolet (UV) spectrophotometry.

Solar simulation in the meso-scale flume

Sunlight is simulated with a solar simulator from Gmbh Steuernagel. The solar lamp (4 KW) emits a wavelength spectrum calibrated to fit natural sunlight at high noon and in the absence of clouds. Figure B-6 shows the measured spectrum from the solar simulator compared to one of the most widely used standard spectra for solar irradiance (CIE publication 85, 1989).

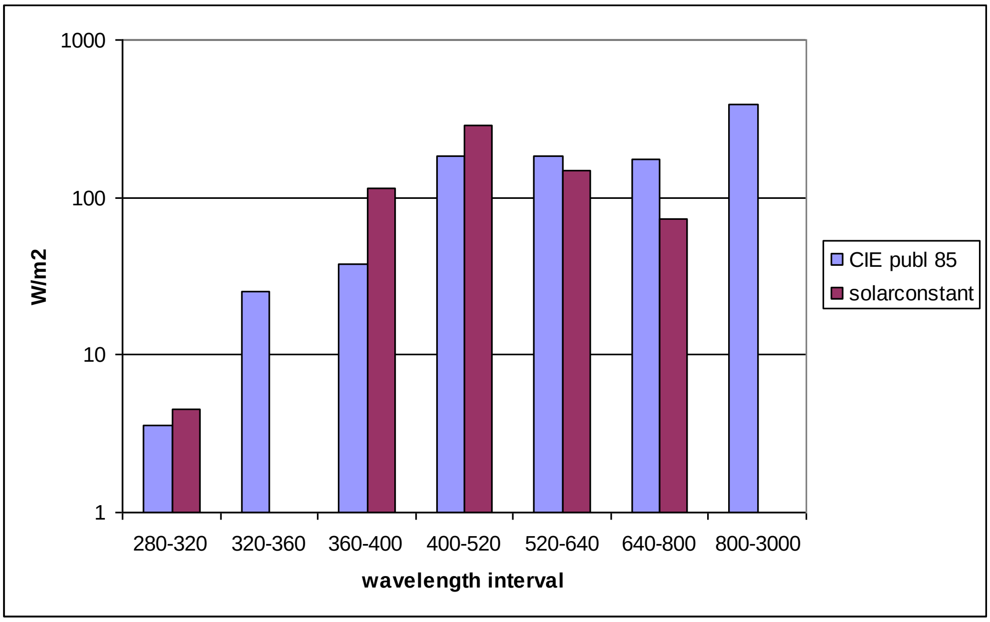

Figure B-6: Measured wavelength compared to standard spectrum suggested in CIE publication 85

The exact exposure of solar irradiance on the oil in the meso-scale flume is somewhat difficult to calculate. Since the oil is moving, it will only be within the irradiated area periodically. The exposure will be highly dependent on the distribution of the oil in the flume and the thickness of the emulsion on the water surface. In Figure B-7, an estimated irradiation per day, using the solar simulator, is compared with the average irradiation per day for selected Norwegian cities.

