Report

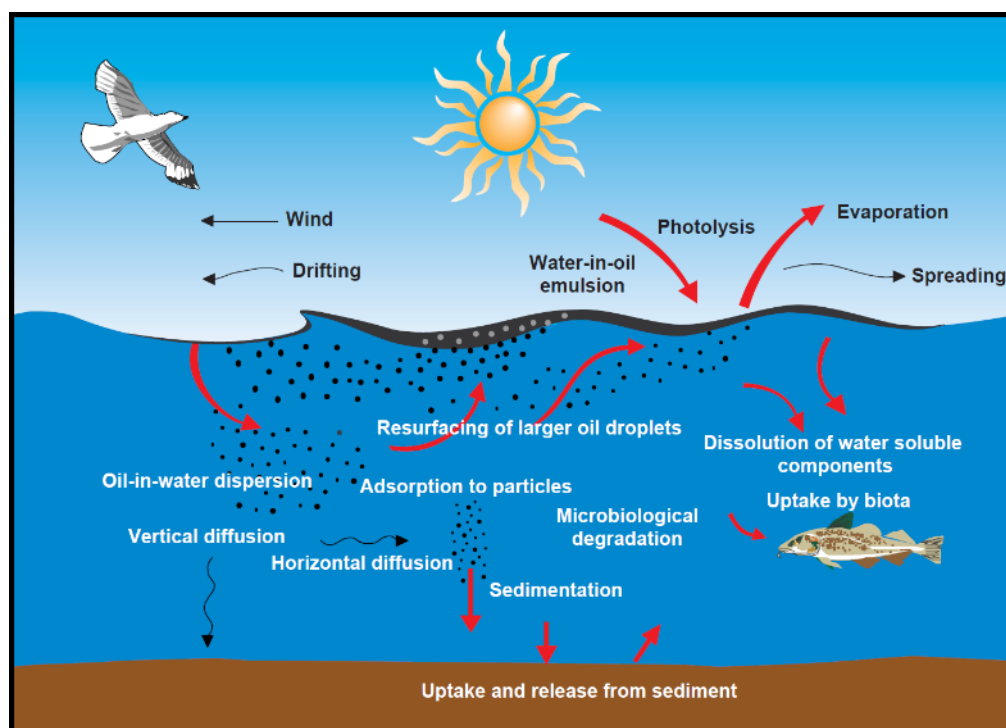## Drivis crude oil – Properties and behaviour at sea

In relation to oil spill response

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Drivis crude oil – Properties and behaviour at sea

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ABSTRACT

A weathering study oil has been performed on the Drivis crude oil. In addition, dispersibility testing was also conducted in order to establish a "window of opportunity" for the use of oil spill dispersants in a spill response scenario.

The obtained laboratory data were used as input in the SINTEF Oil Weathering Model (OWM) to predict the weathering properties of Drivis if spilled at sea. The weathering properties of Drivis crude oil were also discussed in relation to oil spill response by mechanical containment and recovery, and chemical dispersion.

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Table of contents

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 Drivis crude oil when weathered on the sea surface.

Drivis is categorized as a medium density paraffinic crude oil (0.838 g/mL) with low asphaltene content of 0.05 wt. %, and a low to medium wax content of 1.9 wt. % compared with other Norwegian oils. The fresh unweathered oil has a very low pour point (< -12 °C), but increases rapidly with the initial evaporative loss. High initial evaporative loss also results in an increase of the asphaltene and wax content, which contribute in stabilising the water-in-oil (w/o) emulsions.

Drivis formed stable emulsions with medium to low viscosities and with a rapid water uptake. The maximum water content was found to reach about 80 vol. %. However, the emulsion effectively released water when adding the emulsion breaker (Alcopol O 60 %) with a concentration of 2000 ppm by weight. Emulsion breaker may be used during an oil spill operation to remove or reduce water from the emulsion, normally applied after recovery and prior to transfer to storage tank to minimize the storage volume.

The prediction of mass balance indicates that Drivis will be removed from the sea surface within 1-2 days in high wind speeds (15 m/s), and nearly removed within 5 days in wind conditions 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 Drivis crude oil the flash point is predicted to be above 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. Drivis will reach this limit within 5-6 hours after a spill at calm wind speed (2 m/s), and more rapidly at higher wind speeds.

In low wind speed of 2 m/s, Drivis formed emulsions of relatively low viscosities (<1000 mPa.s), which may pose a challenge with boom leakage during the first 24 hours. At higher wind speeds, the emulsions predicted to surpass the 1000 mPa.s within the first 6 hours after a spill. The emulsion viscosities were predicted to remain below 20 000 mPa.s during the first five days, and reduced flowability towards traditional weir skimmers will likely not be a problem. However, in cases when high viscosity of the oil/emulsion is not a limiting factor, high pour point may cause solidification (i.e. elastic properties) of the oil on the sea surface. Solidification typically arises when the pour point of the oil is 10-15 °C above the sea temperature, and this phenomenon may occur for Drivis after 12 hours weathering at high wind speeds (10 m/s).

Drivis has a potential for use of oil spill dispersants. The oil was estimated to be easily dispersible with dispersant (Dasic NS) for viscosities in the range of 500 mPa.s (non-breaking waves, <5 m/s) to 3000 mPa.s (breaking waves, > 5 m/s), and not dispersible for emulsion viscosities higher than 10 000 mPa.s. The predicted time-window for dispersant application indicates that Drivis is chemically dispersible up to 2 days of weathering in low wind speed of 2 m/s at 5 and 10 °C, but the time-window subsequently reduces with higher winds speeds.

In general, when the 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 with use of firefighting (Fi-Fi) systems, thrusters or MOB boats after dispersant application may enhance the rate of dispersion. Drivis crude oil was estimated to exhibit reduced chemically dispersibility less than 10 000 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 worldwide. Due to large variations in different crude oils' physical and chemical properties, their behaviour and fate may vary greatly if spilled at sea. 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 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.

Dispersibility studies of the oil spilled after 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 (Ptil) 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 Environmental Technology in Trondheim has performed a weathering study of the Drivis crude oil on request from Statoil ASA. The obtained dataset were used to predict the weathering properties of Drivis if spilled at sea under different weather condition. The study included a meso-scale study in addition to dispersibility testing.
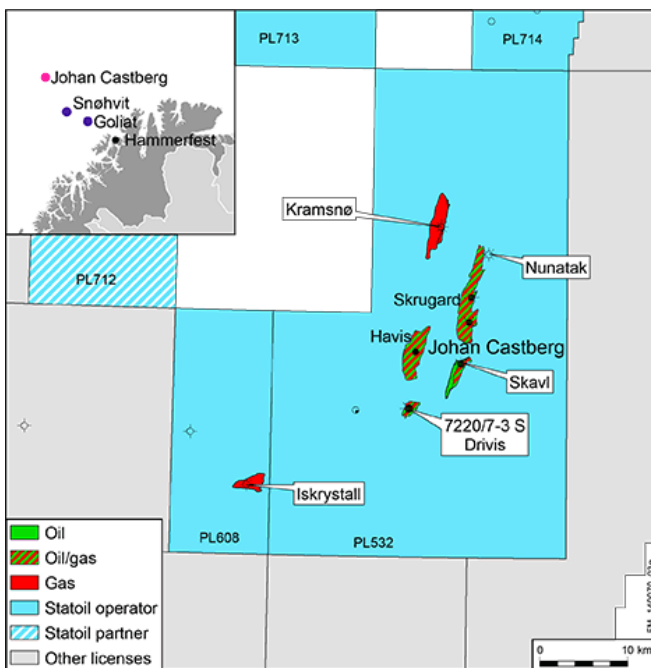
Johan Castberg was discovered in 2011 and contains oil and gas. The discovery is located in the Barents Sea about 110 kilometres north of the Snøhvit field. The water depth is about 370 metres. The reservoir contains Middle to Lower Jurassic sandstones. A joint development is planned for Johan Castberg, 7220/7-1 (Havis) and 7220/7-3 S (Drivis). In December 2015, it was decided to continue studying a development concept that includes a production, storage and offloading vessel (FPSO).

http://www.norskpetroleum.no/en/facts/discovery/72208-1-johan-castberg/

Statoil is operator for production licence PL532 with an ownership share of 50%. The licence partners are Eni Norge AS (30%) and Petoro AS (20%).

Figure 1-1: Location of the Johan Castberg discovery. Drivis prospect /Well 7220/7-3 S. Source: http://www.statoil.com/en/NewsAndMedia/News/2014/Pages/02May_Drivis.aspx

2 Experimental results and discussion

2.1 Small scale laboratory testing results

The bench-scale methodology is thoroughly described in Appendix B. The small-scale weathering results of Drivis crude oil were compared with similar data from the Johan Castberg oil field (Skrugard and Havis), in addition to Grane (North Sea) and Norne (Norwegian Sea) crude oils listed in Table 3-1. Drivis crude oil used in this study was given the laboratory identification: SINTEF ID 2014-0116.

Table 2-1: Oils compared with Drivis crude oil data in the report

Oil	SINTEF-ID	Report Number	Reference
Havis	2012-0243	A24356	Strøm and Johnsen, 2013
Skrugard	2011-0559	A22589	Øksenvåg, 2012
Grane	1997-0253	F98038	Strøm and Daling, 1997
Norne	1997-0276	A98126	Singsaas *et al.*, 1998

2.1.1 Chemical composition and physical properties

The chemical composition of Drivis and the other crude oils for comparison are shown in Figure 2-1 as GC/FID chromatograms, whereas the wax and asphaltene content, and physical properties are given in Table 2-3 and Table 2-4, respectively. Appendix D shows the composition groups derived from the chemical characterization of the fresh oil on GC/MS.

Gas chromatographic flame ionization detector (GC/FID) characterization

The chemical composition of Drivis, as characterized by gas chromatography (GC), is shown in Figure 2-1. The same figure also presents the gas chromatographic characterization of the corresponding residues (150°C+, 200°C+, and 250°C+) that verify the artificial evaporation of the oil by use of distillation (topping) in the laboratory. Figure 2-2 includes GC-chromatograms of the other crude oils used for comparison.

The GC-chromatograms show the *n*-alkenes as systematic narrow peaks where the peaks to the left in the chromatogram represent the components with the lowest boiling point. As can be seen in Figure 2-1, these components are gradually removed with higher distillation temperature. The more complex components such as resins and naphthenes are not easily separated as the *n*-alkanes and form a broad and poorly defined bump below more pronounced peaks. The bump is often described as "Unresolved Complex Mixture", or UCM. Heavier compounds such as asphaltenes ($> n$C40) are not possible to analyse with this technique. Drivis is a paraffinic crude oil reflecting low wax/paraffinic components in the range of nC$_{20}$-nC$_{30}$ and a minor content of UCM.

Gas chromatography (GC/FID) is also an important tool for oil characterisation and for oil spill identification the initial step. Common screening parameters used for identification, as well as for the degree of biodegradation, 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. These parameters for Drivis and other crude oils are given in Table 2-2.

Table 2-2: nC$_{17}$/Pristane and nC$_{18}$/Phytane ratios for fresh Drivis crude oil and other Norwegian oils

Oil	nC$_{17}$/Pristane	nC$_{18}$/Phytane
Drivis	1.2	2.4
Havis	1.3	2.7
Skrugard	0.3	0.6
Grane	1.6	3.0
Norne	1.3	1.9

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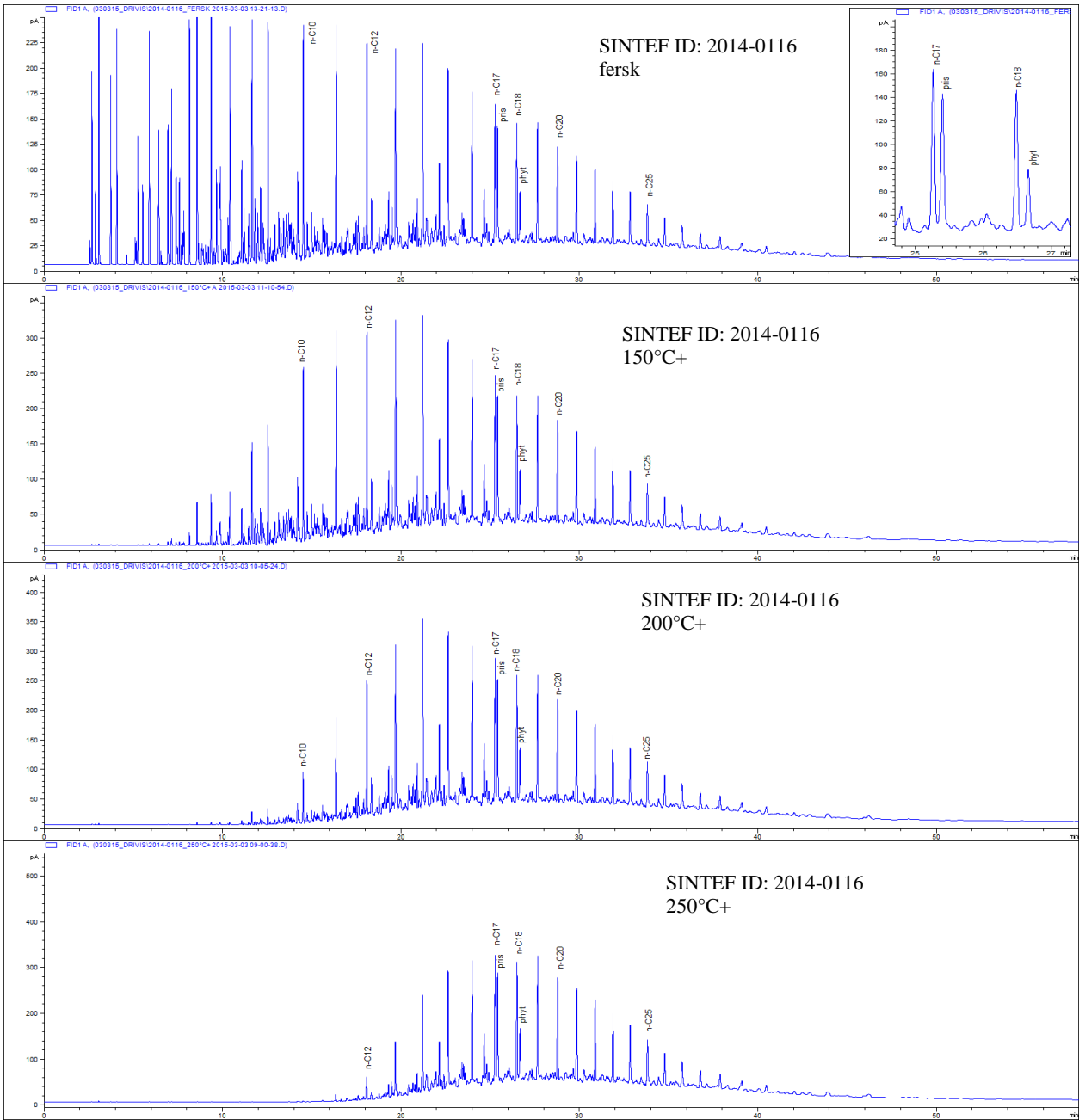
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Figure 2-1: GC/FID chromatograms of fresh sample and evaporated residues of Drivis crude oil
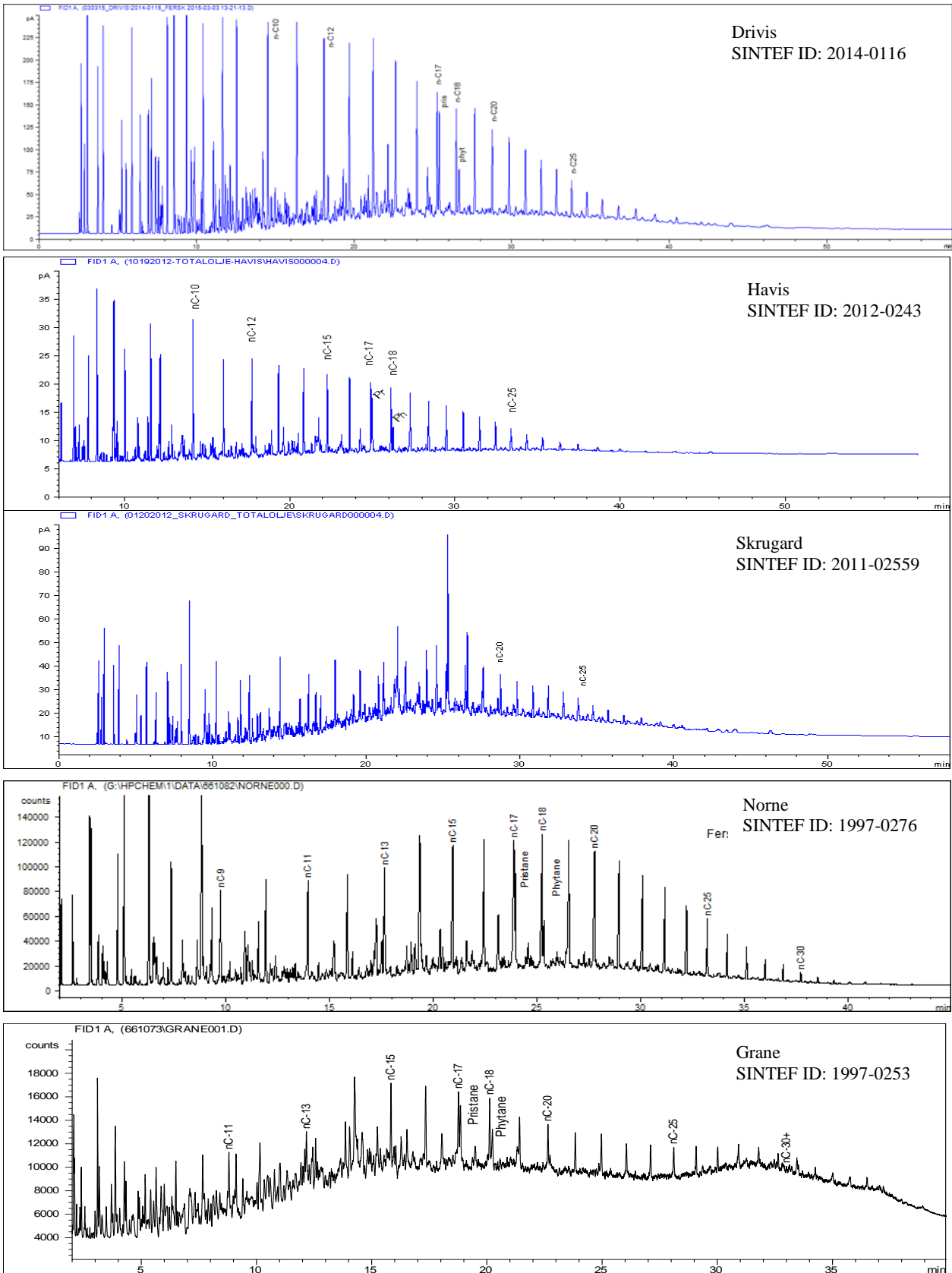
Figure 2-2: GC/FID chromatograms for fresh oils used for comparison

Asphaltene and wax content fresh and weathered residues

The chemical properties of asphaltene and wax are given in Table 2-3. Drivis (fresh oil) has a low contents of both asphaltenes (0.03 wt. %) and wax (1.9 wt. %), and is most comparable to Skrugard. Grane exhibits the highest content of asphaltenes (1.4 wt. %) and is regarded as an asphaltenic crude oil, whilst Norne is a waxy crude oil with very high content of wax (13 wt. %) in the fresh oil.

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

Oil	Residue	Asph. "hard" (wt. %)	Wax (wt. %)
Drivis	Fresh	0.05	1.9
	150°C+	0.07	2.3
	200°C+	0.07	2.7
	250°C+	0.09	3.3
Havis	Fresh	0.14	4.5
	150°C+	0.16	5.2
	200°C+	0.17	5.5
	250°C+	0.20	6.5
Skrugard	Fresh	0.05	1.9
	150°C+	0.05	2.0
	200°C+	0.06	2.1
	250°C+	0.06	2.4
Grane	Fresh	1.4	3.2
	150°C+	1.4	3.3
	200°C+	1.4	3.3
	250°C+	1.5	3.6
Norne	Fresh	0.1	13
	150°C+	0.1	14
	200°C+	0.1	15
	250°C+	0.1	16

Physical properties of fresh and weathered residues

Physical properties of Drivis and the other crude oils for comparison are listed in Table 2-4. Drivis exhibits the highest evaporative loss of 45 vol. % for the 250°C+ residue whilst the evaporative loss of Havis (34 vol. %) is an intermediate of Drivis and Skrugard (23 vol. %). The high-density Grane crude oil exhibits a very low evaporative loss of 13 vol. %, only.

Densities, pour points, flash points, viscosities and interfacial tensions of the fresh oil and the weathered residues of Drivis are most similar to those properties of Havis crude oil. Norne has high viscosities due to the very high content of wax.

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Table 2-4: Physical parameters of Drivis in comparison with other Norwegian 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⁻¹)	IFT (mN/m) ini.
Drivis	Fresh	0	100	0.838	-	-12	13	27
	150°C+	20	83	0.866	54	9	179	28
	200°C+	31	72	0.878	93	15	904	27
	250°C+	45	59	0.892	122	18	7134	29
Havis	Fresh	0	100	0.850	-	3	226	26
	150°C+	15	87	0.869	61	15	809	24
	200°C+	21	82	0.875	86	18	2222	24
	250°C+	34	69	0.887	125	24	9869	20
Skrugard	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	-
Grane	Fresh	0	100	0.942	26	-24	1330	-
	150°C+	3	98	0.948	70	-18	1980	-
	200°C+	5	96	0.950	92	-15	2830	-
	250°C+	13	89	0.960	139	-6	5970	-
Norne	Fresh	0	100	0.863	-	21	16600	-
	150°C+	5	95	0.869	42	24	12350	3775
	200°C+	13	86	0.877	79	27	21100	8370
	250°C+	22	80	0.883	112	30	30100	15445

-: No data available

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2.1.2 Emulsifying properties of Drivis crude oil

Emulsification

Emulsification is the mixing of seawater droplets into spilled oil at the water's surface (water-in-oil emulsion), forming a weathered oil product that 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 emulsified oil can be more difficult to recover and also be difficult to chemically disperse.

The emulsifying properties of Drivis were studied by use of the rotating cylinders as described in Hokstad et al., 1993. In general, residues of 150°C+, 200°C+ and 250°C+ are made for each oil in order to produce data for stability, viscosity, water uptake and effectiveness of application of an emulsion breaker. Four cylinders of each residue of each oil are prepared to study in parallel: stability testing and water uptake (rotating cylinder 1); viscosity / water update (rotating cylinder 2); effectiveness of emulsion breaker at dosage of 500 ppm (wt.%) (rotating cylinder 3); and effectiveness of emulsion breaker at dosage of 2000 ppm (wt.%) (rotating cylinder 4).

Emulsions containing the 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. The colour of the emulsions after 24 hours rotation was medium brownish with a yellow tint.

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 conducted 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 derived from kinetics is defined as the consumed time in hours needed to incorporate half of the maximum water uptake, and is derived from the tabulated data for each residue.

The $t_{1/2}$-values for the Drivis emulsions express a rapid water uptake particularly for the 150 and 200°C+ residue. The maximum water content of the w/o-emulsion is high ~ 80 vol. % for the 200 and 250°C+ residue. The 91 vol. % water content observed for the 150°C+ residue is considered a result of "super-saturation" of water in the oil and is unlikely to occur at sea.

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Table 2-5: Water uptake for the evaporated residues of Drivis 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	30	6	3
10 min	44	18	14
15 min	54	25	17
30 min	65	40	25
1 hour	71	52	33
2 hours	78	60	45
4 hours	91*	69	53
6 hours	91*	74	59
24 hours	91*	84	77
$t_{1/2}$	0.21	0.73	1.60

* 91 vol.% due to supersaturation- unlikely to happen in a spill situation at sea.

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 Drivis crude oil was studied by quantifying the amount of water released from the emulsion during 24 hours settling time. In addition, the efficiency of adding emulsion breaker (Alcopol O 60 %) to the emulsion was evaluated. In addition, significant amount of released water of the supersaturated emulsion (150°C+ residue) was observed when the cylinders were rotated once more after settling time. This indicates that minor energy would be required to break such emulsion. The results are tabulated in Table 2-6.

The results indicate that Drivis crude oil forms stable water-in-oil emulsions if spilled at sea and weathered. The effectiveness of applying chemical emulsion breaker was most efficient by using the highest concentration of 2000 ppm (0.2 wt. %).

