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# Report

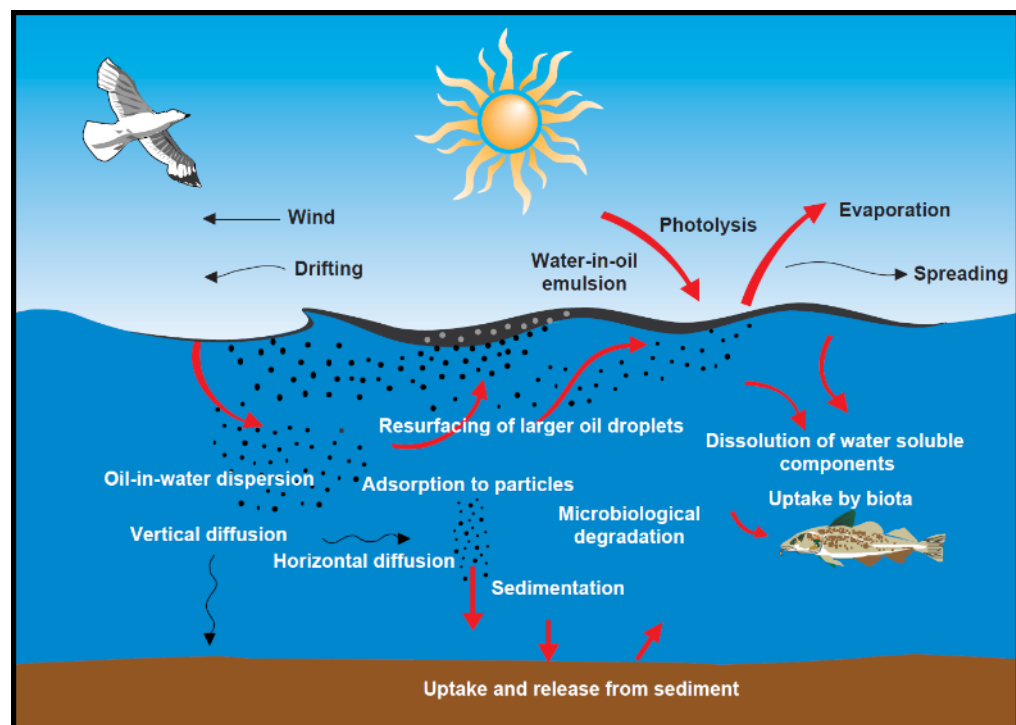
## Wisting Central crude oil – Properties and behaviour at sea

In relation to oil spill response

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# Report

## Wisting Central crude oil – Properties and behaviour at sea

In relation to oil spill response

**KEYWORDS:**Weathering properties;  
Emulsification;  
Dispersibility**VERSION**

2.0

**DATE**

2017-06-02

**AUTHORS**Kristin R. Sørheim  
Oddveig M. Bakken**CLIENT(S)**

OMV Norge

**CLIENT'S REF.**

Svein-Olav Drangeid

**PROJECT NO.**

302002273

**NUMBER OF PAGES/APPENDICES:**

69 including 5 appendices

**ABSTRACT**

A weathering study and dispersibility testing were performed on Wisting Central crude oil at 5°C. The SINTEF Oil Weathering Model (OWM) was used to predict the weathering properties of Wisting Central at 2 and 5°C. The weathering properties were also discussed in relation to oil spill response by mechanical containment and recovery, and chemical dispersion.

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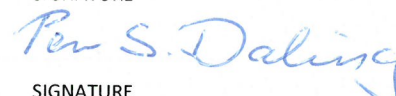
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**REPORT NO.**  
2017:00119**ISBN**  
978-82-14-06714-9**CLASSIFICATION**  
Unrestricted**CLASSIFICATION THIS PAGE**  
Unrestricted

# Document history

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VERSION	DATE	VERSION DESCRIPTION
1.0	2017-05-22	Draft version

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2.0	2017-06-02	Final version approved by OMV Norge
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## Executive summary

Spilled oils undergo changes when weathering on the sea surface that affect behaviour and oil spill countermeasures in various ways. Oil weathering varies over time and with different environmental conditions. This summary gives a brief overview of the main changes predicted for Wisting Central crude oil when weathered on the sea surface. The SINTEF Oil Weathering Model (OWM) has been used to predict the oil weathering properties as a function of time.

Wisting Central is categorized as a medium density naphthenic crude oil (0.838 g/mL) with low asphaltene (0.05 wt. %) and wax content (0.72 wt. %) compared with other Norwegian crude oils. The fresh oil and its residues have very low pour points (<-36 °C). The high initial evaporative loss results in an increase of the asphaltene and wax content, which contribute in stabilising the water-in-oil (w/o) emulsions.

Wisting Central formed low viscous water-in-oil (w/o) emulsions with a relatively slow and low maximum water uptake (60 vol. %). The emulsions of Wisting Central effectively released water (45-60 vol.%) when adding emulsion breaker (Alcopol O 60 %) with concentrations of 500 and 2000 ppm by weight. The lowest concentration of 500 ppm was shown to be sufficient to break the emulsions. Emulsion breaker could effectively be used during an oil spill operation to remove or reduce water from the emulsion, normally injected at the skimmer head prior transfer to storage tank to minimize the storage volume.

The OWM prediction of mass balances show that Wisting Central will be removed from the sea surface within 1 day in high wind speeds (15 m/s) at 2 and 5°C, and nearly removed within 5 days at wind speed of 10 m/s due to the high degree of evaporative loss and natural dispersion/entrainment. However, after 5 days with calm weather conditions (2 m/s wind speed) as much as ~65 % of the oil remains on the sea surface.

Oil spilled on the sea surface assumes to reach the ambient water temperature within short time period. The fire and explosion hazard will be high as long as the flash point of the oil is below the sea temperature. For Wisting Central crude oil, the flash point is predicted to exceed the sea temperature within 15 minutes at 2 m/s wind speeds, and faster at higher wind speeds. Some storage tanks in vessels engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C. Wisting Central will reach this limit within 6 hours after a spill at calm wind speed (2 m/s), and more rapidly at higher wind speeds.

In mechanical recovery operation, low oil/emulsion viscosity < 1000 mPa.s may pose a potential for boom leakage that has to be taken into account with respect to lower vessel speed during recovery. In no breaking wave conditions (wind speeds of 2 and 5 m/s), the oil/emulsion viscosities are below this viscosity limit for > 5 and 2 days, respectively. At higher wind speeds, the emulsions are predicted to surpass 1000 mPa.s within 6-12 hours. Due to the low emulsion viscosities, reduced flowability towards traditional weir skimmers will not be a problem with typically viscosity limit for flowability < 15-20 000 mPa.s for Wisting Central. In cases when high viscosity of the oil/emulsion is not a limiting factor, high pour point may cause solidification on the sea surface (typically arises 10-15 °C above the sea temperature). However, Wisting Central has low pour points (-36 °C), and solidification of the oil residue is not expected on the sea surface at 2 and 5 °C.

Wisting Central has a good potential for use of oil spill dispersant. The oil was estimated to be easily dispersible with use of dispersant (Dasic NS) for viscosities < 3000 mPa.s and showed some reduced dispersible for viscosities > 3000 mPa.s with dispersant to oil ratio (DOR) 1:25. The predicted time-window estimates that the oil/emulsion is good dispersible within 5 days of weathering at sea temperature of 2 and 5 °C. The upper limit for when the oil/emulsion is considered as not dispersible was not reached with use of the MNS high-energy test (breaking waves conditions, reflecting wind speed > 5 m/s), which also implies a wide time-window for use of dispersant for this crude oil. The MNS-test with no dispersant added also showed that Wisting Central has a potential to easily be naturally dispersed into the water column in in breaking waves conditions.

In general, when the oil expects to have a reduced dispersibility within 0.5-1 hour after the dispersant spraying operation, additional energy or use of a higher dispersant dosage and/or repeated dispersant application, particularly in calm sea conditions, may be required to increase the dispersant efficiency. Providing additional

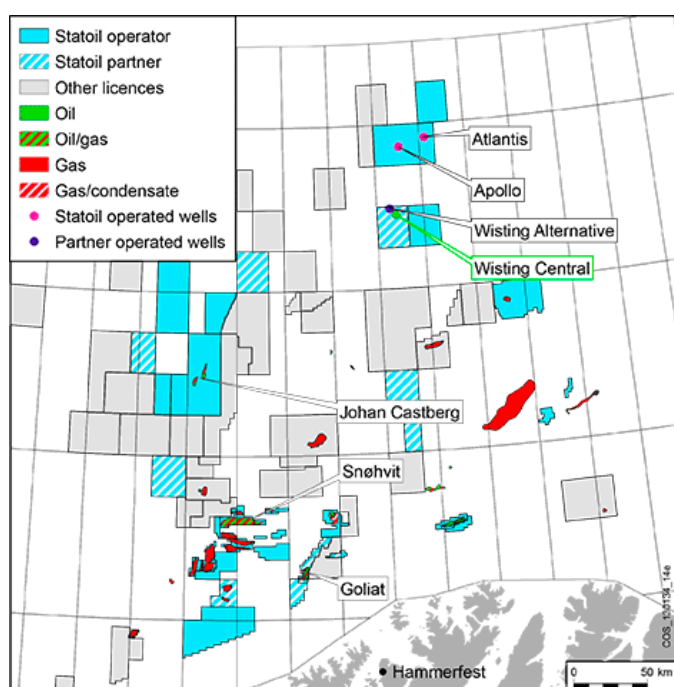
energy with use of firefighting (FiFi) systems, thrusters or MOB boats after the dispersant application may enhance the rate of dispersion. Wisting Central was found to be reduced chemically dispersibility with viscosities > 3000 mPa.s.

## 1 Introduction

New oil types, from heavy crude oil to light crude oils and condensates with varying properties, are continuously coming into production both in Norway and worldwide. Due to large variations in different crude oils' physical and chemical properties, their behaviour and fate may vary greatly if spilled at sea. E.g. 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, having good knowledge about the expected behaviour of oil at sea in case of an accidental spill is highly valuable.

The Deepwater Horizon incident in the Gulf of Mexico (2010) clearly showed how dispersant application efficiency may change as the oil is weathered and emulsified on the sea surface over a longer period. This may form important support for refining operative strategies in terms of where, when and how dispersants could be effectively applied during a response operation.

According to the Norwegian Environment Agency and the Petroleum Safety Authority Norway regulations for petroleum activities (Aktivitetsforskriften §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, Dept. of Environmental Technology has performed a weathering study and dispersibility testing of the Wisting Central crude oil based on a request from OMV Norge. The weathering study was conducted at 5 °C considered as a relevant sea temperature in the Barents Sea. The obtained weathering data were used to predict the weathering properties of the oil by use of the SINTEF Oil Weathering Model (OWM), if spilled at sea under different weather condition at sea temperature of 2 and 5 °C.



Wisting Central II in licence PL537 / Wisting (Hoop area), is located 310 km north of Hammerfest and around 180 km away from the nature reserve Bjørnøya (Bear Island), Wisting Central II is the fifth well in the production license PL537, which was awarded in the 20th licensing round in 2009. The Wisting Central II well is the first horizontal appraisal well in the Barents Sea and sets a new drilling record; it is the shallowest horizontal offshore well drilled from a floating drilling facility. Water depth at Wisting is 402 meters.

OMV (Norge) AS as operator has 25% share in the PL537 license. Joint venture partners are Petoro (20%), Idemitsu (20%), Tullow (20%) and Statoil (15%).

[https://www.omv.com/portal/01/com/omv/OMV\\_Group/upstream/norway/activities\\_in\\_barents\\_sea](https://www.omv.com/portal/01/com/omv/OMV_Group/upstream/norway/activities_in_barents_sea)

[https://www.omv.com/portal/01/com/omv/OMV\\_Group](https://www.omv.com/portal/01/com/omv/OMV_Group)

**Figure 1-1: Location of the Wisting discovery**

<http://subseaworldnews.com/wp-content/uploads/2013/09/Statoil-OMW-Pleased-with-Wisting-Central-Oil-Discovery-in-Barents-Sea.gif>



## 2 Experimental results and discussion

### 2.1 Small-scale laboratory testing results

The methodology of small-scale testing is described in Appendix B. The small-scale weathering results of Wisting Central crude oil were compared with similar data of other crude oils from the Barents Sea region, which include previously study of Wisting Hanssen, Skrugard from the Johan Castberg oil field, Goliat Realgrunnen, and Alta (Table 2-1). The oils in comparison were selected in agreement with OMV Norge. Wisting Central crude oil was given the SINTEF ID 2016-320.

*Table 2-1: Oils compared with Wisting Central crude oil data in the report*

Oil	SINTEF-ID	Report Number	Reference
<b>Wisting Hanssen</b>	Akvaplan-niva AS	Report: 7419-01	Torske and Wasbotten, 2015
<b>Skrugard</b>	2011-0559	SINTEF:A22589	Øksenvåg, 2012
<b>Goliat Realgrunnen*</b>	2001-0729	SINTEF: STF66 F03104	Moldestad et al., 2003
<b>Alta</b>	2015-0029	SINTEF: A27546	Hellstrøm and Johnsen, 2016

\*For simplicity, Goliat Realgrunnen is referred as Realgrunnen throughout this report.

#### 2.1.1 Chemical composition and physical properties

Figure 2-1 shows the chemical composition as the hydrocarbon profile of Wisting Central, whereas the wax and asphaltene content are given in Table 2-3. The physical properties are given in and Table 2-4. Appendix D shows the composition groups derived from the chemical characterization of the fresh crude oil on GC-MS.

##### Gas chromatographic flame ionization detector (GC-FID) characterization

The hydrocarbon profile of the fresh Wisting Central crude oil was analysed by use of gas chromatography (GC) coupled with Flame Ionization detector (FID) (Figure 2-1). The figure includes the gas chromatographic characterization of the evaporated residues of 150°C+, 200°C+, and 250°C+. Figure 2-2 shows the GC-chromatograms of other fresh crude oils in comparison with Wisting Central.

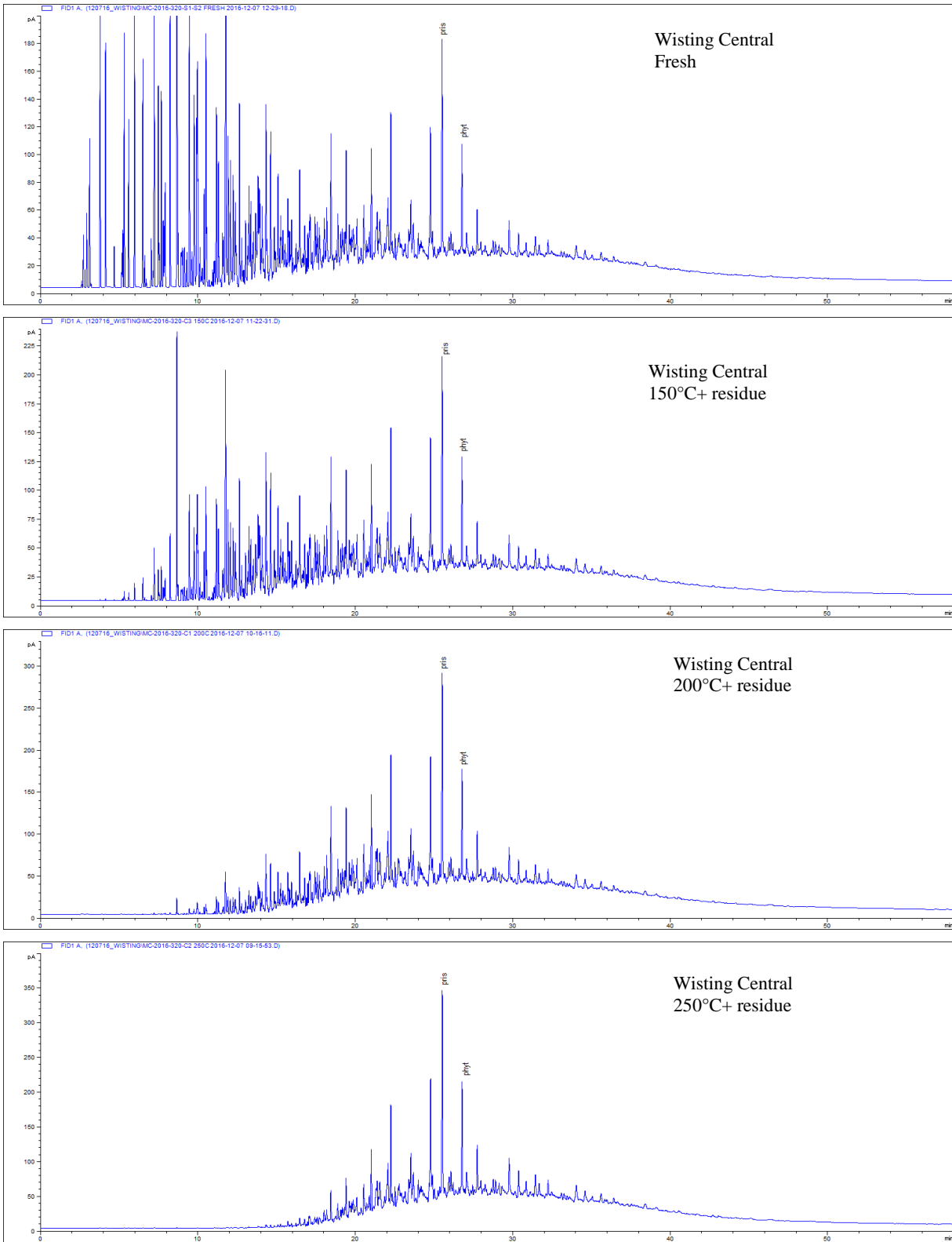
Based on the GC-FID characterisation, Wisting Central is a highly biodegraded (naphtenic) crude oil that lacks of the typically systematic narrow peaks of the straight-chained *n*-alkenes (paraffins). Skrugard is also a biodegraded crude oil with low content of the systematic peaks of *n*-alkanes in the lower range < *n*C13-*n*C15). Wisting Hanssen and Realgrunnen have similarities in their hydrocarbon profiles, where both oils are biodegraded, but also have high peaks of *n*-alkanes with increasing carbon number, reflecting the wax components (> *n*C20). Alta is a typically paraffinic crude oil, which exhibits systematic *n*-alkanes in the area of *n*C5-*n*C36.

GC-FID is also a tool in oil spill identification, where common screening parameters are the *n*C17/pristane and *n*C18/phytane ratios. These ratios give the relation between the *n*-alkanes and isoprenoids (pristane and phytane). Thus, biodegradation results in a reduced ratio between the *n*-alkanes and the isoprenoids. The ratios for Wisting Central and the other crude oils in comparison are given in Table 2-2.

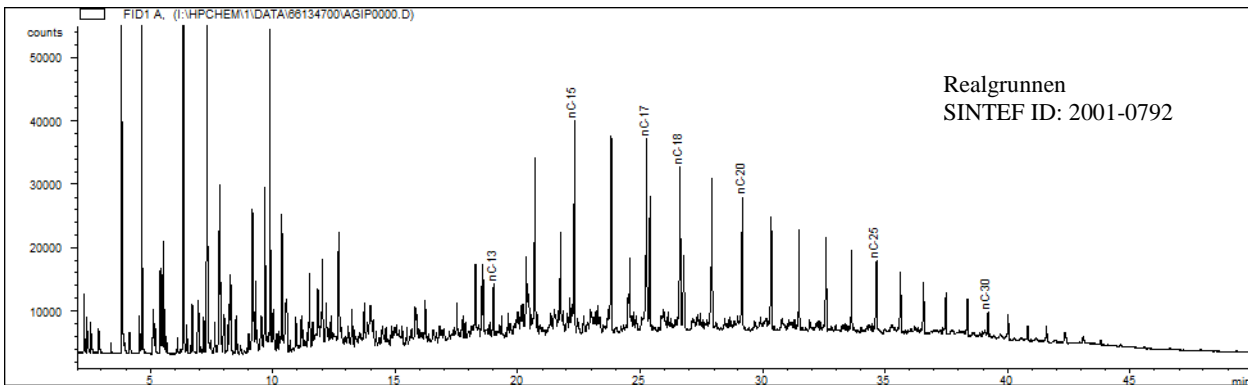
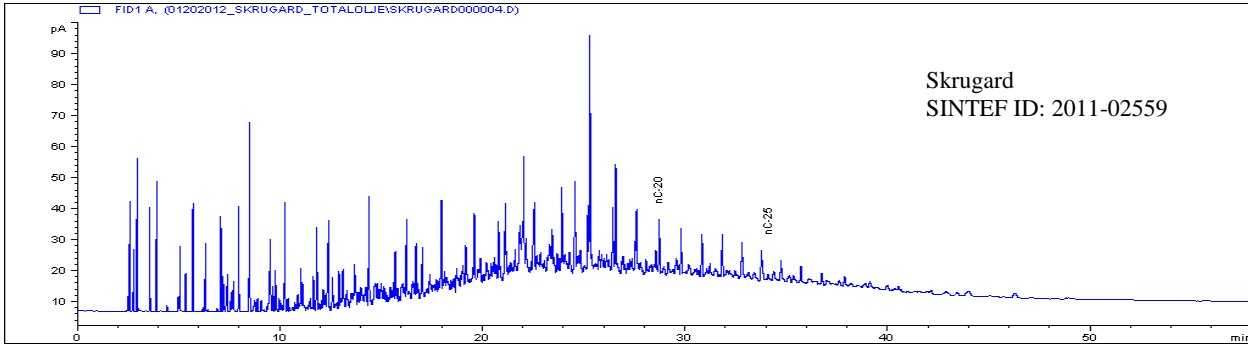
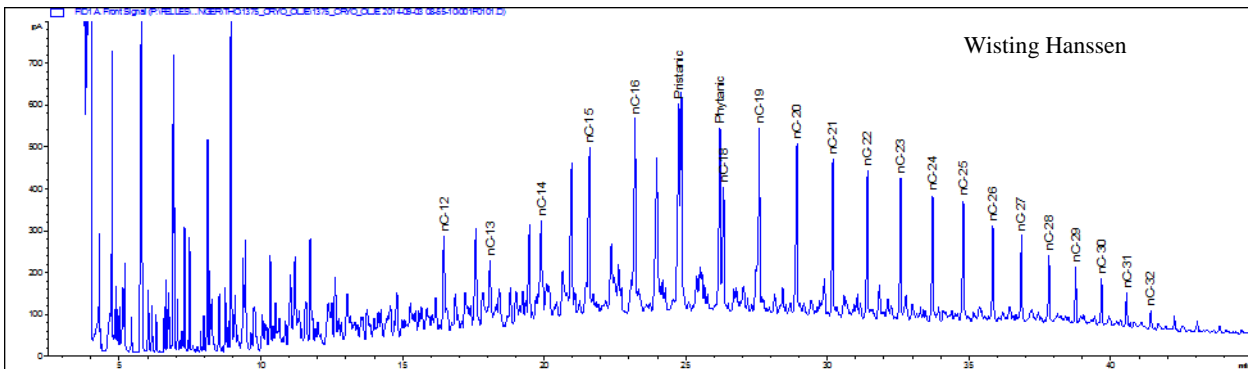
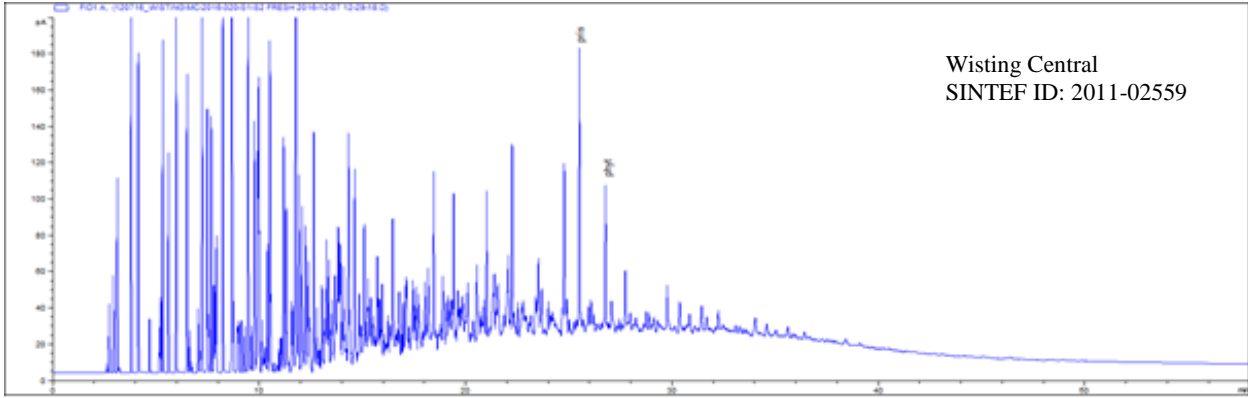
*Table 2-2: *n*C17/Pristane and *n*C18/Phytane ratios*

