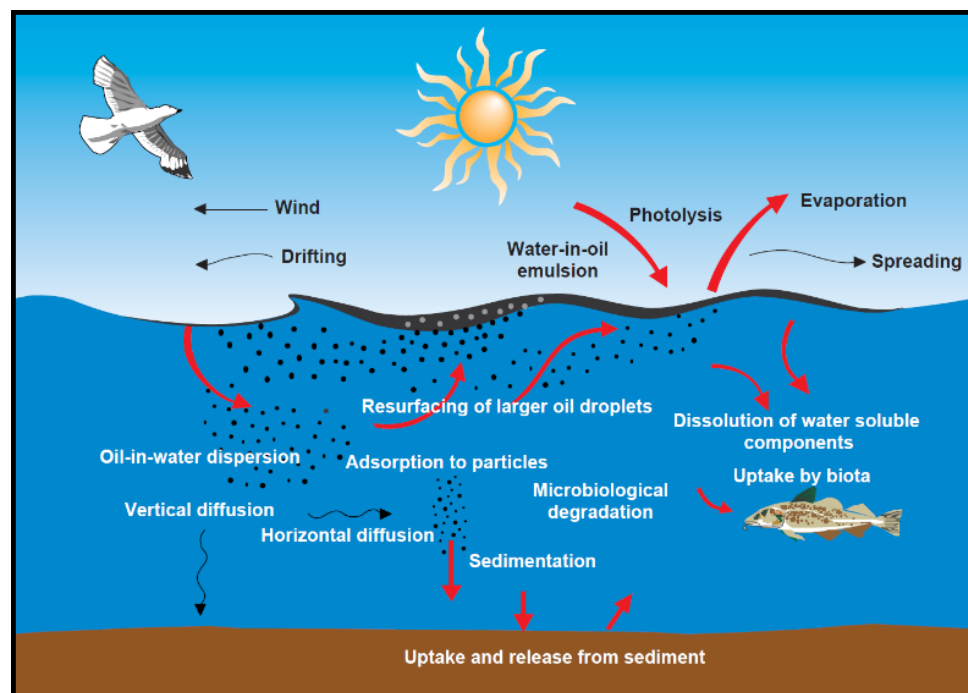# Report

Valhall – Weathering properties and behaviour at sea

In relation to oil spill response

Author(s)
Kristin Rist Sørheim
Oddveig M. Bakken

SINTEF Ocean AS

2021-09-14

Report

Valhall – Weathering properties and behaviour at sea

In relation to oil spill response

REPORT NO.	PROJECT NO.	VERSION	DATE
OC2021 A-063	302006208	2.0	2021-09-14

AUTHOR(S)
Kristin Rist Sørheim
Oddveig M. Bakken

CLIENT(S)
AkerBP ASA

CLIENT'S REF.	NUMBER OF PAGES/APPENDICES:
Harald Kvernstrøm	65 incl. 4 Appendices

CLASSIFICATION	CLASSIFICATION THIS PAGE	ISBN
Open	Open	978-82-7174-421-2

ABSTRACT

A standardized weathering study has been conducted on Valhall crude oil at 13 °C in 2021. Dispersibility testing on Valhall included the dispersant Dasic Slickgone NS to estimate the viscosity limits and time window for dispersant use. In a previous study on Valhall (Moldestad et al., 2001), the dispersibility limits were based on Corexit 9500A.

The SINTEF Oil Weathering Model (OWM) is used to predict the weathering properties of Valhall at sea. The weathering properties of Valhall are also discussed in relation to oil spill response.

![DNV-GL Management System Certification ISO 9001 ISO 14001 OHSAS 18001]

PREPARED BY	CHECKED BY	APPROVED BY
Kristin Rist Sørheim	Per S. Daling	Andy Booth
Kristin R Sørheim	*Per S. Daling*	*AnBah*
Kristin R. Sørheim (Sep 14, 2021 16:09 GMT+2)	Per S. Daling (Sep 14, 2021 16:16 GMT+2)	Andy Booth (Sep 14, 2021 16:07 GMT+2)

Document History

VERSION	DATE	VERSION DESCRIPTION
1.0	2021-07-12	Draft version for review
2.0	2021-09-14	Final version

Table of Contents

1 Executive summary

Spilled oils undergo changes when weathered on the sea surface. These changes affect oil behaviour and consequently oil spill preparedness. Oil weathering varies over time and with different environmental conditions. The lifetime of an oil spill at sea depends on the oil's properties, emulsification, release scenario, and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the sea surface. Based on input from the experimental weathering data of the oil, the SINTEF Oil Weathering Model (OWM) has been used to predict the properties of oil as it weathered over time. This summary gives a brief overview of the main changes predicted for Valhall crude oil when weathered on the sea surface.

Compared to many other Norwegian crude oils, this weathering study of Valhall 2021 shows the following properties relevant for the behaviour, if spilled at sea:

- Valhall is a paraffinic crude oil with medium density (0.842 g/mL) with a content of volatile (42 vol %, 250°C+) that cause a moderate degree of evaporative loss: E.g. after 12 hours the evaporative loss is in the range of 25-35 wt. %.
- The combination of a medium content of wax (4.99 wt.%), asphaltenes (0.04 wt.%), and density, Valhall forms stable water-in-oil emulsions with high water uptake of 70-75 vol .%
- The emulsion formed are expected to be persistent on the sea surface. E.g. the OWM predictions indicate a lifetime at 15 m/s wind speed of 2 days. In calmer weather conditions the lifetime is predicted to be >5 days.
- As much as 65 % of the oil can still remain on the sea surface in very calm weather conditions (2 m/s wind speed) after 5 days, but due to the emulsification the overall volumes the oil has increased with a factor of 1.5 times relative to the volume of oil released.
- In winter conditions, the residue at sea may form semi-solid lumps/material due to the high pour point of the 200 and 250°C+residues (+21 to +24 °C) representing about 3 hours to 2 days weathering at sea. In summer conditions, a remaining residue may solidify at sea after 2-3 days but expect to be less pronounced than in winter conditions.

Risk of fire /explosion hazard in oil spill response:

If free gas is not associated with an oil release (e.g. surface release of stabilized oil at 1 atm.), the flash point of the oil is the most important parameter when evaluating the potential for fire /explosion hazard. In such cases when the oil is spilled on the sea surface it assumes to reach the ambient water temperature within a short time period. The fire hazard, based on the volatile components from the oil, may be high if the flash point of the oil is below the sea temperature. For Valhall, the flash point is predicted to exceed the sea temperature within the first 15 minutes at wind speeds (10-15 m/s), and within 0.5 hours at lower winds speeds (2-5 m/s). However, for larger surface release rates, the time for the flash point to exceed the sea temperature can be extended. Moreover, some storage tanks in vessels engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C. Valhall reaches this limit (60 °C) in 3 hours after a spill at calm wind speed (2 m/s) at summer and 6 hours in winter conditions respective, and more rapidly at higher wind speeds. However, this limit is not considered at relevant for oil recovery vessels with A class certification for transport of liquids (Class I/II, flash point < 60 °C).

A "safety" zone should be established early and downwind from the spill site before any response actions in case of an acute oil spill involving free gas. In a response operation, explosimeters should be utilized to measure concentrations of free gas to minimize the risk for fire and explosion hazard at the spill site.

Effect of adding emulsion breaker:

The emulsions formed were stable but easily released (75-100%) water when adding concentrations (500 and 2000 ppm by weight) of the emulsion breaker (Aerosol OT-SE surfactant). The highest concentration (2000 ppm) was shown to be slightly more effective than 500 ppm. Use of emulsion breaker may effectively be used during an oil spill operation to remove or reduce water from the recovered oil/emulsion which minimizes the storage volume. Emulsion breakers are normally injected at the skimmer head prior to transferring the collected oil/water to storage tanks,

Mechanical recovery :
The risk for boom leakage in a mechanical recovery operation is more of a concern for low viscous emulsions (lower than 1000 mPa.s) compared to emulsions that are more viscous. Boom leakage is also influenced by other factors such as operational speed and weather conditions. This study shows that the emulsion viscosities of Valhall surpassed 1000 mPa.s about 6-9 hours at 5 m/s wind speed (5 and 15 °C), and about 2-3 hours at 10 m/s wind speed at 5 and 15 °C. Moreover, viscosities larger than 15-20 000 mPa.s are known to reduce the flowability of the oil/emulsion when using traditional weir skimmers. However, Valhall has predicted emulsion viscosities lower than this limit within 5 days weathering at summer and winter conditions.