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

Residue	Emulsion breaker	Water-in-oil emulsion (vol. %) at 5 °C		Stability ratio**	Stability ratio after rotation
		Reference	24 hours *		
150°C+	none	91	91	1.00	0.38
200°C+	none	84	85	1.00	0.95
250°C+	none	77	75	0.91	1.00
150°C+	Alc. O 60 % 500 ppm	91	36	0.05	-
200°C+	Alc. O 60 % 500 ppm	84	57	0.25	-
250°C+	Alc. O 60 % 500 ppm	77	76	0.95	-
150°C+	Alc. O 60 % 2000 ppm	91	12	0.01	-
200°C+	Alc. O 60 % 2000 ppm	84	9	0.01	-
250°C+	Alc. O 60 % 2000 ppm	77	17	0.06	-

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

Viscosity of emulsified residues

Table 2-7 gives the viscosities of water-free residues and the corresponding residues after emulsification at 5 °C with 50 vol. %, 75 vol. % and the maximum water. As a non-Newtonian fluid, the viscosities of Drivis emulsions are dependent on the shear rate, thus the viscosities are higher at a lower share rate (10 s^{-1}) compared to higher shear rates (100 s^{-1}). This decrease in viscosity with increasing shear rate is for the waterfree residue likely caused by breaking up the wax lattice structure with increased mechanical force. In general, Drivis shows an increasing emulsion viscosity with increasing degree of weathering (evaporating and water uptake).

Table 2-7: Viscosity of water-free residues and emulsions of Drivis at 5 °C

Residue	Water content (vol. %)	Viscosity (mPa·s) 5 °C	
		10 s^{-1}	100 s^{-1}
Fresh	0	13	11
150°C+	0	179	87
200°C+	0	904	300
250°C+	0	7134	1336
150°C+	50	864	311
200°C+	50	1167	509
250°C+	50	2937	1378
150°C+	75	1941	577
200°C+	75	2653	661
250°C+	-	-	-
150°C+	90	1169	217
200°C+	86	2346	345
250°C+	78	11131	164

- *No date due to water uptake < 75 vol. %*

2.1.3 Chemical dispersibility

The dispersibility testing included:

- Effectiviness of five different dispersants to find most optimal and relevant dispersant
- Dosage testing of the best/relevant dispersant.
- Systematic dispersant testing with the selected dispersant on weathered /emulsified samples as a basis to predict the time-window for effective use of dispersant by use of the SINTEF Oil Weathering Model (OWM).

Screening and dosage testing of dispersants

A screening testing was performed using the low energy test (IFP, reflecting non-breaking waves < 5 m/s wind speed) to investigate the effectiveness of different dispersants. The screening test was performed at the 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 express the highest dispersibility effectiveness.

The dosage testing was performed using a similar emulsion as for the screening study at 5 °C using the Dasic NS dispersant. This testing involved Dispersant-to-Oil/Emulsion ratios (DOR /DER) of 1:25, 1:50, 1:100 and 1:200. The dosage testing gives information about the design conditions for optimal use of dispersant agent. The results are presented in

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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 of the oil with use of high energy.

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

Dispersant (DOR/DER 1:25)	Efficiency dispersant (200°C+ /50 vol. % emulsion)	
	IFP	Viscosity (10s⁻¹)
Corexit 9500	76	685
Dasic NS	77	685
Finasol OSR 52	39	685
Gamlen OD 4000	57	685
Radiagreen OSD	59	685

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

Dispersant (dosage rate)	Efficiency of dispersant on 200°C+/50 vol. % emulsion*	
	IFP	MNS
Dasic NS (1:25)	37	100
Dasic NS (1:50)	35	100
Dasic NS (1:100)	23	100
Dasic NS (1:200)	7	98

The viscosity of the emulsion was 1167 mPa·s (10s⁻¹)

Systematic dispersant testing

Based on the screening testing, Dasic NS was chosen for the continued systematic testing of Drivis to determine the time window for dispersant use. Dasic NS is the dispersant agent in NOFO's stockpile, and a dosage rate of 1:25 (4 wt.%) is used as the standard procedure used to establish the time window for dispersant application. Table 3-10 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: Effectiviness of dispersant on weathered Drivis oil/emulsions at 5 °C

Residue	Water content (vol. %)	Viscosity (mPa·s) 10 s⁻¹	Viscosity (mPa·s) 100 s⁻¹	Effectiveness (%) IFP	Effectiviness (%) MNS
150°C+	0	179	87	67	100
200°C+	0	904	300	20	100
250°C+	0	7134	1336	<5	15
150°C+	50	864	311	32	100
200°C+	50	1167	509	32	100
250°C+	50	2937	1378	<5	86
150°C+	75	1941	577	24	91
200°C+	75	2653	661	16	50
250°C+	-	-	-	-	-
150°C+	91	1169	217	50	100
200°C+	91	2346	345	36	51
250°C+	81	11131	164	5	11

- *No date due to water uptake < 75 vol. %*

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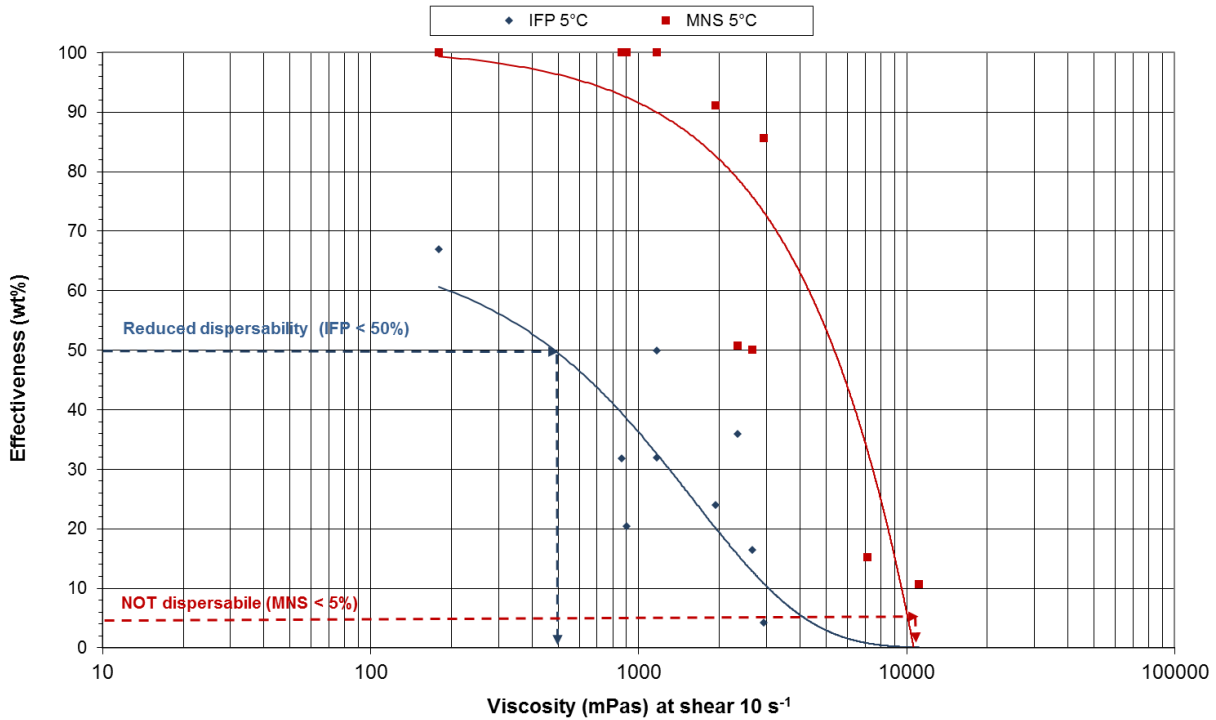
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Figure 2-4: Dispersant effectiveness of the Drivis crude oil and its weathered residues and emulsions at 5 °C

Drivis is considered to be dispersible for viscosities 500 mPa·s reflecting viscosities where the IFP-test produce 50 % effectiveness in non-breaking waves conditions (< 5 m/s), and up to 3000 mPa.s with the MNS-test reflecting breaking waves conditions (> 5m/s). However, the viscosity limit from the IFP-test is considered as most conservative, and were therefore chosen as input for prediction of time-window with use of the SINTEF Oil Weathering Model (OWM). The viscosity limit where Drivis is not dispersible with effectiveness lower than 5 % using the MNS-test was estimated to 10 000 mPa·s. The dispersibility limits are given in Table 2-11.

Table 2-11: Estimated viscosity limits for Drivis for use of dispersant and criteria for definition of time window

Dispersibility	Criteria (wt. %)	Dispersibility limits based on oil viscosities (mPa·s)
Chemically dispersible	IFP efficiency > 50 %* MNS efficiency < 75 %**	500 3000
Not chemically dispersible	MNS efficiency < 5 %	10000

Reflecting non-breaking waves > 5 m/s wind speed. Need of additional energy might be required to enhance the effectiveness of dispersant use in calm weather conditions.
** Reflecting breaking waves > m/s wind speed

2.2 Meso-scale laboratory testing

In general, the meso-scale laboratory testing give valuable operational information about the oil's behaviour under more realistic conditions as weathering processes are allowed to occur simultaneously. The flume testing is therefore considered as a supplement to the small-scale testing. The obtained meso-scale data are used for comparison with predicted behaviour and thus validates the predictions. The description of the meso-scale flume is given in Appendix B.2. This section provides an overview of the tabulated results of the meso-flume testing, visual observations, and estimated mass balance of Drivis at 5 °C.

The results obtained for Drivis in the meso-scale laboratory experiment are presented in Table 2-12, and show an increase in the water content, evaporative loss and emulsion viscosity throughout the experiment. However, after 48 hours the experiment was ended due to insignificant amount of emulsion /oil on the surface. No dispersant was therefore applied onto the surface. The oil/emulsion of Drivis was easily dispersed/entrained into the water column producing relatively large water droplets, where a significant amount of these droplets were adsorbed to the cooling elements (coil) placed in the bottom in the flume basin. This phenomenon was probably caused by a combination high pour point of the weathered oil, low water temperature, and high water content in the emulsified oil. This prevented resurfacing of the larger oil droplets during the experiments and hence, reduced the mass of surface oil faster than expected.

Table 2-12: results from the meso-scale weathering experiment of Drivis at 5 °C

Sample no	Time (hours)	Water content (vol. %)	Evaporative loss (wt. %)	Viscosity (mPa.s) 10 s^{-1}	Oil in water ppm*
1	0.5	65	16	-	167
2	1	69	18	138	122
3	2	72	20	199	151
4	4	67	23	1473	161
5	6	58	25	1171	124
6	24	-	-	-	-
7	48	-	-	1222	-

- No measured data
* ppm = parts per million by weight.

The weathering properties of Drivis derived from the meso-scale flume basin experiments were compared with the predicted properties of evaporation loss and emulsion viscosities by use of the SINTEF Oil Weathering Model (OWM). In addition, the estimated massbalance from the flume experiment and visual observations are also described in the sub-sections below.

2.2.1 Evaporation

Figure 2-5 shows the estimated evaporative loss in the meso-scale testing compared to the predicted evaporation by use of Oil Weathering Model (OWM), at 5 °C. The calculated evaporative loss from the meso-scale test corresponds well up to 6 hours with the predictions based on laboratory data.
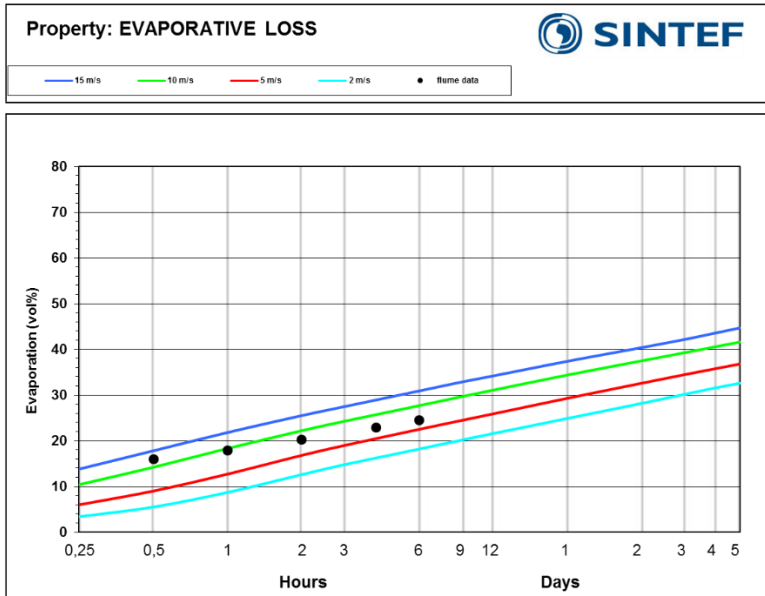
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Figure 2-5: Shows the predicted evaporative loss compared to the observed evaporative loss during the flume testing

2.2.2 Emulsion viscosity and water content

Figure 2-6 shows the measured emulsion viscosities of Drivis from the flume experiments compared to the predicted evaporation by use of Oil Weathering Model (OWM), at 5 °C. The measured data from the meso-scale is in accordance with the predictions based on laboratory data within 1 day of weathering. In general, increasing water content contributes to higher emulsion viscosities.

The meso-scale experiment showed high water uptake (~ 60-70 vol. %) of Drivis during the first hours of weathering with oil/emulsion of larger water droplets and emulsion that is more unstable. This phenomenon may be observed in a spill scenario, particular in breaking wave conditions.
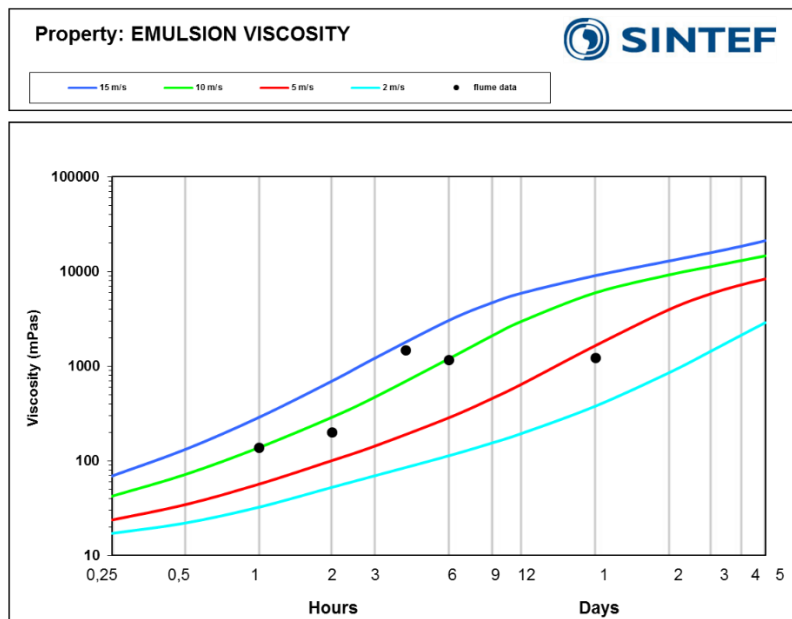
Figure 2-6: Predicted emulsion viscosities for Drivis at sea surface compared to measured viscosities from the flume testing

2.2.3 Mass balance

The main processes of the mass balance for oil spilled at sea are:

- Evaporative loss
- Surface oil
- Dispersed oil into the water column

In addition, the mass balances from the flume basin also includes the estimated parameters:
- Amount of oil sampled
- Amount of oil sticking to the flume wall

The amount of oil evaporated, oil on surface, dispersed and sampled oil was calculated, and the oil adsorbed onto the flume walls and the coils was estimated. Table 2-13 shows values for the mass balance of Drivis during weathering in flume experiment after 6 hours. Figure 2-7 shows the mass balance of Drivis after 6 hours.

Table 2-13: Mass balance for Drivis during the meso-scale laboratory test at 5 ºC after 6 hours of weathering

Mass balance (% of initial oil) of Drivis	6 hours weathering , 5 °C
Evaporated	25
Oil on water surface	5*
Dispersed oil	10
Sampled amount of oil	6
Oil adsorbed to the flume walls	5*
Adsorbed to cooling coil	49*

= value estimated from observations and pictures
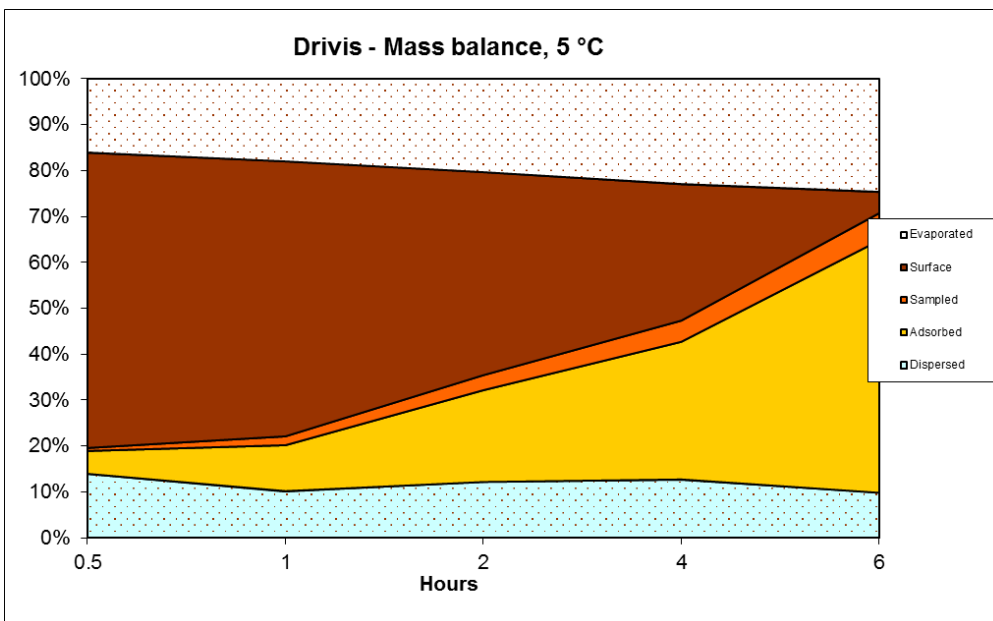
Figure 2-7: Mass balance of Drivis in the meso-scale flume test after 6 hours weathering

2.2.4 Visual observations

A selection of pictures taken during the flume experiment at 5 °C is presented below. Artificial sunlight simulated using a solar simulator was turned on for photographing, but otherwise turned off during the weathering time (no photo-oxidation). Note: Based on previously observations the oil/emulsion may be significantly lighter in appearance /colour with the solar simulator turned on.

- Sample 0 (start): The oil is black in colour and was distributed evenly on the flume water surface. Oil droplets (1-4 mm) were pushed down into the water column by the wave.
- Sample 1 (30min): The oil was still black in appearance and did not seem to have emulsified. Using the solar simulator the oil appeared more brown/grey (shimmering).
- Sample 2 (1 hour): The oil became thicker and emulsification had started. Large oil droplets (4-15 mm) were observed in the water column.
- Sample 3 (2 hours): The oil/emulsion continued to get more thicker – continued to emulsify. The emulsion was still evenly distributed on the water surface.
- Sample 4 (4 hours): The oil continued emulsify and became even thicker. The water column had changed colour to a light brown and there were observed large oil droplets in the water column. It was observed less oil/emulsion on the surface.
- Sample 5 (6 hours): The emulsion became more "smoother" and there was significantly less oil/emulsion on the surface.
- Sample 6 (12 hours): Less emulsion/oil on the surface.
- Sample 7 (24 hours): Almost no oil/emulsion left on the surface. The wave was switched off to gather enough oil/emulsion for surface sampling. The water column was now a mixture of oil droplets and water – it seems that the oil was naturally dispersed.
- Sample 8 (48 hours): Insignificant oil/emulsion on the surface. The experiment was decided to be terminated without dispersant application. The estimated amount of emulsion on the surface was about 50 mL and was considered to small amount to be added any dispersant.

Summary discussion

When the water-level was lowered after ending the experiment, it was observed that the cooling-coils in the bottom of the flume were covered with a layer of oil/emulsion. The surface oil was easily dispersed/entrained into the water column by the wave action producing small and larger water droplets, however, a larger fraction of the oil droplets (millimetre size) did not resurface naturally during the experiment, but were presumably "trapped" by the slightly cooler coils. This was likely caused by a combination of the low water temperature and the relatively high pour points of the evaporated oil, and the high water content emulsion. However, it is expected that the Drivis crude oil could have a potential to easily undergo naturally dispersion/entrainment into the water column in an oil spill situation with breaking waves conditions, where the larger oil droplets in (mm size) may have the ability to resurface naturally when the sea calms down. However, resurfacing was not observed in the flume experiment for Drivis crude oil.

Sample 0 (start): The crude oil is black and was easily distributed on the water surface.
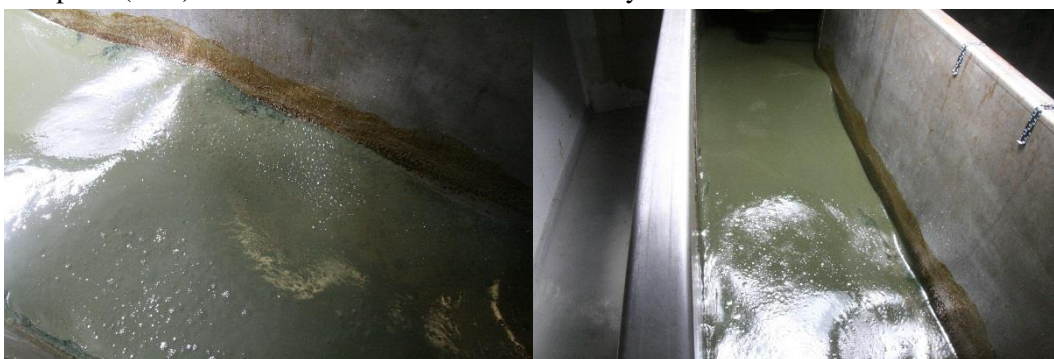
Sample 1 (30 min.): The oil appeared to be more brown/greyish with the solar simulator turned on. The oil was still evenly distributed on the surface of the flume.
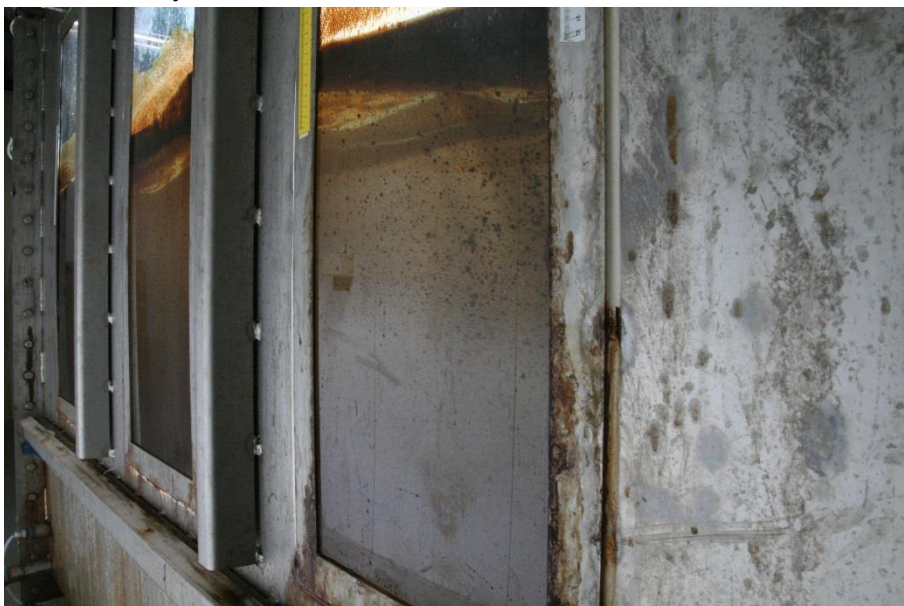
Sample 1 (30 minutes): Large oil droplets (1-4 mm) observed in the water column. The photo is taken on the far side of the wave.