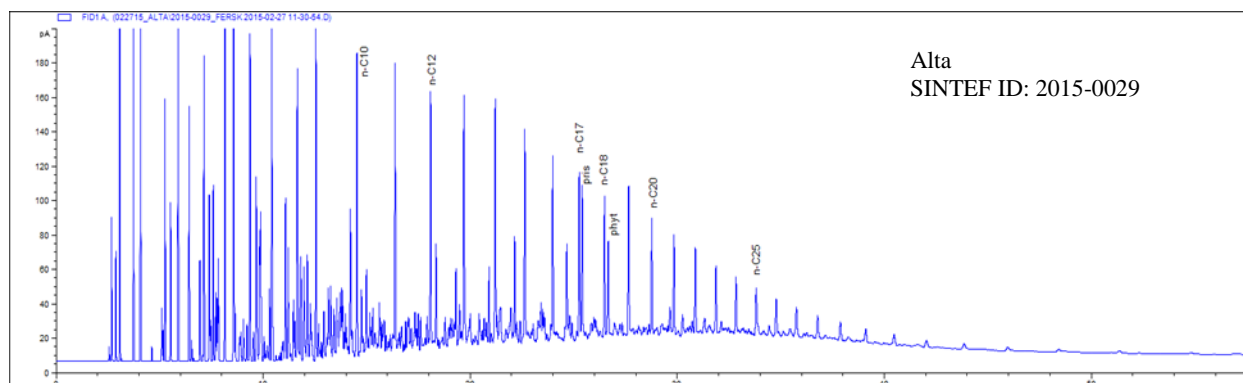
Oil	<i>n</i> C17/Pristane	<i>n</i> C18/Phytane
<b>Wisting Central</b>	-	-
<b>Wisting Hanssen</b>	0.9	1.5
<b>Skrugard</b>	0.3	0.6
<b>Realgrunnen</b>	1.5	2.4
<b>Alta</b>	1.1	1.5

-: Ratios not possible to obtain due to lack of *n*-alkanes of *n*C17 and *n*C18



**Figure 2-1: GC/FID chromatograms of fresh sample and evaporated residues of Wisting Central crude oil**





Alta  
SINTEF ID: 2015-0029

**Figure 2-2: GC/FID chromatograms for fresh oils used for comparison**

### Asphaltene and wax content fresh and weathered residues

The chemical properties of asphaltene and wax are given in Table 2-3. Wisting Central has low content of both asphaltene (0.05 wt. %) and wax (0.71 wt. %), and is most comparable to the Skrugard crude oil. Wisting Hanssen, Realgrunnen and Alta have all medium content of wax compared to other Norwegian crude oils, and exhibit low contents of asphaltene. Although, Realgrunnen has a slightly higher content of both wax and asphaltenes compared with the other oils.

**Table 2-3: Asphaltene ("hard") and wax content for different oils and their residues**

Oil type	Residue	Asph. "hard" (wt. %)	Wax (wt. %)
<b>Wisting Central</b>	Fresh	0.05	0.71
	150°C+	0.06	0.84
	200°C+	0.07	0.97
	250°C+	0.08	1.2
<b>Wisting Hanssen</b>	Fresh	0.03	3.3
	150°C+	0.03	3.7
	200°C+	0.03	4.1
	250°C+	0.04	4.6
<b>Realgrunnen</b>	Fresh	0.14	5.1
	150°C+	0.17	5.8
	200°C+	0.19	6.5
	250°C+	0.21	7.4
<b>Skrugard</b>	Fresh	0.05	1.9
	150°C+	0.05	2.0
	200°C+	0.06	2.1
	250°C+	0.06	2.4
<b>Alta</b>	Fresh	0.03	3.1
	150°C+	0.03	3.7
	200°C+	0.04	4.2
	250°C+	0.04	5.1

### Physical properties of fresh and weathered residues

Physical properties of Wisting Central and the other crude oils for comparison are listed in Table 2-4. Wisting Central and Alta crude oil exhibit the highest evaporative loss, which also reflect the lowest densities. Wisting Central has very low pour points for both the fresh oil and the residues (<-36°C), which reflects lack of paraffins. The pour points for the other crude oils increase with increasing evaporative loss, and Alta and Realgrunnen reach both high pour points of the 200 and 250°C+ residue (12-18°C). Wisting Central, Wisting

Hanssen and Skrugard have low viscosities for the fresh oil and their residues, whilst Realgrunnen reaches the highest viscosity particularly for the 250°C+ residue due to the high wax content. The flash points of the oils are more or less comparable within the oils.

**Table 2-4: Physical parameters of Wisting Central in comparison with other crude oils**

Oil type	Residue	Evap. (vol. %)	Residue (wt. %)	Density (g/mL)	Flash point (°C)	Pour point (°C)	Visc. (mPa.s) 5°C (10 s <sup>-1</sup> )	IFT (mN/m) ini.
<b>Wisting Central</b>	Fresh	0	100	0.838	-	<-36	10	30
	150°C+	17	85	0.859	40	<-36	25	28
	200°C+	29	74	0.871	79	<-36	62	29
	250°C+	42	61	0.883	120	<-36	206	29
<b>Wisting Hanssen</b>	Fresh	0	100	0.845	21	<-33	97	24
	150°C+	10	90	0.857	61	-12	74	-
	200°C+	18	82	0.862	83	-3	167	-
	250°C+	28	72	0.869	111	3	320	-
<b>Skrugard</b>	Fresh	0	100	0.871	-	<-36	32	-
	150°C+	6	95	0.879	61	-33	54	-
	200°C+	11	91	0.884	88	-21	70	-
	250°C+	23	78	0.891	119	6	171	-
<b>Realgrunnen</b>	Fresh	0	100	0.857	-	-12	21	22
	150°C+	14	88	0.869	45	9	1411	21
	200°C+	24	78	0.877	84	18	3890	23
	250°C+	34	68	0.884	124	18	10300	23
<b>Alta</b>	Fresh	0	100	0.827	-	-15	49	19
	150°C+	19	83	0.853	40	3	277	21
	200°C+	29	74	0.863	76	12	698	22
	250°C+	43	61	0.876	117	15	3606	22

-: No data

## 2.1.2 Emulsifying properties of Wisting Central crude oil

### 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 also increases the total volume of oil due to the uptake of water into the oil. Highly stable emulsified oil can be more difficult to recover and may be difficult to chemical disperse.

The emulsifying properties of Wisting Central were studied by use of the rotating cylinders as e.g. described in Hokstad et al., 1993, see Appendix B. Four parallels of the residues of 150°C+, 200°C+ and 250°C+ were made in order to produce data for stability, viscosity, maximum water uptake, kinetics, and the effectiveness of application of emulsion breaker. The emulsions of maximum water content after 24 hours rotation are shown in Figure 2-3, below. The figure shows from left to right emulsions prepared from the residues of 150°C+, 200°C+ and 250°C+, respectively.



*Figure 2-3: The rotating cylinders at the start and after 24 hours of rotation at 5 °C*

### Water uptake and maximum water content

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

Wisting Central expresses low rate of water uptake for the 150°C+ residue, but reaches a high water content of 78 vol. % after 24 hours rotating time (Table 2-5). The 200 and 250°C+ residues emulsified faster compared to the 150°C+ residue, but reach a lower maximum water content of 62 and 52 vol. %, respectively.

**Table 2-5: Water uptake for the evaporated residues of Wisting Central crude oil at 5 °C**

Mixing time	150°C+ (Vol. % water)	200°C+ (Vol. % water)	250°C+ (Vol. % water)
Start	0	0	0
5 min	8	12	12
10 min	14	15	19
15 min	14	15	25
30 min	25	31	40
1 hour	32	43	46
2 hours	39	55	50
4 hours	56	63	52
6 hours	69	66	52
24 hours	78	67	52
t <sup>1/2</sup>	1.70	0.63	0.25

### Stability and efficiency of emulsion breaker

Overall, the findings of stability and the efficiency of emulsion breakers is important in a mechanical recovery situation because separating the oil from water enables optimal use of available storage facilities/tankers. The emulsified oil volume decreases considerably with treatment of an emulsion breaker as water is removed.

The emulsion stability of Wisting Central crude oil was studied by quantifying the amount of water released from the emulsion during 24 hours settling time. In addition, the effectiveness of adding the emulsion breaker Alcopol O 60 % to the emulsion was evaluated. The results are tabulated in Table 2-6. The oil formed stable emulsions, but the emulsions were easily broken when applying emulsion breaker with concentrations of 500 and 2000 ppm (wt.).

**Table 2-6: Stability of emulsion and the effectiveness of emulsion breaker at 5 °C of Wisting Central**

Residue	Emulsion breaker	Water-in-oil emulsion (vol. %) at 5 °C		Stability ratio**	Stability ratio after rotation
		Reference	24 hours *		
150°C+	none	78	77	0.95	0.86
200°C+	none	67	67	1.00	1.00
250°C+	none	52	52	1.00	1.00
150°C+	Alc. O 60 % 500 ppm	78	3	0.01	-
200°C+	Alc. O 60 % 500 ppm	67	12	0.06	-
250°C+	Alc. O 60 % 500 ppm	52	9	0.09	-
150°C+	Alc. O 60 % 2000 ppm	78	6	0.02	-
200°C+	Alc. O 60 % 2000 ppm	67	6	0.03	-
250°C+	Alc. O 60 % 2000 ppm	52	6	0.09	-

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 during 24 hours settling. Stability ratio of 1 implies a totally stable emulsion

-no data

### Viscosity of emulsified residues

The viscosity expresses the oils ability to resist gradually 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 applies on so-called *non-Newtonian* oils, the viscosity of such oils decreases.

The viscosities of the water-free residues and emulsified residues of Wisting Central at 5°C is given in Table 2-7. The fresh oil and the water-free residues overall behave more or less as *Newtonian* fluids at shear rates of 10, 100 and 1000  $s^{-1}$ , although a slightly decrease in viscosity is observed for the 250°C+ residue. The w/o-emulsions behave more as *non-Newtonian* fluids, where the viscosities are higher at a lower share rate (10  $s^{-1}$ ) compared to higher shear rate (100  $s^{-1}$ ) due to increasing degree of weathering (evaporating and water uptake). Overall, the viscosities of the emulsions are low for Wisting Central. The yield stress, the force that must be applied to make the oil to begin to flow, is tabulated in Appendix E. The low yield stress substantiate that the oil has a potential to easily be spread on the sea surface.

**Table 2-7: Viscosity of residues / emulsions of Wisting Central at 5 °C**

Residue	Water content (vol. %)	Viscosity (mPa.s) 5 °C		
		10 $s^{-1}$	100 $s^{-1}$	1000 $s^{-1}$
<b>Fresh</b>	0	10	9	10
<b>150°C+</b>	0	25	25	35
<b>200°C+</b>	0	62	60	59
<b>250°C+</b>	0	206	162	157
<b>150°C+</b>	50	178	162	-
<b>200°C+</b>	50	439	355	-
<b>250°C+</b>	50	1229	774	-
<b>150°C+</b>	75	1060	338	-
<b>200°C+</b>	75	2058	614	-
<b>250°C+</b>	75	4734	1125	-
<b>150°C+</b>	83	810	219	-
<b>200°C+</b>	70	1857	762	-
<b>250°C+</b>	56	1622	966	-

\*not applicable

### 2.1.3 Chemical dispersibility

The dispersibility testing of Wisting Central crude oil included:

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

#### Screening and dosage testing of dispersants

The screening testing was performed using the low energy test (IFP), reflecting non-breaking waves (< 5 m/s wind speed) according to the Norwegian dispersant testing regulations. The screening testing was performed at a standard temperature of 13°C, using a 200°C+ residue emulsified with 50 vol. % seawater. The results from the screening testing are presented in Table 2-8, where Dasic NS and Corexit 9500 expressed the highest dispersibility effectiveness (86 and 82 %, respectively).



**Table 2-8: Screening testing on Wisting Central crude oil using the IFP-test at standard temperature of 13 °C**

Dispersant (DOR/DER =1:25)	Efficiency dispersant (200°C+ /50 vol. % emulsion)*
<b>Corexit 9500</b>	82
<b>Dasic NS</b>	86
<b>Finasol OSR 52</b>	72
<b>Gamlen OD 4000</b>	69
<b>Radiagreen OSD</b>	60

\* The viscosity of the emulsion 289 mPa.s ( $10s^{-1}$ )

The dosage testing was performed at 5°C, using a 200°C+ residue emulsified with 50 vol. % seawater with use of the high energy-test (MNS) and low-energy test (IFP). Based on the screening testing, the Dasic NS dispersant was chosen in accordance with the client. The dosage testing gives information about the design conditions for optimal use of dispersant agent with the dispersant-to-oil/emulsion ratios (DOR /DER) of 1:25, 1:50, 1:100 and 1:200, and no dispersant added. The results are presented in Table 2-9, and show an increasing effectiveness for the IFP-test with higher applied DOR. The MNS-results were all high at the different dosages indicating high dispersibility in breaking waves conditions (> 5 m/s wind speed). This was also measured with no dispersant added (> 90 % effectiveness MNS test)) which is not commonly observed for crude oils.

**Table 2-9: Dosage testing on Wisting crude oil using the IFP-and MNS-test at 5 °C**

Dispersant (DOR/DER)	Efficiency of dispersant on 200°C+/50 vol. % emulsion*	
	IFP	MNS
<b>Dasic NS (1:25)</b>	80	100
<b>Dasic NS (1:50)</b>	68	100
<b>Dasic NS (1:100)</b>	25	90
<b>Dasic NS (1:200)</b>	14	100
<b>No dispersant</b>	0	93

\*The viscosity of the emulsion 439 mPa.s ( $10s^{-1}$ )

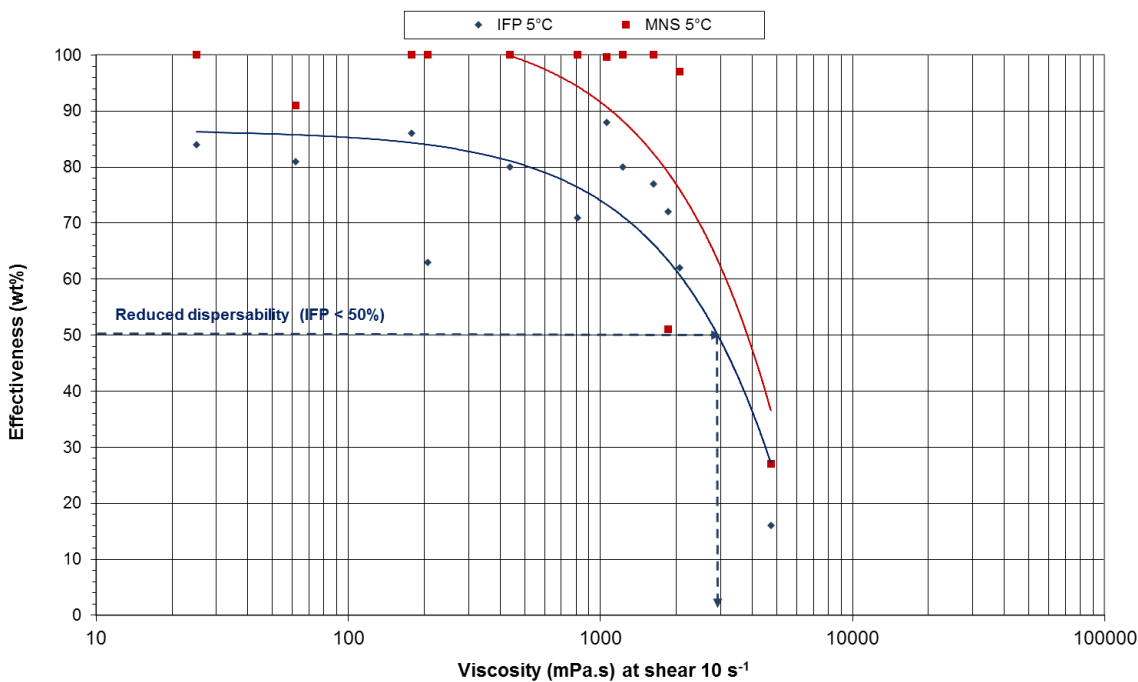
### **Systematic dispersant testing of the oil dispersibility at varying weathering**

Based on the screening testing, Dasic NS was chosen for the continued systematic testing of the oil dispersibility at varying weathering to determine the time window for dispersant use. Dasic NS is also the dispersant agent in NOFO's stockpile, and a dosage rate of 1:25 (4 wt.%) is used as the standard procedure used to establish the time window for dispersant application.

Table 2-10 shows the results from this testing as basis to estimate the dispersibility limits expressed as a function of effectiveness and viscosities (see Figure 2-4). The "window of opportunity" was predicted by use of the SINTEF Oil Weathering Model (OWM) based on the input data (dispersibility limits).

**Table 2-10: Effectiveness of dispersant on weathered Wisting Central oil/emulsions at 5 °C**

Residue	Water content (vol. %)	Viscosity (mPa.s) 10 s <sup>-1</sup>	Viscosity (mPa.s) 100 s <sup>-1</sup>	Effectiveness (%)	
				IFP	MNS
150°C+	0	25	25	84	100
200°C+	0	62	60	81	91
250°C+	0	206	162	63	100
150°C+	50	178	162	86	100
200°C+	50	439	355	80	100
250°C+	50	1229	774	80	100
150°C+	75	1060	338	88	100
200°C+	75	2058	614	62	97
250°C+	75	4734	1125	16	27
150°C+	83	810	219	71	100
200°C+	70	1857	762	72	51
250°C+	56	1622	966	77	100



**Figure 2-4: Dispersant effectiveness of the Wisting Central oil/emulsion at 5 °C**

Wisting Central was found to be good dispersible for viscosities lower than 3000 mPa.s reflecting viscosities where the IFP-test produce 50 % effectiveness. Reduced dispersability is expected with viscosities above 3000 mPa.s. It should be emphasized that reduced dispersability means that the oil/emulsion is still dispersible, but may require additional energy to enhance effective dispersion. The viscosity limit where Wisting Central is not dispersible, expressed with effectiveness lower than 5 % using the MNS-test, was not reached in the laboratory. This indicates that Wisting Central is expecting to have a wide window of opportunity for dispersant use. The dispersibility limits are also summarised in Table 2-11.

*Table 2-11: Estimated viscosity limit for Wisting Central for use of dispersant and criteria for definition of time window*

<b>Dispersibility</b>	<b>Criteria (wt. %)</b>	<b>Dispersibility limits based on oil viscosities (mPa.s)</b>
<b>Chemically dispersible</b>	IFP efficiency > 50 %	3000
<b>Not chemically dispersible</b>	MNS efficiency < 5 %	-

*-: The limit was not reached in the laboratory*

### 3 Predictions with SINTEF Oil Weathering Model (OWM)

#### 3.1 Description of SINTEF OWM

A systematic stepwise laboratory procedure developed at SINTEF (Daling et al., 1990) is 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 Wisting Central crude oil was conducted at 5 °C and the analytical parameters were further used as input to the SINTEF Oil Weathering Model (OWM) (version 4.0 beta). The experimental design for the study of Wisting Central crude oil 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 3-1. 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 time 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.

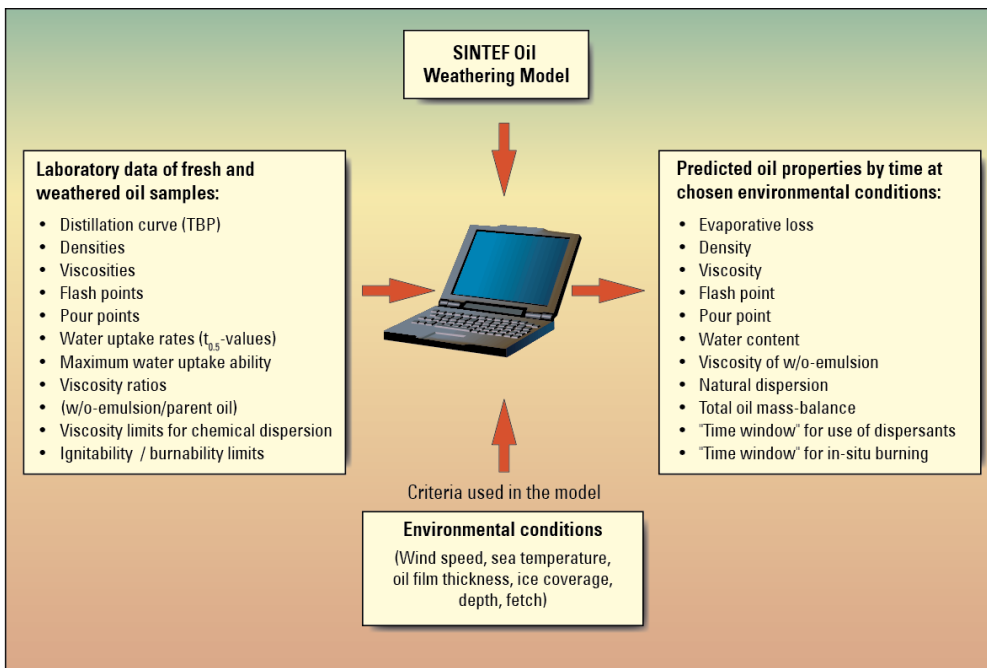


Figure 3-1: Schematic input data to the SINTEF OWM and the predicted output oil properties

#### Spill scenario

A standard surface release from the OWM was used as the spill scenario.