Chemical dispersion:
Valhall is expected to have potential for chemical dispersion in both winter and summer conditions but overall requires energy in terms of breaking waves and /or artificial energy to enhance the dispersion. The oil was found to be good dispersible with the dispersant Dasic NS (DOR; dispersant-to-oil ratio 1:25) for viscosities <800 mPa.s, and not (poor) dispersible >8000 mPa.s. In the field, if the viscosity of is reduced dispersible (800-8000 mPa.s), additional energy (e.g. thrusters, Fire Fighting (Fi-Fi) systems or MOB (Man overboard boats) or higher DOR and/or repeated dispersant application may increase dispersant effectiveness.

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

High-capacity water flushing (mechanical dispersion):
The emulsification is the limiting factor for this strategy. The predicted film thickness is > 0.2-0.3 mm which is the estimated upper limit for effective use of water flushing. Water flushing is therefore not a main response option for Valhall but could be a supplementary method in areas with thin oil films e.g., metallic /rainbow appearance in very calm weather conditions.

 Monitoring and remote sensing: Monitoring and remote sensing should be used a support in a response operations for Valhall.

Short summary differences between Valhall 2021 vs. Valhall 2000
Many similarities in physico-chemical properties, but some differences for Valhall 2021:
- Higher evaporative loss of the 200 and 250°C+ residue.
- Higher density of 250°C+ residue
- Lower viscosities of the waterfree residues 200 and 250°C+

Valhall 2021 emulsification:
- Lower kinetics water uptake
- Lower water uptake
- Lower emulsions viscosities

Valhall 2021 OWM predictions:
- Higher evaporative loss
- Higher emulsion viscosity mainly due to higher evaporative loss (most impact at winter conditions)
- Higher pour point (most impact in winter conditions)
- Slower water uptake
- Dispersibility limits: The viscosity limit for when the oil sis expected to be good dispersible is higher in 2021, whilst the viscosity limit for when the oil is expected not (poor) dispersible is the same: >800 mPa.s and < 8000 mPa.s (Valhall 2021) vs. > 400 mPa.s and < 8000 mPa.s (Valhall 2001)

Based on the results from the dispersibility testing, mechanical recovery should still be the main response strategy for Valhall followed by dispersant use. Use of dispersants requires breaking waves /artificial energy in very calm sea conditions for being efficient.

2 Introduction

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

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 Ocean has performed a standardized small-scale weathering study on Valhall (2021) at 13 °C. The obtained laboratory data have been used to predict the weathering properties of Valhall by use of the SINTEF Oil Weathering Model (OWM). Information about the Valhall field is given, below (Figure 2-1).

Valhall is a field in the southern part of the Norwegian sector in the North Sea. Block: 2/8. The water depth is 70 metres. Valhall was discovered in 1975, and the initial plan for development and operation (PDO) was approved in 1977. Production started in 1982.

The Valhall area consists of a field center with five platforms connected by bridges, and four wellhead platforms that are remotely controlled from the field center. The field is powered with electricity from shore.

Valhall produces oil from chalk in the Upper Cretaceous Hod and Tor Formations. Reservoir depth is 2400 metres. The Tor Formation chalk is fine-grained and has good reservoir quality.

Oil and NGL (Natural Gas Liquids) are routed via pipeline to the Ekofisk field and further to Teesside in the UK. Gas is sent via Norpipe to Emden in Germany.

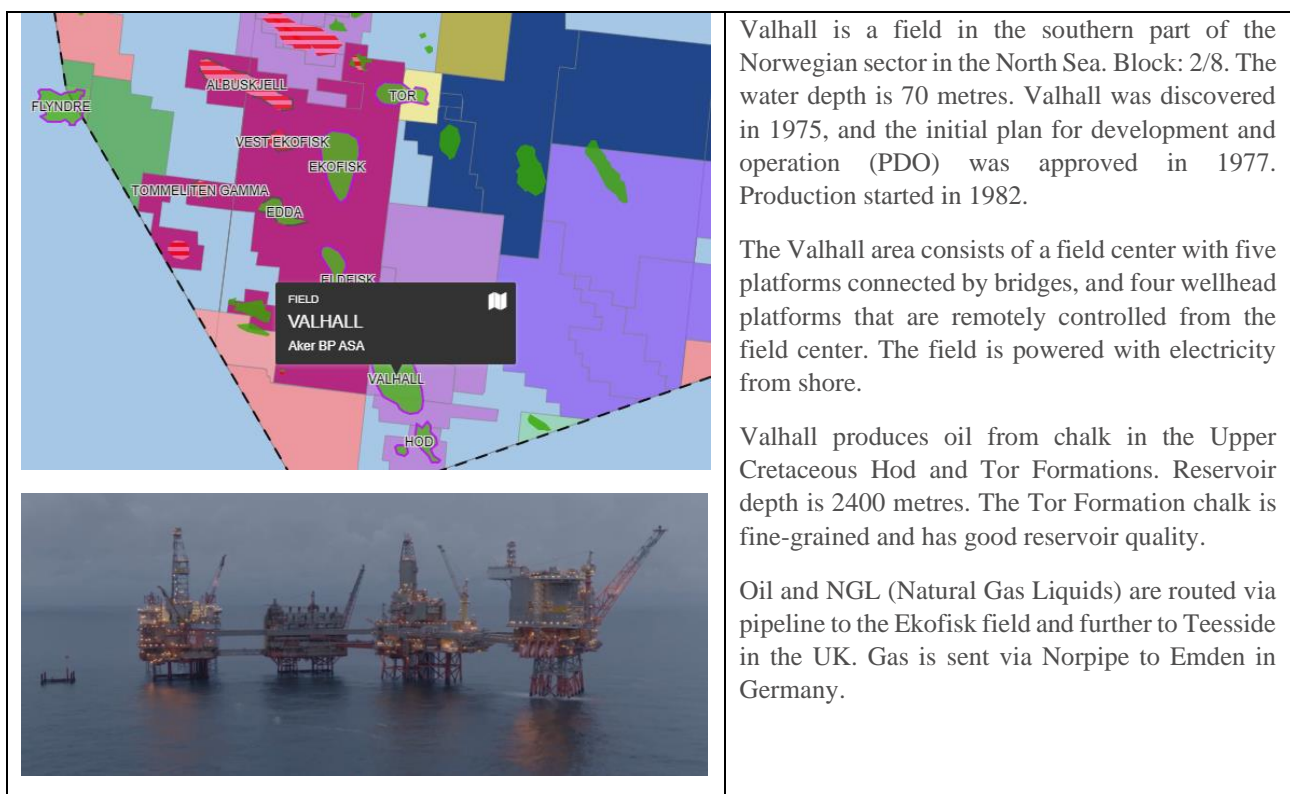*Figure 2-1*   *https://www.norskpetroleum.no/en/facts/field/valhall/*; *https://akerbp.com/en/asset/valhall/*

3 Small-scale laboratory testing of Valhall

Description of the oil sample of Valhall for testing and the experimental setup for the small-scale weathering and dispersibility methods are described in Appendix B. Physico-chemical parameters and weathering properties of Valhall from 2021 were compared with a previous study on Valhall from 2000 (Moldestad et al., 2001), this in agreement with AkerBP.