Sample 2 (1 hour): Minor changes from sample 1 (30 minutes).
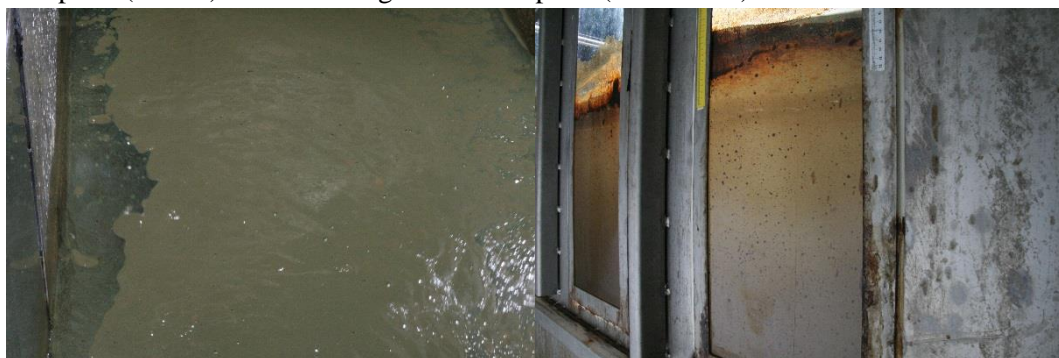
Sample 4 (4 hours): The oil/emulsion has been thicker with increasing viscosity.

Sample 5 (6 hours): Continuous emulsion formation.

Sample 6 (12 hours): Very little oil left on the surface, and no visible large oil droplets in the water column.

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Left: Sample 7 (24 hours): No change visually changes from 12 hours weathering. Right: Sample 8 (48 hours): The wave action was turned off and the oil/emulsion was collected. Estimated oil/emulsion: ~50 mL.

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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 Drivis 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 Drivis 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.
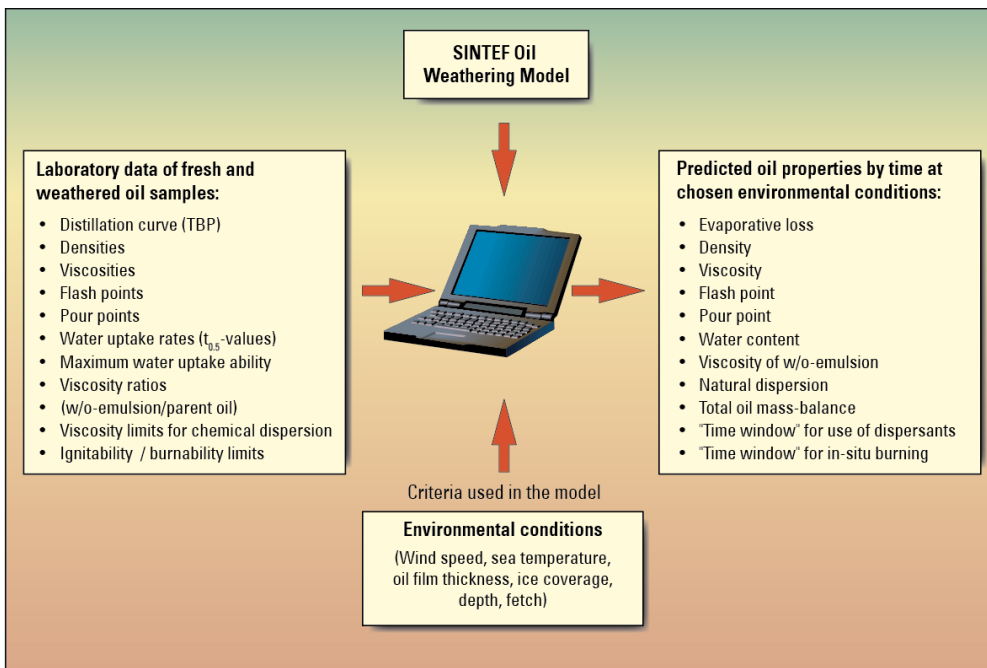

Figure 3-1: Schematic input data to the SINTEF OWM and the predicted output oil properties

Spill scenario
A standard surface release 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 small-scale testing. The terminal film thickness varies among these categories based on experimental (field) experience. Drivis 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 Drives were 5 °C in addition to 10 °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 Drivis 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:	5 °C and 10 °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 Drivis has drifted on the sea surface, the following prediction charts can be used to determine the remaining oil/emulsion's chemical, physical and emulsifying properties.

Table 3-2 gives examples for the following scenario:

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

Table 3-2: Weathering properties for Drivis obtained from the prediction charts after 12 and 24 hours of weathering

Property	12 hours 5 °C, 10 m/s	12 hours 10 °C, 10 m/s	24 hours 5 °C, 10 m/s	24 hours 10 °C, 10 m/s
Evaporation, wt. %	31	33	34	37
Water content, vol. %	64	64	77	77
Flash point, °C	95	100	104	110
Pour Point, °C	14	16	17	19
Viscosity, mPa·s*	3000	2700	5900	5400

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

Property: **EVAPORATIVE LOSS**
Oil Type: **DRIVIS 5DEG**
Description: **SINTEF ID: 2014-0116**
Data Source: **SINTEF Materials and Chemistry (2016), Weatherir** OWModel

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

Pred. date: Oct. 28, 2016

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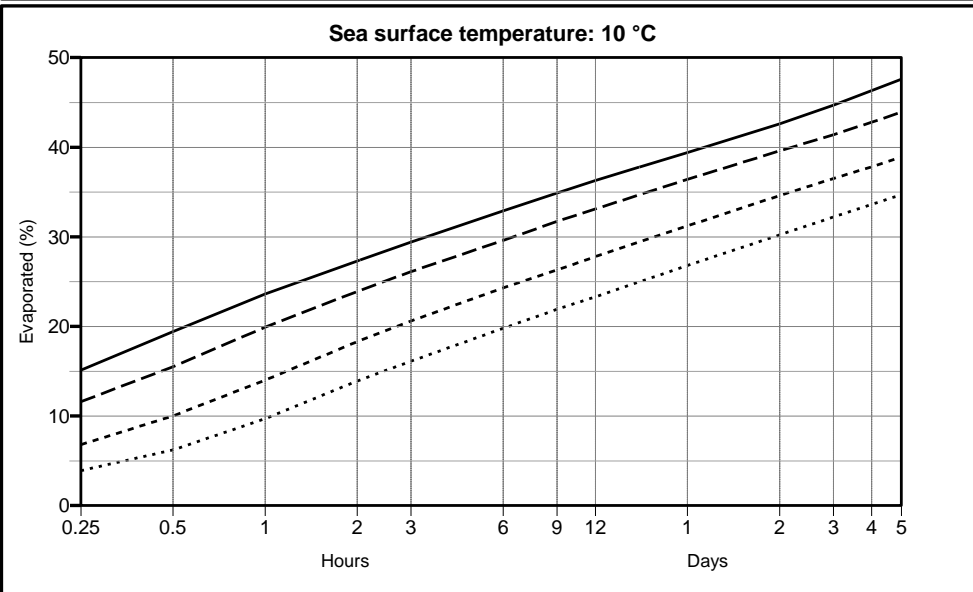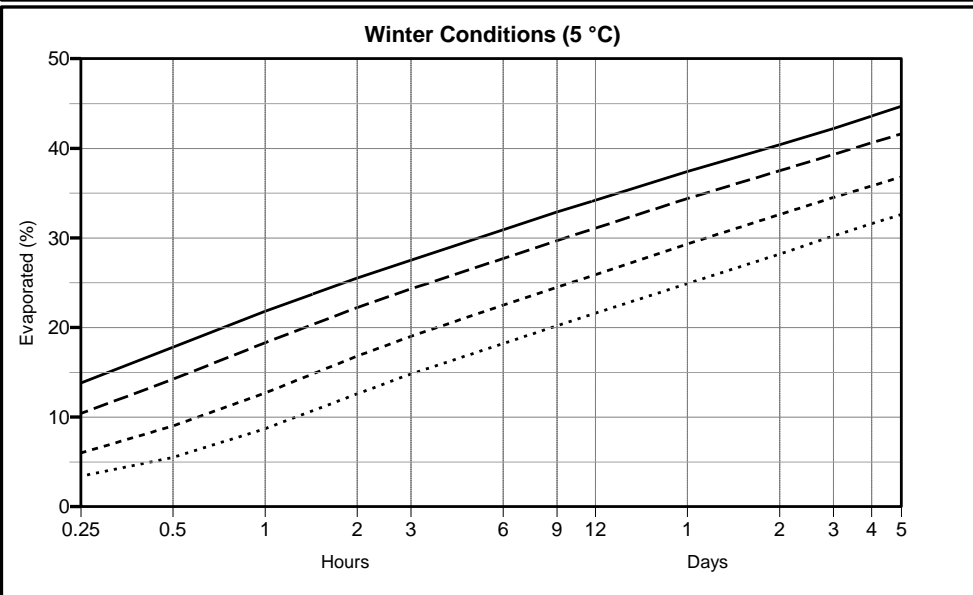---- Wind Speed (m/s): 5
····· Wind Speed (m/s): 2

Figure 3-2: Evaporative loss of Drivis crude oil predicted at sea temperatures of 5 °C and 10 °C

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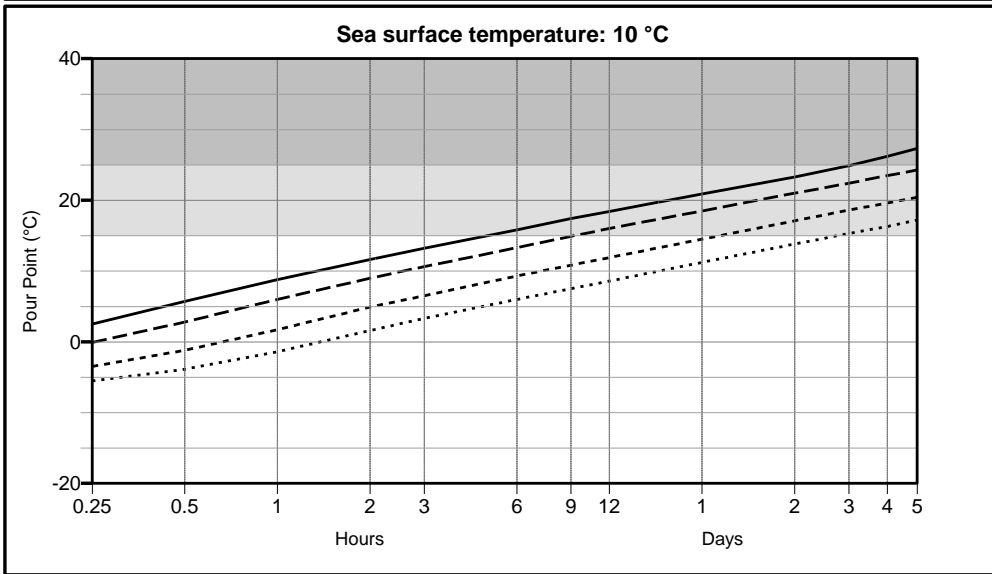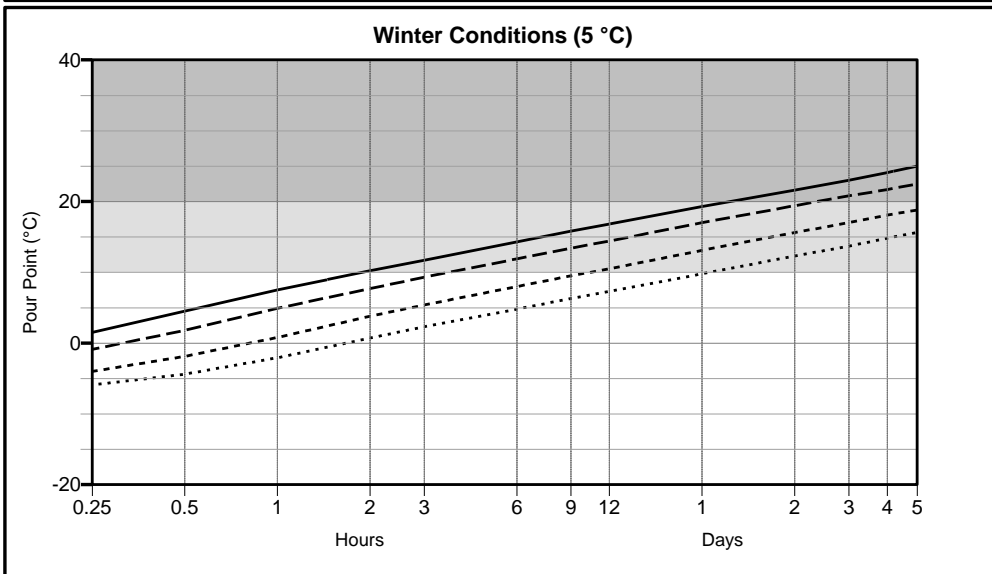REPORT NO.
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Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: DRIVIS 5DEG
Description: SINTEF ID: 2014-0116
Data Source: SINTEF Materials and Chemistry (2016), Weatherir

SINTEF

OWModel

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

Pred. date: Oct. 28, 2016

——— Wind Speed (m/s): 15	☐ No fire hazard
– – – Wind Speed (m/s): 10	▨ Fire hazard in tankage (<60 °C)
- - - Wind Speed (m/s): 5	▧ Fire hazard at sea surface (below sea temperature)
····· Wind Speed (m/s): 2	
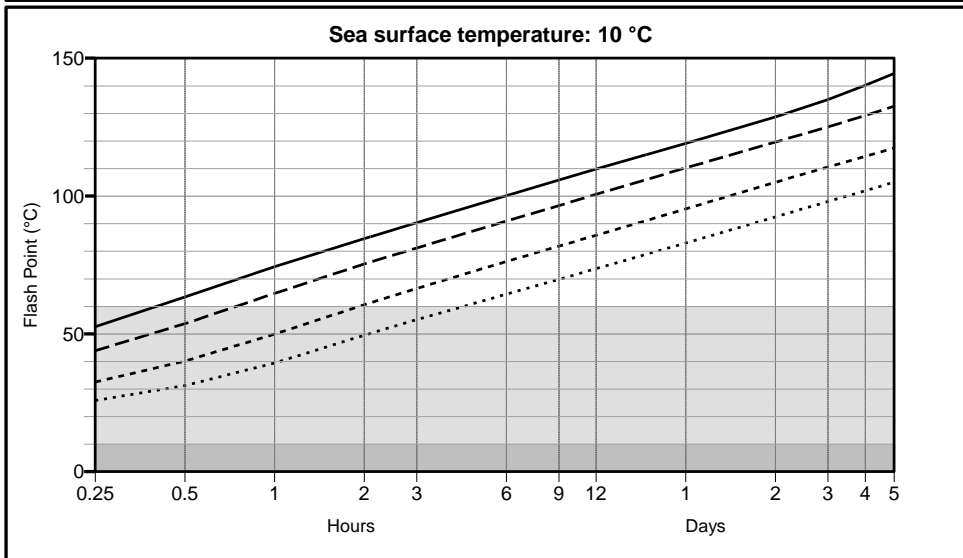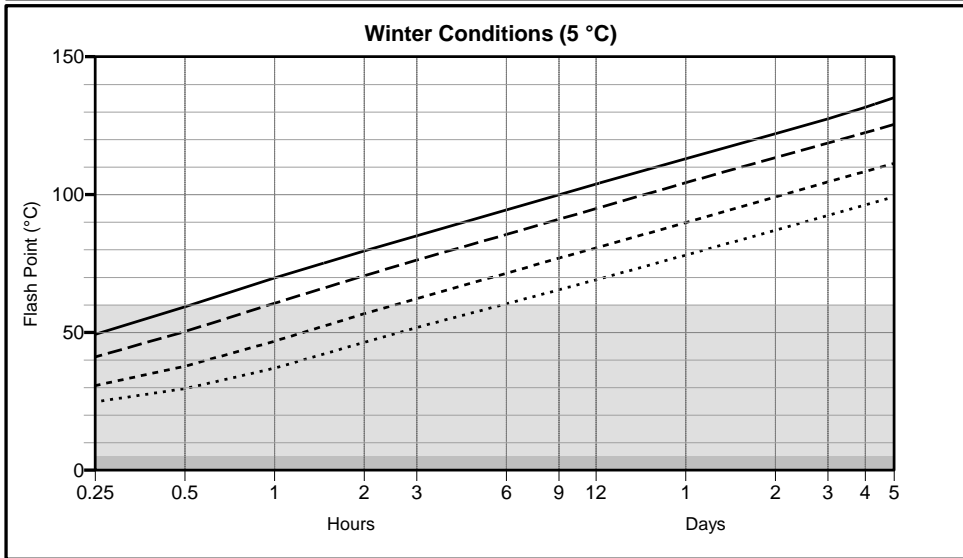
Based on flash point measurements of weathered, water-free oil residues.

Figure 3-3: Flash point of Drivis predicted at sea temperatures of 5 °C and 10 °C

Property: POUR POINT FOR WATER-FREE OIL
Oil Type: DRIVIS 5DEG
Description: SINTEF ID: 2014-0116
Data Source: SINTEF Materials and Chemistry (2016), Weatherin OWModel

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

Pred. date: Oct. 28, 2016

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

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

Figure 3-4: Pour point of Drivis predicted at sea temperatures of 5 °C and 10 °C

Property: WATER CONTENT
Oil Type: DRIVIS 5DEG
Description: SINTEF ID: 2014-0116
Data Source: SINTEF Materials and Chemistry (2016), Weatherin OWModel

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

Pred. date: Oct. 28, 2016

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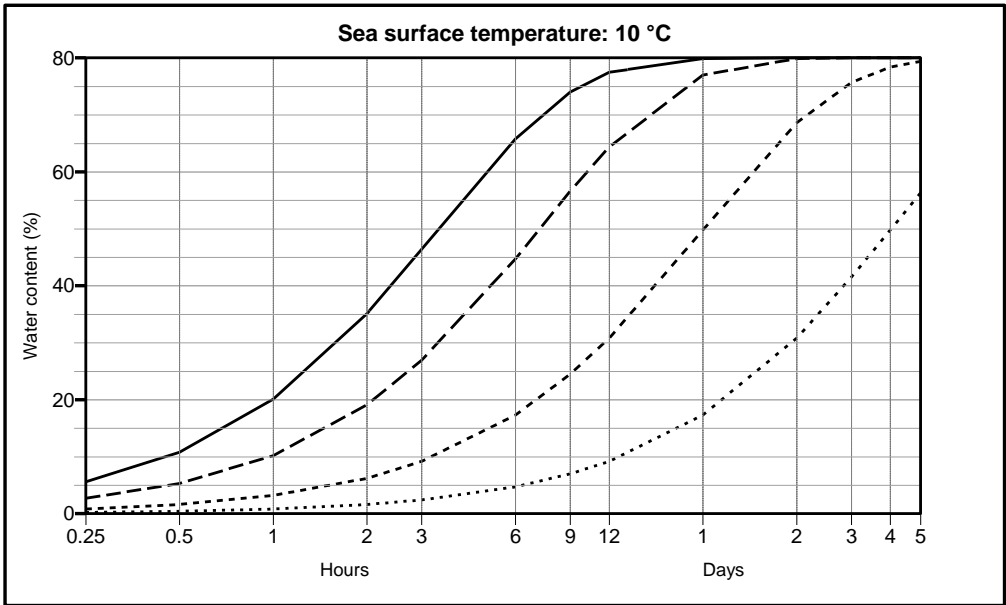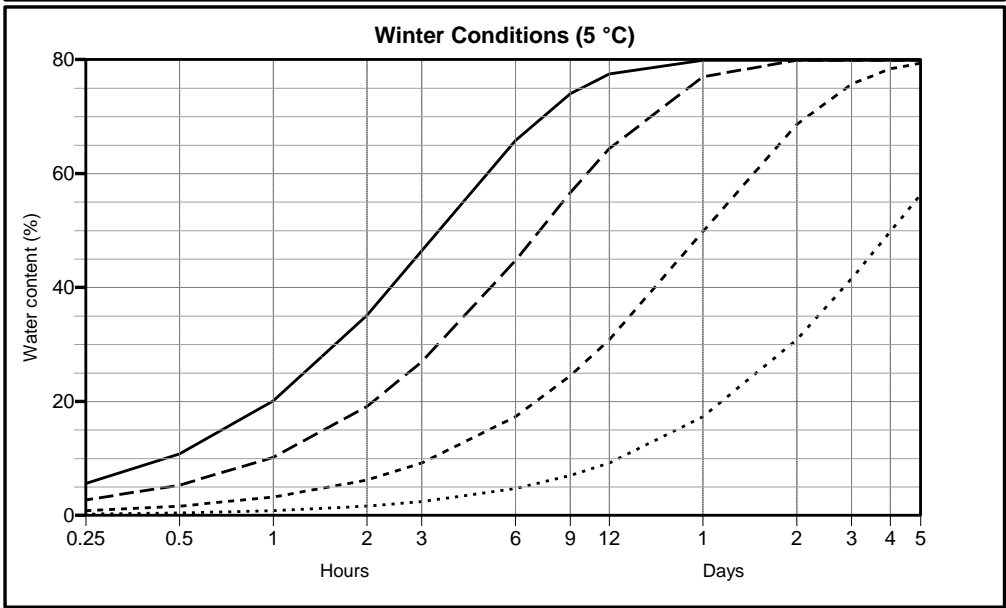- - - - Wind Speed (m/s): 5
······ Wind Speed (m/s): 2

*Figure 3-5: Water content of Drivis predicted at sea temperatures of 5 °C and 10 °C*

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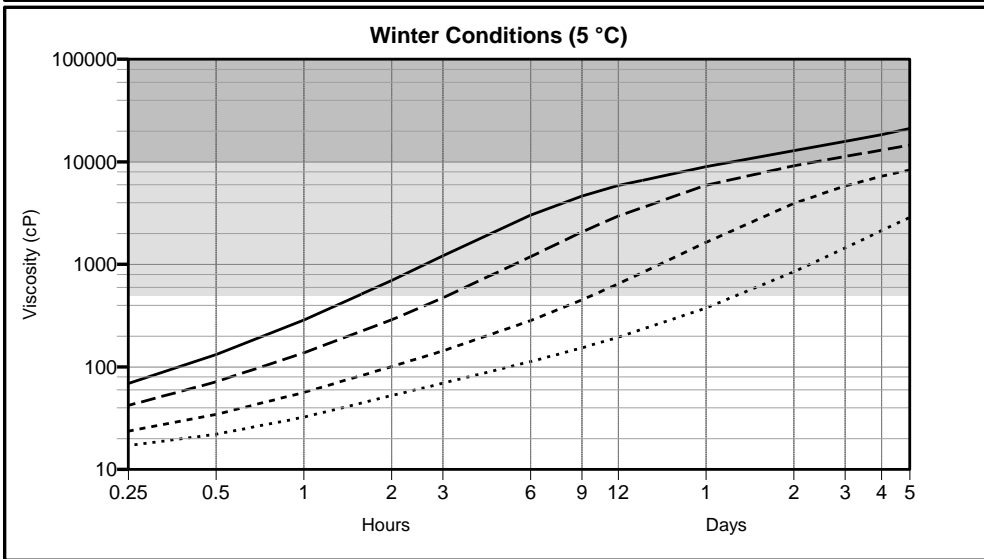REPORT NO.
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Property: VISCOSITY OF EMULSION
Oil Type: DRIVIS 5DEG
Description: SINTEF ID: 2014-0116
Data Source: SINTEF Materials and Chemistry (2016), Weatherir

⊙ **SINTEF**

OWModel

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

Pred. date: Oct. 28, 2016

—— Wind Speed (m/s): 15   ☐ Chemically dispersible (<500 cP)
– – Wind Speed (m/s): 10   ▨ Reduced chemical dispersibility
- - - Wind Speed (m/s): 5   ▨ Poorly / slowly chemically dispersible (>10000 cP)
· · · · · Wind Speed (m/s): 2

Winter Conditions (5 °C)

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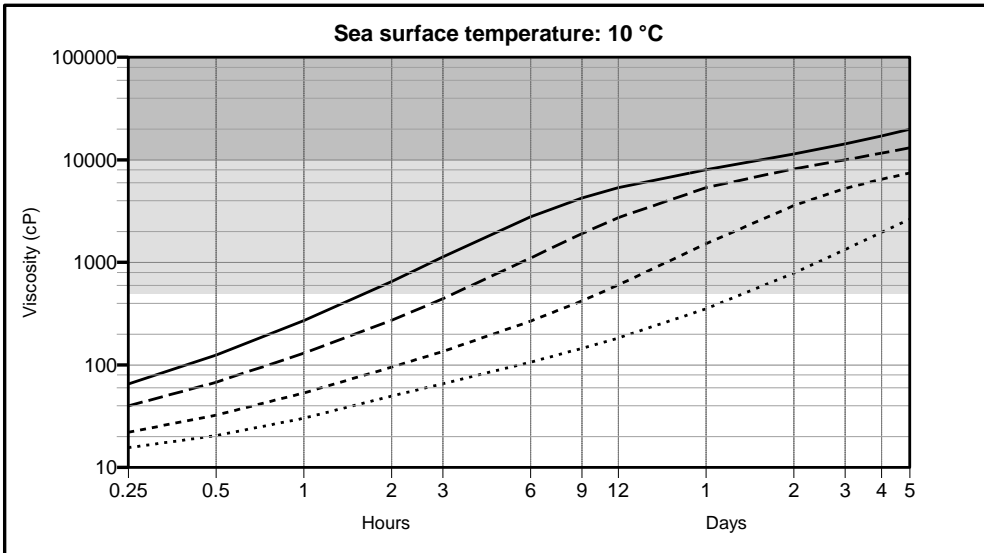
Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.
Chemical dispersability information based on experiments under standard laboratory conditions.