#### Oil film thickness

In the OWM, the oils are categorized as condensate, emulsifying crude, low emulsifying crude, heavy bunker fuel or refined distillate based on experimental results obtained in the laboratory. The terminal film thickness varies among these categories based on experimental (field) experience. Wisting is categorized as emulsifying oil.

### Sea temperature

The prevailing weather conditions greatly influence the weathering rate of oil on the sea surface. Two sets of predictions are given in this report. Due to the location of the oil field, the prediction temperatures chosen for Wisting Central were 2 and 5 °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 3-1.

**Table 3-1: 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

## 3.2 Prediction of Wisting Central weathering properties

### Input to the OWM

Oil type:	Crude oil
Geographical area:	Barents Sea
Terminal oil film thickness:	1 mm
Release rate:	1.33 metric tonnes/minute for 15 minutes; a total of 20 metric tonnes
Sea temperature:	2 °C and 5 °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 can be used to determine the weathering properties of the oil/emulsion. Table 3-2 gives examples for the following scenario:

- Drift time: 12 and 24 hours
- Sea temperature: 2 °C / 5 °C
- Wind speed: 10 m/s

**Table 3-2: Example of the weathering properties for Wisting Central obtained from the OWM predictions after 12 and 24 hours of weathering**

Weathering property	12 hours 2 °C, 10 m/s	12 hours 5 °C, 10 m/s	24 hours 2 °C, 10 m/s	24 hours 5 °C, 10 m/s
Evaporation, wt. %	31	32	34	35
Water content, vol. %	51	51	60	60
Flash point, °C	93	96	103	107
Pour Point, °C	-36	-36	-36	-36
Viscosity, mPa·s*	850	770	1600	1430

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

**Property: EVAPORATIVE LOSS**  
**Oil Type: WISTING CENTRAL 5C, 2017**  
**Description: SINTEF ID:2016-320**  
**Data Source: Sintef Ocean (2017), Weathering data used**

OWModel

Surface release - Terminal Oil film thickness: 1 mm  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 08, 2017

— Wind Speed (m/s): 15  
 - - - Wind Speed (m/s): 10  
 ····· Wind Speed (m/s): 5  
 ····· Wind Speed (m/s): 2

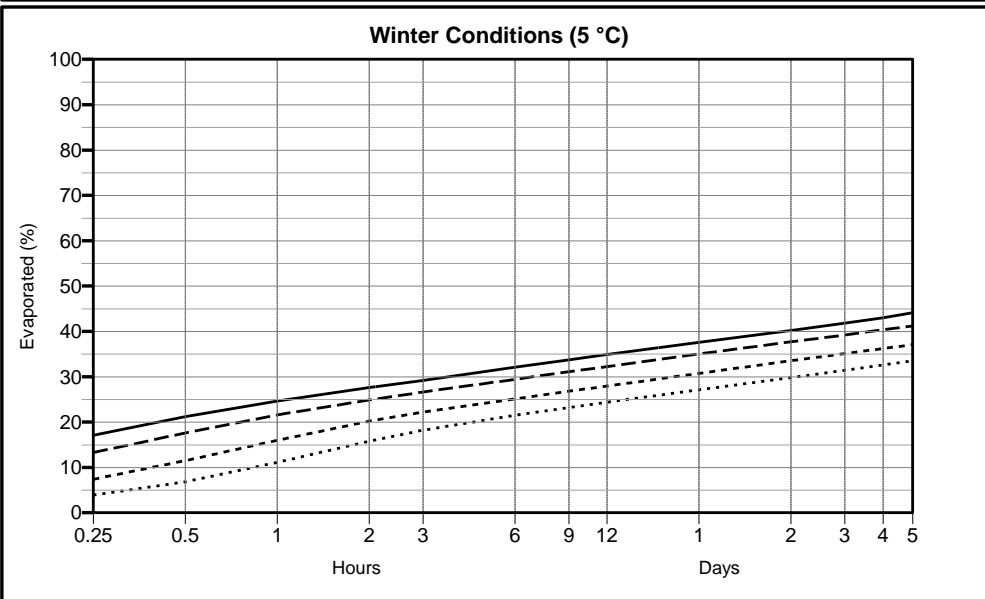
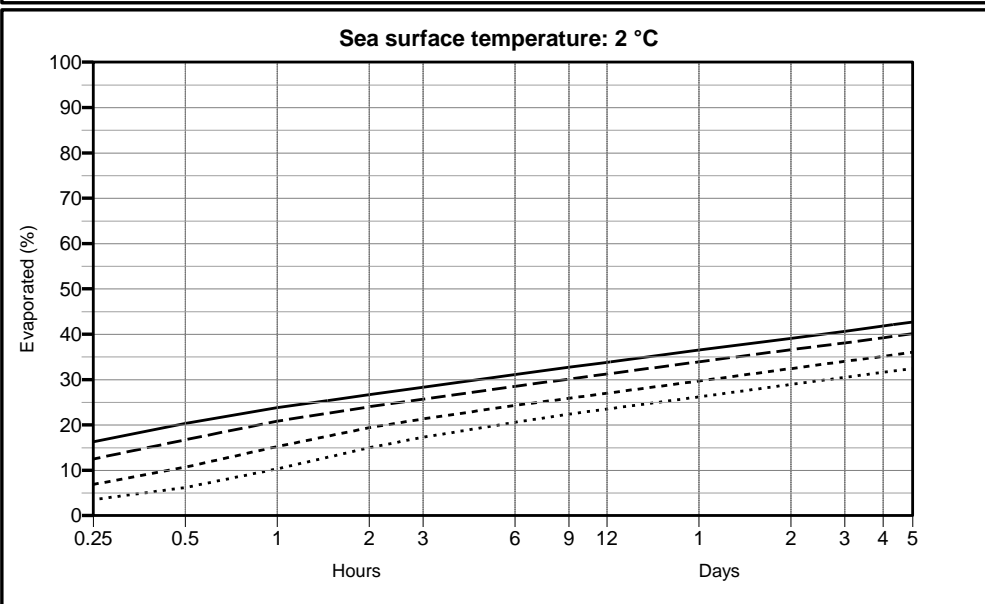


Figure 3-2: Evaporative loss of Wisting Central crude oil predicted at sea temperatures of 2°C and 5°C

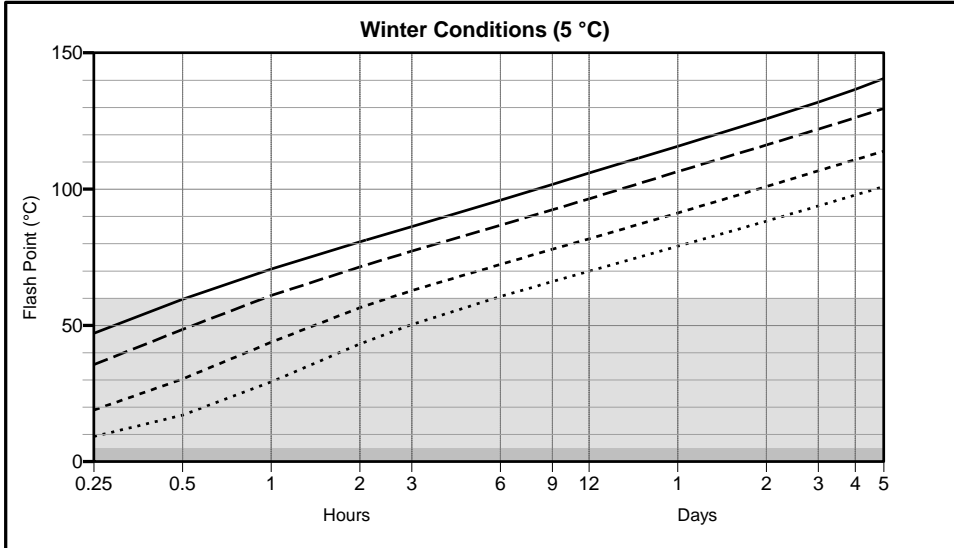
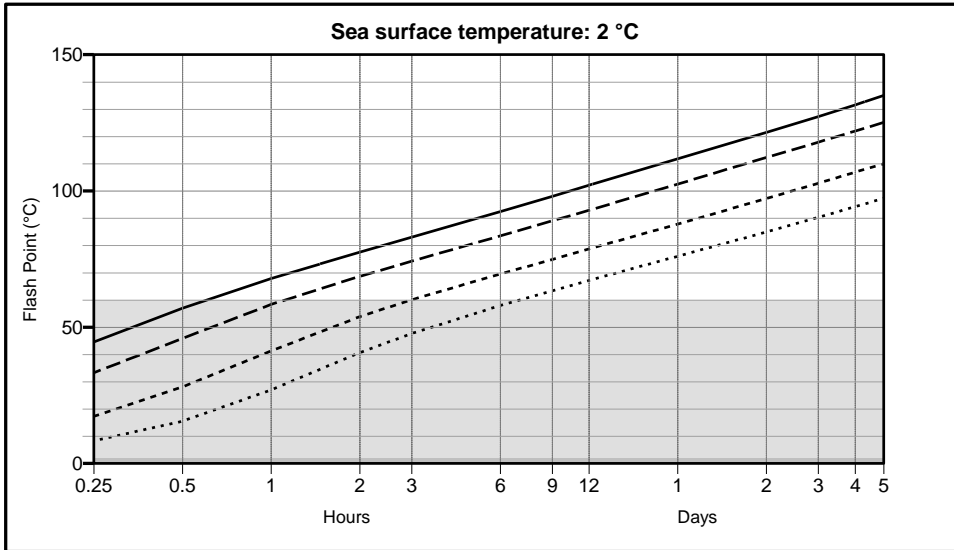
**Property: FLASH POINT FOR WATER-FREE OIL**  
**Oil Type: WISTING CENTRAL 5C, 2017**  
**Description: SINTEF ID:2016-320**  
**Data Source: Sintef Ocean (2017), Weathering data used**

OWModel

Surface release - Terminal Oil film thickness: 1 mm  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 08, 2017

- Wind Speed (m/s): 15
- - - Wind Speed (m/s): 10
- · · · Wind Speed (m/s): 5
- · · · · Wind Speed (m/s): 2
- No fire hazard
- Fire hazard in tannage (<60 °C)
- Fire hazard at sea surface (below sea temperature)



Based on flash point measurements of weathered, water-free oil residues.

**Figure 3-3: Flash point of Wisting Central predicted at sea temperatures of 2°C and 5°C**

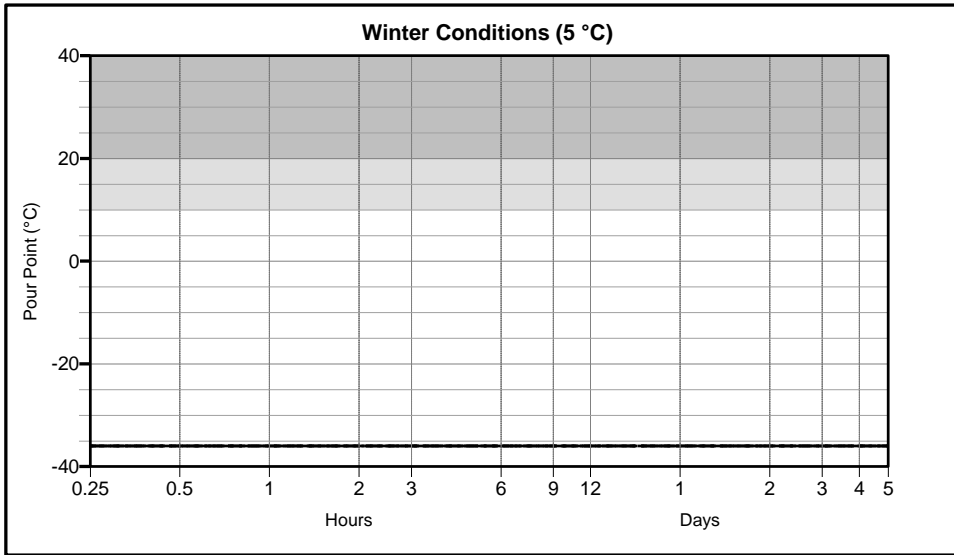
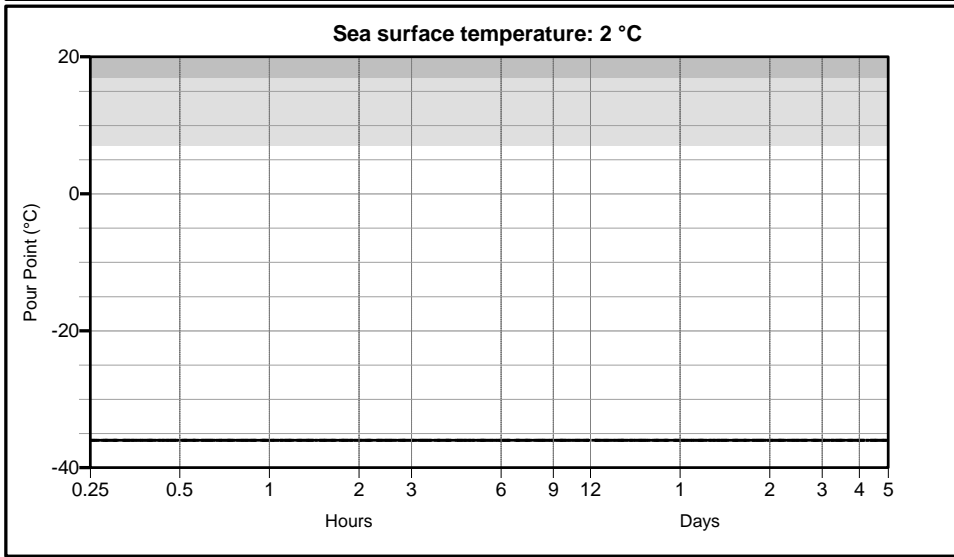
**Property: POUR POINT FOR WATER-FREE OIL**  
**Oil Type: WISTING CENTRAL 5C, 2017**  
**Description: SINTEF ID:2016-320**  
**Data Source: Sintef Ocean (2017), Weathering data used**

OWModel

Surface release - Terminal Oil film thickness: 1 mm  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 08, 2017

- Wind Speed (m/s): 15
- - - Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
- · · · · Wind Speed (m/s): 2
- Chemically dispersible
- ▒ Reduced chemical dispersibility
- Poorly / slowly chemically dispersible



Based on pour point measurements of weathered, water-free oil residues.

**Figure 3-4: Pour point of Wisting Central predicted at sea temperatures of 2°C and 5°C**



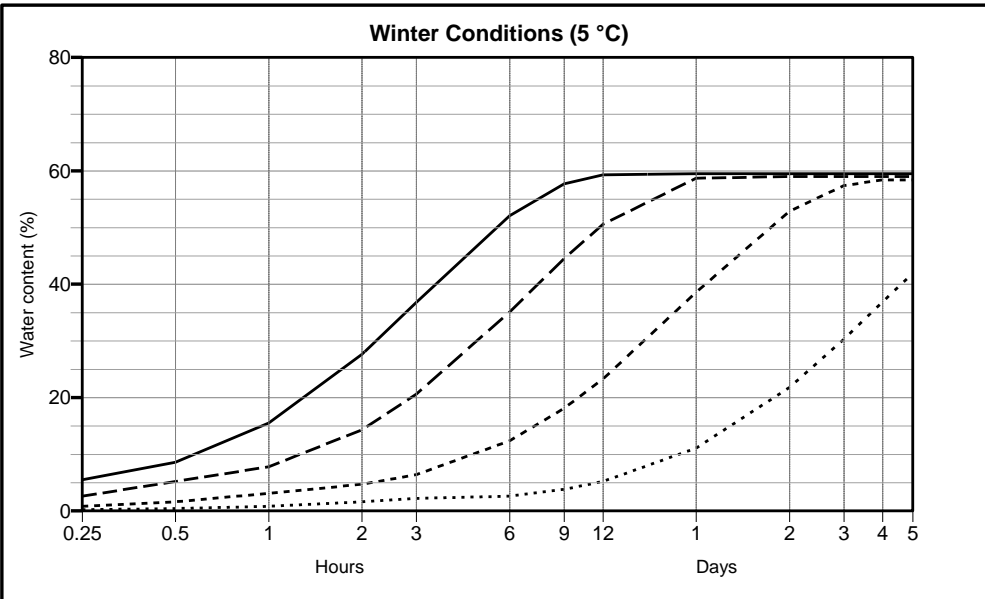
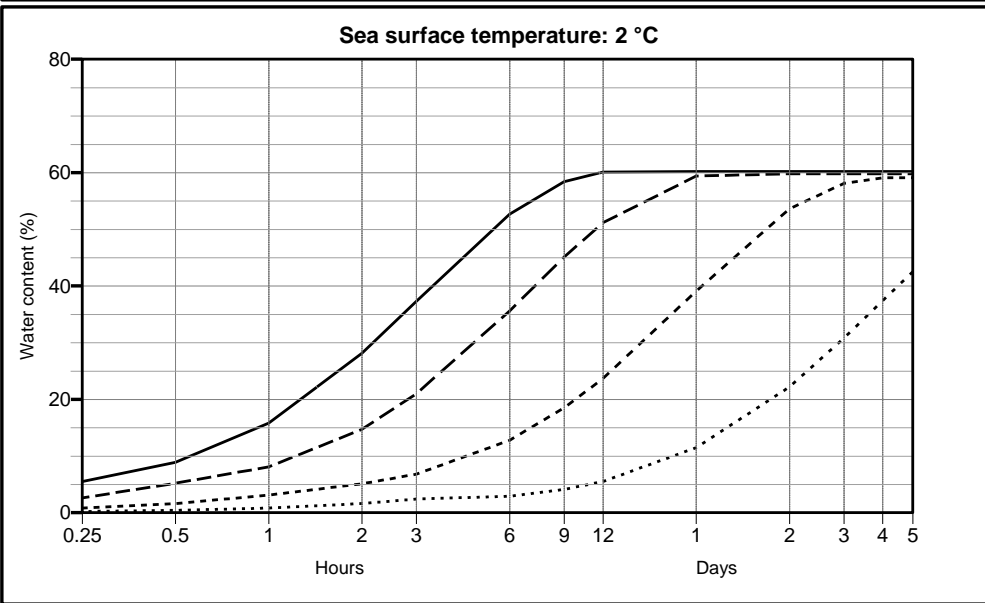
**Property: WATER CONTENT**  
**Oil Type: WISTING CENTRAL 5C, 2017**  
**Description: SINTEF ID:2016-320**  
**Data Source: Sintef Ocean (2017), Weathering data used**

OWModel

Surface release - Terminal Oil film thickness: 1 mm  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 08, 2017

- Wind Speed (m/s): 15
- - - Wind Speed (m/s): 10
- · · · Wind Speed (m/s): 5
- · · · · Wind Speed (m/s): 2



**Figure 3-5: Water content of Wisting Central predicted at sea temperatures of 2°C and 5°C**

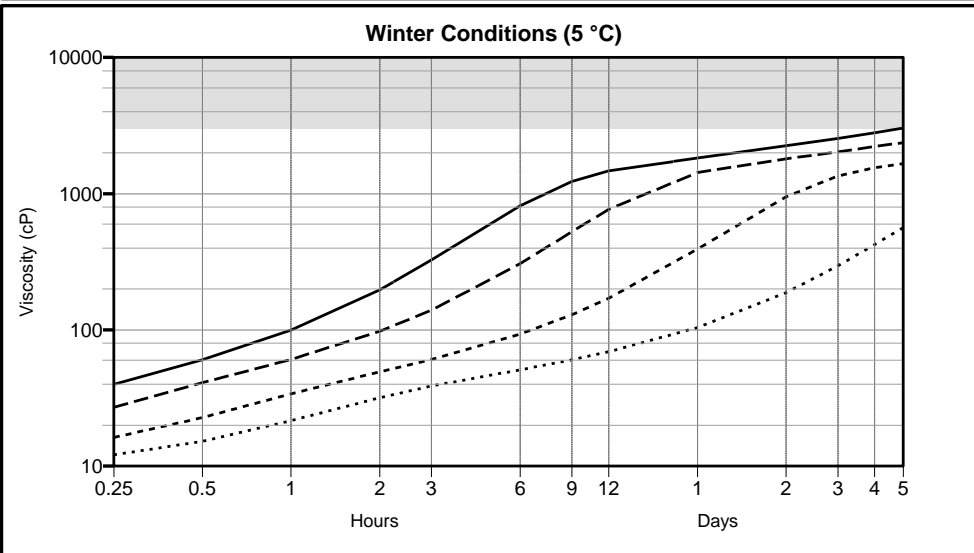
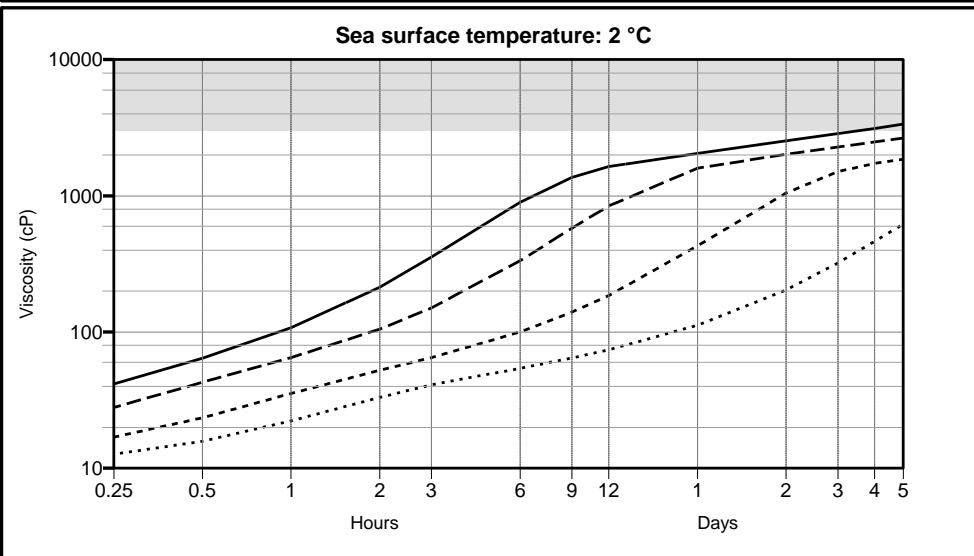
Property: VISCOSITY OF EMULSION  
 Oil Type: WISTING CENTRAL 5C, 2017  
 Description: SINTEF ID:2016-320  
 Data Source: Sintef Ocean (2017), Weathering data used

OWModel

Surface release - Terminal Oil film thickness: 1 mm  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 08, 2017

— Wind Speed (m/s): 15      □ Chemically dispersible (<3000 cP)  
 - - - Wind Speed (m/s): 10      ■ Reduced chemical dispersibility  
 ····· Wind Speed (m/s): 5  
 ······ Wind Speed (m/s): 2



Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.  
 Chemical dispersability information based on experiments under standard laboratory conditions.