3.1 Gas chromatographic (GC-FID) characterization

The hydrocarbon profile of Valhall was analysed by use of gas chromatography (GC) coupled with Flame Ionization detector (FID). Figure 3-1 illustrates the GC-FID outputs (gas chromatograms) of the fresh oil of Valhall and the corresponding evaporated residues at three different degrees of evaporative loss of volatiles with boiling points 150, 200 and 200°C+ (see Appendix B.2). The loss of low molecular weight (volatiles) compounds (shown towards the left of the chromatogram) at the three temperatures mimics that of natural weathering (evaporative loss at sea) corresponding to approximately 0.5-1-hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface. The GC-FID also provides support for the artificial evaporation of the crude oil by use of distillation.

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

Figure 3-1 shows that Valhall is a typical paraffinic crude oil with a main range of n-alkanes from nC_5 to nC_{30}. Valhall from 221 and 2000 also have great similarities in their hydrocarbon profile, as shown in Figure 3-2.

GC/FID is an important tool for oil characterization and for oil spill identification as an initial step. Common screening parameters used for identification, as well as for the degree of biodegradation, are the nC_{17}/Pristane and nC_{18}/Phytane ratios. Table 3-1 shows the ratios of Valhall 2021 in comparison with the previous tested Valhall 2000. The ratios show small variations between Valhall 2021 and Valhall 2000, however Valhall 2021 has lower ratios than Valhall 2000 that can be due to some extend biodegradation in the reservoir.

Table 3-1 nC_{17}/Pristane and nC_{18}/Phytane ratios*

Oil name	nC$_{17}$/Pristane	nC$_{18}$/Phytane
Valhall 2021	1.8	2.0
Valhall 2000	2.1	2.3

*Ratios > 1 typical for paraffinic oils, ratios < 1 typical for very biodegraded /naphthenic oil.
-: no data obtained
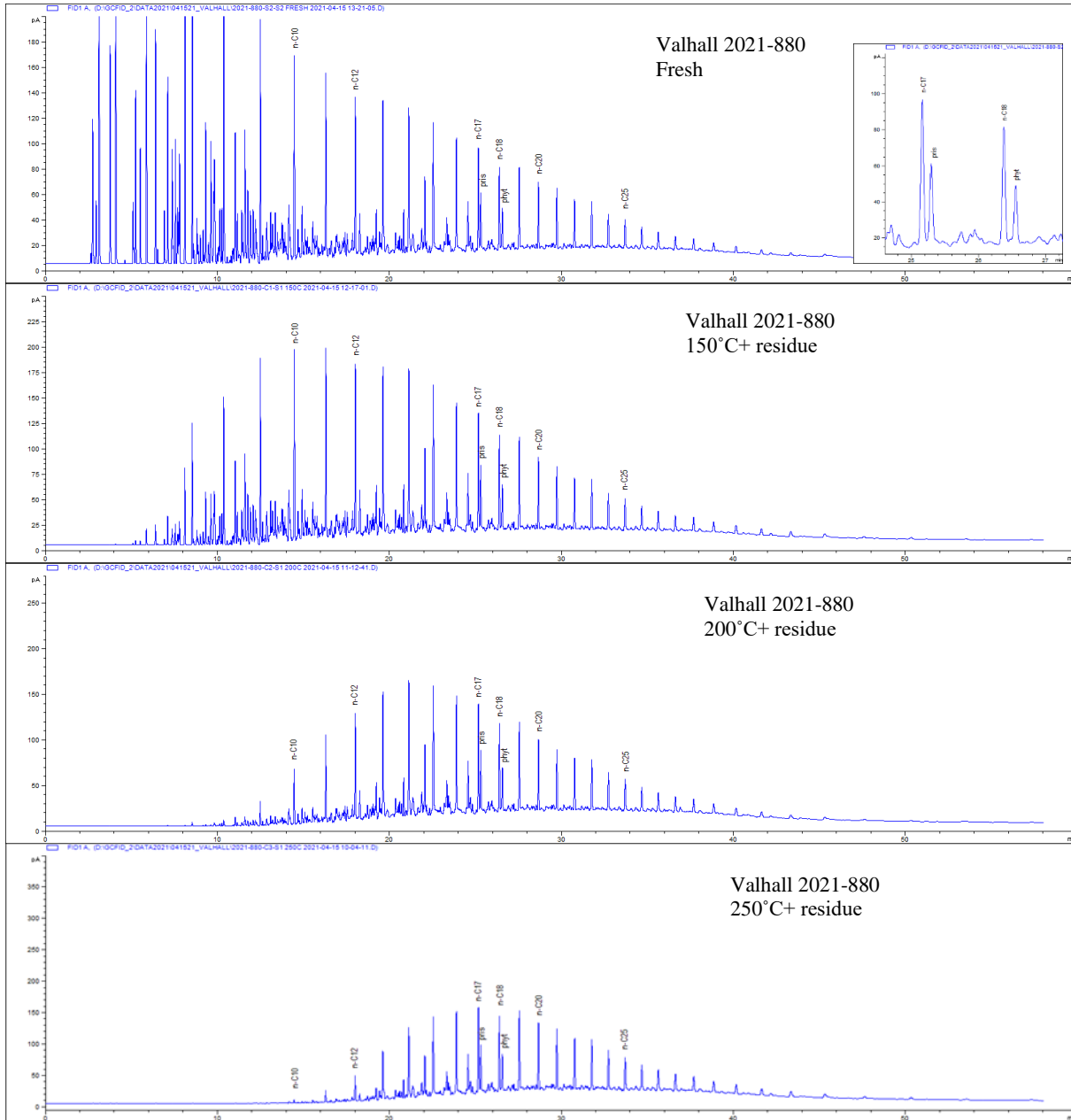
Figure 3-1   GC-FID chromatograms of fresh sample and evaporated residues of Valhall 2021.

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 9 of 65

Figure 3-2   GC-FID chromatograms for fresh oils of Valhall 2021 and Valhall 2000. The retention times may differ between the chromatograms due to different temperature programs (relative comparison).

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 10 of 65

3.2 Asphaltenes and wax content of the fresh and weathered residues

The content of asphaltenes and wax of Valhall 2021 in comparison with Valhall 2000 are given in Table 3-2. The Valhall crude oils (2021 and 2000) 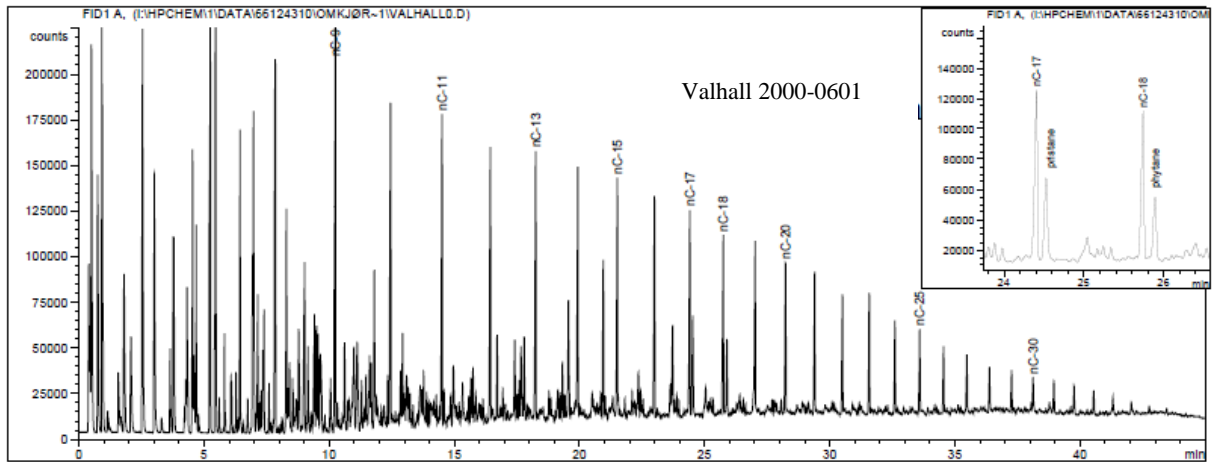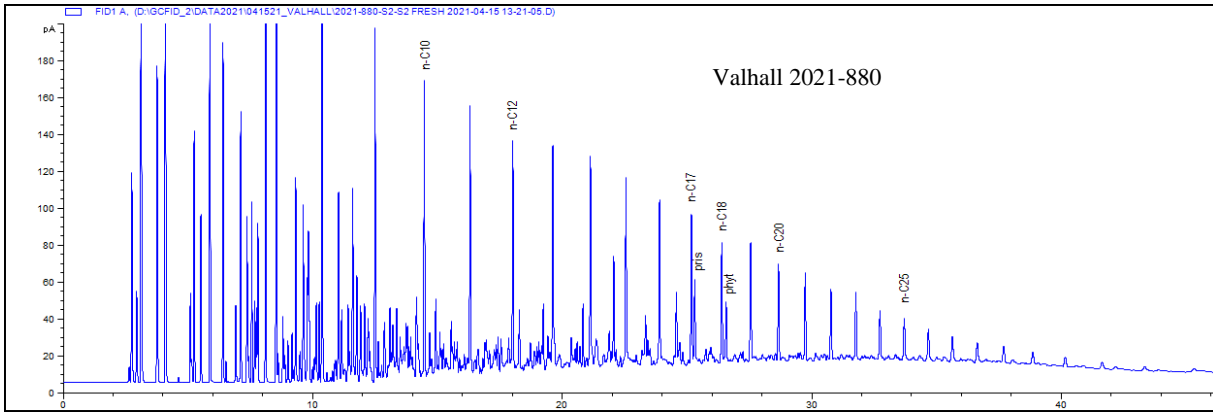have both a medium content of wax of the fresh oil (4.99-5.13 wt.%) and low contents of asphaltenes (0.04-0.07 wt.%), in comparison with other Norwegian crude oils.