Figure 3-6: Viscosities of Drivis emulsions predicted at sea temperatures of 5 °C and 10 °C. Predictions are based on measurements performed at a shear rate of 10 s⁻¹

Property: MASS BALANCE
Oil Type: DRIVIS 5DEG
Description: SINTEF ID: 2014-0116
Data Source: SINTEF Materials and Chemistry (2016), Weatherir

SINTEF

OWModel

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

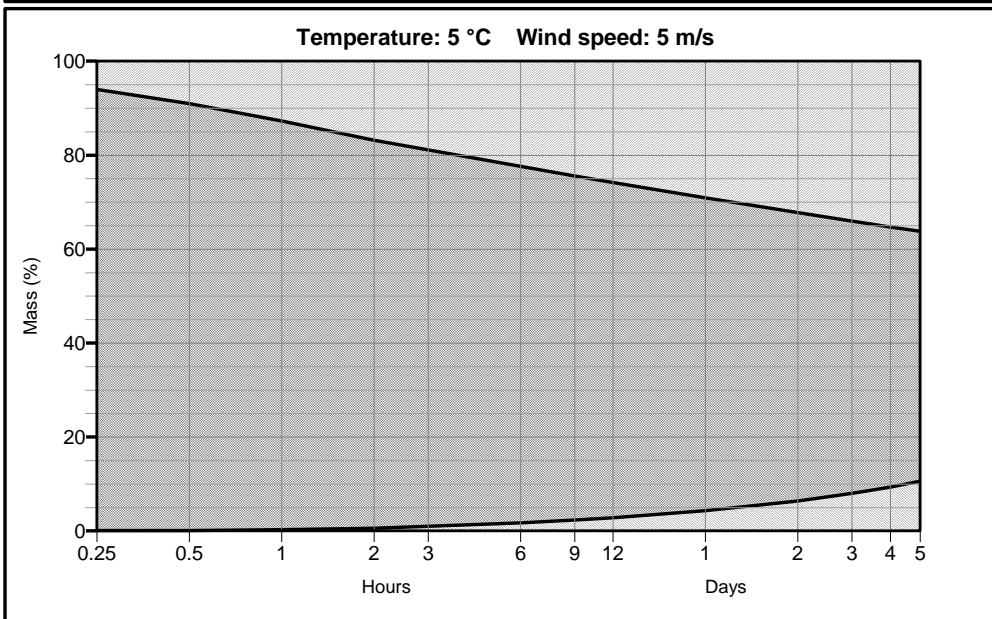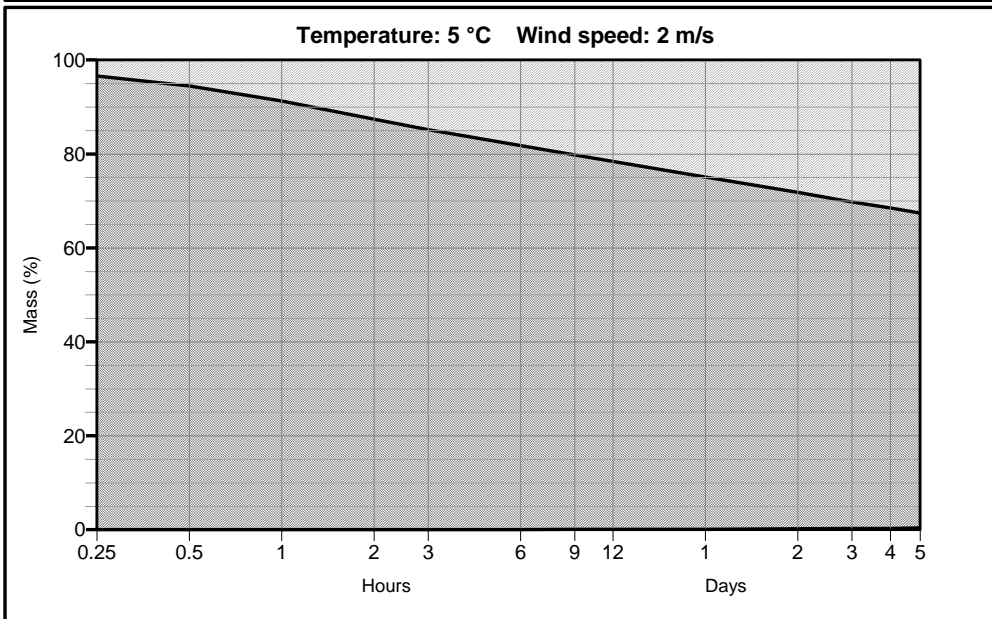Pred. date: Oct. 28, 2016

Evaporated
Surface
Naturally dispersed

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

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Property: MASS BALANCE
Oil Type: DRIVIS 5DEG
Description: SINTEF ID: 2014-0116
Data Source: SINTEF Materials and Chemistry (2016), Weatherir OWModel

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

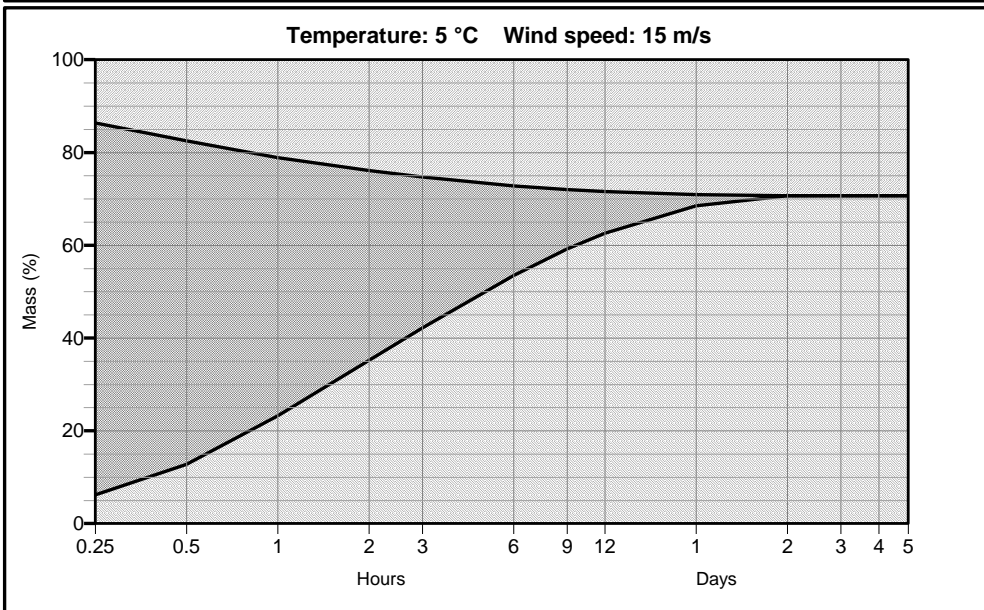Pred. date: Oct. 28, 2016

Evaporated
Surface
Naturally dispersed

Figure 3-8: Predicted mass balance for Drivis at 5°C and wind speeds of 10 and 15 m/s

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Property: MASS BALANCE
Oil Type: DRIVIS 5DEG
Description: SINTEF ID: 2014-0116
Data Source: SINTEF Materials and Chemistry (2016), Weatherir

OWModel

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

Pred. date: Oct. 28, 2016

- Evaporated
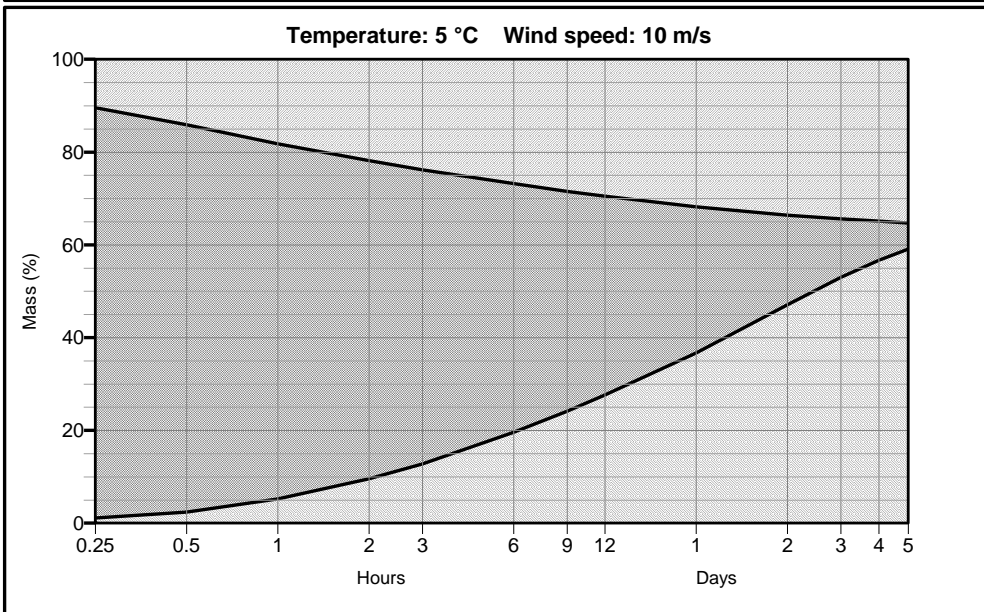- Surface
- Naturally dispersed

Figure 3-9: Predicted mass balance for Drivis at 10 °C and wind speeds of 2 and 5 m/s

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Property: MASS BALANCE
Oil Type: DRIVIS 5DEG
Description: SINTEF ID: 2014-0116
Data Source: SINTEF Materials and Chemistry (2016), Weatherir

SINTEF

OWModel

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

Pred. date: Oct. 28, 2016
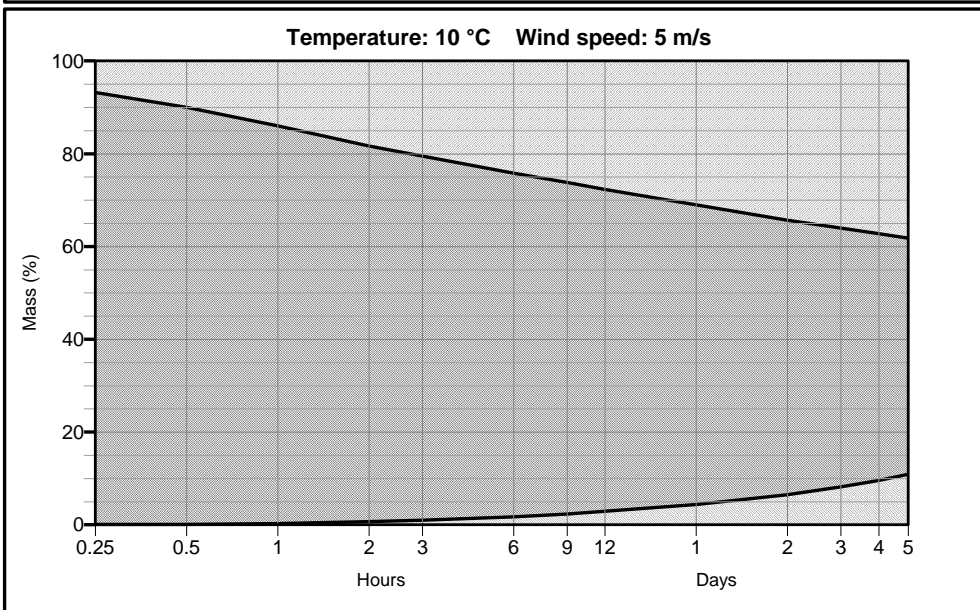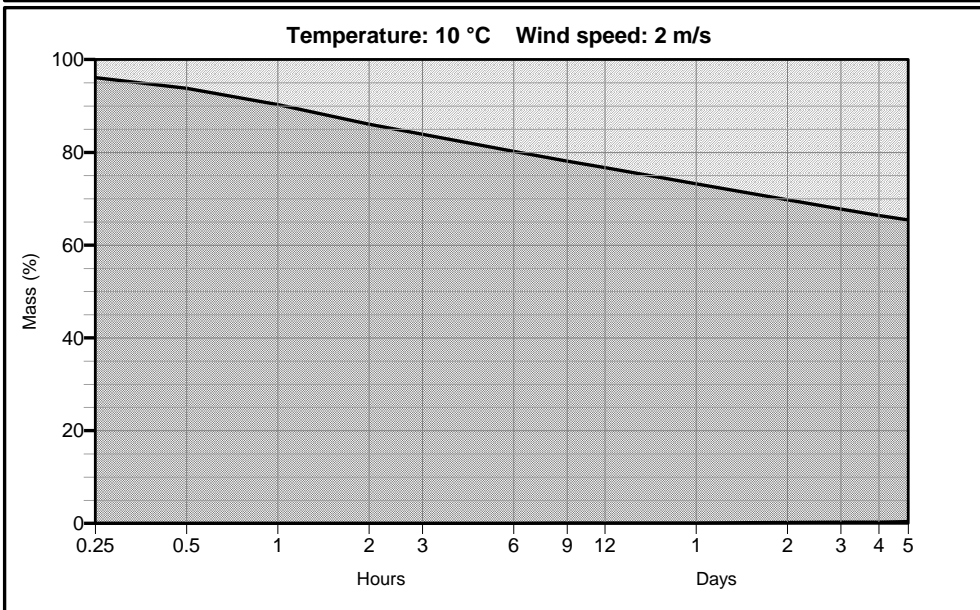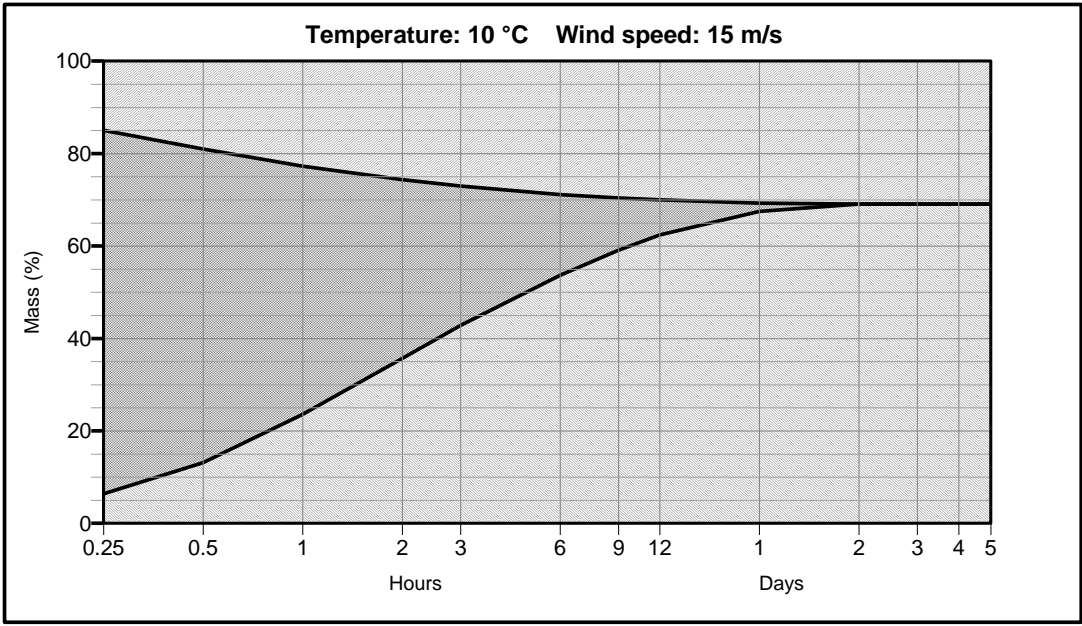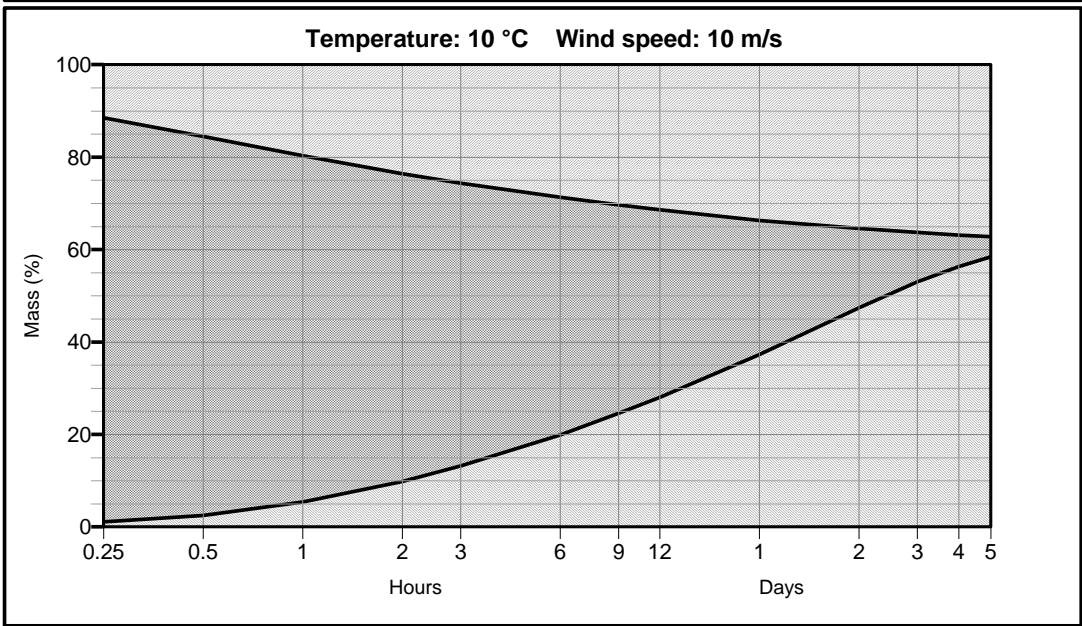
- Evaporated
- Surface
- Naturally dispersed

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

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4 OWM predictions - Comparison of Drivis with other crude oils

Weathering predictions of Drivis were compared to a selection of other Norwegian crude oils. The crude oils chosen for comparison are Havis and Skrugard from the Johan Castberg field in the Barents Sea, Norne from the Norwegian Sea, and Grane from the North Sea. 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 Drivis and the oils used for comparison are presented in Figure 4-1 below. Drivis has the highest predicted evaporative loss, while the heavy Grane exhibits the lowest evaporative loss in comparison.
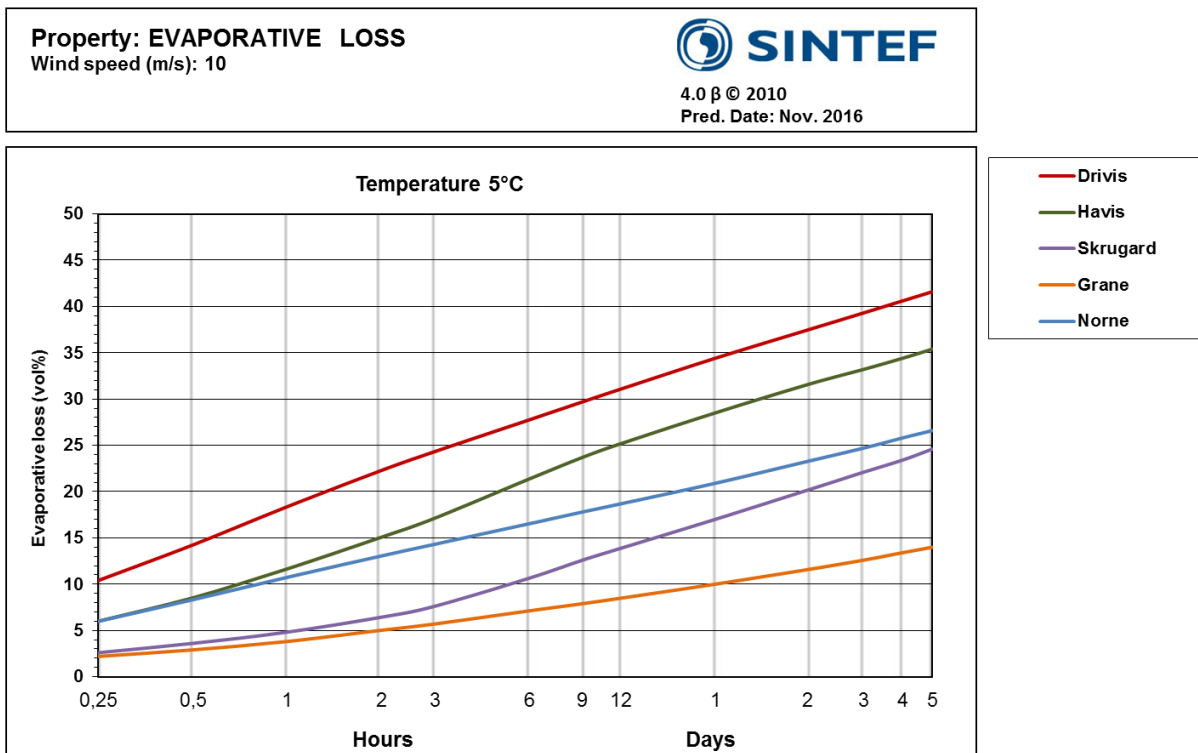

Figure 4-1: Predicted evaporative loss at 5 °C and 10 m/s for Drivis compared to other oils

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 Drivis and other oils in comparison are shown in Figure 4-2. None of the oil show any fire or explosion hazard 15 minutes after release where the flash points is far beyond the sea temperature of 5 °C.
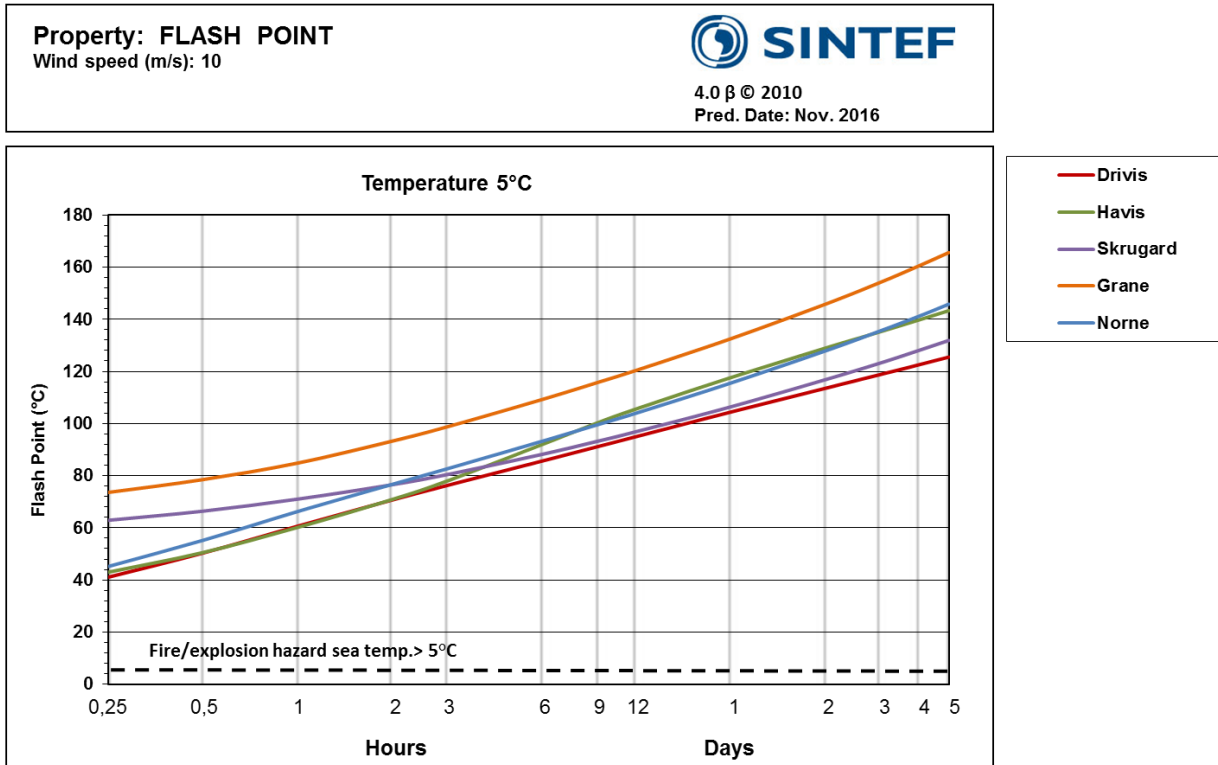

Figure 4-2: Predicted flash point at 5 °C and 10 m/s for Drivis compared to other oils

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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 are most pronounced for waxy /paraffinic crude oil, such as Norne and Havis. High pour points may prevent the dispersant to soak into the oil slick and influence on the dispersant effectiveness.