**Figure 3-6: Viscosities of Wisting Central emulsions predicted at sea temperatures of 2°C and 5°C. Predictions are based on measurements of emulsions performed at a shear rate of 10 s<sup>-1</sup>**

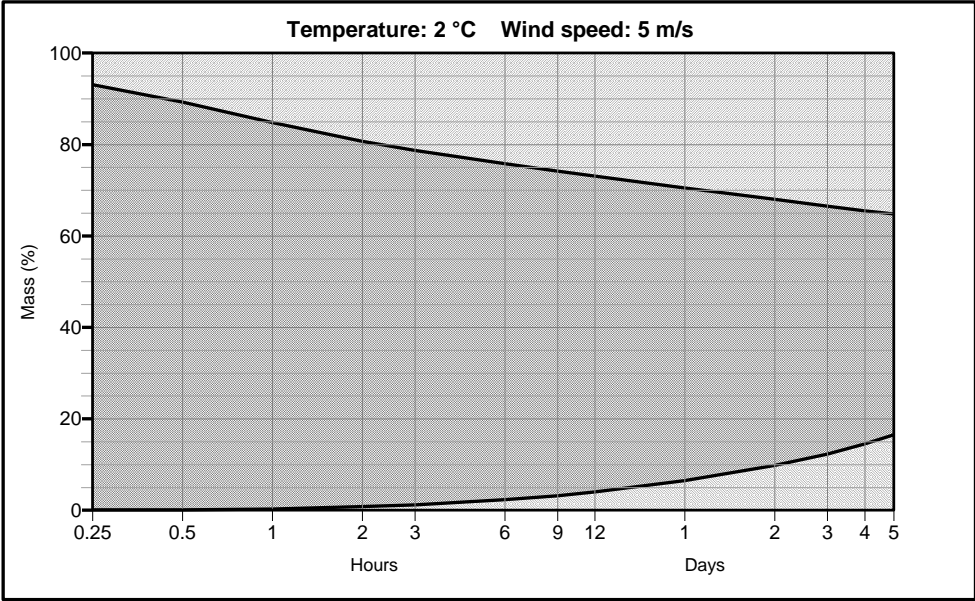
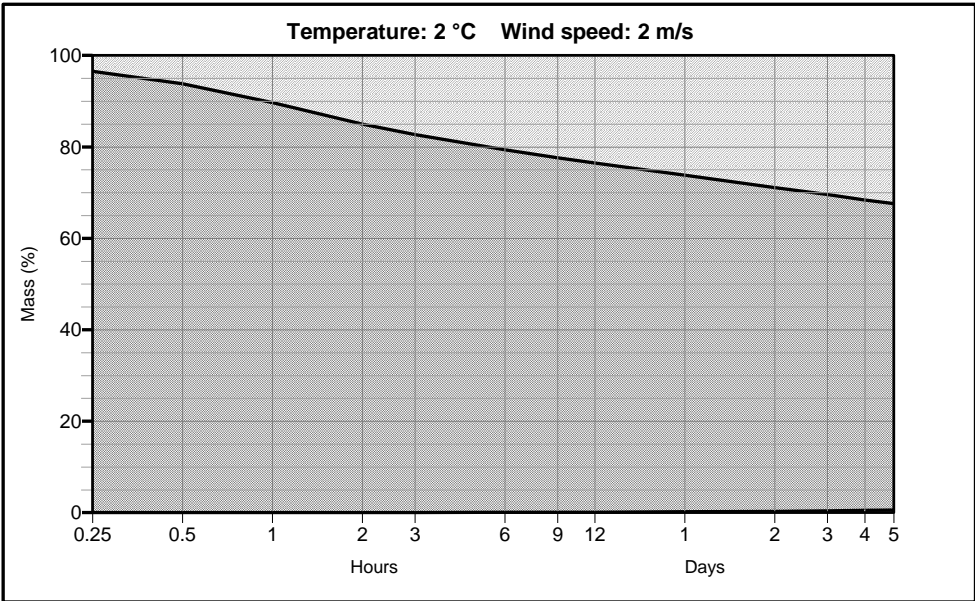
**Property: MASS BALANCE**  
**Oil Type: WISTING CENTRAL 5C, 2017**  
**Description: SINTEF ID:2016-320**  
**Data Source: Sintef Ocean (2017), Weathering data used**

OWModel

Surface release - Terminal Oil film thickness: 1 mm  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 08, 2017

- Evaporated
- Surface
- Naturally dispersed



**Figure 3-7: Predicted mass balance for Wisting Central at 2°C and wind speeds of 2 and 5 m/s**

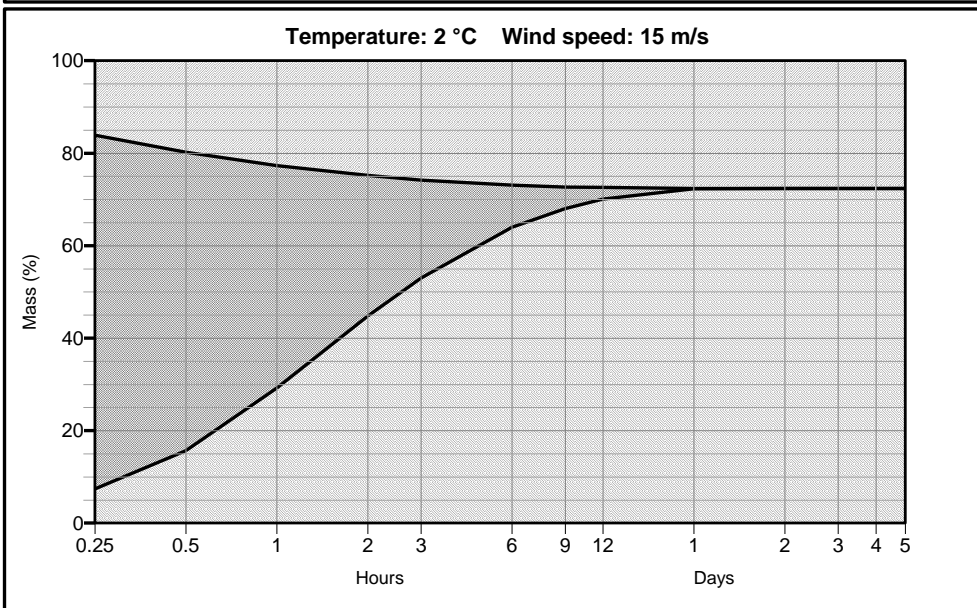
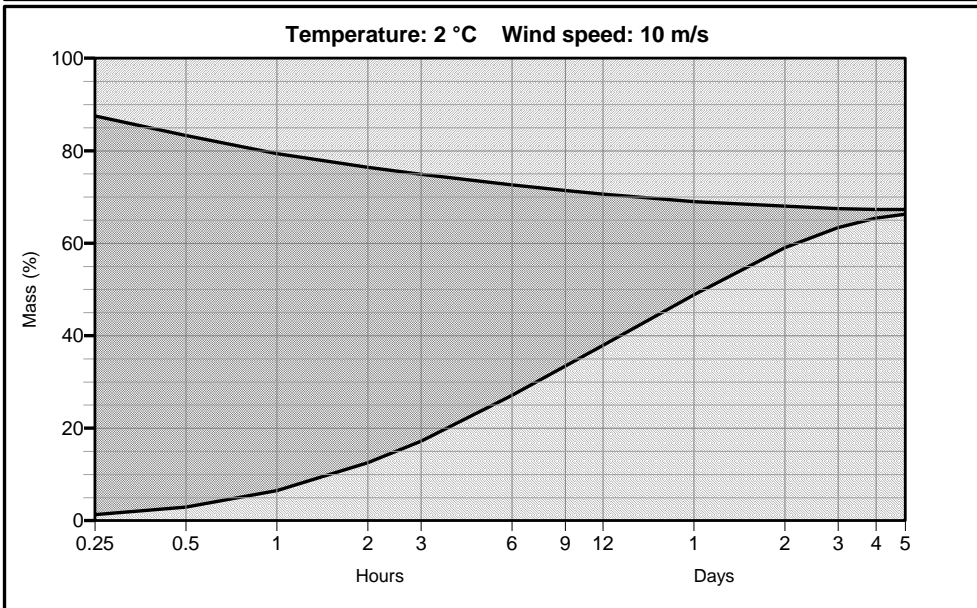
**Property: MASS BALANCE**  
**Oil Type: WISTING CENTRAL 5C, 2017**  
**Description: SINTEF ID:2016-320**  
**Data Source: Sintef Ocean (2017), Weathering data used**

OWModel

Surface release - Terminal Oil film thickness: 1 mm  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 08, 2017

- Evaporated
- Surface
- Naturally dispersed






**Figure 3-8: Predicted mass balance for Wisting Central at 2°C and wind speeds of 10 and 15 m/s**

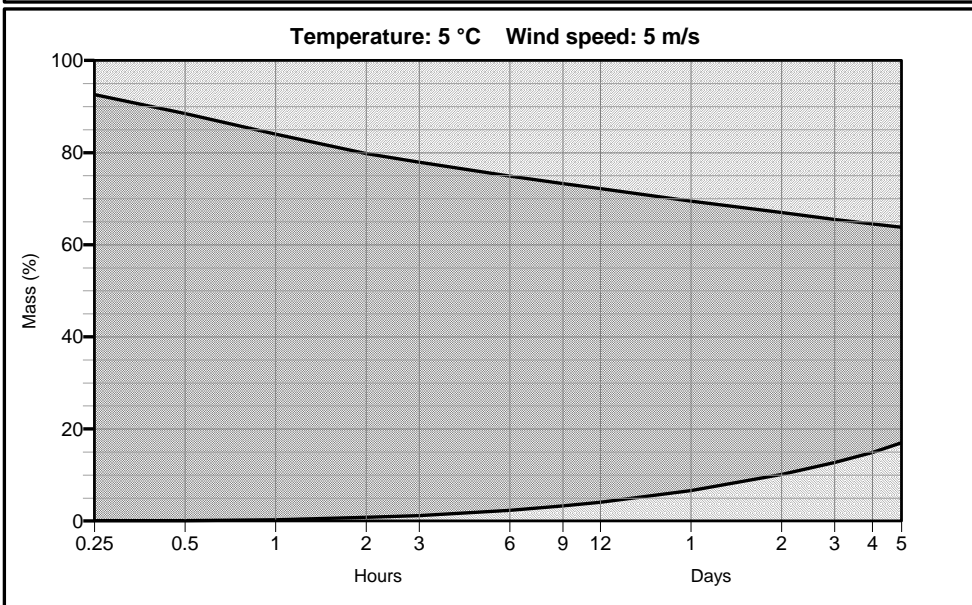
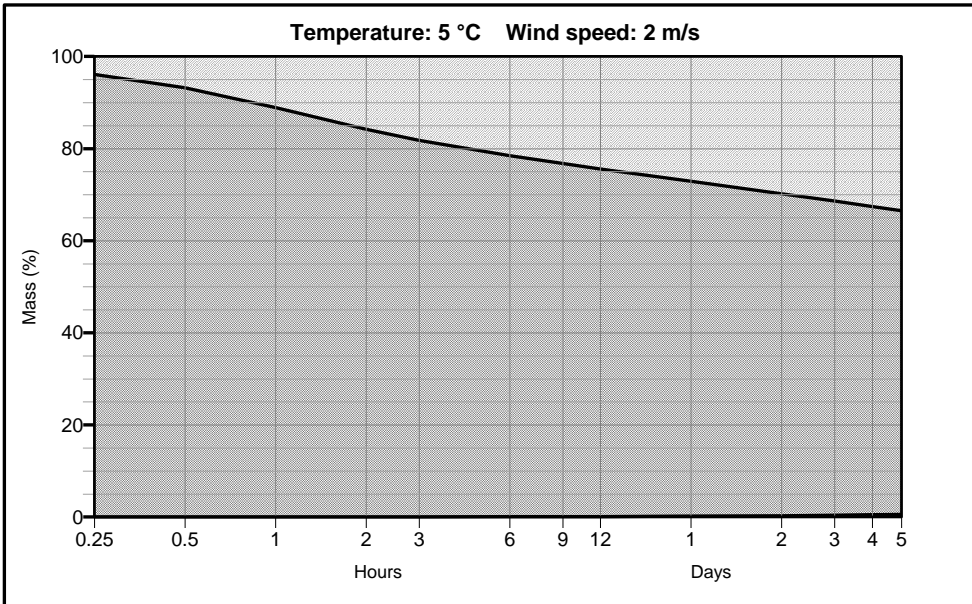
**Property: MASS BALANCE**  
**Oil Type: WISTING CENTRAL 5C, 2017**  
**Description: SINTEF ID:2016-320**  
**Data Source: Sintef Ocean (2017), Weathering data used**

OWModel

Surface release - Terminal Oil film thickness: 1 mm  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 08, 2017

-  Evaporated
-  Surface
-  Naturally dispersed



**Figure 3-9: Predicted mass balance for Wisting Central at 5°C and wind speeds of 2 and 5 m/s**

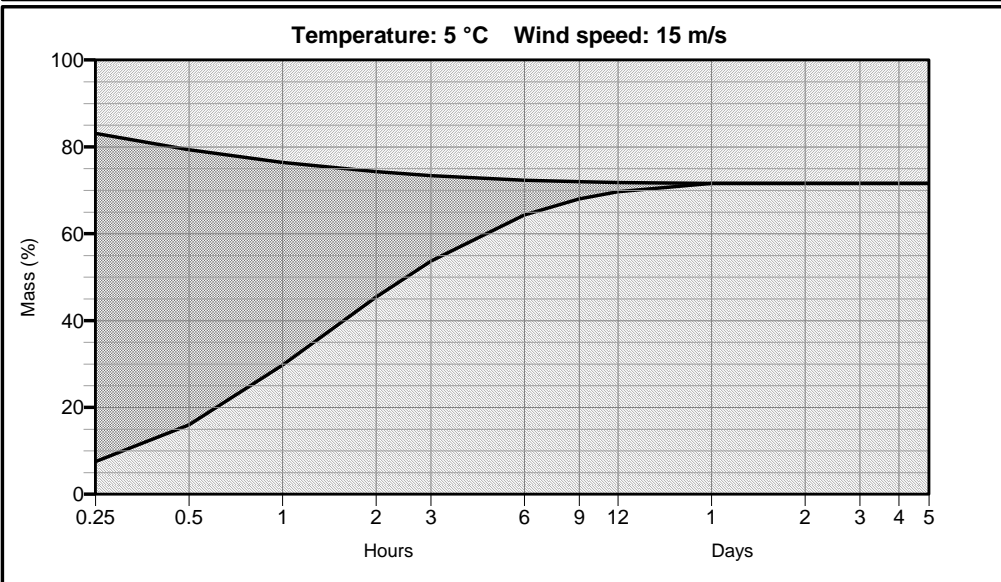
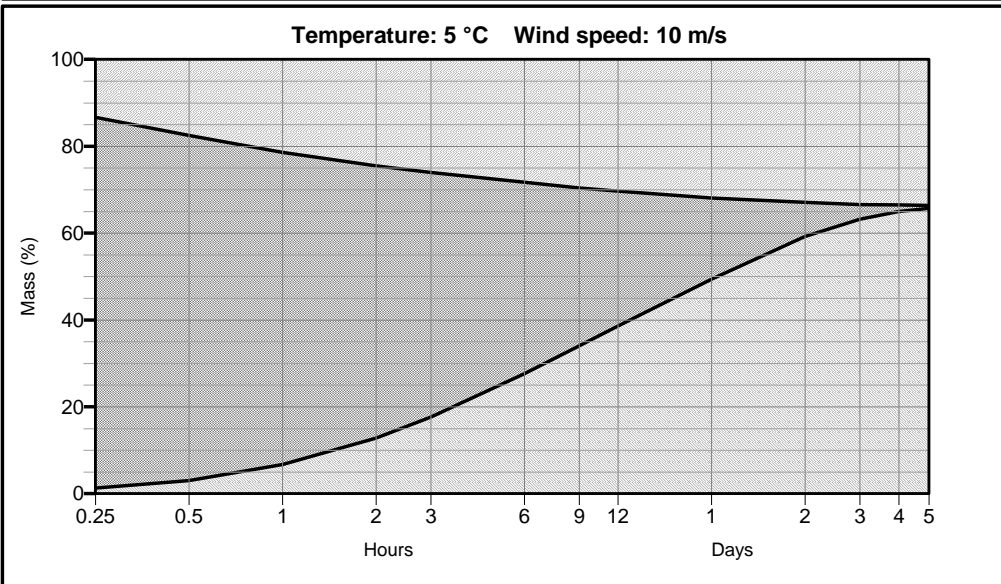
**Property: MASS BALANCE**  
**Oil Type: WISTING CENTRAL 5C, 2017**  
**Description: SINTEF ID:2016-320**  
**Data Source: Sintef Ocean (2017), Weathering data used**

OWModel

Surface release - Terminal Oil film thickness: 1 mm  
 Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: May. 08, 2017

- Evaporated
- Surface
- Naturally dispersed



**Figure 3-10: Predicted mass balance for Wisting Central at 5°C and wind speeds of 10 and 15 m/s**

## 4 OWM predictions - Comparison of Wisting Central with other crude oils

Weathering predictions of Wisting Central were compared to a selection of other crude oils from the Barents Sea. The crude oils chosen for comparison are Wisting Hanssen, Skrugard from the Johan Castberg field, Realgrunnen and Alta. The presented comparisons given in the figures below are based on predictions at 5 °C and wind speed of 10 m/s.

### 4.1 Evaporative loss

The evaporative loss of Wisting Central and the oils used for comparison are presented in Figure 4-1 below. Wisting Central and Alta have similar and the highest predicted evaporative, while the Skrugard exhibits the lowest evaporative loss due to its high density in comparison with the other oils.

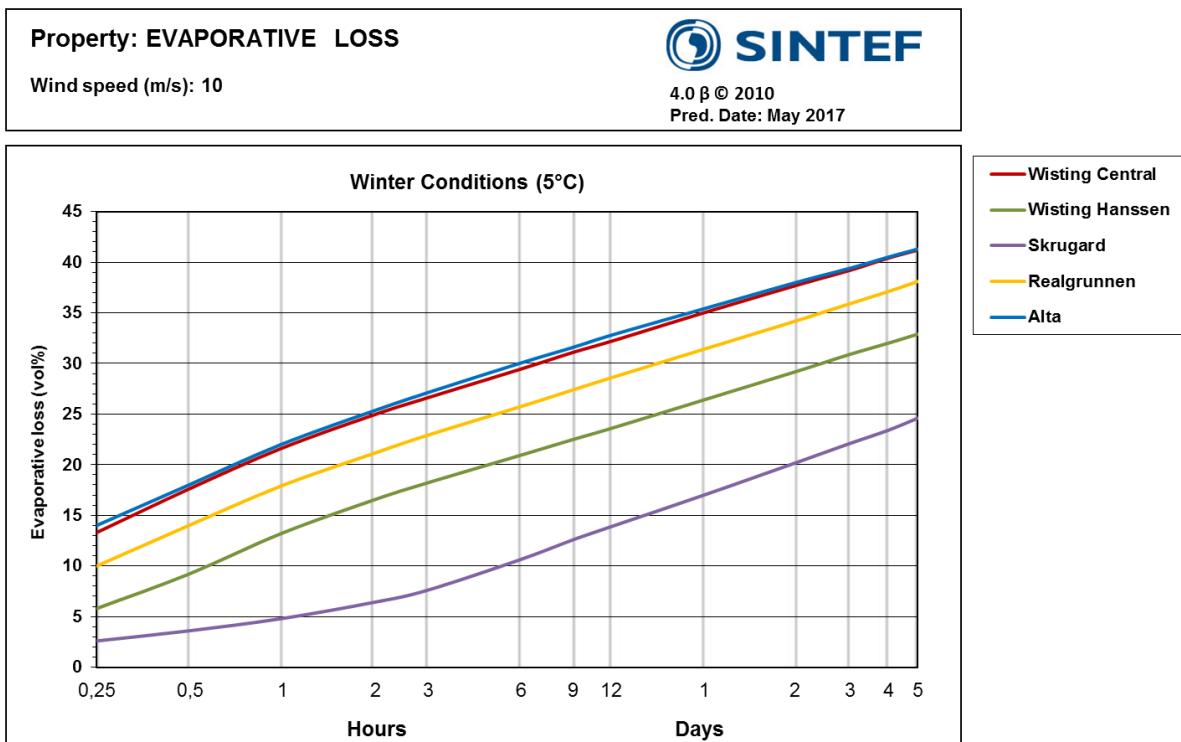


Figure 4-1: Predicted evaporative loss at 5 °C and 10 m/s for Wisting Central compared to other oils

## 4.2 Flash point

As oil spilled on the sea surface, the temperature of the oil is cooled to the ambient water temperature within a short period. The fire hazard will be high as long as the flash point of the oil is below the sea temperature. The fire hazard dependent on the proportions of volatile components in the oil is usually over within few minutes due to the rapid evaporation of those components. The flash points of Wisting Central and other oils in comparison are shown in Figure 4-2. None of the oils show any fire or explosion hazard 15 minutes after release where the flash points is far beyond the sea temperature of 5 °C.