Table 3-2   *Asphaltene ("hard") and wax content of Valhall 2021 vs. Valhall 2000*

Oil type	Residue	Asph* (wt. %)	Wax (wt. %)
Valhall 2021	Fresh	0.04	4.99
	150°C+	0.05	6.04
	200°C+	0.06	7.03
	250°C+	0.07	7.96
Valhall 2000	Fresh	0.07	5.13
	150°C+	0.08	6.33
	200°C+	0.09	7.22
	250°C+	0.11	8.14

*n-heptane (nC_7) precipitation

3.3 Physical properties of the fresh and weathered residues

The physical properties of Valhall 2021 are listed in Table 3-4 in comparison Valhall 2000.

Overall, Valhall 2021 and Valhall 2000 have many similarities in their physical properties, although there are some differences. Valhall 2021 has a slightly higher evaporative loss, higher density and pour point (250°C+) than Valhall 2000. Both oils have low pour point of the fresh oil (-6 °C) that increase rapidly to considerably higher pour points with increasing evaporative loss (+24 and +21 °C for the 250°C+residue). Valhall 2021 has lower viscosities than Valhall 2000, e.g. for the 250°C+residue the viscosity for Valhall 2021 is 2850 mPa.s ($10s^{-1}$) vs. 5560 mPa.s for the similar residue for Valhall 2000. However, the viscosity of the emulsions (Figure 3-7) has normally most impact on the behaviour of the spilled oil at sea. The interfacial tension of fresh oil Valhall 2021 is 15 mN/m.

Table 3-3   *Physical properties of Valhall 2021 in comparison with Valhall 2000.*

Oil type	Residue	Evap. (vol. %)	Residue (wt. %)	Density (g/mL)	Flash point (°C)	Pour point (°C)	Visc. (mPa.s) 13°C ($10\ s^{-1}$)
Valhall 2021	Fresh	0	100	0.8422	-	-6	21
	150°C+	20.9	82.6	0.8783	36.5	9	149
	200°C+	33.3	71.0	0.8962	84.5	21	560
	250°C+	41.6	62.3	0.9087	121	24	2859
Valhall 2000	Fresh	0	100	0.8413	-	-6	82
	150°C+	20.2	80.8	0.878	-	9	230
	200°C+	30.2	71.5	0.893	-	15	2160
	250°C+	38.5	63.3	0.905	-	21	5560

-:No data

The True Boiling Point curves (TBP) of Valhall 2021 in comparison with Valhall 2000 are shown in Figure 3-3. Valhall 2021 exbibits a higher distilled cumulative loss than Valhall 2000, that also reflect the higher evaporative loss of the 150, 200 and 250°C+ residues (Table 3-4), reflecting the evaporative loss at sea.
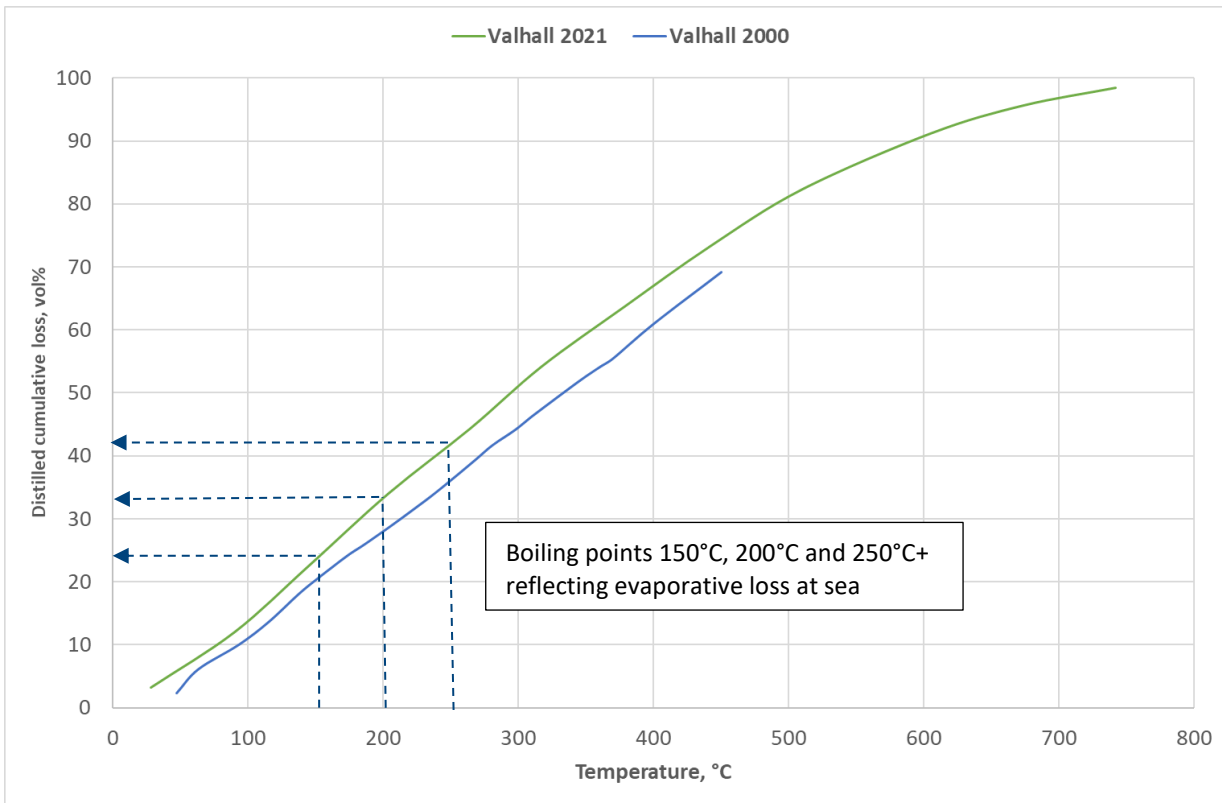
Figure 3-3　　　*TBP of Valhall crude oils. TBP of Valhall 2021 from simulated distillation (Simdist GC). TBP of Valhall 2000 from crude assay.*

3.4 Viscosity of fresh oil and water-free residues with different shear rates

The viscosity describes the oils' ability to resist gradual deformation by increasing shear, where viscosities of so-called *Newtonian* oils remain constant independent on the applied shear rate (s^{-1}) at a given temperature. The opposite when shear is applied on so-called *non-Newtonian* oils the viscosity of such oils decreases. The dynamic viscosities (mPa.s) of Valhall 2021 fresh oil and water-free residues are given in Table 3-4 with increasing shear rates (10, 100 and 1000 s^{-1}) at 13 °C. The fresh oil and the residues 150, 200 and 250°C+ of Valhall 2021 clearly exhibit *non-Newtonian* behaviour at 13 °C, i.e., viscosities depending on the shear rates. Non-Newtonian behaviour is also pronounced for the emulsion of Valhall (Figure 3-7).