Drivis has low initial pour point that increases with increased evaporative loss as shown in Figure 4-3, and semi-solid properties could potentially pose a challenge within a day weathering at sea. Both the naphthenic Skrugard and asphaltenic Grane express low pour points compared with to the other crudes with more paraffinic features. The waxy Norne expresses very high pour points with high degree of solidification.
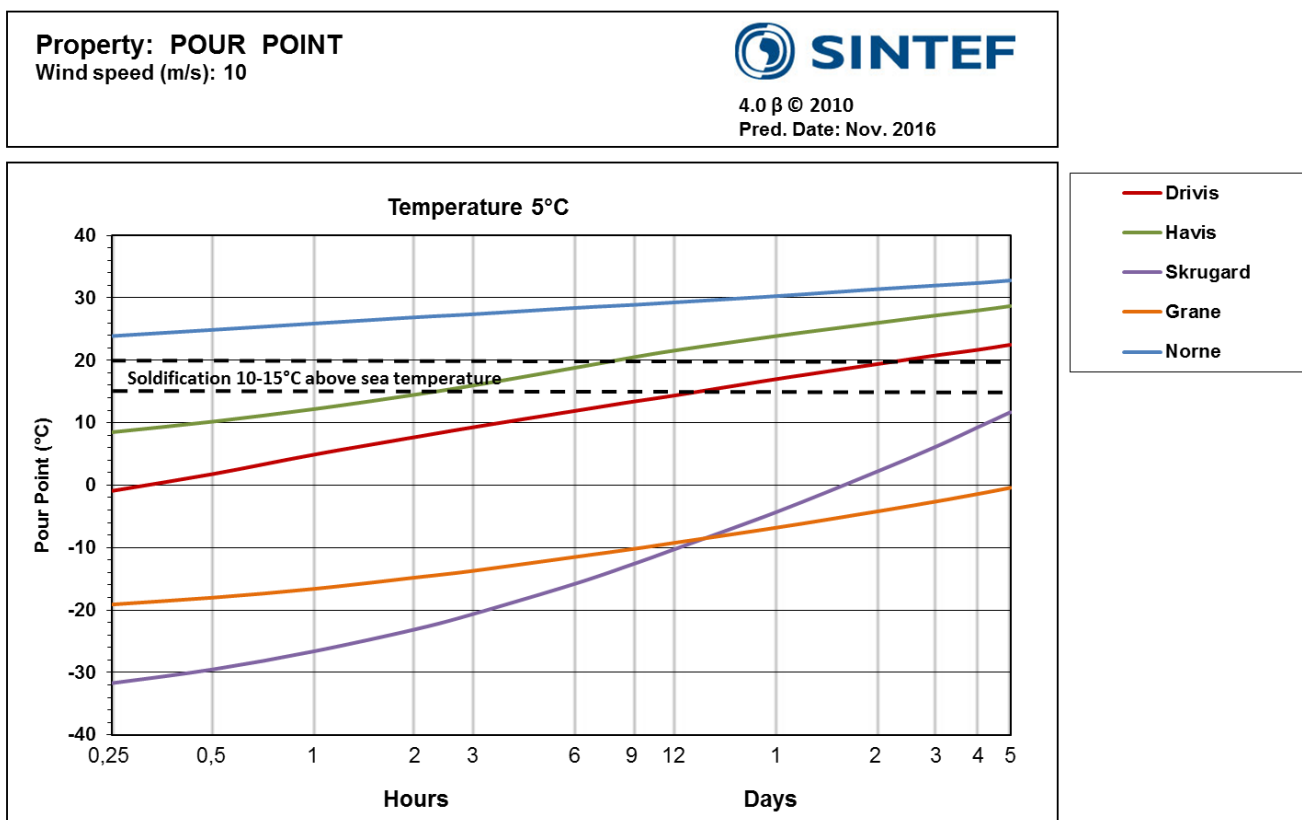

Figure 4-3: Predicted pour point at 5 °C and 10 m/s for Drivis compared to other oils

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4.3.1 Water content

Water uptake and content for Drivis and the oils used for comparison are shown in Figure 4-4. The maximum water uptake of Drivis is similar to Skrugard (80 vol. %), but the Drivis has a slower water uptake. The naphtenic Skrugard and asphaltenic Grane have both rapidly water uptake, but the high-density Grane reaches a low maximum water content of approximately 55 vol. %. The very waxy Norne has slow and reaches as low water uptake.
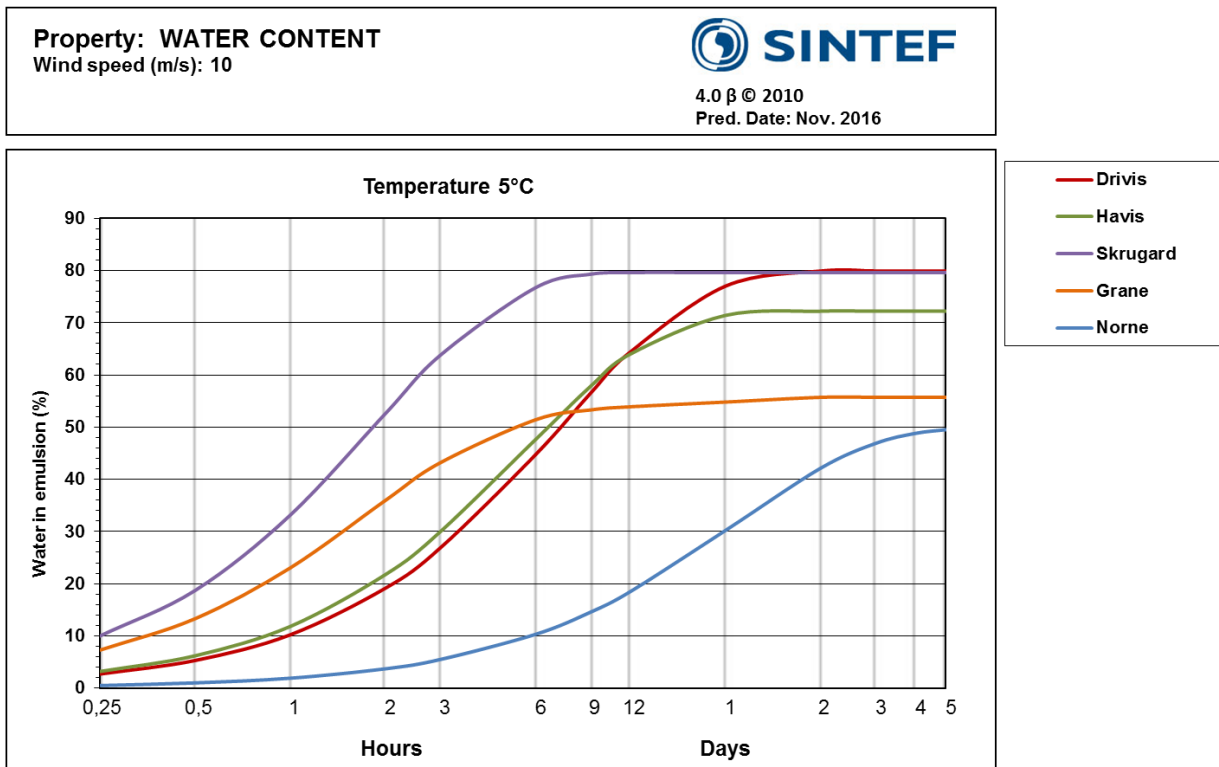
Figure 4-4: Predicted water content at 5 °C and 10 m/s for Drivis compared to other oils

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4.3.2 Emulsion viscosity

Figure 4-5 show the predicted emulsion viscosities of Drivis and the other oils in comparison. The emulsion viscosities of Drivis have similarities with Havis and Skrugard, but reaches somewhat higher viscosity after 5 days of weathering. The asphaltenic high-density Grane has high viscosities, whilst the very waxy Norne has very high initial viscosity that decreases after weathering whereas the waxy structure beaks up during emulsification.
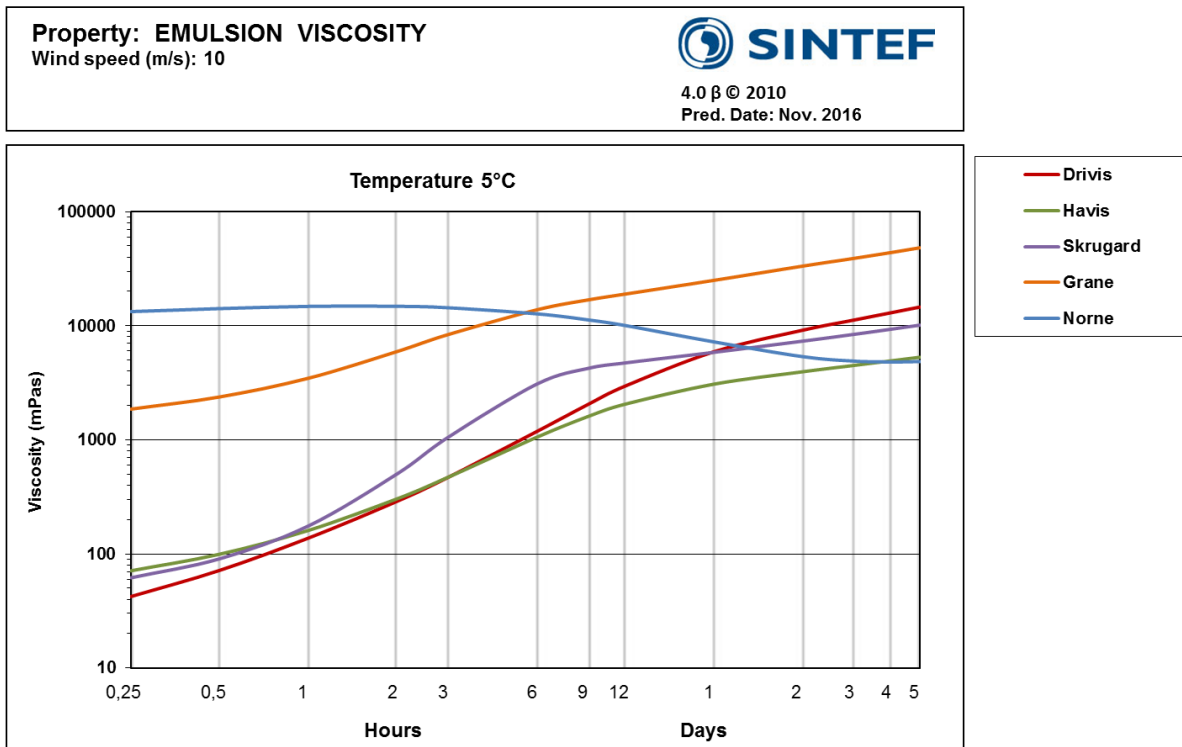
Figure 4-5: Predicted emulsion viscosity at 5 •C and 10 m/s for Drivis compared to other oils

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 Drivis surface oil compared to the other oils in comparison. Drivis and Havis have very similar mass balances and have the lowest remaining surface oil after 5 days of weathering due to high evaporative loss and natural dispersion /entrainment.

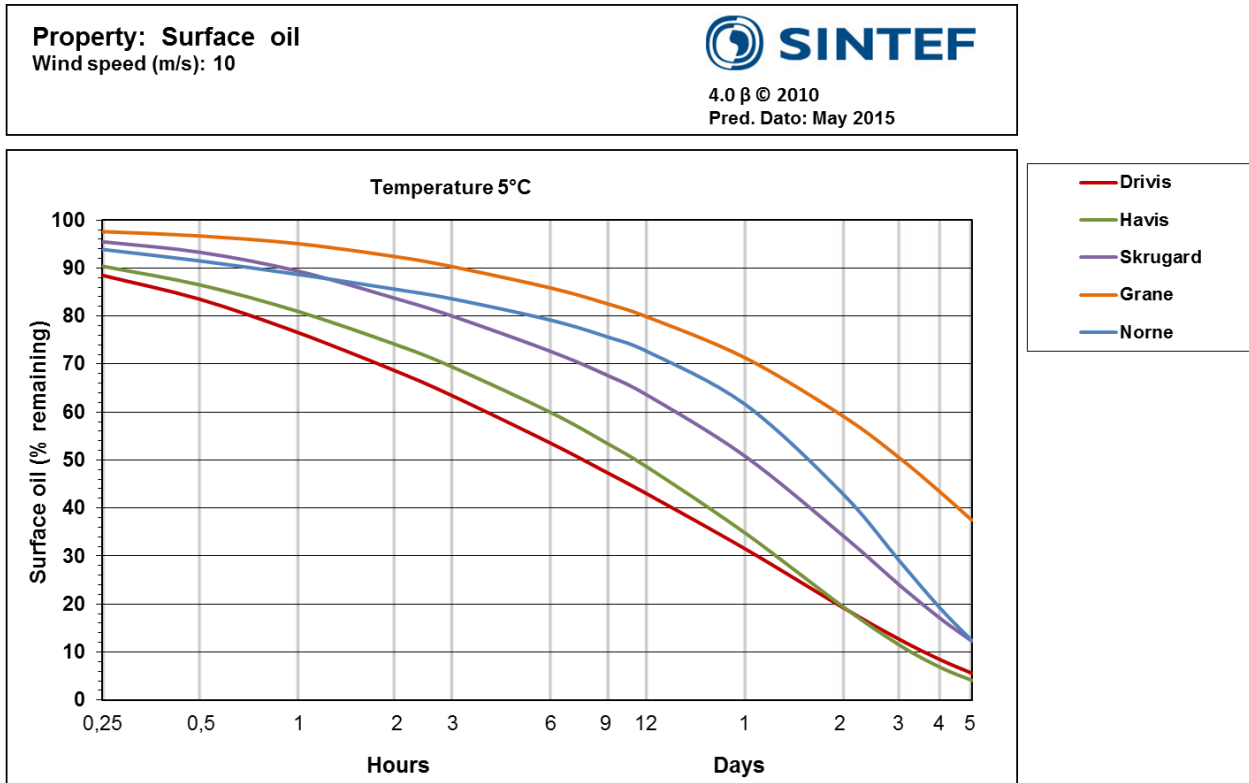*Figure 4-6: Predicted remaining surface oil at 5 °C and 10 m/s for Drivis compared to other oils*

5 Weathering properties of Drivis crude oil related to oil spill properties

5.1 Oil properties

Drivis is a medium density crude oil (0.838 g/mL) with a relatively low wax content (1.9 wt. %), and low asphaltene content (0.05 wt. %) compared with Norwegian crude oils. Drivis is categorised as a paraffinic crude oil and forms stable water-in-oil (w/o) emulsions with water maximum water content of ~ 80 vol %. The high evaporation loss of light components causes an increase in the relative content of wax and asphaltenes that contribute stabilizing emulsions of the oil.

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 Drivis the flash point will be above the sea temperature within the first 15 minutes after a spill in at 5 and 10 °C, as shown in Figure 5-1 below.

Some vessels engaged in oil recovery operations may not be classified to carry liquids with flash point lower than 60 °C (e.g. towing vessels, smaller cargo or vessels available in the emergency). For Drivis, this limit will be reached within approximately 6 hours in low wind conditions (2 m/s) at 5 °C, and more rapidly at 10 °C, and with higher wind speeds.
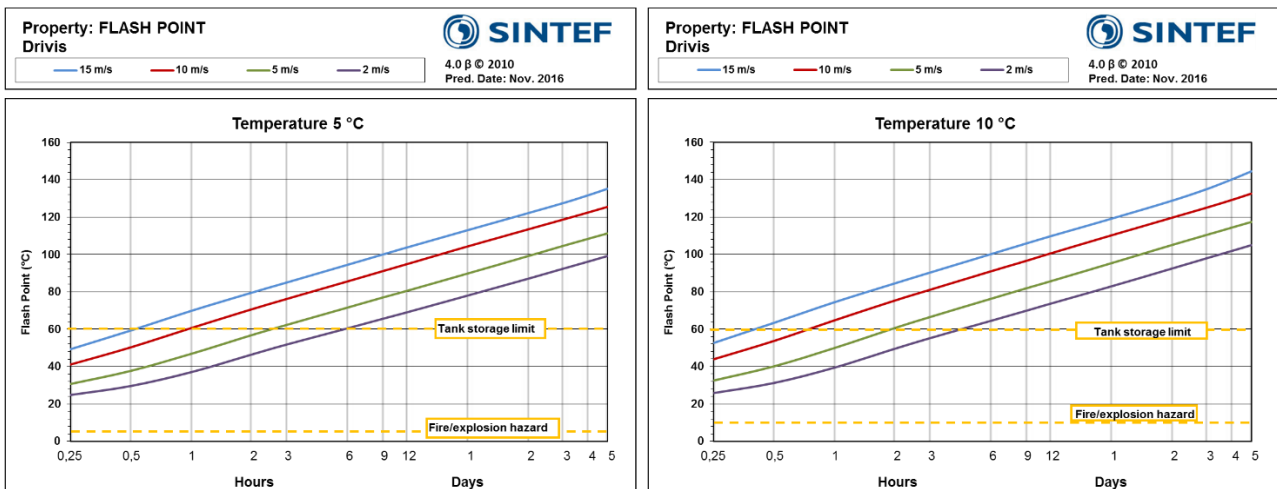

Figure 5-1: Flash point at different sea states for Drivis crude oil at 5 °C and 10 °C

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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 water is mixed into the oil with formation of emulsions, the total volume increases. Drivis forms stable w/o-emulsions with relatively high water content causing a high increase in the total volume. Figure 5-2 shows this increase of volume relative to the volume of the remaining surface oil at 10 m/s wind and at both 5 and 10 °C. At both temperatures, the volume of the emulsion is predicted increase significantly (4-4.5 times) of the originally spilled oil volume within one day of weathering.
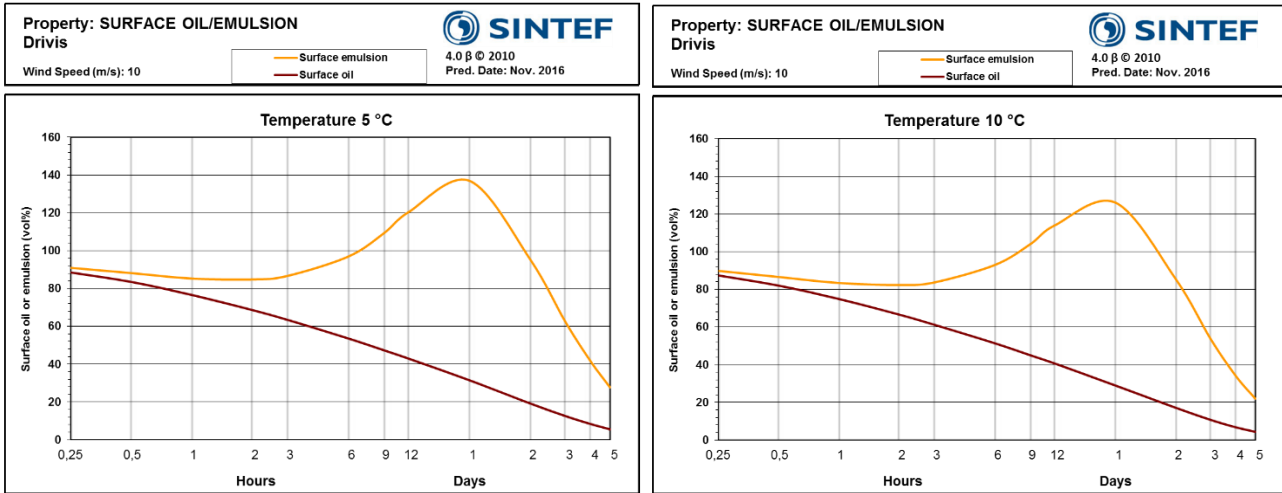

Figure 5-2: Difference in the total slick volume of Drivis due to emulsification compared to non-emulsified oil. Decrease in total volume due to evaporation and natural dispersion at 10 m/s wind speed at temperatures of 5 °C and 10 °C

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 not added directly on the oil spill at sea surface.

Figure 5-3 illustrates the relative volumetric composition of water-in-oil emulsion and free-water, for the 150 and 250°C+ residue (reflecting 0.5 and 1 week weathering, respectably) with and without addition of emulsion breaker (Alcopol O 60 %). The effectiveness of the emulsion breaker is relative to the dosage applied, with 2000 ppm by weight causing a higher release of water compared to application of 500 ppm. Use of emulsion breaker could be considered for Drivis, as the stable emulsions with high water uptake require large storage capacity when recovered.
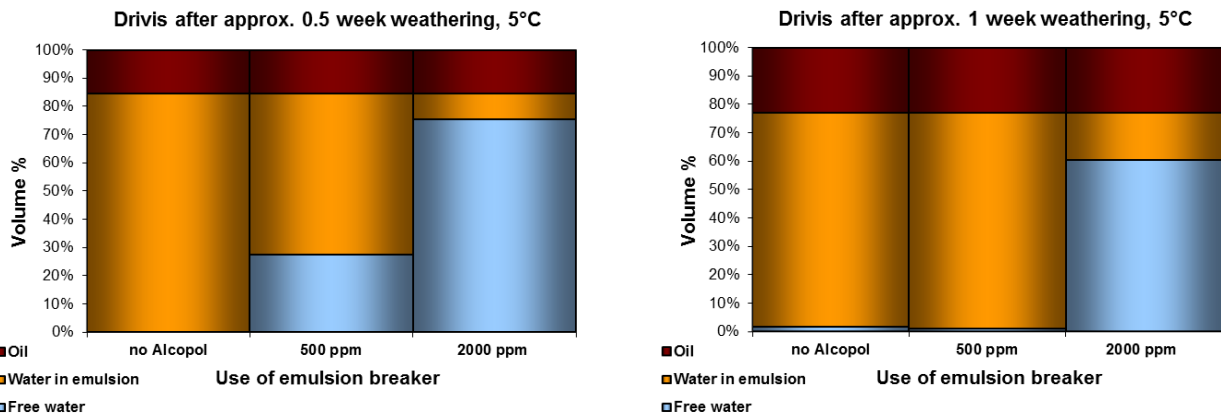
Figure 5-3: Relative volumetric composition of water-in-oil emulsion and free-water after approximately 0.5 week (left) and 1 week (right) of weathering of Drivis.