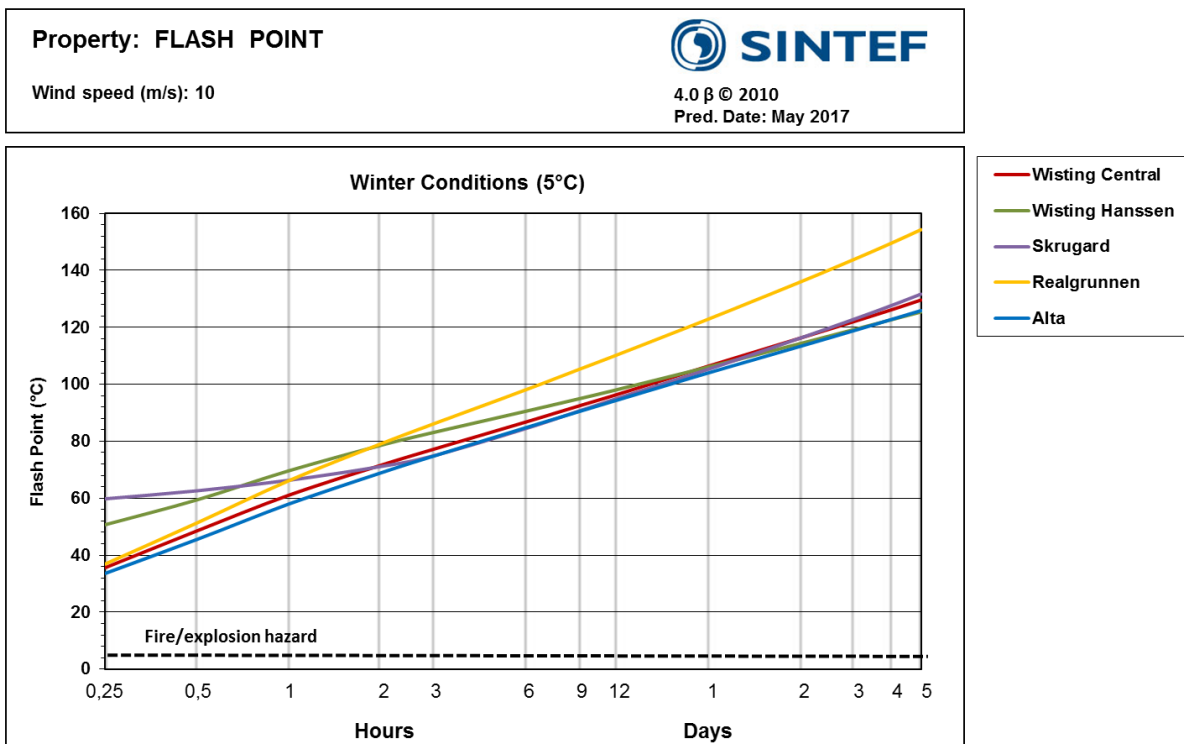


Figure 4-2: Predicted flash point at 5 °C and 10 m/s for Wisting Central compared to other oils



### 4.3 Pour point

Pour point depends on the oil's wax content and the amount of light components that are able to keep the waxes dissolved in the oil phase. In addition, the asphaltene content prevents 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 on the dispersant effectiveness. The pour points of Wisting Central and the other oils for comparison are given in Figure 4-3.

Wisting Central has very low pour points for the fresh oil and its residues, and similar, Skrugard also expresses low pour points and none of this oils will solidify at sea at the selected weather condition. Realgrunnen and Alta have the highest pour points and could therefore potentially pose a challenge with solidification at sea.

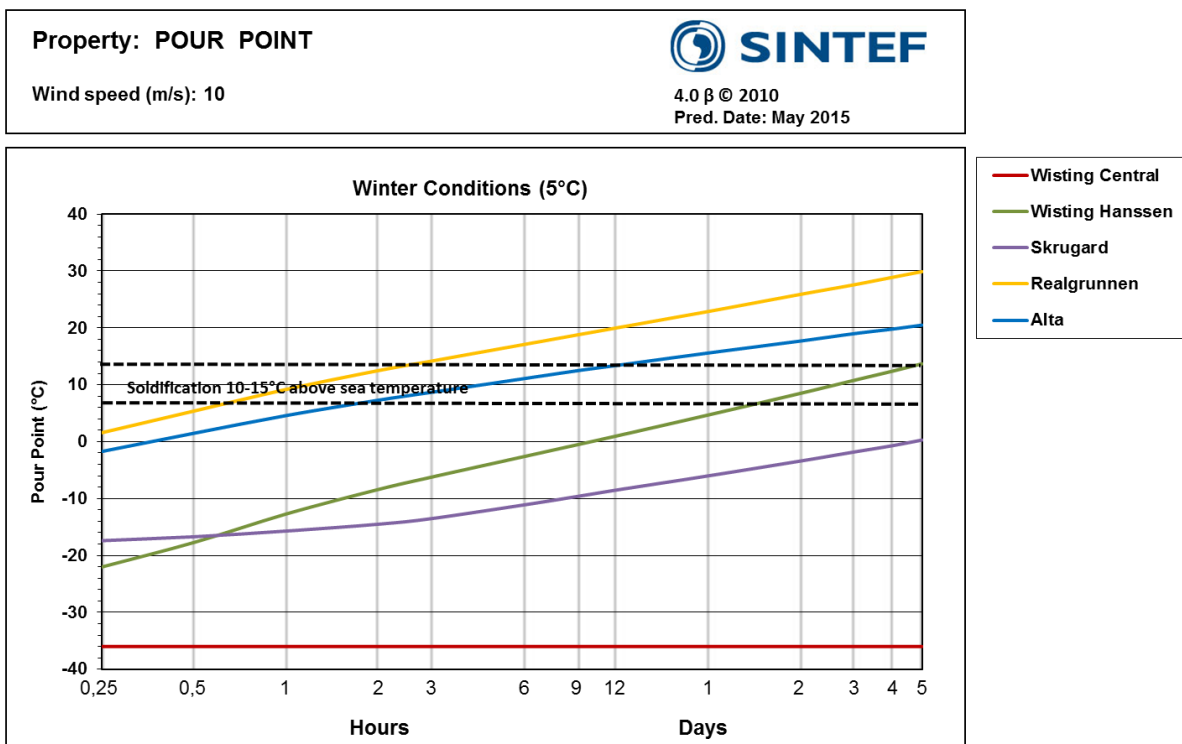


Figure 4-3: Predicted pour point at 5 °C and 10 m/s for Wisting Central compared to other oils

### 4.3.1 Water content

Water uptake and content for Wisting Central and the oils used for comparison are shown in Figure 4-4. The maximum water uptake of Wisting Central is similar to Wisting Hanssen (60 vol. %), but the Wisting Central has a slower water uptake. Skrugard and Alta have both rapidly and high maximum water uptake of 80 vol. %.

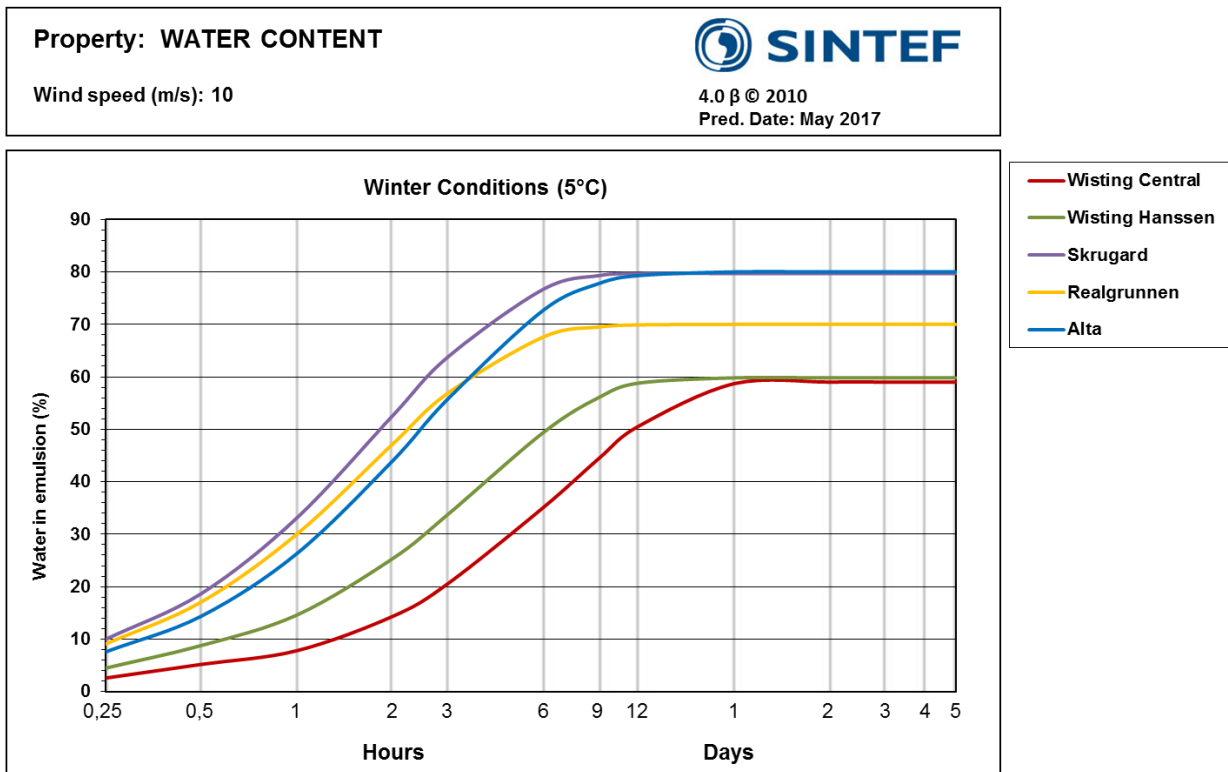


Figure 4-4: Predicted water content at 5 °C and 10 m/s for Wisting Central compared to other oils

### 4.3.2 Emulsion viscosity

Figure 4-5 show the predicted emulsion viscosities of Wisting Central and the other oils in comparison. Wisting Central has low emulsion viscosities compared with the other crude oils. Realgrunnen has the highest emulsion viscosities, whilst Wisting Hanssen, Skrugard and Alta end up with more or less similar viscosities after five days of weathering.

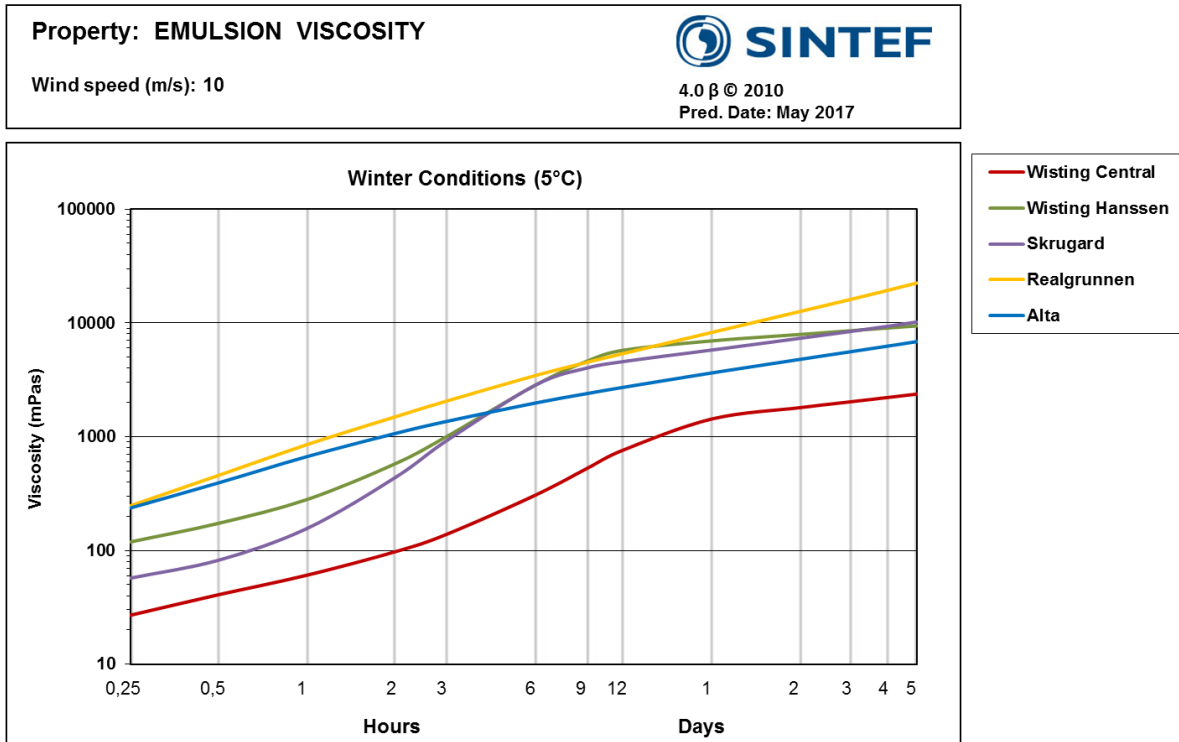
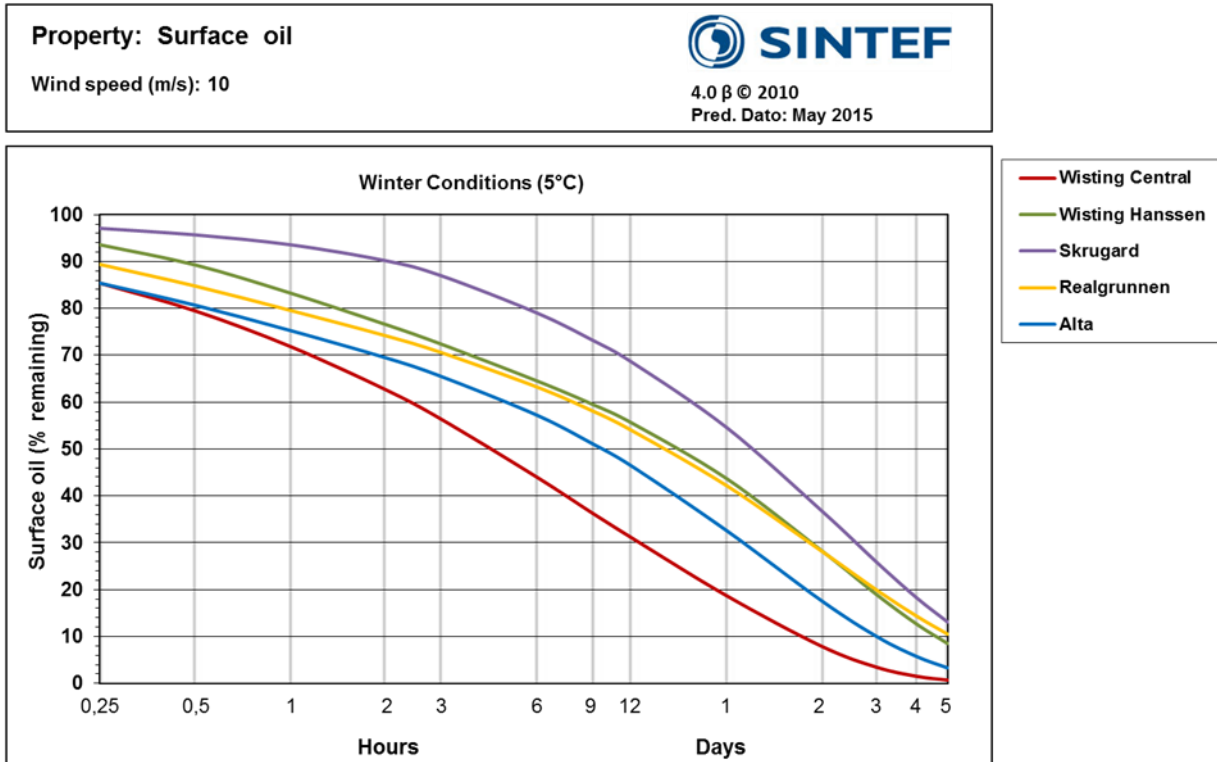


Figure 4-5: Predicted emulsion viscosity at 5 °C and 10 m/s for Wisting Central compared to other oils

### 4.3.3 Surface oil

Due to evaporative loss and natural dispersion/entrainment, the amount oil on the sea surface will gradually be reduced. Figure 4-6 illustrates the predicted mass balance of the Wisting Central surface oil compared to the other oils in comparison. Wisting Central has the lowest remaining surface oil during 5 days of weathering due to high evaporative loss and natural dispersion /entrainment. Skrugard expresses the highest remaining surface oil. Wisting Hanssen and Realgrunnen have comparable and similar remaining surface oil.



**Figure 4-6: Predicted remaining surface oil at 5 °C and 10 m/s for Wisting Central compared to other oils**

## 5 Weathering properties of Wisting Central crude oil related to oil spill

### 5.1 Oil properties

Wisting Central is a medium density crude oil (0.838 g/mL) with low content of wax (0.71 wt. %) and asphaltene (0.05 wt. %), compared with other Norwegian crude oils. Wisting Central is categorised as a naphthenic (biodegraded) crude oil, as shown in Figure 2.1 for chromatographic characterization (GC-FID) of the oil. The hydrocarbon profile shows that the crude oil lacks of the systematic *n*-alkanes (paraffins). Wisting Central has very low pour point ( $< -36^{\circ}\text{C}$ ) for the fresh oil and residues. The oil forms water-in-oil (w/o) emulsions maximum water uptake  $\sim 60$  vol. % and with low emulsion viscosities.

Knowledge of the alterations in physical and chemical properties caused by weathering processes are of importance for oil spill response.

### 5.2 Flash point – Fire/explosion hazard

As oil is spilled on the sea surface, the temperature of the oil will be cooled to the ambient water temperature within a short period. The fire hazard will be at its greatest as long as the flash point of the oil is below the sea temperature. For Wisting Central the flash point will be above the sea temperature within the first 15 minutes after a spill in at 5 and 10  $^{\circ}\text{C}$ , as shown in Figure 5-1 below.

Some vessels/storage tanks engaged in oil recovery operations may not be classified to carry liquids with flash point lower than 60  $^{\circ}\text{C}$  (e.g. towing vessels, smaller cargo or vessels available in the emergency). For Wisting Central, this limit will be reached within approximately 6 hours in low wind conditions (2 m/s) at 2 and 5 $^{\circ}\text{C}$ , and more rapidly with higher wind speeds.

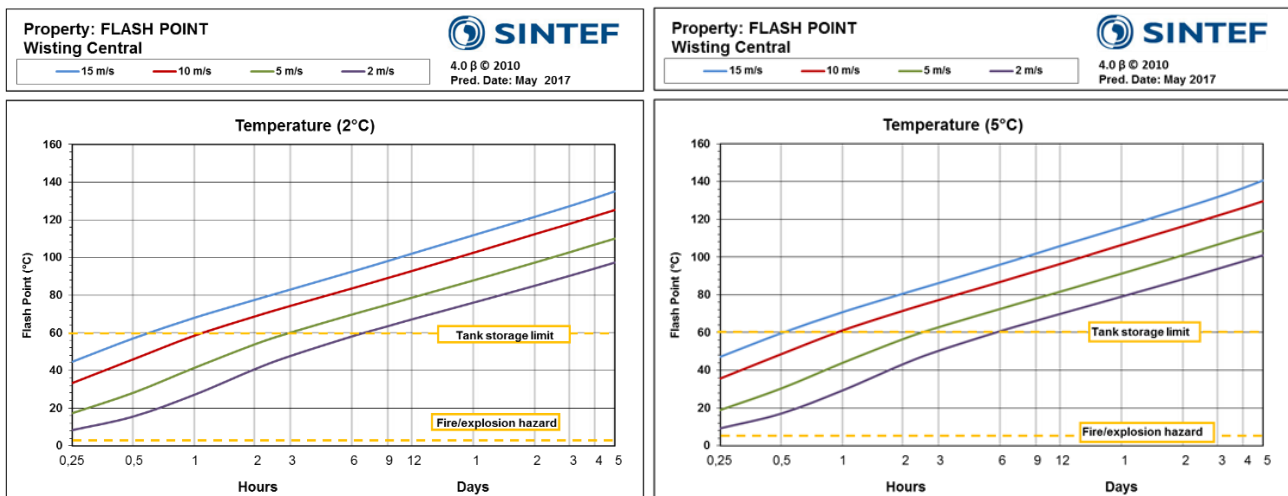
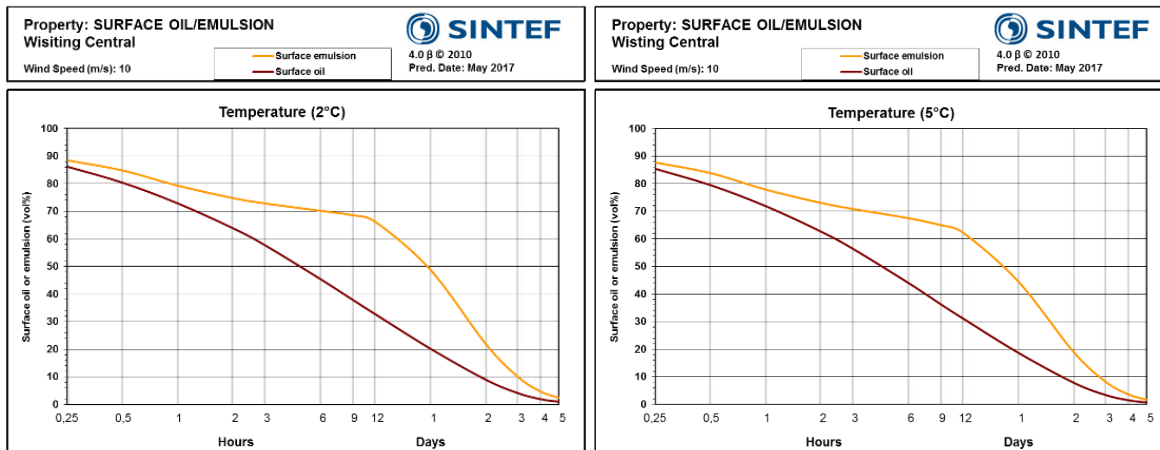


Figure 5-1: Flash point at different wind speeds for Wisting Central crude oil at 2 $^{\circ}\text{C}$  and 5 $^{\circ}\text{C}$

### 5.3 Emulsion formation

The total amount of oil on the sea is reduced due to evaporation and natural dispersion/entrainment in the early stage of weathering. However, as seawater is mixed into the oil with formation of emulsions, the total volume increases. Figure 5-2 illustrate this increase of volume relative to the volume of the remaining surface oil at 10 m/s wind and at both 2 and 5°C. At both temperatures, the volume of the emulsion increases 2-2.5 times of the originally spilled oil volume within 12 hours weathering.



**Figure 5-2: Difference in the total slick volume of Wisting Central due to emulsification compared to non-emulsified oil. Decrease in total volume due to evaporation and natural dispersion at 10 m/s wind speed at temperatures of 2°C and 5°C**

### 5.4 Addition of emulsion breaker

Emulsion breaker can be used during an oil spill operation to increase water release from an emulsion, normally after recovery prior to transfer to storage tank. The emulsion breaker is normally injected at the skimmer head prior the entering to storage tank. The use of emulsion breaker could be considered for Wisting Central, to increase the storage capacity when recovered

Figure 5-3 illustrates the relative volumetric composition of water-in-oil emulsion and free-water, for the 150 and 250°C+ residue (reflecting approx. 0.5 and 1 week weathering, respectively) with and without addition of emulsion breaker (Alcopol O 60 %). The effectiveness of the emulsion breaker is relative to the dosage applied, with 500 and 2000 ppm by weight, where the emulsions released 45-60 vol. % water. A concentration of 500 ppm could be considered as a sufficient concentration to break the emulsion.