Table 3-4　　　*Viscosities of fresh oil and residues of Valhall 2021 with increasing shear rates (s^{-1}) at 13 °C.*

Oil type	Residue	Visc. (mPa.s) 13°C (10 s^{-1})	Visc. (mPa.s) 13°C (100 s^{-1})	Visc. (mPa.s) 13°C (1000 s^{-1})
Valhall 2021	Fresh	21	17	12
	150°C+	149	106	52
	200°C+	560	365	158
	250°C+	2859	949	405

3.5 Emulsifying properties

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

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 12 of 65

rotating cylinders method (Mackay and Zagroski, 1982) was used to study the emulsifying properties, and the procedure for maximum water uptake is described in Hokstad et al., 1993 (Appendix B).

3.5.1 Emulsification

Emulsification testing of Valhall 2021 were conducted on the residues of 150℃+, 200℃+ and 250℃+ to produce data for stability, viscosity, maximum water uptake, kinetics, and the effectiveness of the emulsion breaker application. Emulsions of maximum water content after 24 hours rotation are shown in Figure 3-4, below. The figure shows from left to right four emulsions prepared from the residues of 150℃+, 200℃+ and 250℃+, respectively.
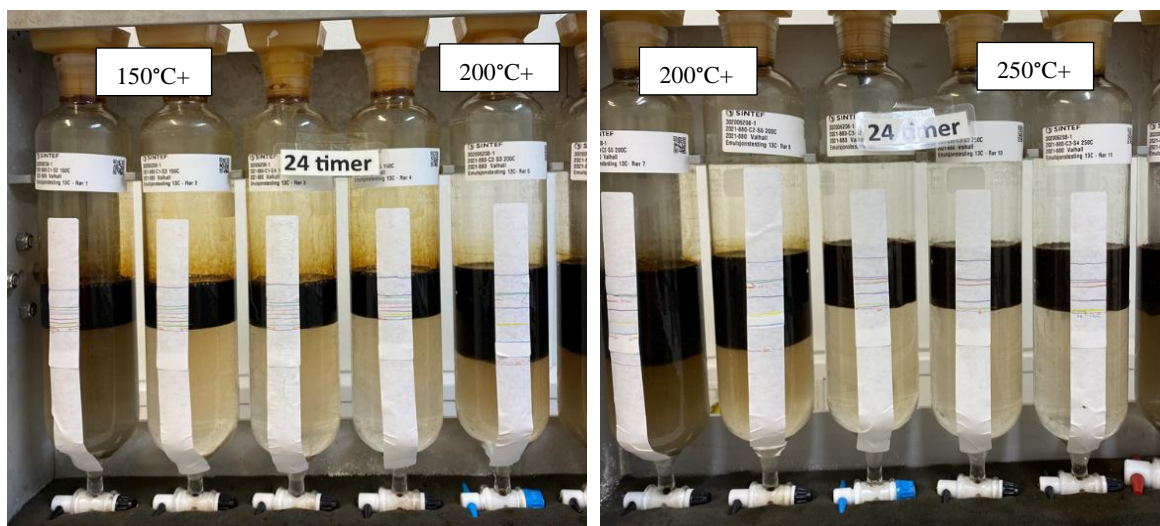

Figure 3-4   Rotating cylinders of water-in-oil (w/o) emulsions of Valhall 2021 after 24 hours at 13 °C.

3.5.2 Water uptake

The rate (kinetics) of water content in the water-in-oil (w/o) emulsions as a function of time is tabulated in Table 3-5. The $t_{1/2}$ values are defined as the time (hours) it takes to incorporate <u>half</u> of the maximum water uptake (vol. %) in 24 hours (rotating time). Valhall 2021 expressed relatively high-water uptakes for all the residues 150℃+, 200℃+ and 250℃+, which ranged from 61 to 85 vol. % (Table 3-5).

Table 3-5   Kinetics ($t_{1/2}$) for the emulsified residues of Valhall 2021 at 13 °C

Mixing time	150°C+ * (vol. % water)	200°C+ * (vol. % water)	250°C+ * (vol. % water)
Start	0	0	0
5 min	15	7	6
10 min	27	8	6
15 min	32	8	12
30 min	42	29	29
1 hour	49	48	54
2 hours	53	66	64
4 hours	56	74	65
6 hours	59	78	66
24 hours	61	81	67
t ½	**0.26**	**0.85**	**0.57**

Depending on weather situation and release rate, the residues are corresponding to approximately 0.5-1-hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface.

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 13 of 65

3.5.3 Efficiency of emulsion breaker and stability of emulsions

In mechanical recovery operations, separating oil from water enables optimal use of available storage (i.e. facilities/tankers), and the efficiency of this separation can be enhanced by applying emulsion breakers. The effectiveness of the emulsion breaker Aerosol OT-SE surfactant was evaluated on different residues of emulsified Valhall 2021. The choice of emulsion breaker was selected in agreement with Aker BP.

The results show that the emulsified oil volume decreased significantly after treatment with the emulsion breaker in all residues, as water was released from the emulsion (Table 3-6). The emulsions were almost totally broken when adding the emulsion breaker (Aerosol OT-SE). Adding 2000 ppm of the emulsion breaker, relative to the oil was shown to be slightly more efficient to break the emulsion compared with a lower concentration of 500 ppm.

The emulsion stability was studied by quantifying the amount of volume fraction of water released from the emulsion after 24 hours settling time. Valhall 2021 formed stable w/o-emulsions of the 150, 200 and 250°C+ residues, as shown in the first main row of Table 3-6.

Table 3-6   Stability of emulsion and the effectiveness of emulsion breaker at 13 °C of Valhall 2021

Residue Valhall 2021	Emulsion breaker	Water-in-oil emulsion (vol. %) at 13 °C		Stability ratio**	% Effect. (released water)
		Reference	24 hours settling *		
150°C+	None	61	61	1.00	0
200°C+	None	81	81	0.98	20
250°C+	None	67	66	0.98	20
150°C+	Aerosol OT-SE 500 ppm	61	9	0.06	94
200°C+	Aerosol OT-SE 500 ppm	81	14	0.04	96
250°C+	Aerosol OT-SE 500 ppm	67	33	0.25	75
150°C+	Aerosol OT-SE 2000 ppm	61	0	0.00	100
200°C+	Aerosol OT-SE 2000 ppm	81	3	0.01	99
250°C+	Aerosol OT-SE 2000 ppm	67	14	0.08	92

ppm: parts per million
* Reference: w/o emulsion after 24 hours rotation
*: w/o-emulsion after 24 hours rotation and 24 hours settling.
** Stability ratio of 0 implies a totally unstable emulsion after 24 hours settling; all the water is settled out for 24 hours settling. Stability ratio of 1 implies a totally stable emulsion.