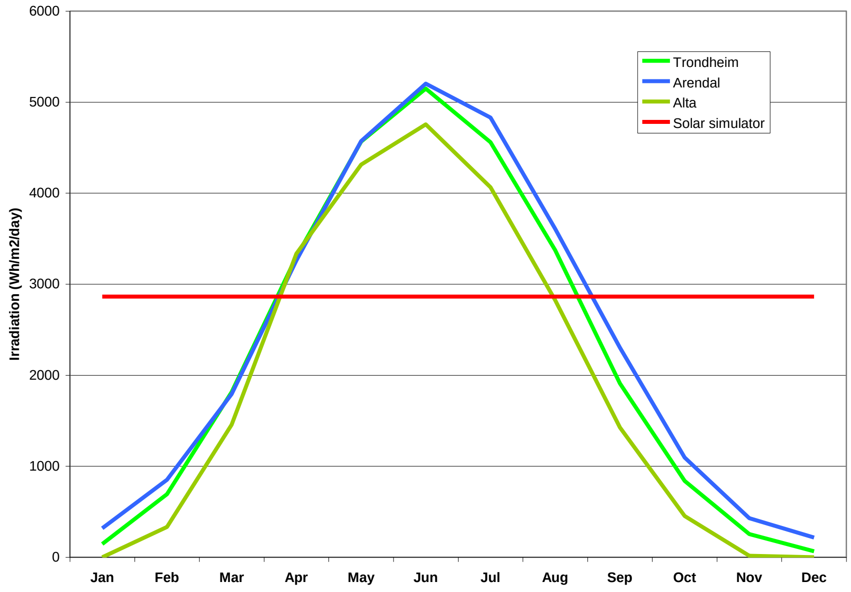

Figure B-7: Daily Irradiation for some Norwegian cities throughout the year compared with the estimated daily irradiation in the meso-scale flume

The simulated irradiance seems to be the approximate average of the daily irradiance throughout the year. It should be noted, however, that the simulations are not considering clouds. The real irradiation will be lower than that predicted in Figure B-7.

C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Oda crude oil is given in Table C-1 to C-3.The oil weathering predictions were based on the weathering study at 13 °C.

Table C-1: Physical and chemical properties for Oda crude oil

Properties of fresh oil	**Value**
Density (g/mL)	0.8204
Pour point (°C)	-3
Reference temperature (°C)	13
Viscosity at ref. temp. (mPa·s = cP) *	10
Asphaltenes (wt. %)	0.44
Wax Content (wt. %)	5.58
Dispersible for visc. <	5000
Not dispersible for visc. >	15000

** Measured at shear rate 100 s^{-1}*

Table C-2: True boiling point (TBP) curve for Oda crude oil

Temp. (°C)	**Cumulative yield (vol. %)**
36	5.6
69	8.9
98.5	14.3
126	20.6
158	24.5
174	30
196	33.8
216	54.99
235	40.8
254	44.4
271	48
287	51
302	53.9
316	56.7
329	59.3
343	61.6
368.5	65.9
380	67.8
391	69.5
402	71.2
431.5	75.8
450	78.6
467	81
496	83

**TBP from Stock tank oil PVT. Compositional Analysis of MDT Oil samples from Well 8/10-B-3 H, Oda field- Weatherford Laboratories Sept. 2018*

Table C-3: Lab weathering data for Oda crude oil at 13 °C

Properties	**Fresh**	**150°C+**	**200°C+**	**250°C+**
Boiling Point Temp. (°C)	-	199	255	315
Vol. Topped (%)	0	25.5	35.5	46.4
Weight Residue (wt. %)	100	78.3	68.9	58.2
Density (g/mL)	0.8024	0.8622	0.8757	0.8901
Pour point (°C)	-3	12	18	24
Flash Point (°C)	-	40.5	76.5	116.5
*Viscosity of water-free residue (mPa.s =cP)	10	125	423	1146
**Viscosity of 50% emulsion (mPa.s = cP)	-	538	992	8610
**Viscosity of 75% emulsion (mPa.s = cP)	-	2487	6548	-
**Viscosity of max water (mPa.s = cP)	-	6312	17805	31081
Max. water cont. (vol. %)	-	91	84.4	76.2
(T1/2) Halftime for water uptake (hrs)	-	0.1	0.22	0.24
Stability ratio	-	1	1	1

** Measured at shear rate 100* s^{-1}
*** Measured at shear rate 10* s^{-1}
- No data

D Chemical characterization on GC-MS (OSCAR oil profile)

The OSCAR oil profile is based on the quantification of semi-volatile organic hydrocarbons (SVOC) and volatile organic hydrocarbons (VOC) by GC-MS. The composition is divided into individual pseudo-component groups (OSCAR groups) representing the oil from the TBP (True Boiling Point) fractions.