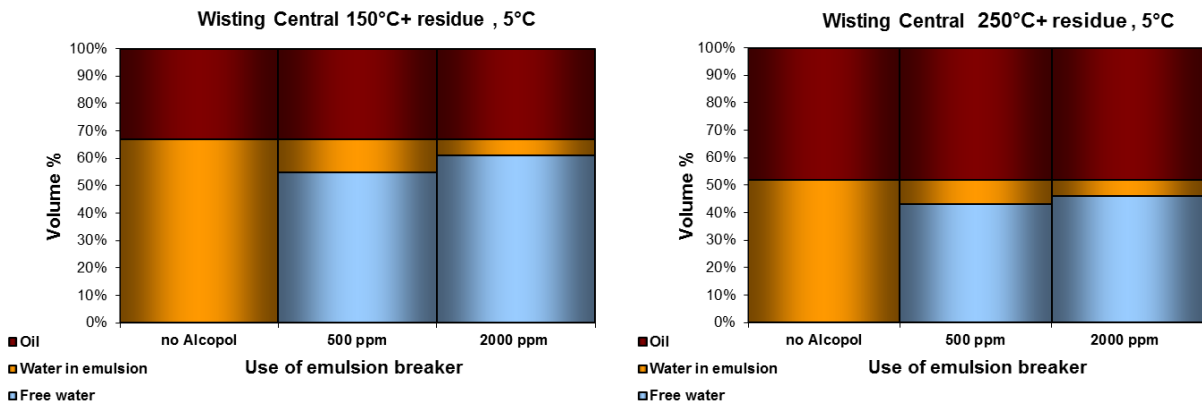


Figure 5-3: Relative volumetric composition of water-in-oil emulsion and free-water after approximately 0.5 week (left) and 1 week (right) of weathering of Wisting Central

### 5.5 Lifetime at sea – 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 5-4 shows the remaining surface oil over time for different wind speeds and temperatures. Considerably larger spills expect to produce longer lifetimes, and individual predictions should be considered in such cases. At high wind speed of 15 m/s, no oil is remained on the sea surface after one day of weathering at 2 and 5°C. However, the variation is strongly dependent on the wind speeds and more oil remains on the sea surface with lower wind.

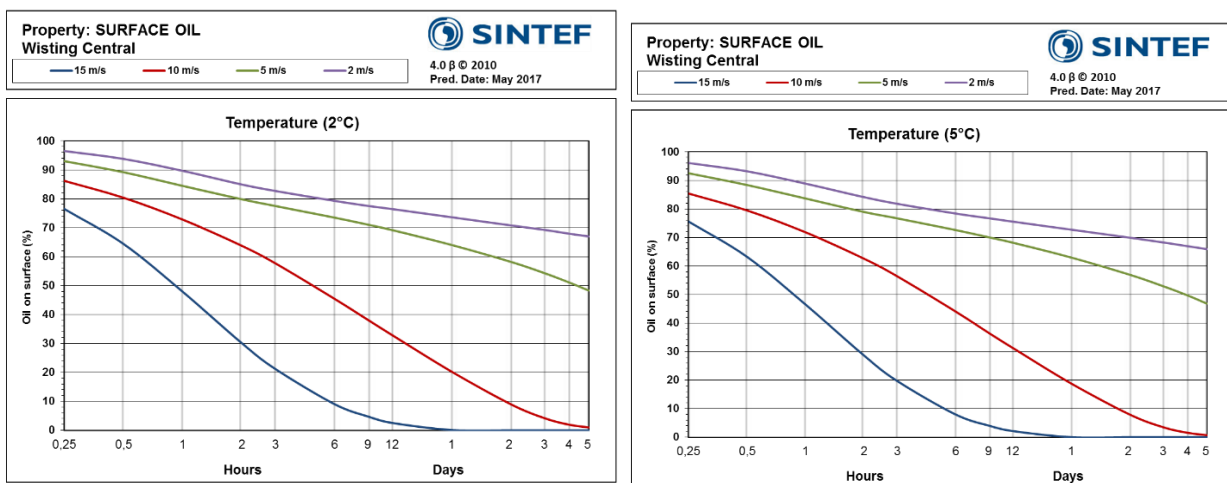


Figure 5-4: Remaining surface oil under different sea states for Wisting Central at 2°C and 5°C

## 5.6 Oil spill response

Mechanical recovery and use of oil spill dispersants are the main oil spill responses at sea in Norwegian sector, today. These response options are discussed for the Wisting Central related to its predicted weathering properties (viscosities). The weathered oil is expected to have a window of opportunity for ignitibility for in-situ burning, but has not been evaluated and predicted in this study.

### 5.6.1 Mechanical recovery

Experiences from Norwegian field trials have demonstrated that the effectiveness of various mechanical clean-up operations is reduced due to the high degree of leakage of the confined oil or w/o-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 set at 1000 mPa.s. However, other factors like operational speed of recovery vessel and weather conditions influence on the risk of boom leakage, and it may therefore be possible to recover oil in calm weather conditions with viscosities higher than this limit. Previously studies at SINTEF have shown that weir skimmers may have reduced recovery rate (m<sup>3</sup>/h) at viscosities in the range 15-20 000 mPa.s (Leirvik et al., 2001).

The emulsion viscosities of Wisting Central are relatively low as shown in Figure 5.5. The emulsion viscosities are predicted to pass 1000 mPa.s after 12 hours at 10 m/s, and > 5 days in calm wind conditions (2 m/s) at 2 and 5°C. With such low oil/emulsion viscosities (< 1000 mPa.s), the speed of the recovery vessel during containment of the oil/emulsion could be lowered to avoid /reduce boom leakage.

The emulsion viscosities of Wisting Central remain far below the 15-20 000 mPa.s limit (Figure 5.5) for effectively use of weir skimmers for all weather conditions, and sufficient flowability towards weir skimmers are therefore expected for this oil. This gives a wide window of opportunity for mechanical recovery with use of e.g. Transrec equipped with traditional weir-skimmer head.

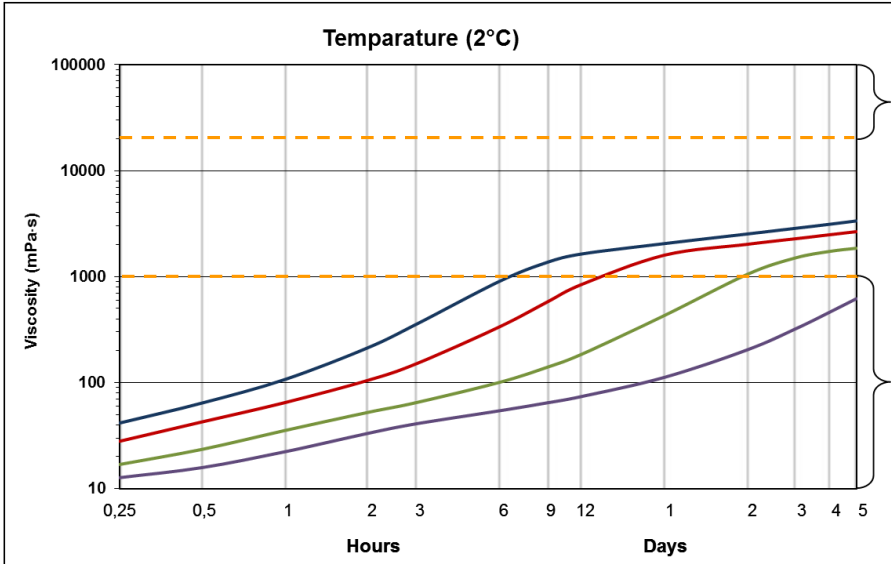
In cases when high viscosity of the oil/emulsion is not a limiting factor, high pour point could cause semi-solid oil when spilled on the sea surface. Such solidification is known to appear with pour points 10-15 °C above the sea temperature. However, Wisting Central exhibit's very low pour points (<-36°C) and solidification will not pose a challenge for this oil when spilled at sea.



Property: EMULSION VISCOSITY  
Wisting Central

— 15 m/s   
 — 10 m/s   
 — 5 m/s   
 — 2 m/s

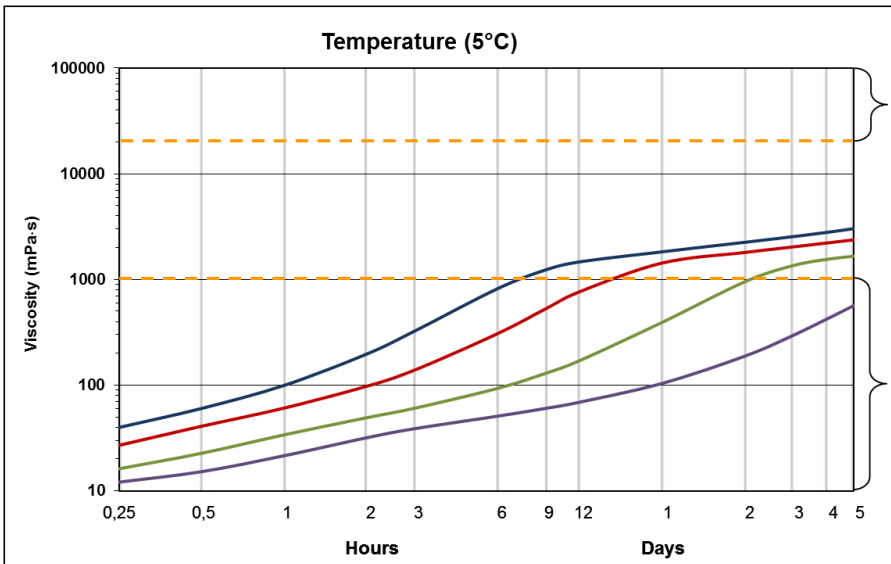
**SINTEF**  
 4.0 β © 2010  
 Pred. Date: May 2017



Property: EMULSION VISCOSITY  
Wisting Central

— 15 m/s   
 — 10 m/s   
 — 5 m/s   
 — 2 m/s

**SINTEF**  
 4.0 β © 2010  
 Pred. Date: May 2017



**Figure 5-5: Predicted emulsion viscosity for Wisting Central at 2°C and 5°C compared with viscosity limits for reduced boom leakage and poor flow to weir skimmers.**

### 5.6.1 Use of oil spill dispersant

Wisting Central crude oil has a good potential for use of oil spill dispersant, and the window of opportunity for use of the dispersant (Dasic NS) is presented in Figure 5.6.

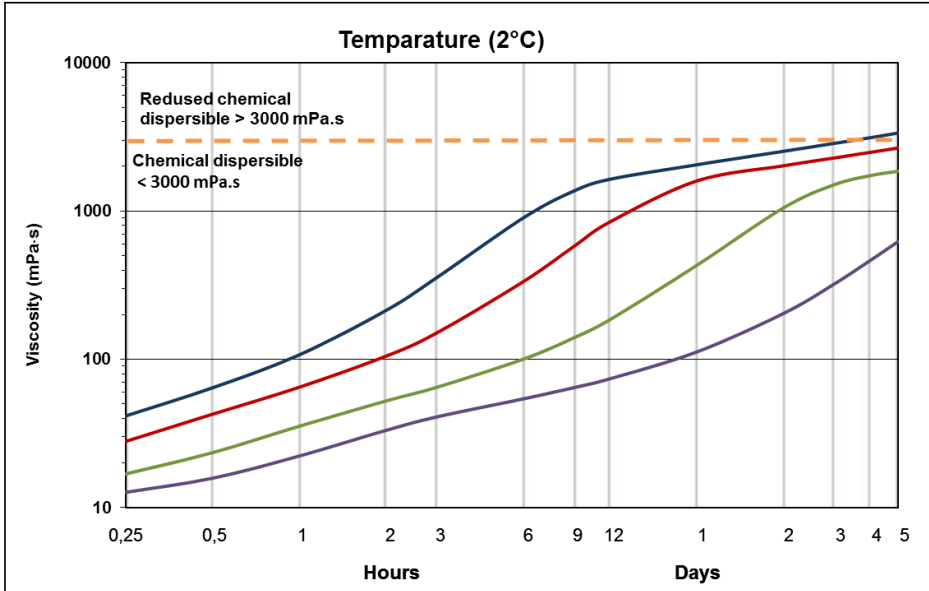
Wisting Central is estimated to be good dispersible for viscosities  $< 3000$  mPa.s, and expressed reduced dispersibility for viscosities  $> 3000$  mPa.s. However, the upper limit for the oil/emulsion is not dispersible was not reached in the dispersibility testing with use of the MNS high-energy test, indicating that this crude oil has a wide time-window for use of dispersant  $> 5$  days of weathering. The MNS-test with no dispersant added also showed that the crude oil has a potential to easily be naturally dispersed/entrained into the water column in in breaking waves conditions ( $> 5$  m/s wind speeds).

In general, when oil expects to have a reduced dispersibility, additional energy or use of a higher dispersant dosage and/or repeated dispersant application, particularly in calm sea conditions, may be required to increase the dispersant efficiency. Providing additional energy through use of firefighting (Fi-Fi) systems, thrusters or MOB boats after dispersant application may in such cases enhance the dispersion rate.

Property: EMULSION VISCOSITY  
Wisting Central

— 15 m/s    — 10 m/s    — 5 m/s    — 2 m/s

**SINTEF**  
 4.0 β © 2010  
 Pred. Date: May 2017



Property: EMULSION VISCOSITY  
Wisting Central

— 15 m/s    — 10 m/s    — 5 m/s    — 2 m/s

**SINTEF**  
 4.0 β © 2010  
 Pred. Date: May 2017

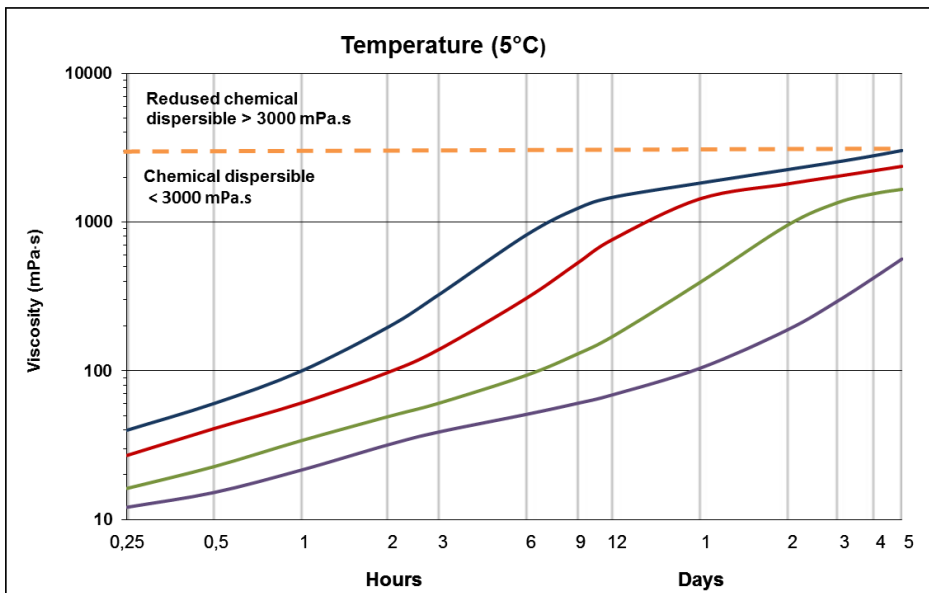


Figure 5-6: Time window for use of chemical dispersant as a function of emulsion viscosity for Wisting Central at 2 and 5°C

## 6 Categorization map of Wisting Central

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

**Naphtenic 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 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 is not related to all naphtenic oils.

**Paraffinic oils**, 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 w/o-emulsions.

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

**Waxy oils** often exhibit high pour points due to large content of wax components (typically > 6 wt. %). These oils have a tendency to solidify producing elastic properties on the sea surface, particularly observed at low seawater temperatures. Solidification is pronounced if the seawater temperature typically is 10-15 °C below the pour point. Waxy crude oils typically exhibit a light to medium evaporative loss. The water uptake can vary extensively, whereas the w/o-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 oils including Wisting Central is presented in Figure 6-1 below. Wisting Central is categorized as a highly biodegraded naphtenic crude oil.

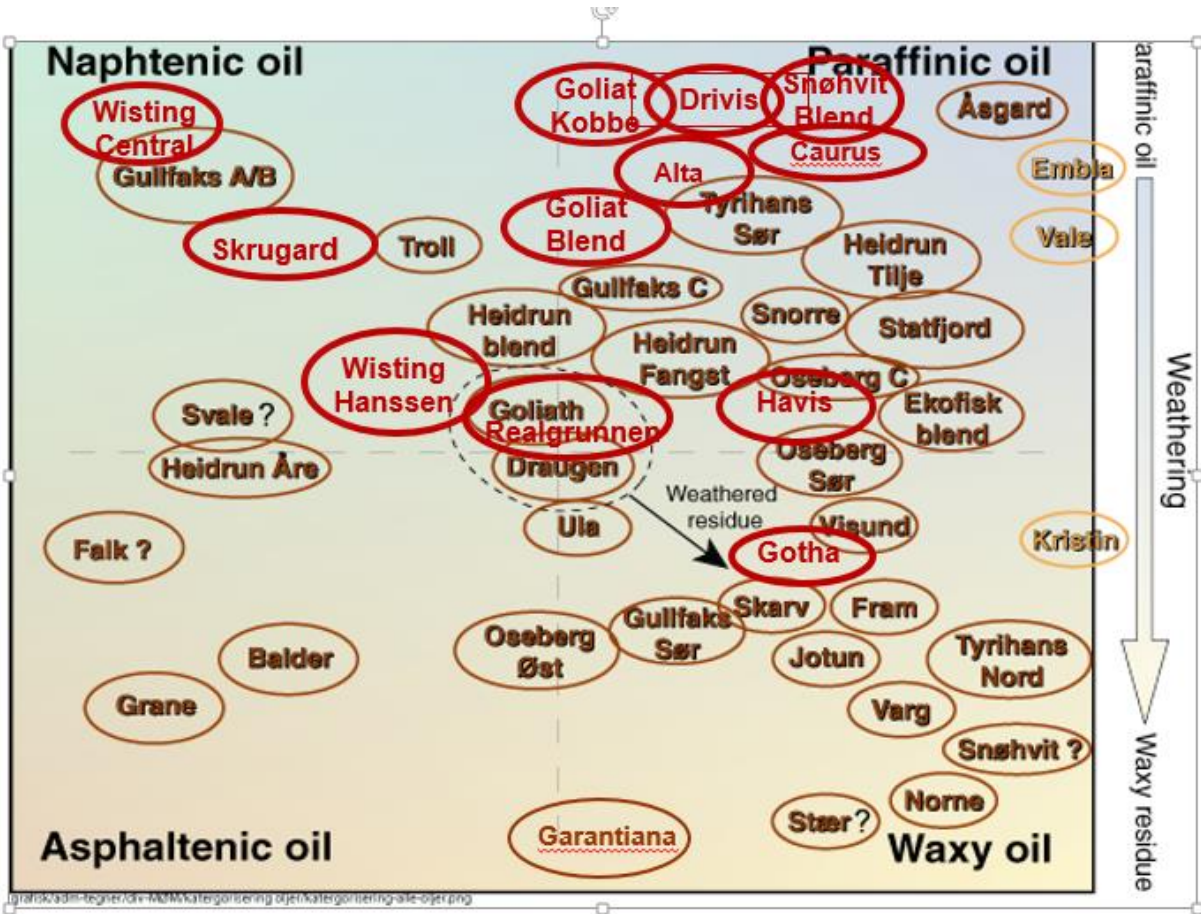


Figure 6-1: Categrization of a selection of Norwegian crude oils including Wisting Central and oils used for comparison (the oil with red rings are other oils from the Barents Sea).

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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 heteroatomic organics see Figure A-1.

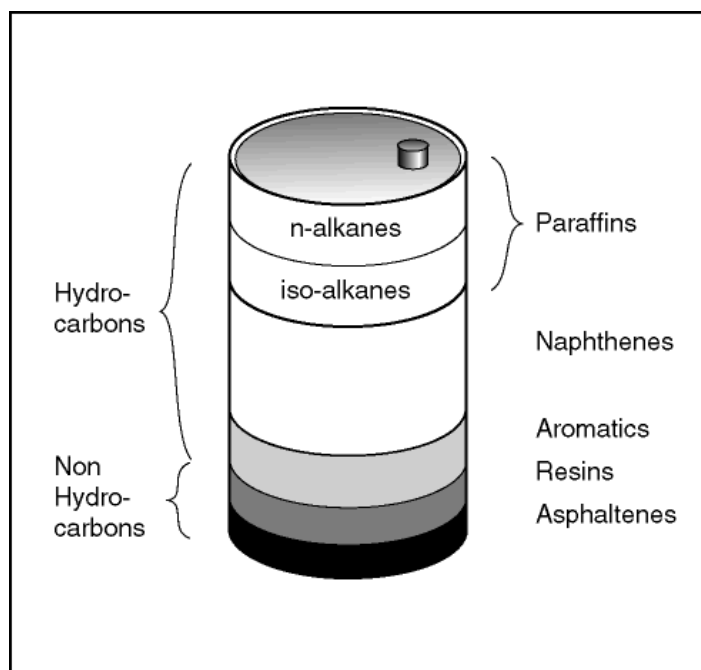


Figure A-1: The chemical composition of crude oils

#### A.1.1 Hydrocarbons

The majority of 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 isoalkane 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 Heteroatomic organics**

In addition to pure hydrocarbons, 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. The two most important groups of heteroatomic organic compounds are resins and asphaltenes.

### Resins

Resins are relatively polar compared to the hydrocarbons, 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

This 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 1000-10000). Asphaltenes may be classified as "hard" or "soft" on the basis of the method of determination. Crude oils may contain up to 6 wt. % "hard" and 10 wt. % "soft" asphaltenes.

## **A.2 Main oil categories – Related to weathering**

The relative composition of oils will differ extremely, resulting in great variations in physical properties and following, behaviour after a spill at sea.

Related to weathering oils can roughly be divided into 3 main categories:

- Crude oils
- Light oils
- Condensates

**Crude oils** contain relatively more of the heavier components than the other two categories, and the 250°C+ residue (corresponds to 0.5 to 1 week after a spill at sea) evaporates less than 50 vol. %. The heavier components make possible formation of stable water-in-oil (w/o) emulsions, which reduces the 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 differentiated in the reservoir terminology. However, related to weathering studies, it is suitable to deal with the light oils as a separate category. Light oils have a high content of light components, and the 250°C+ residue evaporates less than 50 - 70 vol. %. In contrast to condensates light oils also contain heavier components. The content of these heavier, emulsion-stabilizing components cause that light crudes may emulsify water. These w/o emulsions are, however, very unstable. A light oil will spread less than a condensate, and a final film thickness of 0.5 mm is estimated.