Figure 3-5 (left) shows image of the stable emulsions of Valhall 2021 after 24 hours stand still (150, 200 and 250 °C+). Figure 3-5 (right) illustrates the % effectivity of settling (low values means minor water has been released from the emulsions), and % effectivity of adding emulsion breaker, high values (75-100 %) means that water has effectively been released from the emulsions.
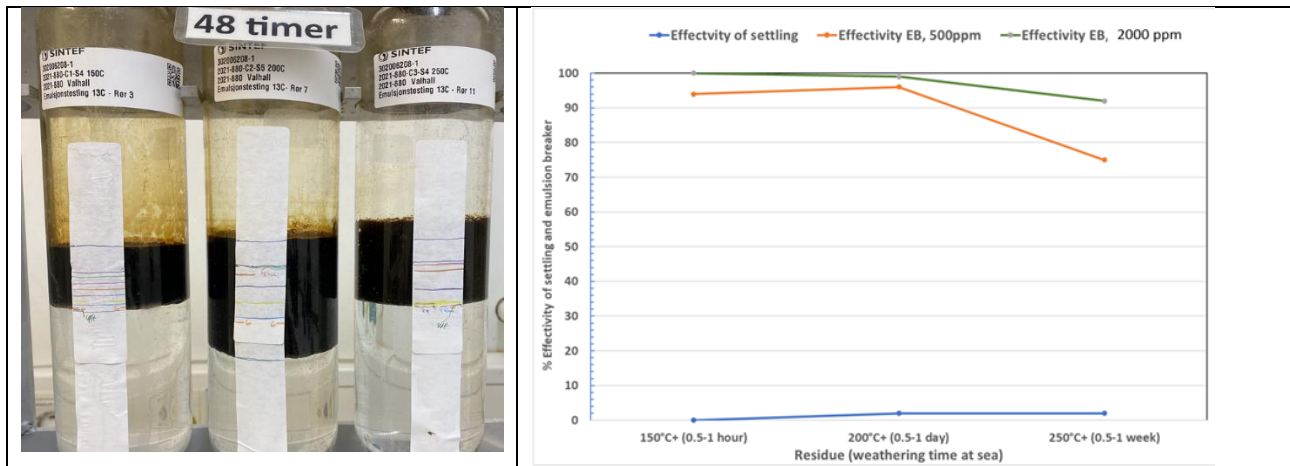
Figure 3-5   Left: Stable (w/o) emulsions of Valhall 2021 after 24 hours rotating followed by 24 hours stand still (s at 13 °C. Right: % efficiency of settling, and emulsion breaker (EB) on Valhall 2021. High % effectivity means that water has been released from the emulsion.

3.5.4 Emulsion viscosities

The viscosities of emulsified residues of Valhall 2021 are given in Table 3-7 (including waterfree residues, Table 3-4). The emulsions behave as *non-Newtonian* fluids due to the increasing degree of weathering (evaporation and water uptake), with higher viscosities at a lower shear rate (10 s^{-1}) compared to the viscosities measured at higher shear rate (100 s^{-1}).

Table 3-7   Viscosities waterfree residues and emulsions of Valhall 2021 at 13 °C

Residue Valhall 2021	Water content (vol. %)	Viscosity (mPa.s) 10 s^{-1}	Viscosity (mPa.s) 100 s^{-1}
Fresh	0	21	15
150°C+	0	149	91
200°C+	0	560	301
250°C+	0	2859	949
150°C+	50	528	211
200°C+	50	1720	637
250°C+	50	3890	859
150°C+	75	578	293
200°C+	75	3011	1013
250°C+	75	5812	1297
150°C+	63	588	234
200°C+	81	1654	549
250°C+	75	5480	805

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 15 of 65

3.6 Chemical dispersibility

The dispersibility testing of Valhall 2021 crude oil included:

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

Screening testing of different dispersants were not performed on Valhall 2021, in agreement with Aker BP. In a previous study (Moldestad et al., 2001), Corexit 9500A was used to estimate the dispersibility (viscosity) limits for dispersant use. In this study, Dasic Slickgone NS was used to estimate dispersibility limits. Dasic Slickgone NS is also the main dispersant agent in NOFO's stockpile, today. The dispersibility limits (viscosities) are further used as input to the SINTEF Oil Weathering Model (OWM) to predict the time-window for dispersant use.

3.6.1 Dosage testing

Dosage testing at 13 °C was performed using Dasic Slickgone NS on the Valhall 2021 emulsion (200°C+ / 50 vol. %). The dosage test helps to identify optimal design conditions for dispersant use and was performed with dispersant-to-emulsion ratios (DER) of 1:25, 1:50, 1:100 and 1:200, and with no dispersant added. The results are presented in Table 3-8 and Figure 3-6. Pictures from the dosage testing on Valhall 2021 are given in Figure 3-7. The results show a clear dosage dependant effect for the high-energy test (MNS), where DER 1:25 and 1:50 showed the highest effects (87-88%). The MNS test produced formation small, dispersed droplets (< 70 -100 µm) reflecting good dispersion by adding the dispersant to the oil (emulsion), see Figure 3-7. For the low-energy test (IFP), the results indicated negligible effect of adding dispersant to the emulsion, producing larger oil droplets in mm size. This means that breaking waves (> 5 m/s wind speeds) or artificial energy in non-breaking waves (< 5 m/s wind speeds) are necessary to disperse surface emulsion of Valhall. No formation of small oil droplets was observed with no dispersant added to the emulsion of Valhall, as shown in Figure 3-7.

Table 3-8   Dosage testing on 200°C+/50% emulsion of Valhall 2021 at 13 °C.

Dispersant (dispersant-to-emulsion ratio)	% Effectiveness IFP	% Effectiveness MNS
Dasic NS (1:25)	3	87
Dasic NS (1:50)	4	88
Dasic NS (1:100)	<0.5	54
Dasic NS (1:200)	< 0.5	43
No dispersant	-	< 0.5

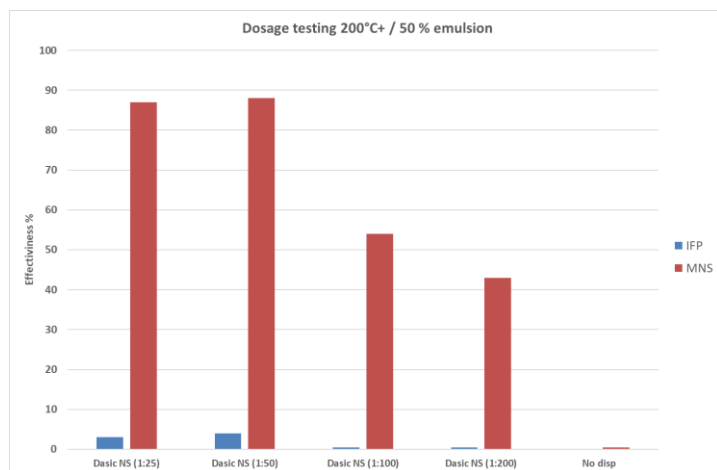**Emulsion viscosity: 1720 mPa.s (10s^{-1})*

Figure 3-6   Results from dosage testing with use of Dasic Slickgone NS on Valhall 2021 (200°C+/50 vol. emulsion).
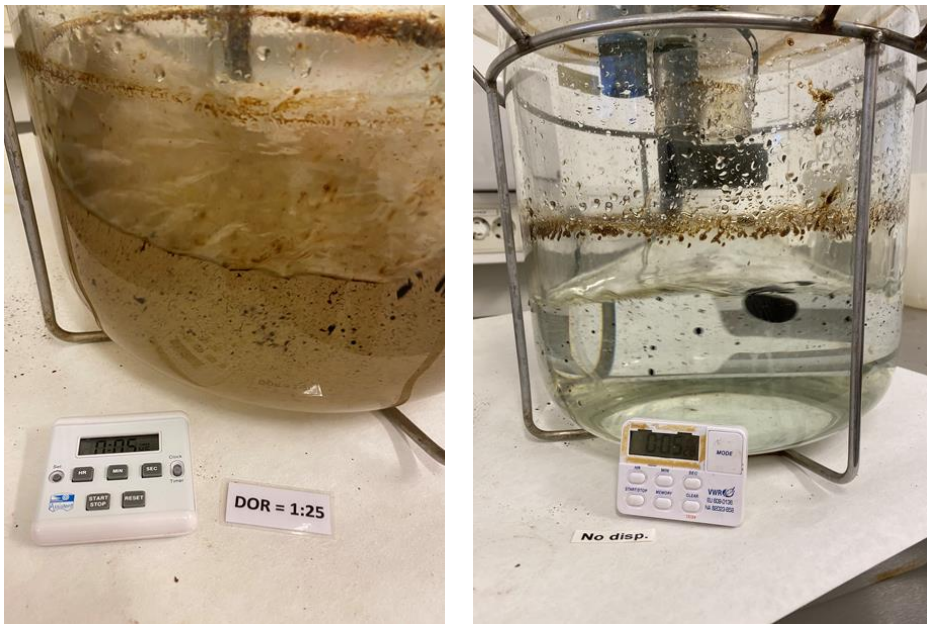
Figure 3-7   *MNS high energy test on 200°C+ 50% emulsion. Left: After adding DOR/DER 1:25 Dasic Slickgone NS. Right: No dispersant added showing no effect on the emulsion.*