Table D-1: Chemical characterization ("oil profile") of Oda fresh oil derived from GC-MS analysis and TBP oil fraction

Oda wt.%	Goups	Pseudo-components
3.000	1	C1-C4 gasses (dissolved in oil)
2.500	2	C5-saturates (n-/iso-/cyclo)
2.116	3	C6-saturates (n-/iso-/cyclo)
0.384	4	Benzene
3.500	5	C7-saturates (n-/iso-/cyclo)
0.656	6	C1-Benzene (Toluene) et. B
6.844	7	C8-saturates (n-/iso-/cyclo)
0.882	8	C2-Benzene (xylenes; using O-xylene)
3.916	9	C9-saturates (n-/iso-/cyclo)
0.702	10	C3-Benzene
3.500	11	C10-saturates (n-/iso-/cyclo)
0.045	12	C4 and C4 Benzenes
5.455	13	C11-C12 (total sat + aro)
0.000	14	Phenols (C0-C4 alkylated)
0.308	15	Naphthalenes 1 (C0-C1-alkylated)
7.192	16	C13-C14 (total sat + aro)
0.000	17	Unresolved Chromatographic Materials (UCM: C10 to C36) 0 0 0
0.000	37	metabolite 1
0.000	38	metabolite 2
0.494	18	Naphthalenes 2 (C2-C3-alkylated)
6.006	19	C15-C16 (total sat + aro)
0.249	20	PAH 1 (Medium soluble polyaromatic hydrocrbns (3 rings-non-alkyltd;<4 rings)
5.751	21	C17-C18 (total sat + aro)
5.500	22	C19-C20 (total sat + aro)
8.712	23	C21-C25 (total sat + aro)
0.288	24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)
32.000	25	C25+ (total)

The SINTEF OSCAR model is a 3-dimensional Oil Spill Contingency And Response model system that calculates and records the distribution (as mass and concentrations) of contaminants on the water surface, on shore, in the water column and in sediments. The model allows multiple release sites, each with a specified beginning and end to the release. This allows time-variable releases at a given location, as well as throughout the study area. The model computes surface spreading, transport, entrainment into the water column, evaporation, emulsification and shore interactions to determine oil drift and fate at the surface. In the water column, horizontal and vertical transport by currents, dissolution, adsorption, settling and degradation are simulated. By modelling the fate of individual pseudo-components, changes in the oil composition due to evaporation, dissolution and degradation are accounted for.

E Yield stress rheology

Yield stress is defined as the force that must be overcome so that an oil can spread / flow like a liquid on the sea (also known as the flow limit). This force is called the fluids "yield stress" or flow limit and is given the unit Pascal (Pa). Many crude oils (and emulsions) are so-called Bingham-plastic fluids at sea temperature. This means that applied force must be exerted on the fluid to make it flow and hence spread and is mainly pronounced for *non-Newtonian* oils where the viscosities varies with the shear rate. Yield stress can be utilized in modelling tool for modelling spreading of oil on the sea surface and for calculation of oil terminal film thicknesses.

The measurements were performed by applying a gradually increasing oscillating force to the sample. The instrument measure the sample's response to the exerted oscillating. The yield stress is derived from measurement of oscillation stress-sweep with increasing applied force on the sample where the deformation of the oil sample is measured. Results from the yield stress measurements of Oda are tabulated in Table E-1, below.

Table E- 1 Yield stress (flow limit) measurements for Oda at 13 °C measured with Physica MRC 300 rheometer

Residue	**Water Content (Vol%)**	**Yield stress (Flow limit) (Pa)**	**Deformation**
Fresh	0	-	-
150°C+	0	4.14	No data
200°C+	0	0.46	0.34
250°C+	0	14.5	1.12
150°C+	50	0.32	3.51
200°C+	50	0.88	4.46
250°C+	50	2.31	0.59
150°C+	75	0.95	0.52
200°C+	75	3.67	0.72
250°C+	65	65	2.45
150°C+	91*	35.9	18.7
200°C+	84*	32.8	3.48
250°C+	76*	48.2	2.50

-: *No yield stress quantified *Maximum water*

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