**Condensates** evaporates typically more than 70 vol. % for the 250°C+ residue. Condensates will not contain components as asphaltenes and heavier waxes, and will not emulsify significantly amounts of water. The spreading is vast, with a final film thickness in the order of 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 the hydrocarbons increases with increasing molecular weight. Furthermore, paraffinic oils have lower density than those containing large amounts of high molecular weight aromatics, naphthenes and asphaltenes.

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:

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

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** *force distance/area speed* and has the unit: dyn·sec/cm<sup>2</sup>. = 1 Poise. The industry is often using the unit mPa.s = centipoise (cP). 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 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 in the area of typically 0.9 – 1 g/ml, the units cSt and cP will often have similar values.

The 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<sup>-1</sup> 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.

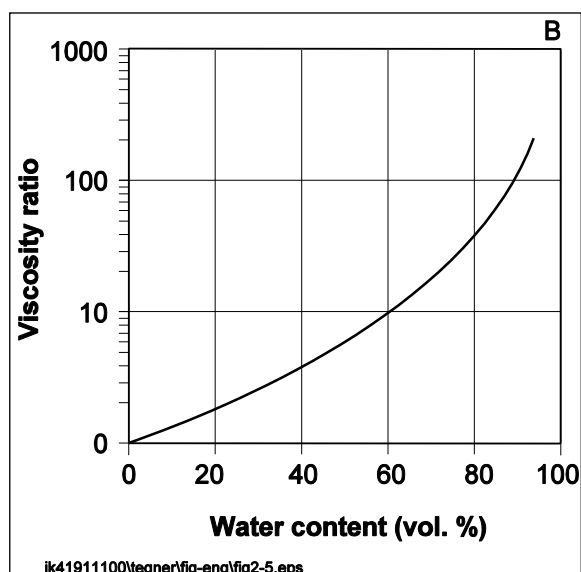


Figure A-2: Example of viscosity ratio as a function of water content

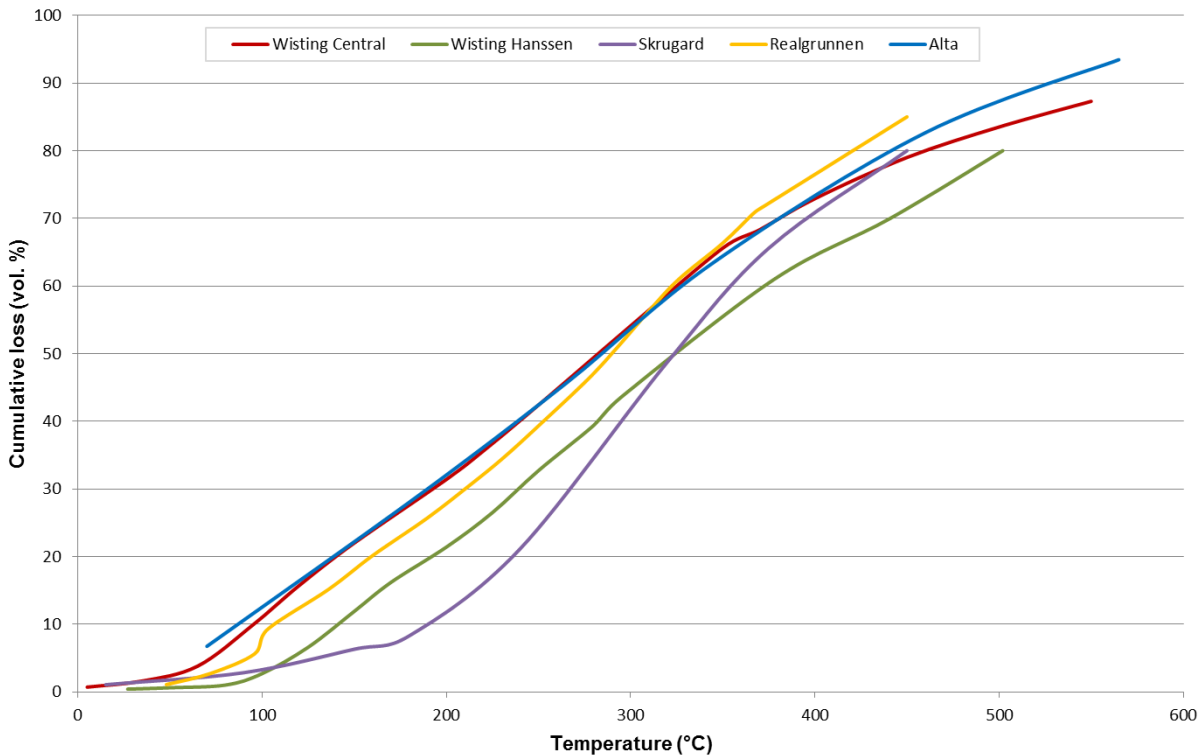
### A.3.2 Pour point

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 *10 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 important information when determining the efficiency of various skimmers, pumping rates and the use of dispersing agents.

### A.3.3 Distillation curve (True Boiling Point curve – TBP)

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 particular 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 for Wisting Central crude oil in comparison with other Norwegian crude oils**

### 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:**

*Moving in an oil slick where the oil's flash point is close to or lower than the sea temperature implies a fire and/or explosion hazard.*

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 is a number of 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 and the release of oil components into the water column, 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.

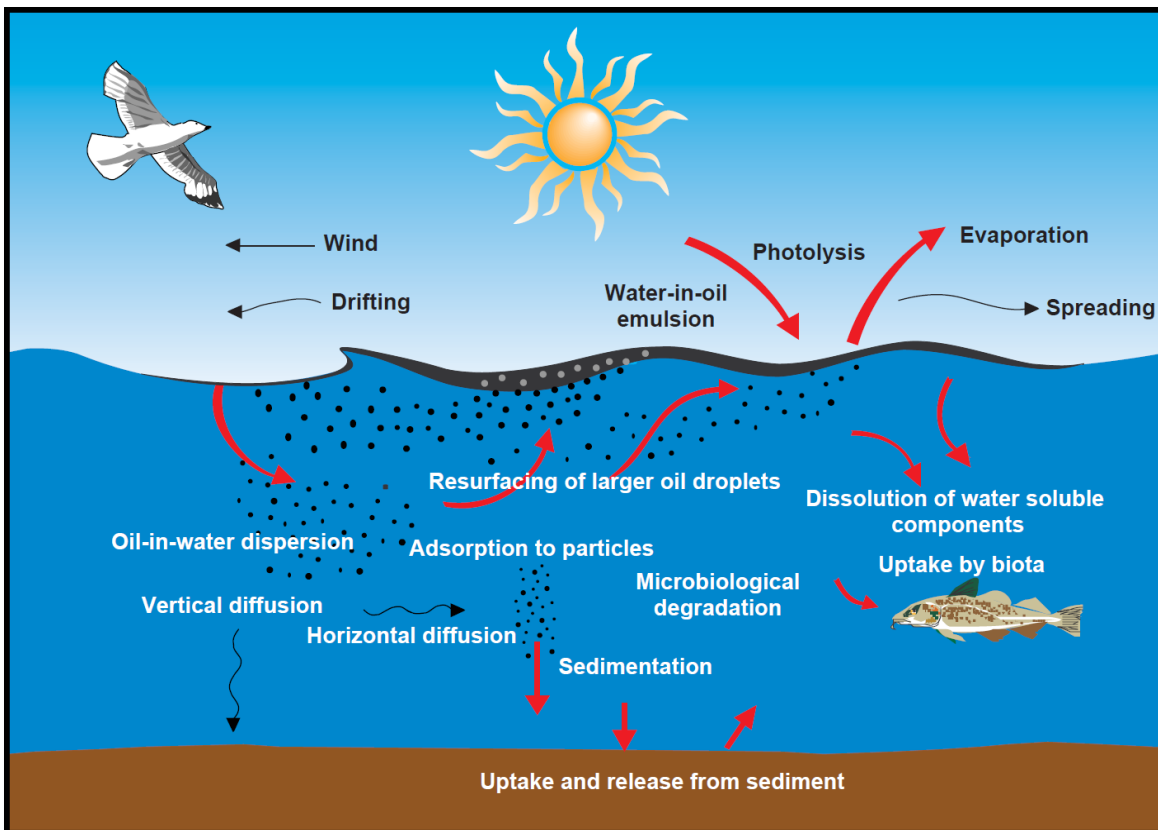
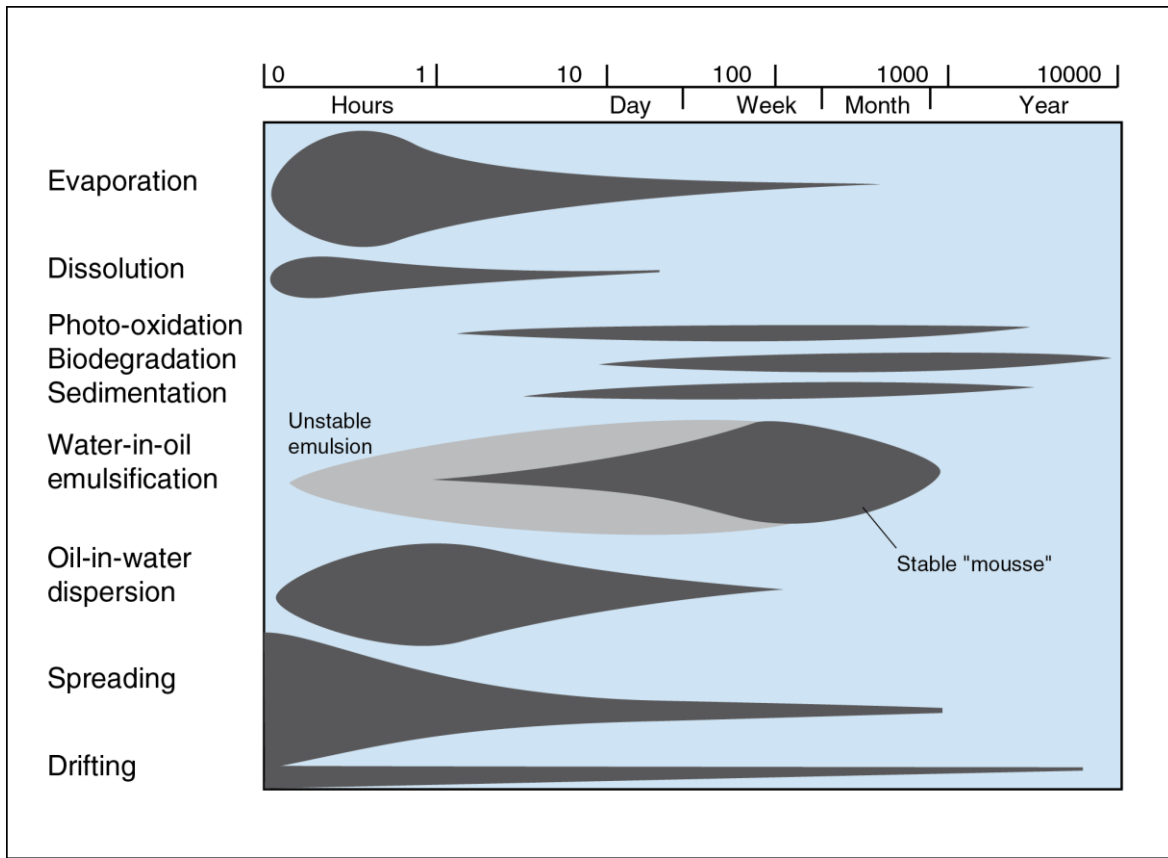


Figure A-4: Illustrating the weathering processes that take place when oil is spilled on the sea surface



**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.

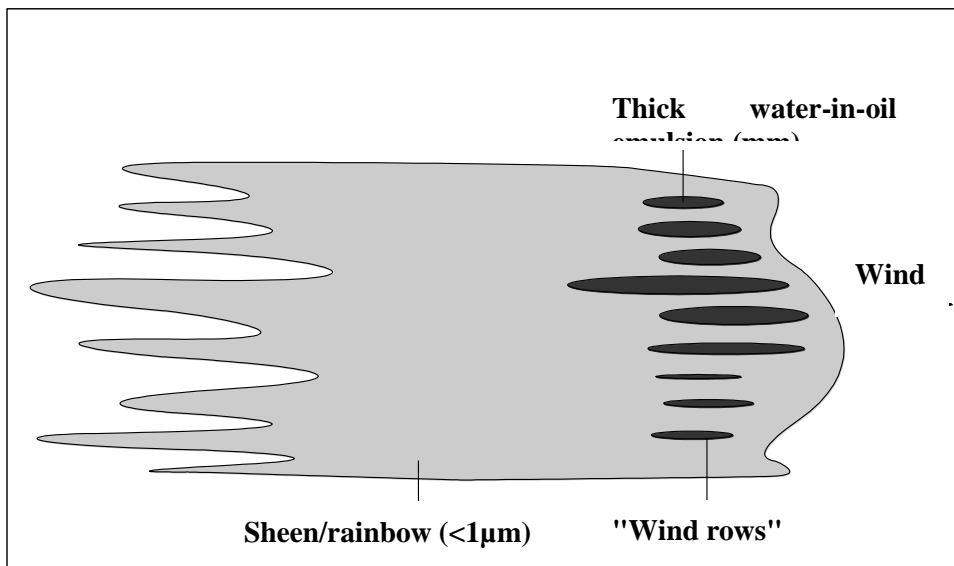
The most significant difference caused by evaporation is the loss of volatile and semi-volatile compounds, which increases the relative amounts of higher molecular weight compounds.

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 retarded if the oil's pour point is 10-15°C below the sea temperature.

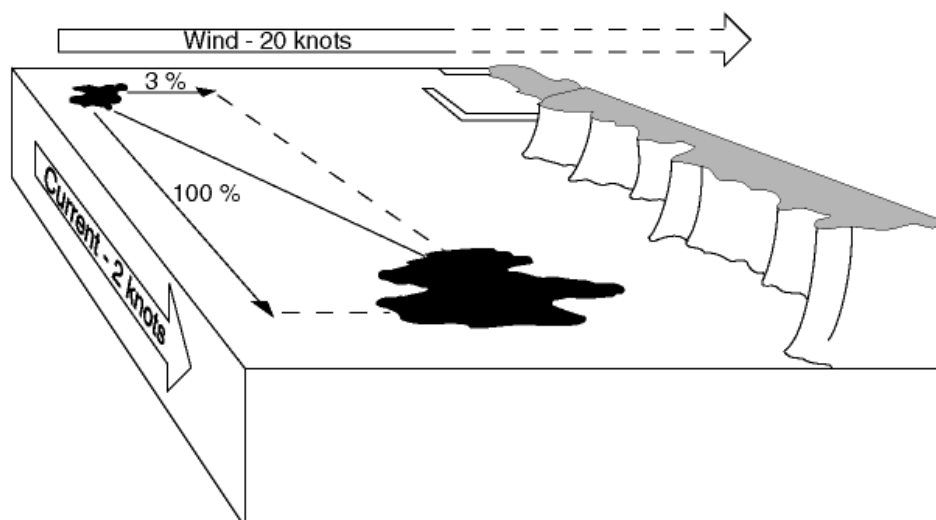
Oceanographic conditions (e.g. wind, waves and currents) affect the spreading process. The oil slick will be broken into windrows aligned in the direction of the wind, see Figure A-6. The thickness of the oil slick varies, often differing by a factor of several thousand. Experience has shown that e.g. 90 vol.% of the oil spilled may consist of patches of w/o emulsion with a film thickness of 1 to 5 mm, which often constitutes less than 10% of the total oil slick area. The remaining 5-10 vol. % usually covers 90% of the spill area in the form of a sheen (<1  $\mu\text{m}$  oil thickness).



**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. As a result of emulsification, the total emulsion volume may increase to as much as six times the original spilled oil volume depending on the properties of the oil. 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.

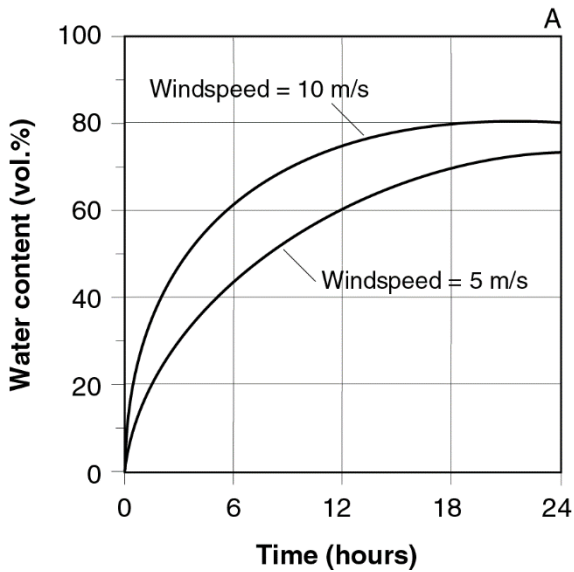
The minimum criterion for the formation of w/o emulsions is the presence of breaking waves (i.e. a wind speed of >5 m/s). Nonetheless, a slow water uptake can also take place during calmer weather. Figure A-8 shows how wind speed influences the w/o formation rate.

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 fairly independent of the prevailing weather conditions as long as 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.

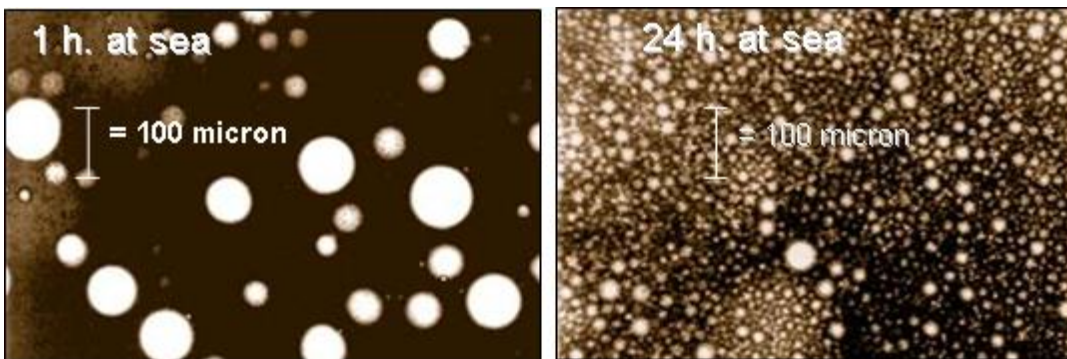
The w/o emulsion formation rate depends on the oil's chemical composition, which varies for different oil types.





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

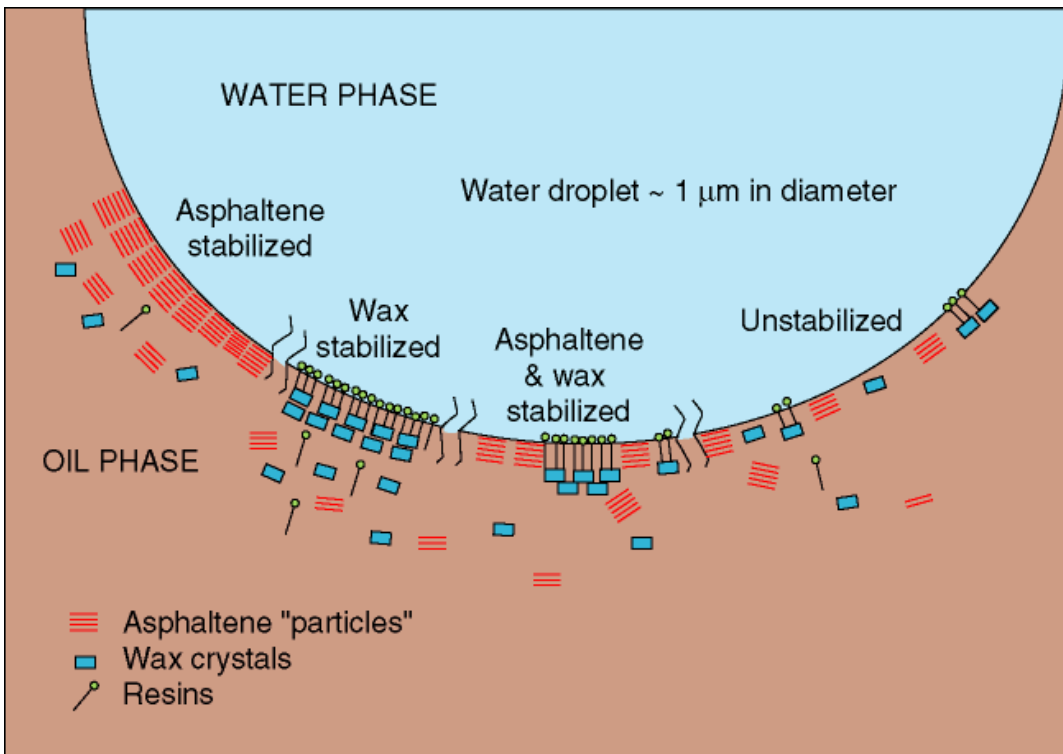
The stability of the w/o emulsion depends on the water droplet size, since not all water droplets in the emulsion are stable. Larger water droplets may be reduced in size by the flexing, stretching and compressing motion of the slick due to wave action, whereas the largest droplets may coalesce and be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

At SINTEF's laboratories we have the possibility to measure the ultra-low interfacial tension (IFT) values of oil/water/surfactant interfaces by the spinning drop apparatus. With our ultra-modern equipment it is possible to measure the IFT in the range from  $1 \cdot 10^{-6}$  to  $2 \cdot 10^3$  mN/m.

#### **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 droplets of diameters, typically  $1 \mu\text{m} - 1 \text{mm}$ , which are then mixed into the water mass. The largest oil droplets will resurface and form a thin oil film (typically  $<50 \mu\text{m}$ ) behind the oil slick. 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 the 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 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. The dispersant reduces the interfacial tension between water and oil and thus promotes dispersion. When effective chemical dispersion is achieved, small oil droplets are formed with diameters typical 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<sub>7</sub>) 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. This contributes to the stability of w/o emulsions, therefore exerting a large influence on the oil's persistence on the sea surface. The photo-oxidized components will stabilize the w/o emulsions. After a long period of weathering at sea, tar balls, mainly consisting of asphaltenes, may be formed and can 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. The various microorganisms prefer specific oil components as their energy source. Bacteria can only degrade oil in contact with water and depend 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 in the water mass.