3.6.2 Systematic dispersant testing and dispersibility limits

A dosage ratio of 1:25 (4 wt.%) is commonly used as the standard procedure to establish the time window for dispersant application. The results from the systematic dispersant testing at 13 °C is tabulated in Table 3-9. At 13 °C the viscosity limit for when the oil-emulsion is not expected to be dispersible expressed as MNS < 5 % was not obtained in the laboratory testing. Therefore, a supplementary test at 5 °C was conducted for the 250°C+ residue to reach higher viscosity and hence lower the dispersant efficiency (Figure 3-10). Figure 3-8 shows the dispersibility limits (viscosities) expressed as a function of % effectiveness.

Table 3-9   *Effectiveness of Dasic Slickgone NS on Valhall 2021 at 13 °C*

Residue	(vol. %)	Visc. (10 s⁻¹)	Effectiveness % IFP	Effectiveness % MNS
150°C+	0	149	68	100
200°C+	0	560	19	100
250°C+	0	2859	5	18
150°C+	50	528	61	100
200°C+	50	1720	3	87
250°C+	50	3890	3	28
150°C+	75	578	66	78
200°C+	75	3011	8	79
250°C+	66	5812	n.a	n.a
150°C+	63	588	63	98
200°C+	81	1654	11	88
250°C+	75	5480	8	21

Table 3-10   Effectiveness of Dasic Slickgone NS on Valhall 2021 at 5 °C.

Residue	(vol. %)	Visc. (10 s⁻¹)	Effectiveness % IFP	Effectiveness % MNS
250°C+	50 (37)	8838	n.a	3
250°C+	75 (51)	10649	n.a	n.a
250°C+	mw (62)	11318	n.a	n.a
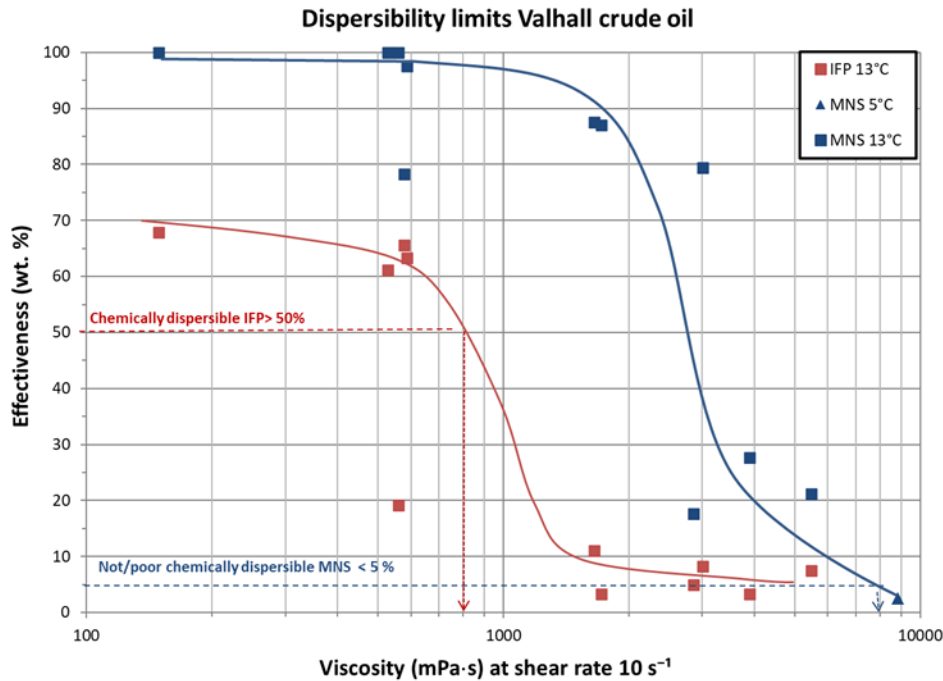
Figure 3-8   Dispersant effectiveness limits on Valhall 2021 at 13 °C.

Valhall 2021 was found to be dispersible for viscosities lower than 800 mPa.s, reflecting > 50 % effectiveness by use of the low energy IFP-test. The upper limit for then Valhall 2021 is not or poor chemically dispersible was estimated to 8000 mPa.s expressed with effectiveness lower than 5 % using the high energy MNS-test. Reduced dispersibility is expected with viscosities between 800 and 8000 mPa.s and means that the oil is still dispersible but may require additional energy and/or higher dispersant dosage to enhance effective dispersion. The dispersibility limits are also summarised in Table 3-11.

Table 3-11   Estimated viscosity limits for Visund for use of dispersant and definition of time window.

Dispersibility	Criteria for effectiveness (wt. %)	Dispersibility limits based on emulsion viscosity (mPa.s)
Chemically dispersible	IFP > 50 %	800
Not/poor chemically dispersible	MNS < 5 %	8000

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 18 of 65

4 Predictions with SINTEF Oil Weathering Model (OWM)

4.1 Description of SINTEF OWM

A systematic stepwise laboratory procedure developed at SINTEF (Daling et al., 1990) was used to isolate and map the various weathering processes that take place when oil is spilled on the sea surface. Laboratory study of Valhall 2021 was conducted at 13 °C, and the analytical data were further used as input to the SINTEF Oil Weathering Model (OWM). The experimental design for the study is described in Appendix B. The input data of Valhall to the SINTEF OWM are 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 4-1. The predictions obtained from the SINTEF OWM are useful tools in the oil spill contingency planning related to the expected behaviour of oil on the sea surface, and to evaluate the time window for operational response strategies in a spill operation. In this report, the presented predictions span a period from 15 minutes to 5 days after an oil spill has occurred. The SINTEF OWM is described in more detail in Johansen (1991), and in the user's guide for the model.
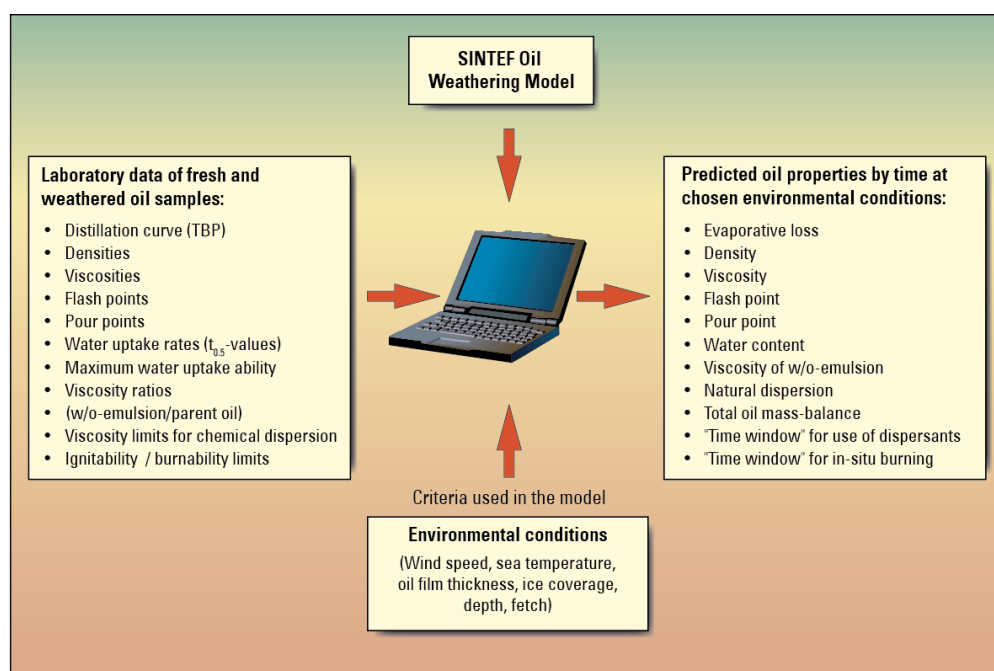

Figure 4-1   Schematic input data to the SINTEF OWM and the predicted output oil properties.