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 sea states and temperature conditions. Considerably larger spills expect to produce longer lifetimes, and individual modelling should be considered in such cases. At high wind speed of 15 m /s, no oil is remained on the sea surface after 5 days weathering at 5 and 10 °C. However, the variation is strongly dependent on the wind speeds and more oil remains on the sea surface with lower wind
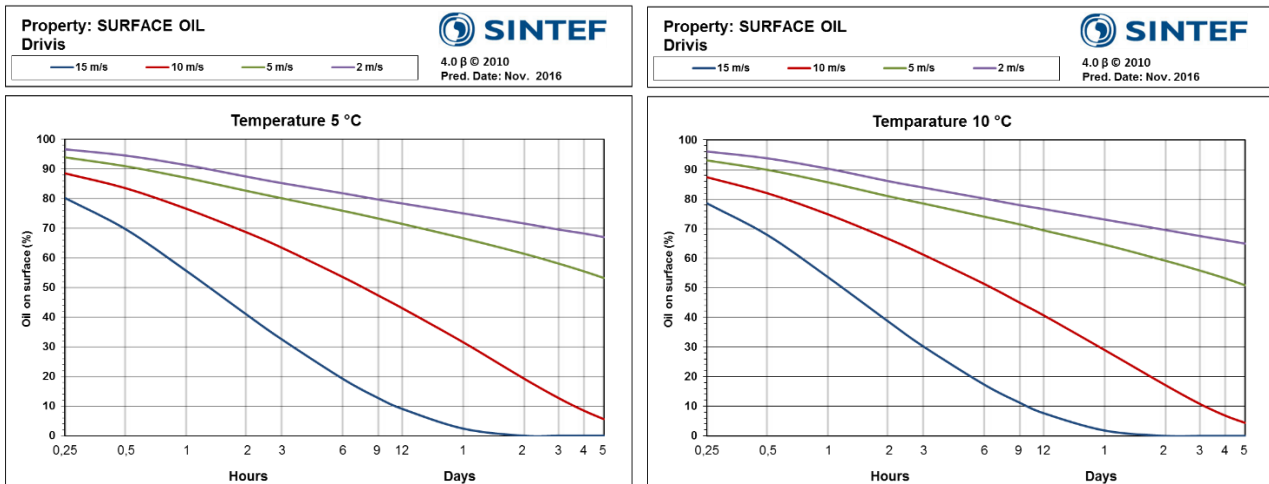

Figure 5-4: Remaining surface oil under different sea states for Drivis at 5 °C and 10 °C

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5.6 Oil spill response

Mechanical recovery and use of oil spill dispersants are the main oil spill responses at sea in Norwegian sector.

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. This 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). A general rule of thumb, a viscosity of 1000 mPa.s is used for an optimal mechanical clean-up operation. It should be emphasized that boom leakage is also influenced by other factors such as the operational speed of recovery vessel and weather conditions, and lower viscosity emulsion also is possible recover in very calm conditions. Studies at SINTEF have shown that weir skimmers may have reduced recovery rate (m³/h) at viscosities in the range 15000-20000 mPa·s (Leirvik et al., 2001). There is insignificant variation in emulsion viscosities predicted at 5 and 10 °C, as illustrated in Figure 5-5.

The initial emulsion viscosities of Drivis are relatively low. The emulsion viscosities are predicted to pass the 1000 mPa·s limit within the first six hours at 10 m/s, and within one day in calm wind conditions (2 m/s). see Figure 6.5. The emulsion viscosities are predicted to remain below the 20 000 mPa·s limit for effectively use of weir skimmers for all predicted 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. However, the efficiencies of different types of skimmers are also influenced on other oil properties such as the wax content and should be considered. It has also been observed that the recovery rate of rope skimmer varies among different categorizations of crudes oils (Singsaas *et al*. 2000).

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. Drivis crude oil has low initial pour point that increases very rapidly with increasing evaporative loss, and hence solidification could pose a challenge for this oil within one day of weathering at sea. The use of high visc. skimmer should therefore be considered, see also Figure 5.3.
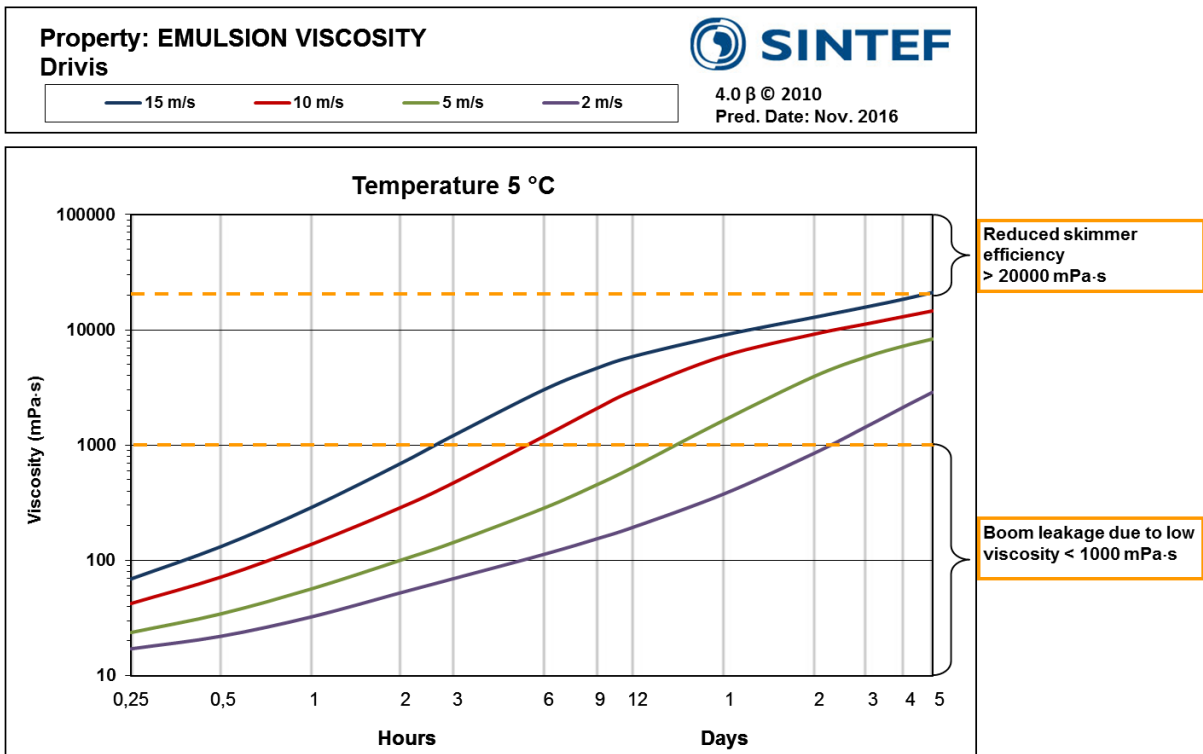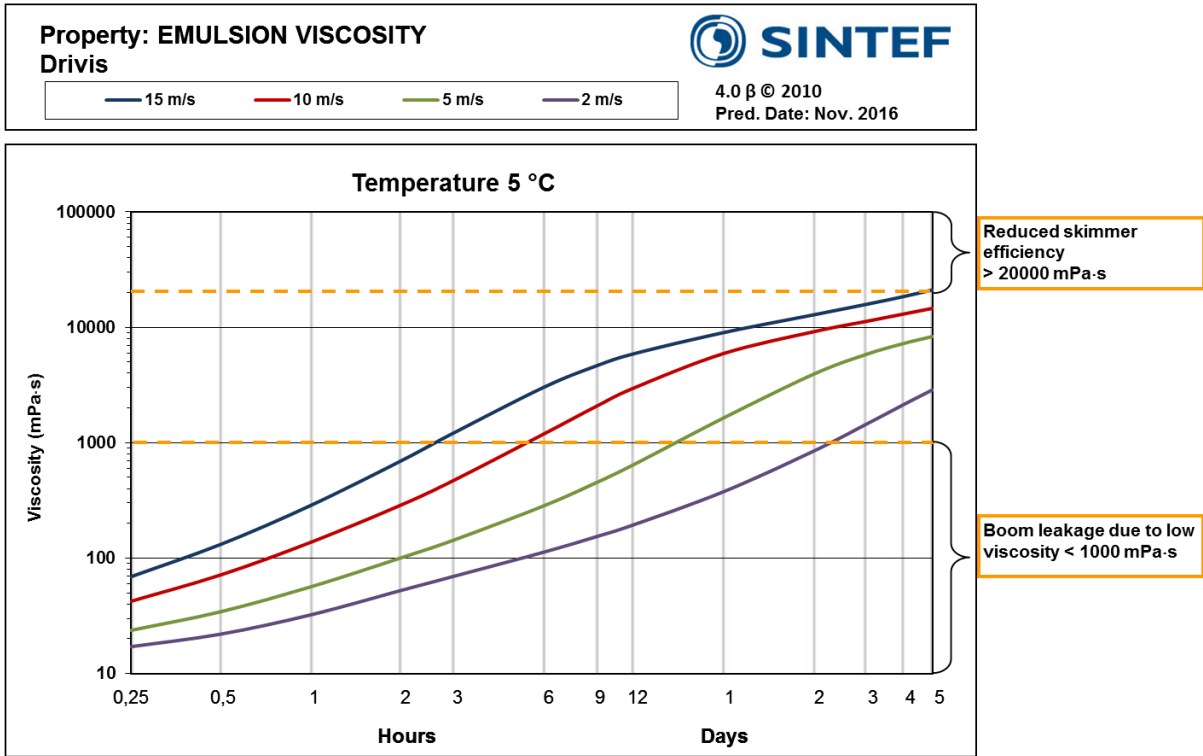
Figure 5-5: Predicted emulsion viscosity for Drivis at 5 °C and 10 °C compared with expected viscosity limits for boom leakage and poor flow to weir skimmers.

5.6.1 Use of oil spill dispersant

Drivis crude oil has a potential for use of oil spill dispersant, and the "window of opportunity" for use of dispersant (Dasic NS) is presented Figure 5-6. The oil is estimated to be dispersible for viscosities in the range of 500 mPa.s (IFP-test) to 3000 mPa.s (MNS-test), reflecting typically non-breaking (< 5m/s wind speed) and breaking waves (>5 m/s speed), respectively. The viscosity limit of 500 mPa.s considered as a conservative estimate and used as input to the SINTEF Oil Weathering Model (OWM) to predict the time-window for dispersant use. The viscosity where Drivis is considered not dispersible was estimated to 10 000 mPa·s.

The predicted time-window for dispersant application indicates that Drivis is chemically dispersible up to 2 days of weathering in low wind speed of 2 m/s at 5 and 10 °C, but the time-window subsequently reduces at higher winds speeds.

In general, when the 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 enhance the dispersion rate.
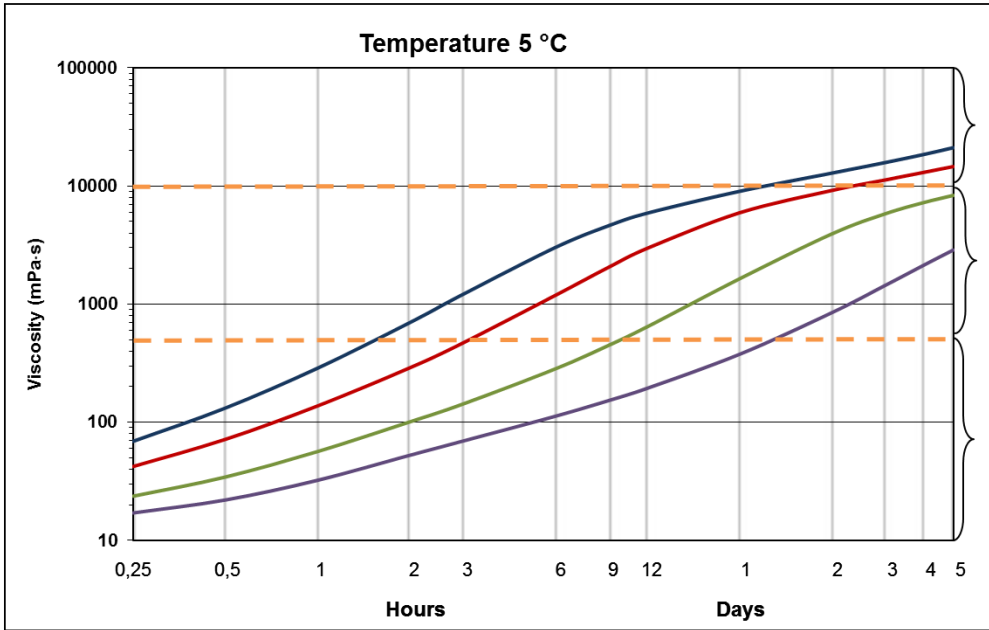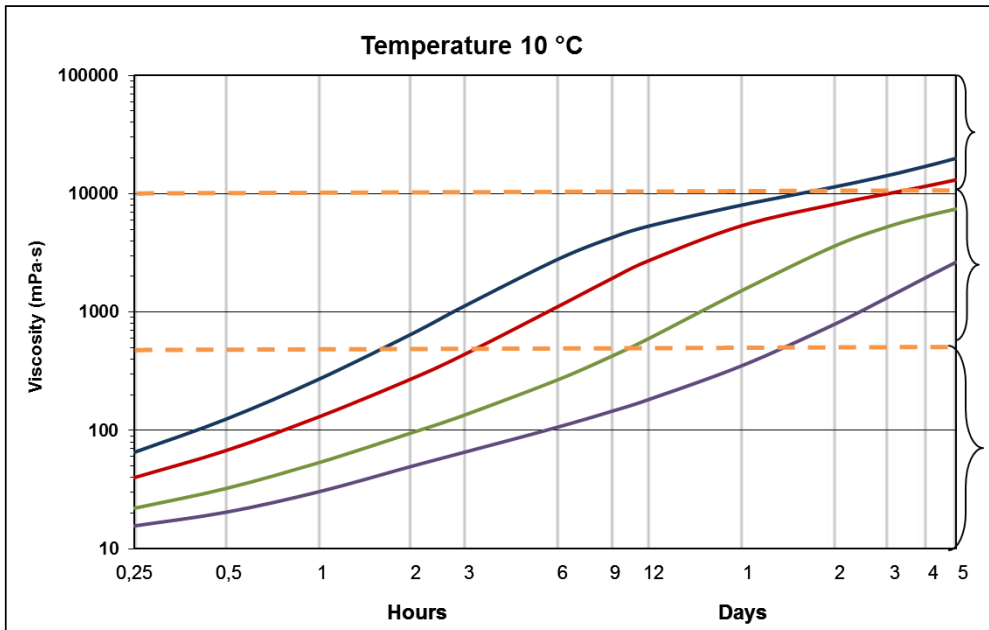
Figure 5-6: Time window for use of chemical dispersant as a function of emulsion viscosity for Drivis at 5 and 10 °C

6 Categorization of Drivis and other Norwegian crude oils and condensates

A semi-quantitative categorization map of crude oils is developed into four main groups of oil: *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.

Paraffinic oils, are often characterized by low to medium density, which reflects high content of light and saturated components, such as paraffins (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, and is 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 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 ºC 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 Drivis is presented in Figure 6-1 below. Drivis is categorized as a (light) paraffinic crude oil.
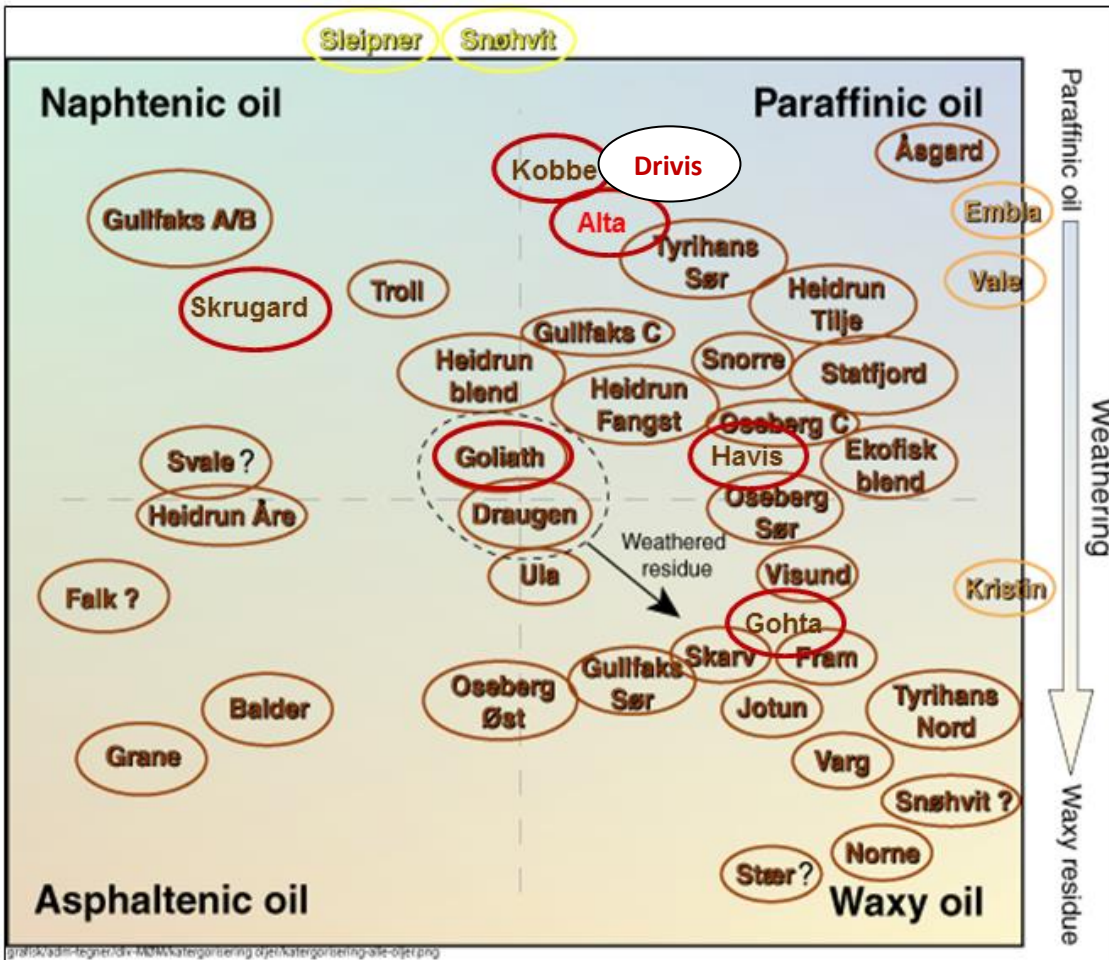
Figure 6-1: Categorization of a selection of Norwegian crude oils including Drivis and oils used for comparison (the oil with red rings are other oils from the Barents Sea).

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A The behaviour of crude oil on the sea surface

The Drivis crude oil was given the SINTEF ID 2014-0116.

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.
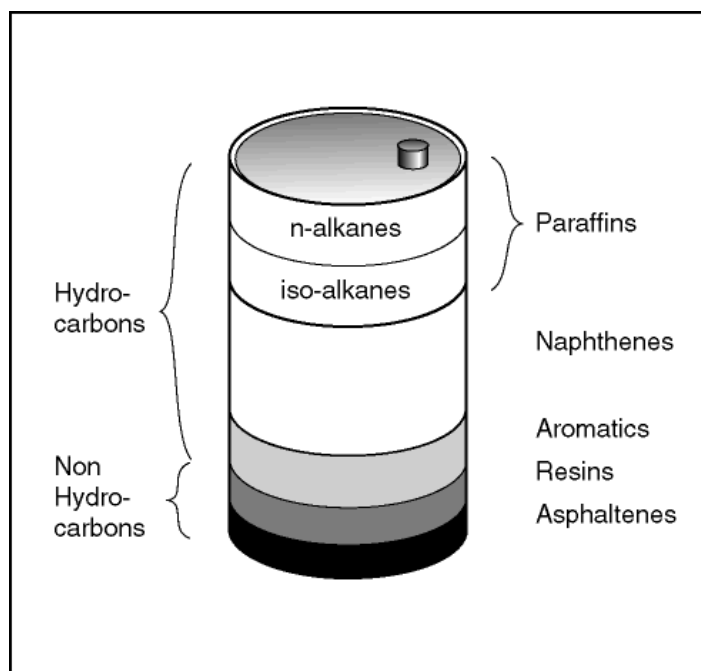
Figure A-1: The chemical composition of crude oils

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.

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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:

$$°API = \frac{141.5}{Secific\ gravity} - 131.5$$

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 is: *force distance/area speed* and has the unit: $dyn \cdot sec/cm^2$. = 1 Poise. The industry is often using the unit $mPa \cdot s$ = centipoise (cP). The viscosity of fresh crude oils can vary from less than 1 to more than 2000 $mPa \cdot s$ (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 quite liquid under turbulent conditions at sea, but can become much more viscous, or even semi-solid in calmer water conditions, or on beaches. Thus, the measurements of the viscosity of w/o-emulsions must be carried out under strictly controlled conditions (defined shear rates and thermal and mechanical history of the sample). At SINTEF a shear rate of 10 s^{-1} is routinely used for expressing viscosity data on w/o-emulsions.

The viscosity of an oil increases with evaporation since the heavier, more viscous components remain in the residue (Mackay et al, 1982). The difference in viscosity for crude oils is approximately 3 to 2000 $mPa \cdot s$ for fresh crude oils and several hundred/thousand $mPa \cdot s$ 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.
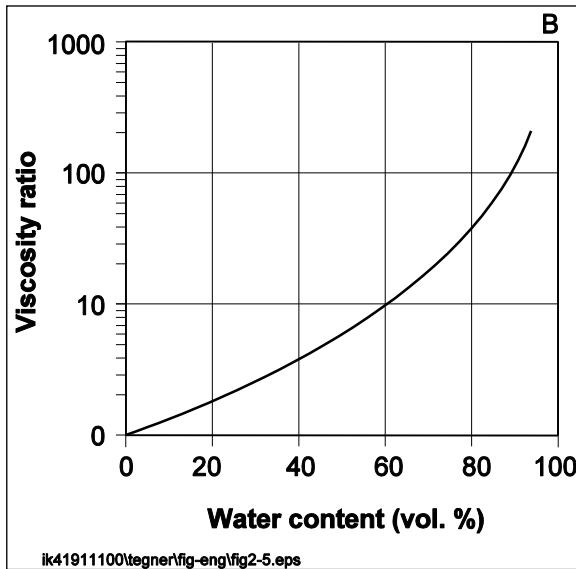
Figure A-2: Example of viscosity ratio as a function of water content

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 vapor 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 vapor pressure, which is a function of its molecular weight and chemical structure. Low molecular weight oil components have a higher vapor 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.
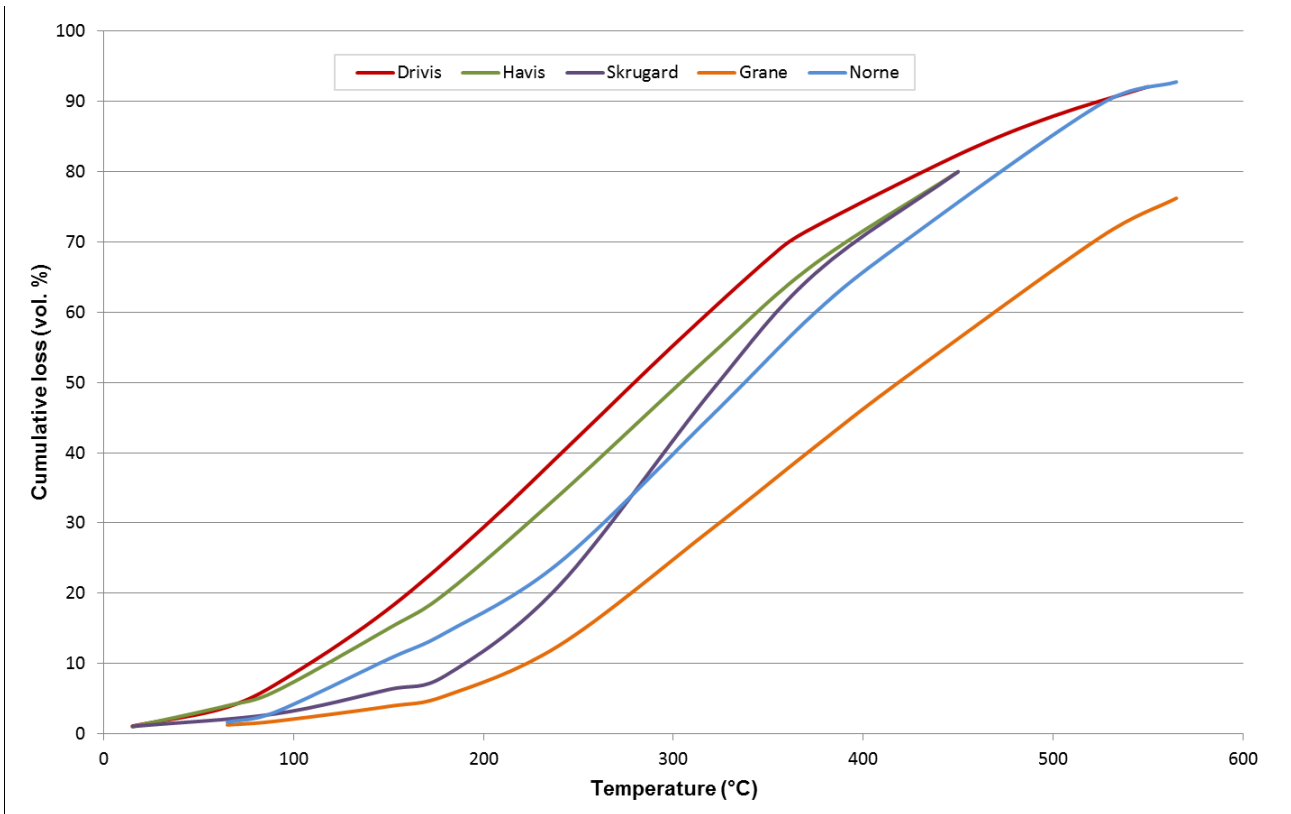
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Figure A-3: Distillation curves for Drivis crude oil in comparison with other Norwegian crude oils