Important factors influencing the biodegradation rate are temperature, the nutritive supply that contain nitrogen and phosphorus, the oxygen supply, oil type and the degree of weathering. Low molecular compounds are degraded more rapidly than the 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). PAHs dissolved in water can be degraded within a few days (Brakstad and Faksness, 2000). Degradation of oil in contact with seawater depends highly on the water/oil interface area. The interfacial area increases as the oil is spread over the sea surface as a thin layer or by chemical or natural dispersion of oil into the water column.

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, and it has been shown that *n*-alkanes are biodegraded within 2-4 weeks at North Sea conditions (Brakstad and Lødeng, 2005). Other higher molecular-weight oil compounds are biodegraded 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 a particular material 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 particular 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.4.10 Deep 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.

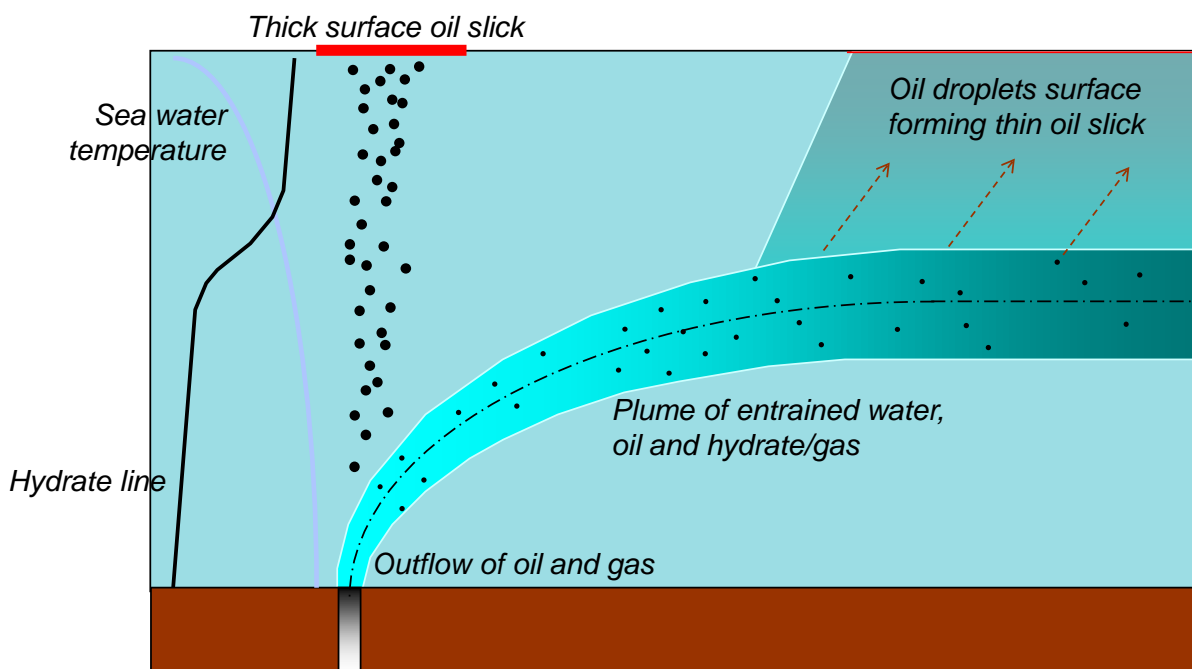
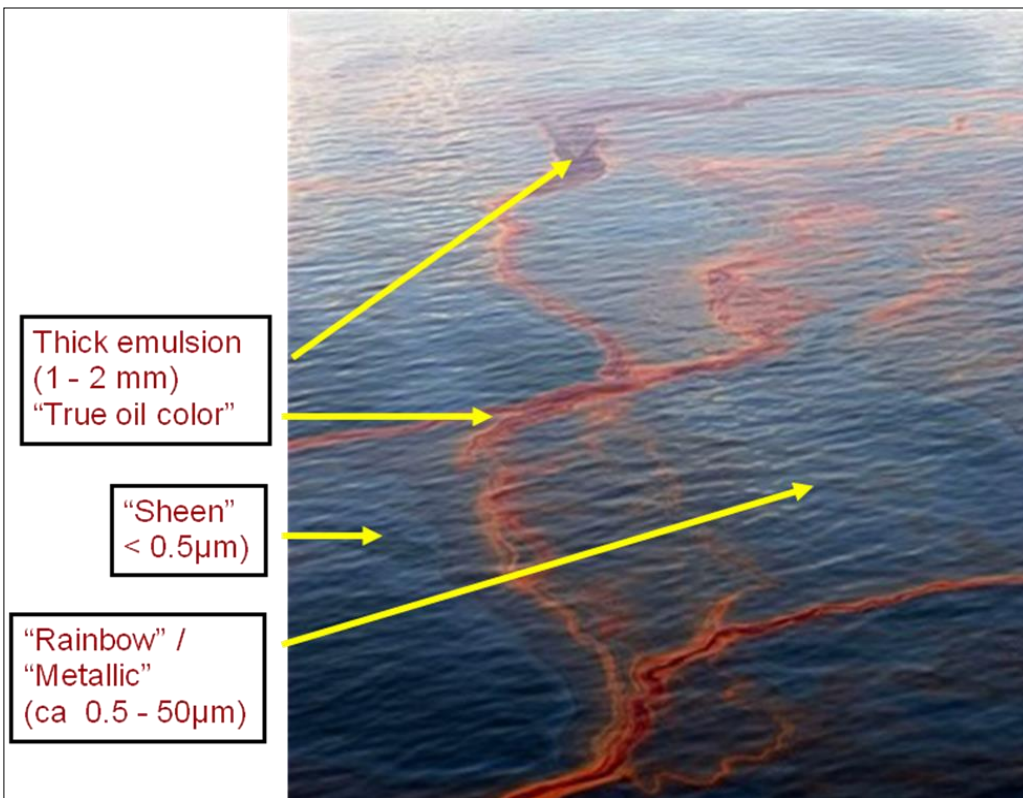


Figure A-11: Illustration of possible creation of thick surface oil slick (> 200  $\mu\text{m}$ ) from deep-water release of oil



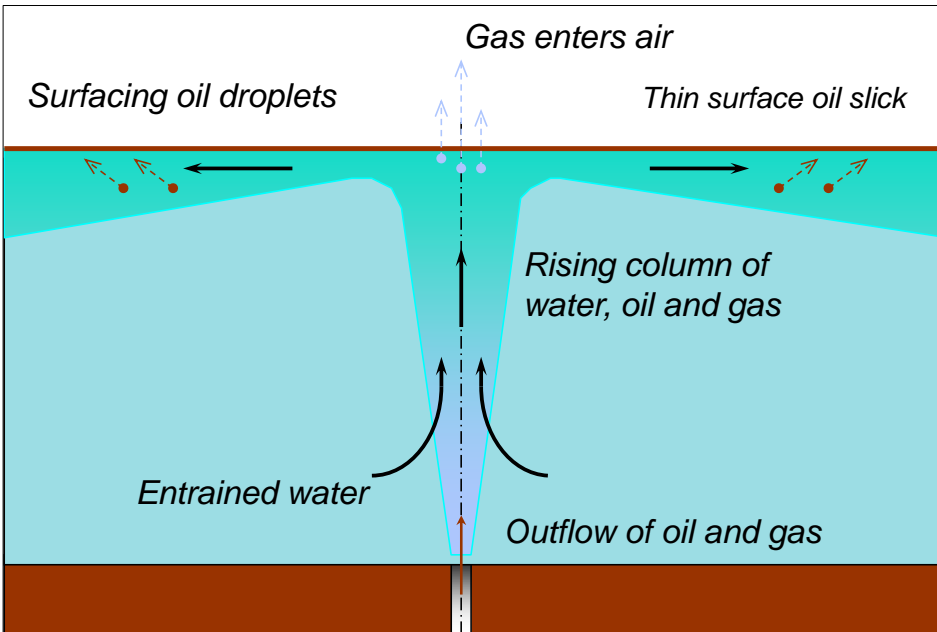
**Figure A-12:** Surface oil slick (initial thickness > 200  $\mu\text{m}$ ) from the experimental deep-water release "DeepSpill" in 2000. Surface oil is emulsifying similar to an oil slick from a surface batch release (from Leirvik et al., 2011)



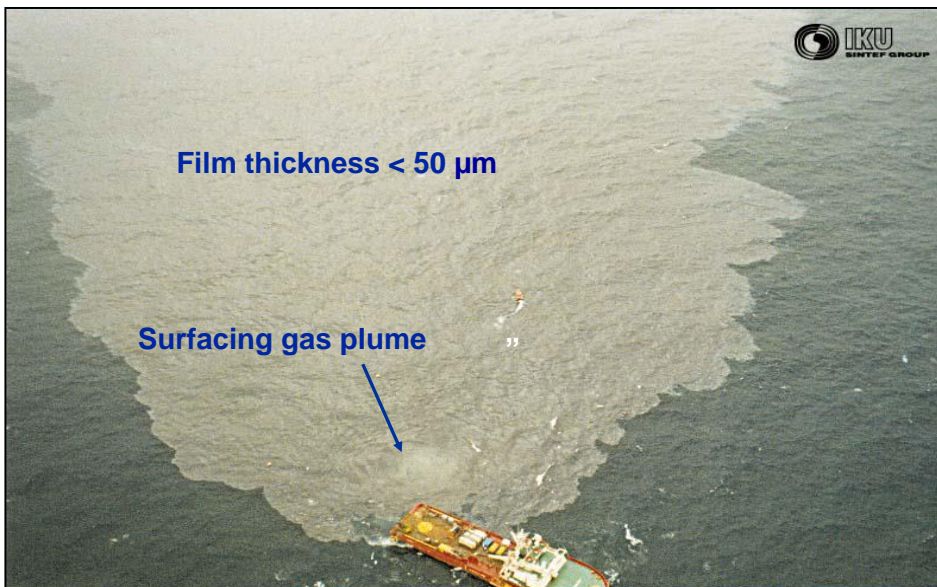
**Figure A-13:** Surface oil slick (initial thickness > 200  $\mu\text{m}$ ) from the DWH deep-water release. Surface oil is emulsifying similar to an oil slick from a surface batch release

#### A.4.11 Shallow 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  $\mu\text{m}$ ) from a shallow subsurface release (<500 m)



**Figure A-15:** Surface oil slick (< 50  $\mu\text{m}$ ) 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)

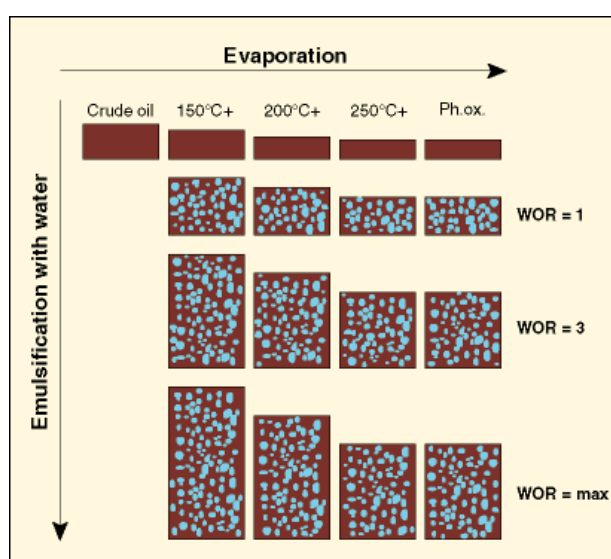
## B Experimental setup

### B.1 Oil samples and test temperature

The Wisting Central crude oil arrived at SINTEF Environmental Technology in 2016. The crude oil was given the unique SINTEF ID 2016-320. The weathering and dispersibility study were performed at 5 °C, regarded as relevant sea temperature in the Barents Sea. Predictions of the weathering properties were conducted at 2 and 5 °C.

### B.2 Small-scale laboratory testing

To isolate and map the various weathering processes at sea, the Wisting Central crude oil was exposed to a systematic, stepwise procedure developed at SINTEF (Daling et al., 1990). The general procedure is illustrated in Figure B-1.



WOR: Water to Oil Ratio

WOR=1: 50 vol.% water

WOR=3: 75 vol.% water

*WOR=max: the maximum water content*

**Figure B-1:** 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 flash point 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)	-	Spinning drop video tensiometer SVT 20 N, Dataphysics

**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-2. 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.



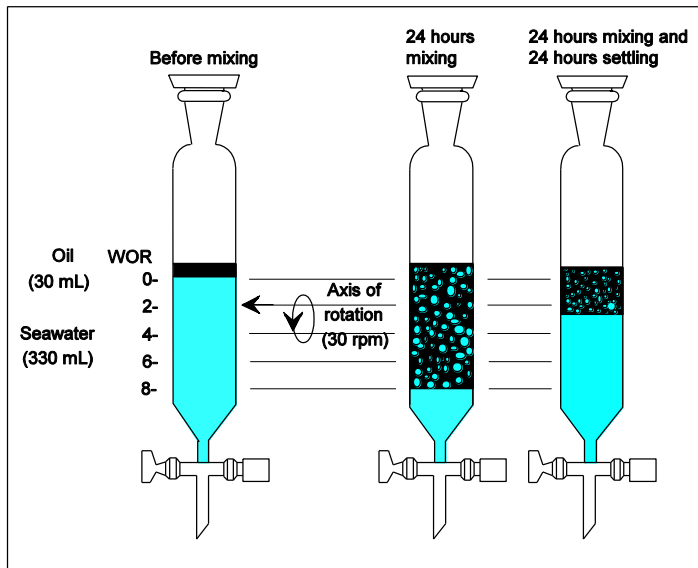


Figure B-2: Principle of the rotating cylinder method

### 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 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 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-3.

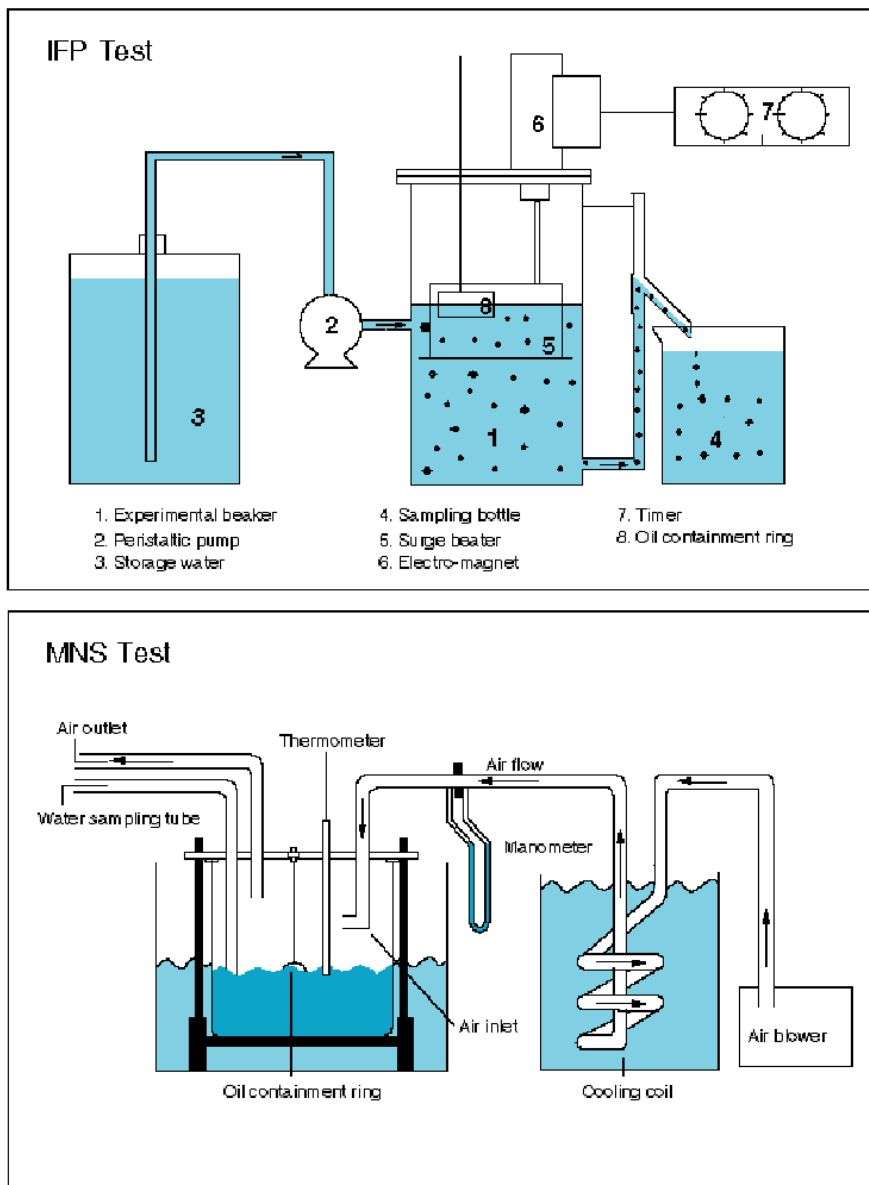


Figure B-3: IFP and MNS test apparatus.

## C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Wisting Central is given in Table C-1 to Table C-3. The oil weathering predictions were conducted at 2 and 5 °C.

**Table C-1: Physical and chemical properties for Wisting Central crude oil at 5 °C**

Properties of fresh oil	Value
Density (g/mL)	0.838
Pour point (°C)	-36
Reference temperature (°C)	5
Viscosity at ref. temp. (mPa.s = cP) *	10
Asphaltenes (wt. %)	0.05
Flash Point (°C)	-
Wax Content (wt. %)	0.71
Dispersible for visc. <	3000
Not dispersible for visc. > **	-
Maximum water uptake (%)	-

\* Measured at shear rate  $10s^{-1}$

\*\* Not reached in the laboratory

- No data

**Table C-2: True boiling point (TBP) curve for Wisting Central crude oil**

Temperature (°C)	Volume (%)*
5	0.7
35	1.6
65	3.8
95	9.9
120	15.7
150	22.0
200	31.4
250	42.4
300	54.1
350	64.6
400	72.9
450	79.0
500	83.5
550	87.3

\*TBP derived from crude assay:

Reference "WICLB479" provided from OMV Norge

**Table C-3: Lab weathering data for Wisting Central crude oil at 5 °C**

<b>Property</b>	<b>Fresh</b>	<b>150°C+</b>	<b>200°C+</b>	<b>250°C+</b>
Boiling Point Temp. (°C)	-	192	250	309
Vol. Topped (%)	0	17.2	29.3	42.1
Weight Residue (wt. %)	100	84.9	73.5	61
Density (g/ml)	0.838	0.859	0.871	0.883
Pour point (°C)	-36	-36	-36	-36
Flash Point (°C)	-	40	79	120
*Viscosity of water-free residue (mPa.s =cP)*	10	25	62	206
*Viscosity of 50% emulsion (mPa.s = cP)**	-	178	439	1229
*Viscosity of 75% emulsion (mPa.s = cP)**	-	1060	2058	4734
*Viscosity of max water (mPa.s = cP)*	-	810	1857	1622
Max. water cont. (vol. %)	-	83	70	56
(T1/2) Halftime for water uptake (hrs)	-	1.7	0.63	0.25
Stability ratio	-	0.95	1.0	1.0

\* Measured at shear rate  $10\ s^{-1}$

\*\*Measured at shear rate  $10\ s^{-1}$

- No data

## D Chemical characterisation of the fresh oil on GC-MS

*Table D-1: Chemical composition of Wisting Central based on GC-MS analysis of fresh oil*

No	Description	Wisting Central, wt. %
1	C1-C4 gasses (dissolved in oil)	1.000
2	C5-saturates (n-/iso-/cyclo)	1.000
3	C6-saturates (n-/iso-/cyclo)	1.849
4	Benzene	0.151
5	C7-saturates (n-/iso-/cyclo)	5.000
6	C1-Benzene (Toluene) et. B	0.984
7	C8-saturates (n-/iso-/cyclo)	8.016
8	C2-Benzene (xylenes; using O-xylene)	1.659
9	C9-saturates (n-/iso-/cyclo)	1.214
10	C3-Benzene	1.127
11	C10-saturates (n-/iso-/cyclo)	4.000
12	C4 and C4 Benzenes	0.057
13	C11-C12 (total sat + aro)	5.943
14	Phenols (C0-C4 alkylated)	0.000
15	Naphthalenes 1 (C0-C1-alkylated)	0.291
16	C13-C14 (total sat + aro)	8.709
17	Unresolved Chromatographic Materials (UCM: C10 to C36) 0 0 0	NA
37	metabolite 1	NA
38	metabolite 2	NA
18	Naphthalenes 2 (C2-C3-alkylated)	0.291
19	C15-C16 (total sat + aro)	6.709
20	PAH 1 (Medium soluble polyaromatic hydrocarbons (3 rings-non-alkylated; <4 rings))	0.139
21	C17-C18 (total sat + aro)	6.861
22	C19-C20 (total sat + aro)	7.000
23	C21-C25 (total sat + aro)	7.859
24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings))	0.141
25	C25+ (total)	30.000

NA – Not analysed

The method for generating the chemical composition is based on the quantification of semi-volatile organic hydrocarbons (SVOC) and volatile organic hydrocarbons (VOC). The composition is divided into individual pseudo-component groups (OSCAR groups) representing the oil, based on the TBP (True Boiling Point) and the chemical characterization by GC/MS analysis.

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, slick 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. OSCAR may compute oil weathering from crude assay data, although the most reliable results are produced if the target oil has been through a standardized set of laboratory weathering procedures established by the SINTEF laboratories. Alternatively, the model may use oil-weathering properties from oils for which data already exist, selecting the oil in the oil database that most closely matches the composition of the oil of concern.

## 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 has to 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 (e.g. OSCAR oil trajectory model) for modelling spreading of oil on the sea surface and for calculation of oil terminal film thicknesses.

The yield stress parameter 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 Wisting Central are tabulated in Table E-1, below. The yield stress is low for this crude oil /emulsion for this oil due to low viscosities and wax.

**Table E- 1 Yield stress (flow limit) measurements for Wisting Central crude at 5°C**

Residue	Water Content (Vol%)	Viscosity (mPa.s), 10s <sup>-1</sup>	Yield stress (Flow limit) (Pa)	Density (g/mL)
Fresh	0	10	ND	0.838
150°C+	0	25	ND	0.859
200°C+	0	62	ND	0.871
250°C+	0	206	ND	0.883
150°C+	50	178	ND	0.941
200°C+	50	439	ND	0.947
250°C+	50	1229	ND	0.953
150°C+	75	1060	0.2	0.983
200°C+	75	2058	0.5	0.986
250°C+	75	4734	5.6	0.989
150°C+	83*	810	2.9	0.996
200°C+	70*	1857	0.5	0.980
250°C+	56*	1622	-	0.992

ND: No yield stress quantified due to Newtonian properties \*Maximum water



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