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.
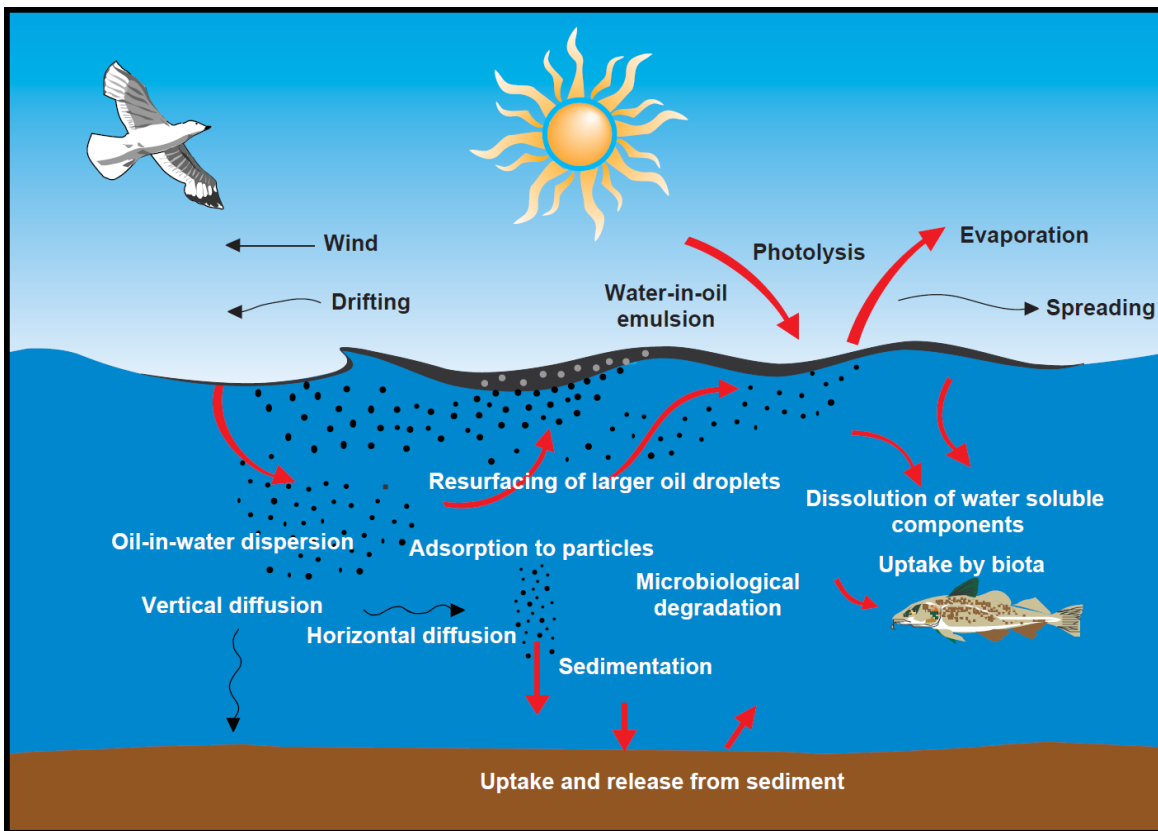

Figure A-4: Illustrating the weathering processes that take place when oil is spilled on the sea surface
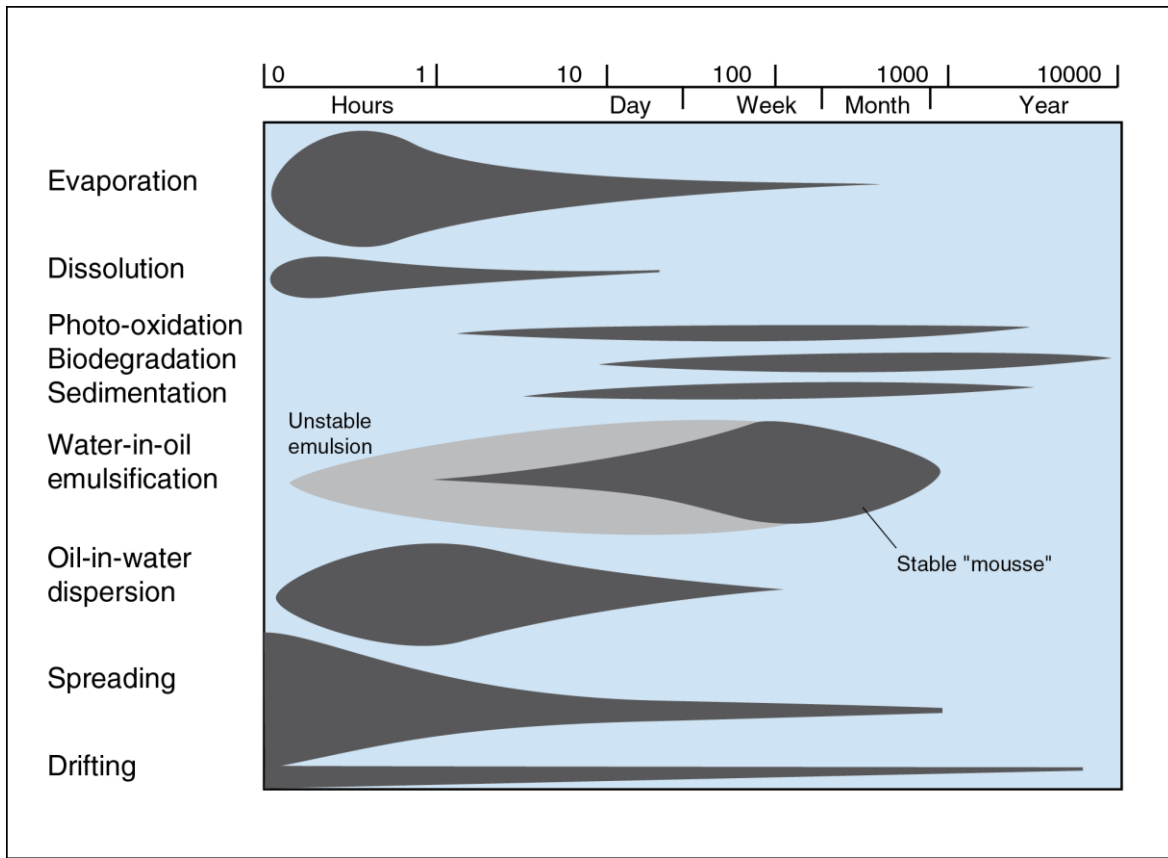
Figure A-5: Weathering processes' relative importance over time. Note: logarithmic scale

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.

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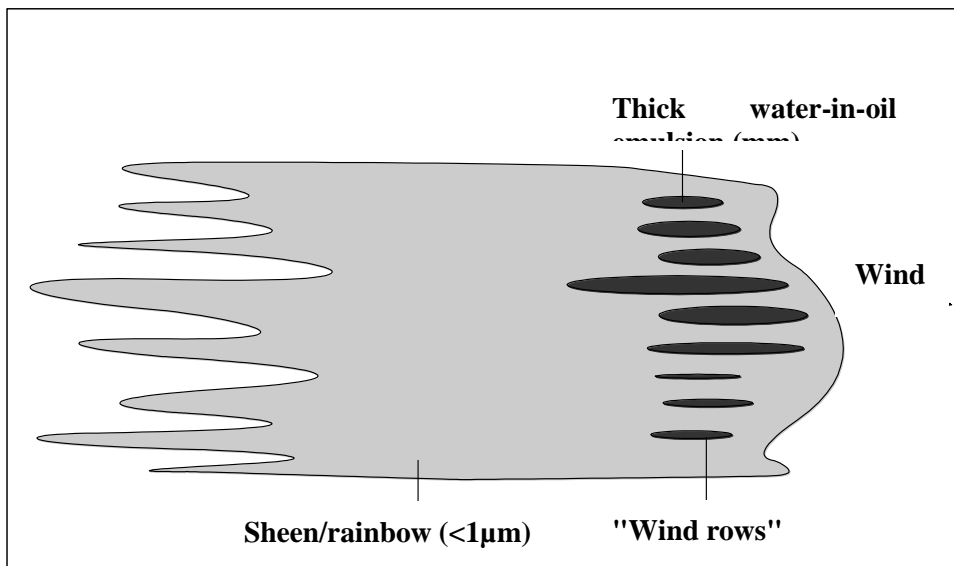
Figure A-6: The spreading of oil spilled on the sea surface and the distribution within the oil slick

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.

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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 o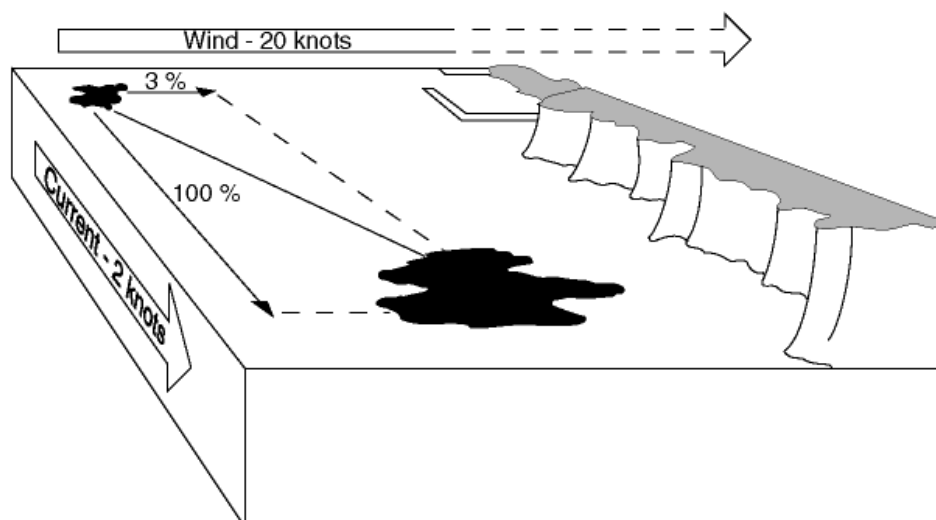il volume depending on the properties of the oil. The formation of w/o emulsions also contributes to keeping oil on the sea surface. A w/o emulsion normally has a higher viscosity than the parent crude oil, so the emulsification process will therefore retard/delay evaporation and the natural dispersion 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.
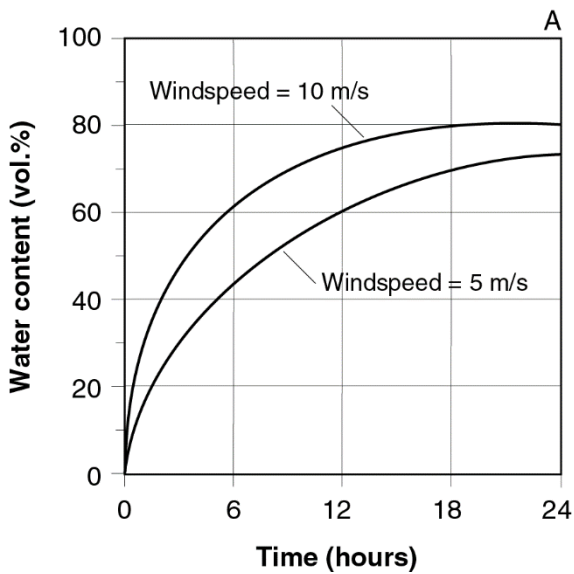
Figure A-8: Example of how weather conditions influence the w/o emulsion formation for typical oils

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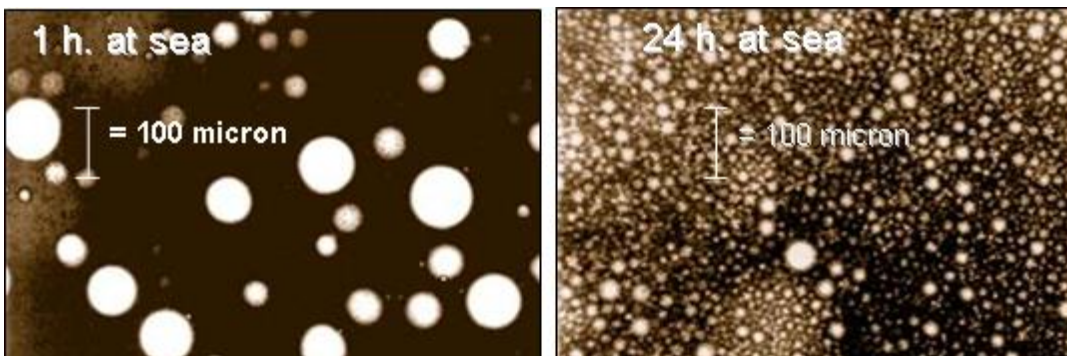
Figure A-9: Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder

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

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

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

Oils that contain large amounts of wax and small amounts of asphaltenes can form w/o emulsions stabilized by a continuous phase's rheological strength (viscosity and elasticity) due to wax structure formed by precipitated wax. Wax stabilized emulsions are characterized by large water droplets and are fairly stable when stored, although they may break down when stress is applied and/or when the emulsion is heated to, e.g. 40-50°C.
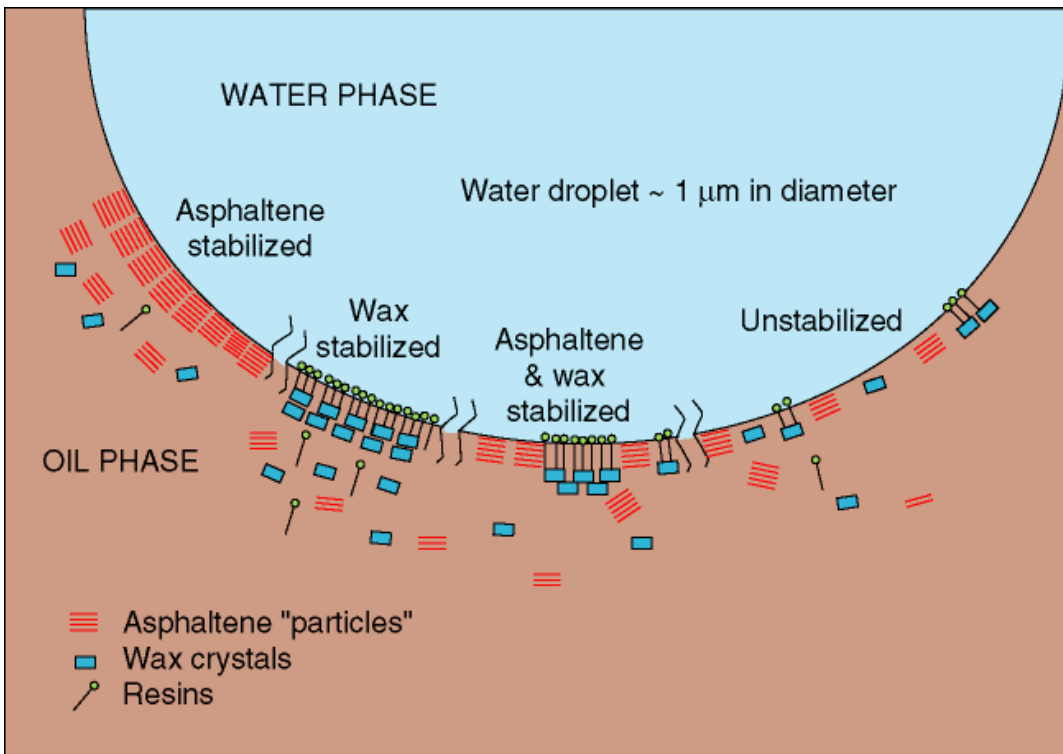
Crude oil- and sea water interfacial tension (IFT) plays a key role in the process of oil droplet formation. The need to both understand and control droplet formation in dispersant system is extremely important. Addition of dispersants reduces the interfacial tension between oil and water that subsequently 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 SINTEFs 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 $1\cdot10^{-6}$ to $2\cdot10^{3}$ 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 μm - 1 mm, which are then mixed into the water mass. The largest oil droplets will resurface and form a thin oil film (typically <50 μm) 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_7) have a potential to be dissolved in the water column (McAuliffe, 1987). Within the various types of hydrocarbons the water solubility decreases from aromatics to naphthenes and from isoalkanes 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 micro-organisms that can break down all types of oil components. The various micro-organisms 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 isoalkanes > 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 by10 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 Løldeng, 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 come in contact with the sea-bed sediment. This can cause some sedimentation of oil droplets to the sea-bed in the vicinity of 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.
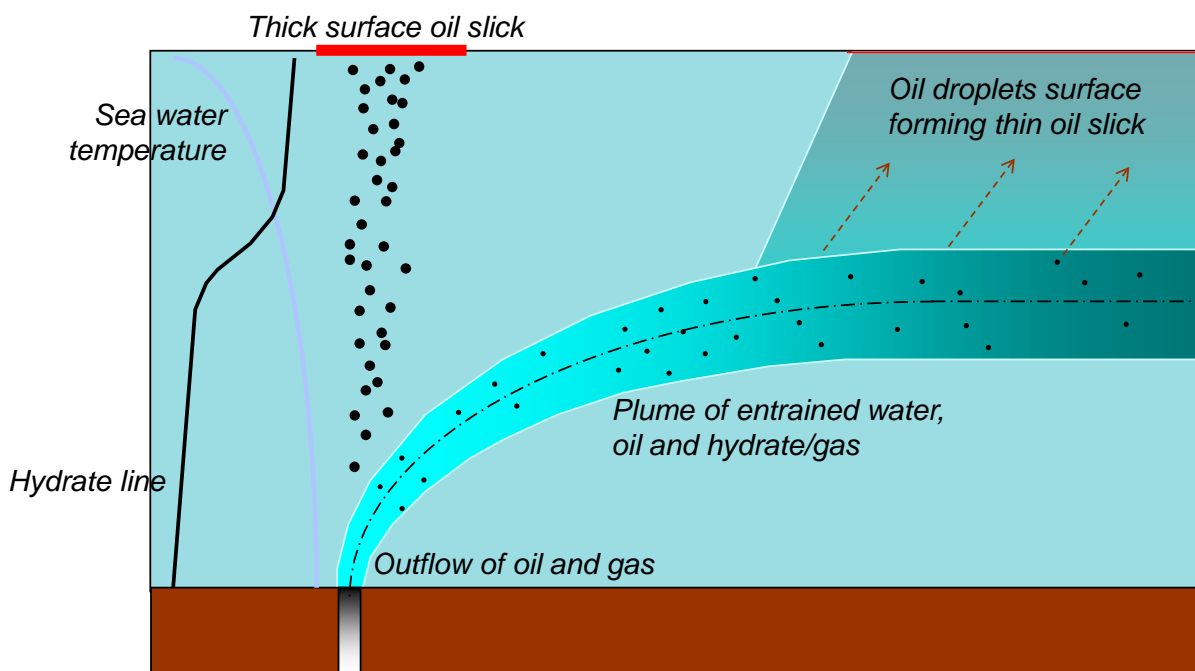
Figure A-11: Illustration of possible creation of thick surface oil slick (> 200 µm) from deep water release of oil
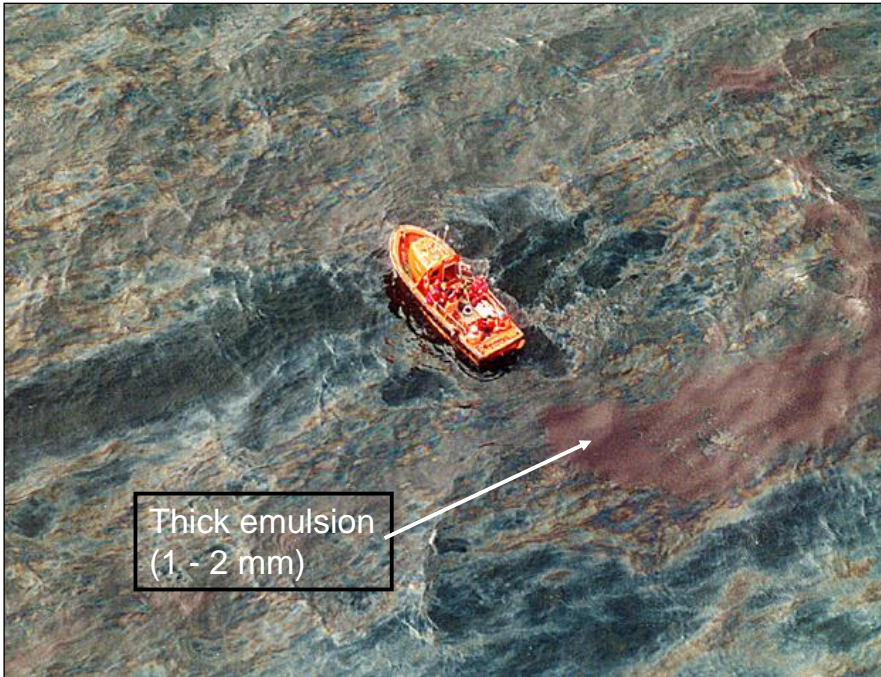
Figure A-12: Surface oil slick (initial thickness > 200 µm) from the experimental deep water release DeepSpill in 2000. Surface oil is emulsifying similar to an oil slick from a surface batch release (from Leirvik et al., 2011)
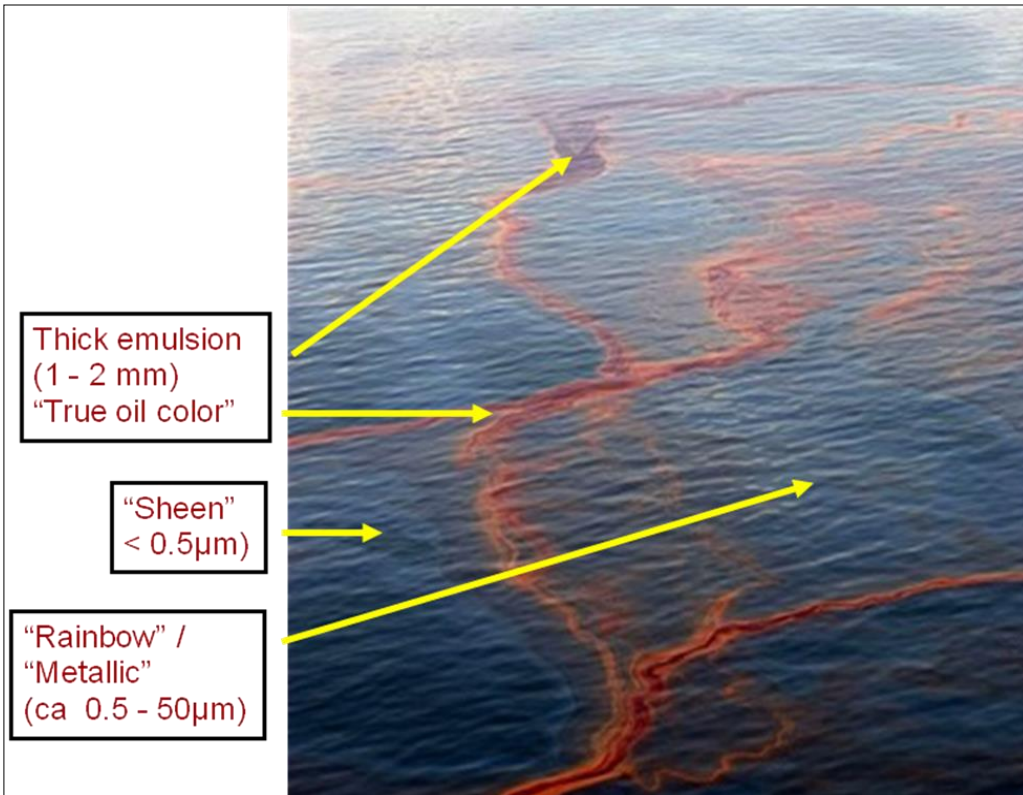
Figure A-13: Surface oil slick (initial thickness > 200 µm) from the DWH deep water release. Surface oil is emulsifying similar to an oil slick from a surface batch release

A.4.11 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 will in many cases be too thin to emulsify (< 200 microns) and evaporation and natural dispersion will be the predominant weathering processes.
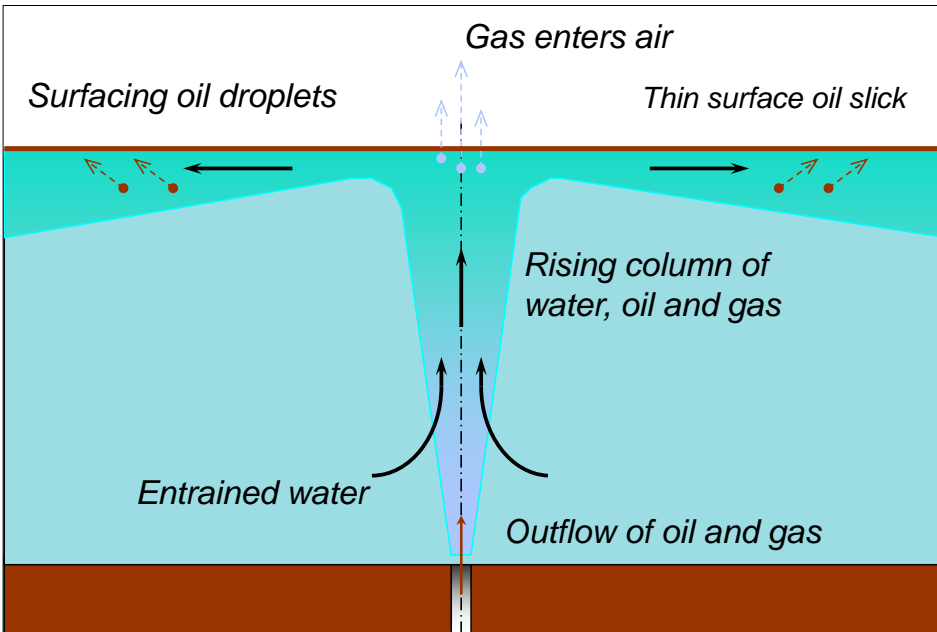

Figure A-14 Illustration of possible creation of thin surface oil slick (< 200 µm) from a shallow subsurface release (<500 m)
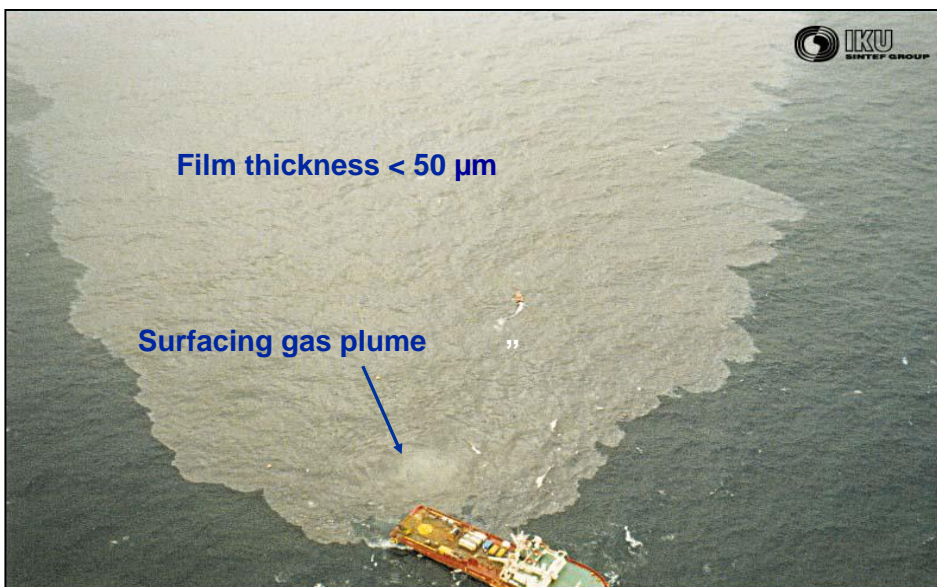
Figure A-15: Surface oil slick (< 50 µm) from experimental subsurface release at 106 m in 1996. The surface oil didn't emulsify and had a very limited life time (hours) due to the low film thickness and high rate of natural dispersion (even at < 10 m/s wind)

B Experimental setup

B.1 Oil samples and test temperature

The Drivis crude oil arrived at SINTEF Environmental Technology in 2014. One red Jerry cans, 20 L, were received. The sample and tag are shown in the photo. The Drivis crude oil was given the unique SINTEF ID 2014-0116.

The weathering and dispersibility study Drivis crude oil were performed at 5 °C, regarded as relevant temperature in the Barents Sea.

B.2 Small-scale laboratory testing

To isolate and map the various weathering processes at sea, the Drivis 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.
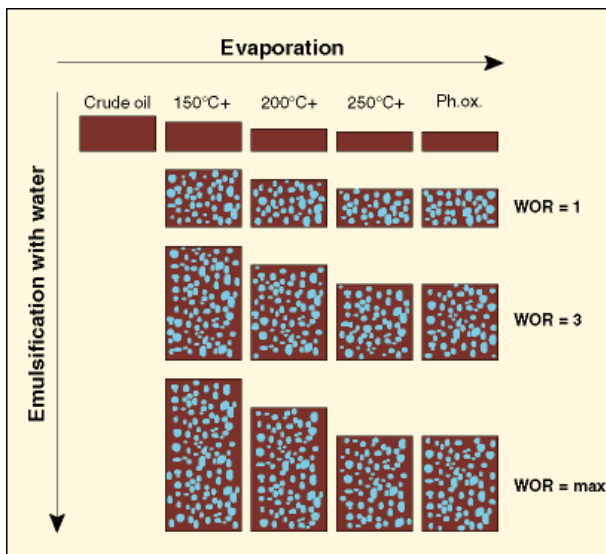
WOR: Water to Oil Ratio

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).

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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.
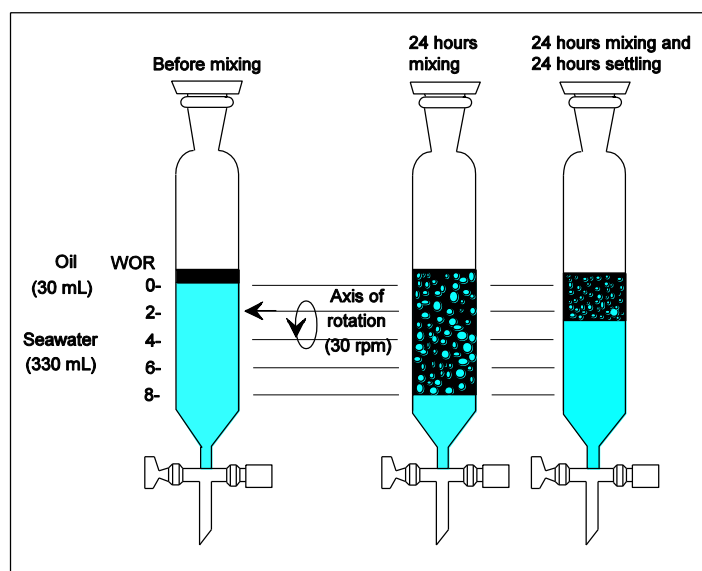
Figure B-2: Principle of the rotating cylinder method

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.

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Both IFP and MNS test apparatus is shown in Figure B-3.

IFP Test

1. Experimental beaker   4. Sampling bottle   7. Timer
2. Peristaltic pump   5. Surge beater   8. Oil containment ring
3. Storage water   6. Electro-magnet

MNS Test

Air outlet

Thermometer

Air flow

Water sampling tube

Manometer

Air inlet

Air blower

Oil containment ring

Cooling coil
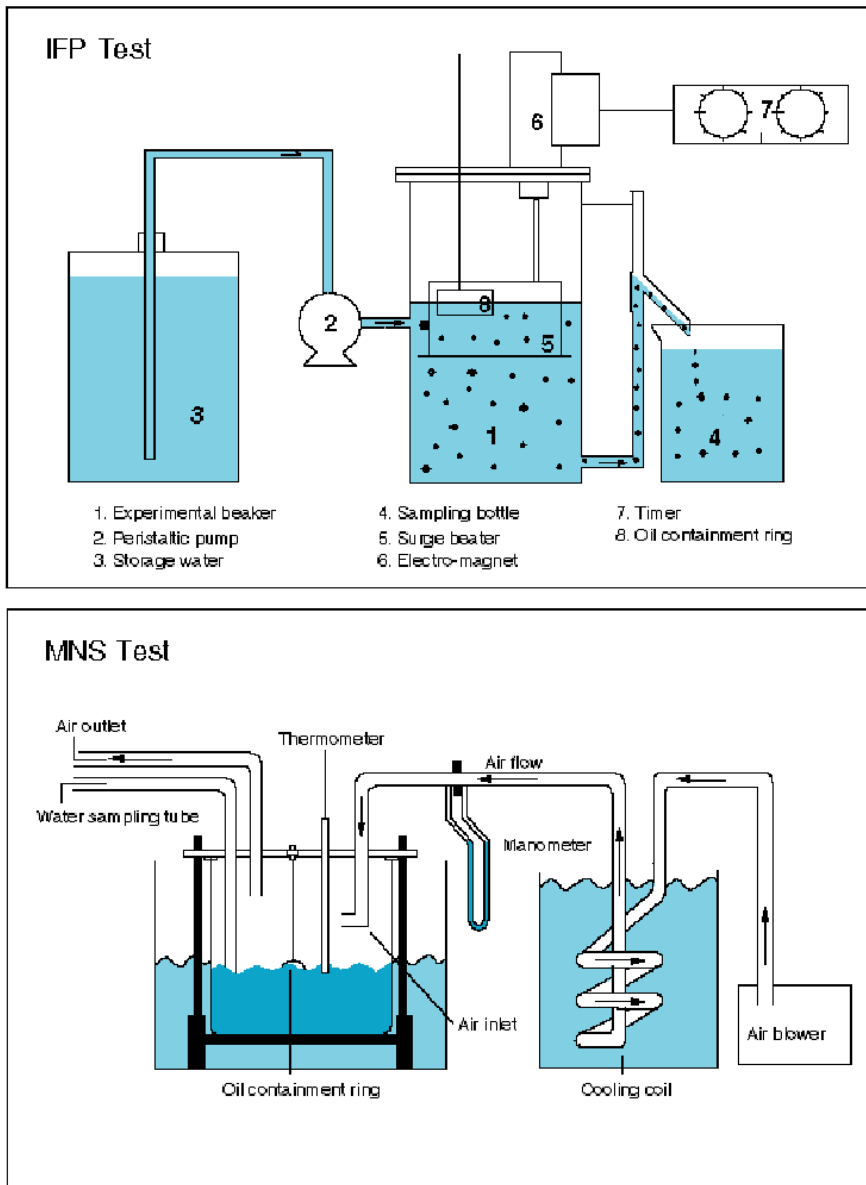
Figure B-3: IFP and MNS test apparatus.

B.3 Meso-scale laboratory testing

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

B.3.1 Description of the flume basin

A meso-scale flume basin (Singsaas *et al.*, 1993), located at SINTEF's Sealab, is routinely used to simultaneously study the weathering processes under controlled conditions. The meso-scale flume basin was

rebuilt in 2006, having state of the art instrumentation. A schematic drawing of the flume is given in Figure B-4.

Approximately 5 m^3 seawater circulates in the 10 metres long flume. The flume basin is located in a temperature controlled room (0°C-20°C). Two fans are placed in a covered wind tunnel, controlling the wind speed. The fans are calibrated to simulate an evaporation rate corresponding to a wind speed of 5-10 m/s on the sea surface.
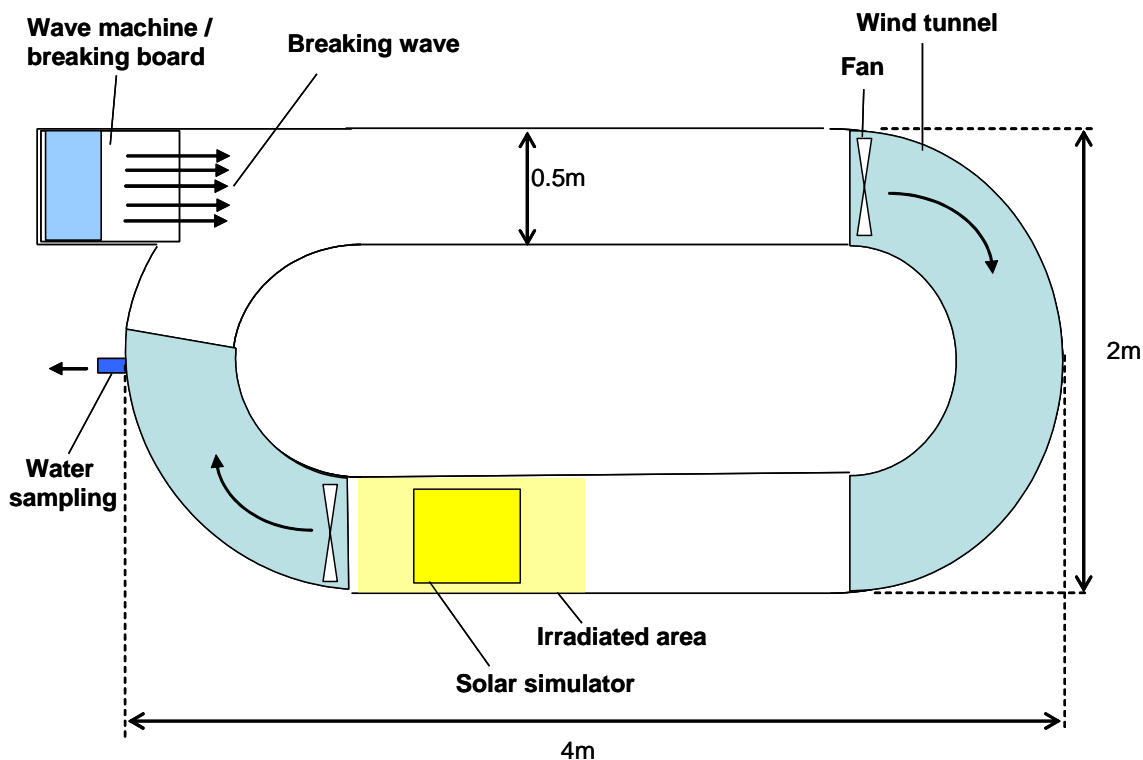
Figure B-4: Schematic drawing of the meso-scale flume

B.3.2 Oil weathering in the flume basin

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

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

Analysis of surface oil/emulsion

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

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

- Viscosity

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- Water content
- Density
- Evaporative loss
- Emulsion stability (for a limited amount of samples)

Analysis of water samples

Water samples are analysed for oil concentration in the water column (droplets and dissolved components). The samples are taken at a depth of 50 cm through a tap in the basin wall into a Pyrex glass bottle (1 L). The sampled water is acidified with some droplets of 10% HCl (pH < 2). The sampling position is shown in Figure B-4. Samples are then extracted by liquid-liquid extraction with dichloromethane (DCM) and quantified by Ultra Violet (UV) spectrophotometer.

Solar simulation in the meso-scale flume

Sunlight is simulated with a solar simulator from Gmbh Steuernagel. The solar lamp (4 KW) emits a wavelength spectrum calibrated to fit natural sunlight at high noon and in the absence of clouds. Figure B-5 shows the measured spectrum from the solar simulator compared to one of the most widely used standard spectra for solar irradiance (CIE publication 85, 1989).
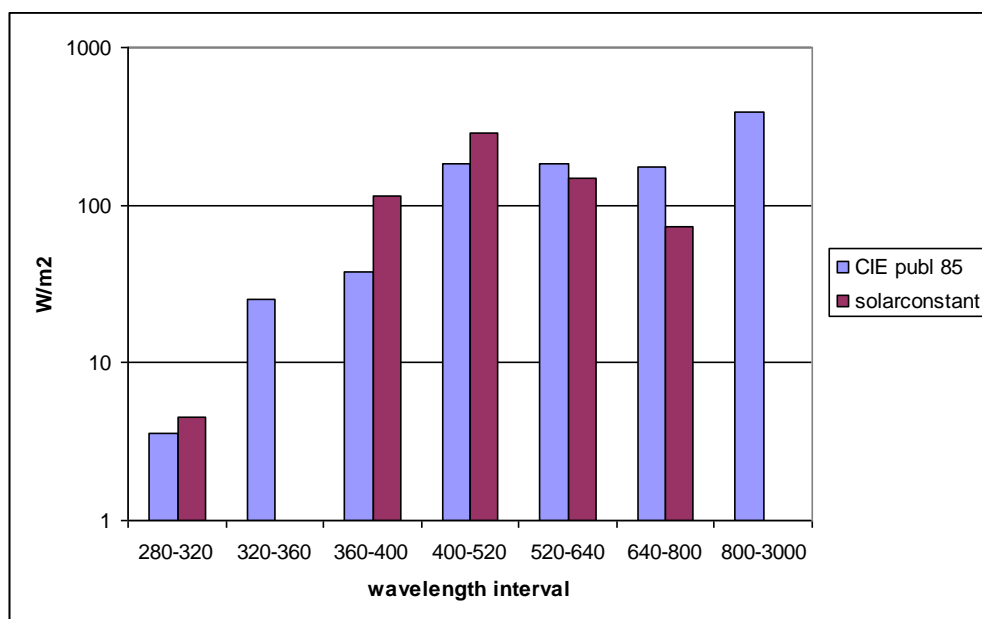
Figure B-5: Measured wavelength compared to standard spectrum suggested in CIE publication 85

The exact exposure of solar irradiance on the oil in the meso-scale flume is somewhat difficult to calculate. Since the oil is moving, it will only be within the irradiated area periodically. The exposure will be highly dependent on the distribution of the oil in the flume and the thickness of the emulsion on the water surface. An estimated irradiation pr. day using the solar simulator is compared with the average irradiation pr. day for selected Norwegian cities in Figure B-6.
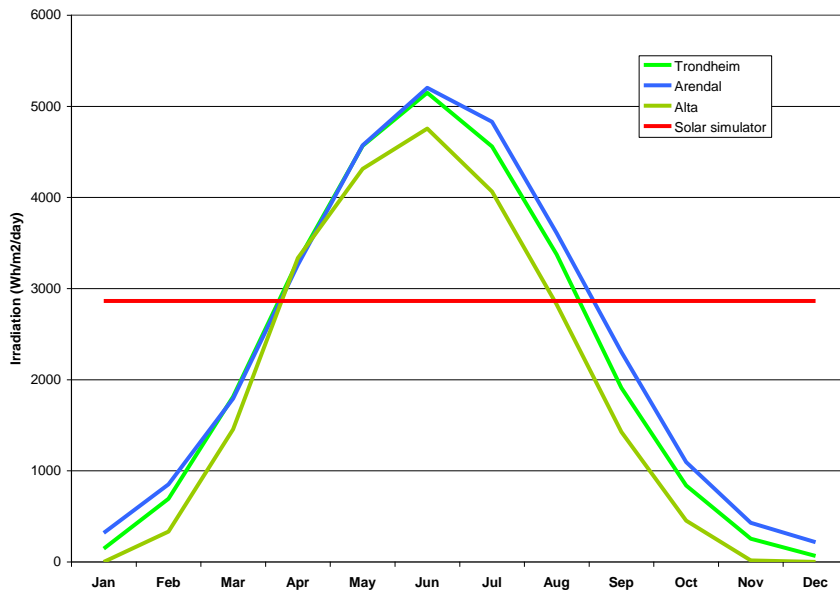
Figure B-6: Daily Irradiation for some Norwegian cities throughout the year compared with the estimated daily irradiation in the meso-scale flume

The simulated irradiance seems to be the approximate average of the daily irradiance throughout the year. However, simulations are not considering clouds. The real irradiation will be lower than that predicted in Figure B-6.

C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Drivis is given in Table C-1 to Table C-3.

Table C-1: Physical and chemical properties for Drivis crude oil at 5 °C

| Properties of fresh oil	Value
Density (g/ml)	0.827
Pour point (°C)	-12
Reference temperature (°C)	5
Viscosity at ref. temp. (mPa·s = cP) *	11
Asphaltenes (wt. %)	0.05
Flash Point (°C)	-
Wax Content (wt. %)	1.94
Dispersible for visc. < **	500
Not dispersible for visc. > **	10000
Maximum water uptake (%)	-

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

** Estimated

- No data

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

Temperature (°C)	Volume (%)*
15	1.1
65	3.8
100	8.6
150	17.8
200	29.4
250	42.3
300	55.3
350	67.6
370	71.5
450	82.4

*TBP from crude assay "DRIVIS201404".

TBP adjusted to fit the lab. data as input to predictions.

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Table C-3: Lab weathering data for Drivis crude oil at 5 °C

Property	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	215	271	313
Vol. Topped (%)	0	19.6	31.0	44.8
Weight Residue (wt. %)	100	83.0	72.2	58.7
Density (g/ml)	0.838	0.866	0.878	0.892
Pour point (°C)	-12	9	15	18
Flash Point (°C)	-	54.0	92.4	121.5
Viscosity of water-free residue (mPa.s =cP)	11	87	300	1336
*Viscosity of 50% emulsion (mPa.s = cP)**	-	864	1167	2937
*Viscosity of 75% emulsion (mPa.s = cP)**	-	1941	2653	-
Viscosity of max water (mPa.s = cP)	-	1169	2346	11131
Max. water cont. (vol. %)	-	90.9	85.7	77.8
(T1/2) Halftime for water uptake (hrs)	-	0.21	0.73	1.6
Stability ratio	-	1	1	0.91

* Measured at shear rate 100 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 Drivis crude oil based on GC/MS analysis of fresh oil

No	Description	Drivis, wt.%
1	C1-C4 gasses (dissolved in oil)	2.000
2	C5-saturates (n-/iso-/cyclo)	2.000
3	C6-saturates (n-/iso-/cyclo)	1.563
4	Benzene	0.437
5	C7-saturates (n-/iso-/cyclo)	2.000
6	C1-Benzene (Toluene) et. B	1.052
7	C8-saturates (n-/iso-/cyclo)	4.948
8	C2-Benzene (xylenes; using O-xylene)	1.581
9	C9-saturates (n-/iso-/cyclo)	3.478
10	C3-Benzene	0.941
11	C10-saturates (n-/iso-/cyclo)	4.000
12	C4 and C4 Benzenes	0.041
13	C11-C12 (total sat + aro)	5.959
14	Phenols (C0-C4 alkylated)	0.000
15	Naphthalenes 1 (C0-C1-alkylated)	0.330
16	C13-C14 (total sat + aro)	9.670
17	Unresolved Chromatographic Materials (UCM: C10 to C36) 0 0 0	0.000
37	metabolite 1	0.000
38	metabolite 2	0.000
18	Naphthalenes 2 (C2-C3-alkylated)	0.454
19	C15-C16 (total sat + aro)	7.546
20	PAH 1 (Medium soluble polyaromatic hydrocrbns (3 rings-non-alkyltd;<4 rings)	0.261
21	C17-C18 (total sat + aro)	7.739
22	C19-C20 (total sat + aro)	9.000
23	C21-C25 (total sat + aro)	6.774
24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)	0.226
25	C25+ (total)	28.000

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

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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

Many crude oils and particularly water-in-oil 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. This force is called the fluids "yield stress" or flow limit and is given the unit Pascal (Pa). The yield stress parametre is derived from measurement of oscillation stress-sweep with increasing applied force on the sample where the deformation of the samples is measured. Results from the yield stress measurements of Drivis are tabulated in Table E-1, below. This information can be utilized in model tool (e.g. OSCAR) for spreading modelling of oil on the sea surface and for modelling /calculation of oil film thicknesses.

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

Residue	Water Content (Vol%)	Viscosity (mPa.s), $10s^{-1}$	Yield stress (Flow limit) (Pa)	Density (g/mL)
Fresh	0	13	NA	0.838
150°C+	0	179	NA	0.866
200°C+	0	904	1.09	0.878
250°C+	0	7134	17.2	0.892
150°C+	50	864	2.39	0.945
200°C+	50	1167	2.89	0.951
250°C+	50	2937	2.55	0.958
150°C+	75	1941	2.78	0.985
200°C+	75	2653	3.95	0.987
250°C+	72*	11298	23.3	0.991
150°C+	90**	1169	3.57	1.009
200°C+	86**	2346	2.81	1.003
250°C+	78**	11131	21.3	0.995

NQ: No yield stress quantified due to Newtonian properties. *Not possible to make 75 vol% emulsions ** Maximum water uptake

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