Oil film thickness

Oils in OWM are categorized as condensate (non-emulsifying oil), low emulsifying oil/condensate, emulsifying oil, heavy bunker fuel or refined distillate. The categorization is based on the experimental results obtained in the laboratory. The terminal film thicknesses vary among these categories based on experimental (field) experience. Valhall is categorized as an emulsifying oil.

Seawater temperature

The prevailing weather conditions greatly influence the weathering rate of oil on the sea surface. Due to the location of the oil field, the prediction seawater temperatures chosen for Valhall 2021 was 5 and 15 °C, reflecting typically winter and summer conditions.

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 4-1.

Table 4-1   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

4.2 Predictions of Valhall oil weathering properties

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

Input to SINTEF OWM

Oil type: Crude oil

Geographical area: North Sea

Terminal oil film thickness: 1 mm

Release rate: 1.33 metric tonnes per min. in 15 min, a total of 20 metric
                                  tonnes (80 m^3/hour or 1900 m^3/day)

Seawater temperatures: 5 and 15 °C

Wind speeds: 2 m/s, 5 m/s, 10 m/s and 15 m/s

Predicted properties

- Evaporative loss
- Viscosity
- Flash point
- Pour point
- Mass balance

The predictions are based on 5 days weathering independently if there is not predicted any remining oil within shorter time. The predictions are shown to indicate the weathering properties in cases there are patches or oil left on the surface up to 5 days.

How to use the prediction charts: an example

If the oil has drifted on the sea surface, the following prediction charts could be used to determine the weathering properties of the oil/emulsion. Table 4-2 gives an example of predicted weathering properties for Valhall 2021.

Table 4-2   *Example of weathering properties of Valhall obtained from the OWM predictions after 12 hours of weathering at 2, 5 and 10 m/s wind speed at 15 °C.*

Weathering properties	12 hours 15 ˚C 2 m/s	12 hours 15 ˚C 5 m/s	12 hours 15 ˚C 10 m/s	12 hours 15 ˚C 15 m/s
Evaporation, wt. %	28	32	35	37
Flash point, ℃	80	95	111	121
Pour Point, ℃	18	21	24	26
Water content, vol.%	19	42	69	75
Viscosity, mPa.s *	590	1610	3860	5200
Mass balance / Oil on surface wt.%	72	67	45	11

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

Property: EVAPORATIVE LOSS	SINTEF
Oil Type: VALHALL 2021	
Description:	
Data Source: Sintef Ocean (2021), Weathering data used	OWModel© 13.0

| Surface release | 2.0 |
| Amount/duration of oil spill : 20 metric tons 15.0   minute | Pred. date: Jul. 06, 2021 |

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

Sea surface temperature: 5°C

Sea surface temperature: 15°C
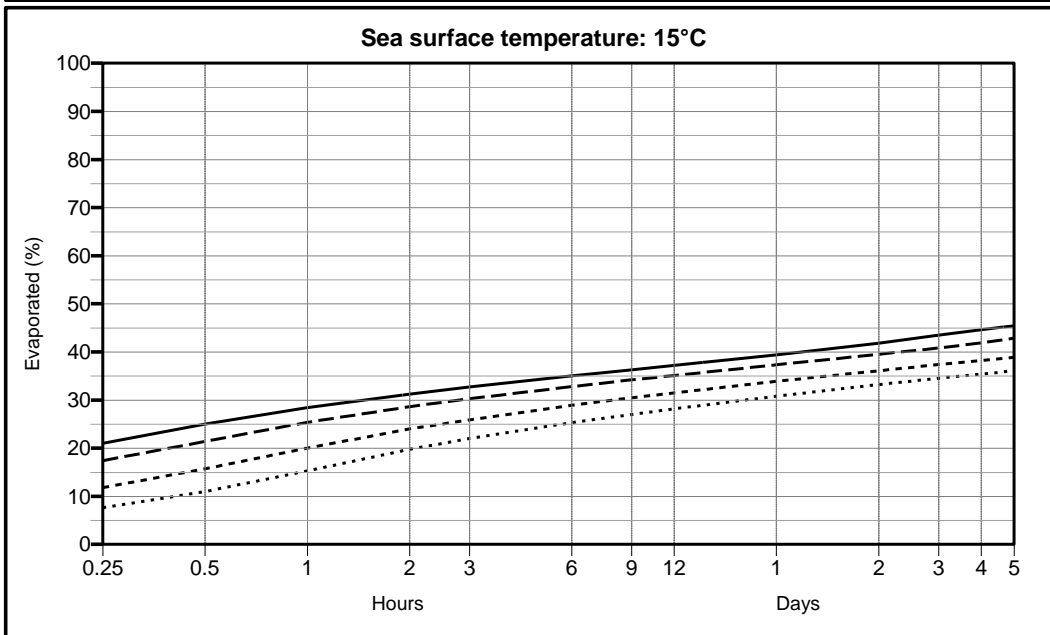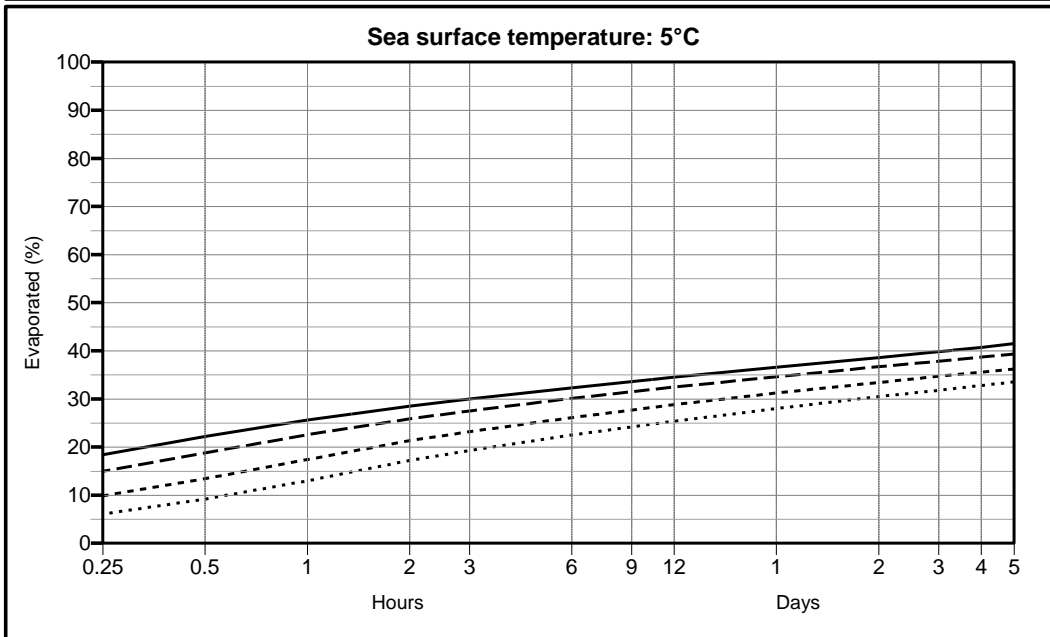
Figure 4-2   Evaporative loss of Valhall 2021 predicted at sea temperatures of 5 and 15 °C.

Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: VALHALL 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

OWModel© 13.0

Surface release
Amount/duration of oil spill : 20 metric tons 15.   /minute

2.0
Pred. date: Jul. 06, 2021

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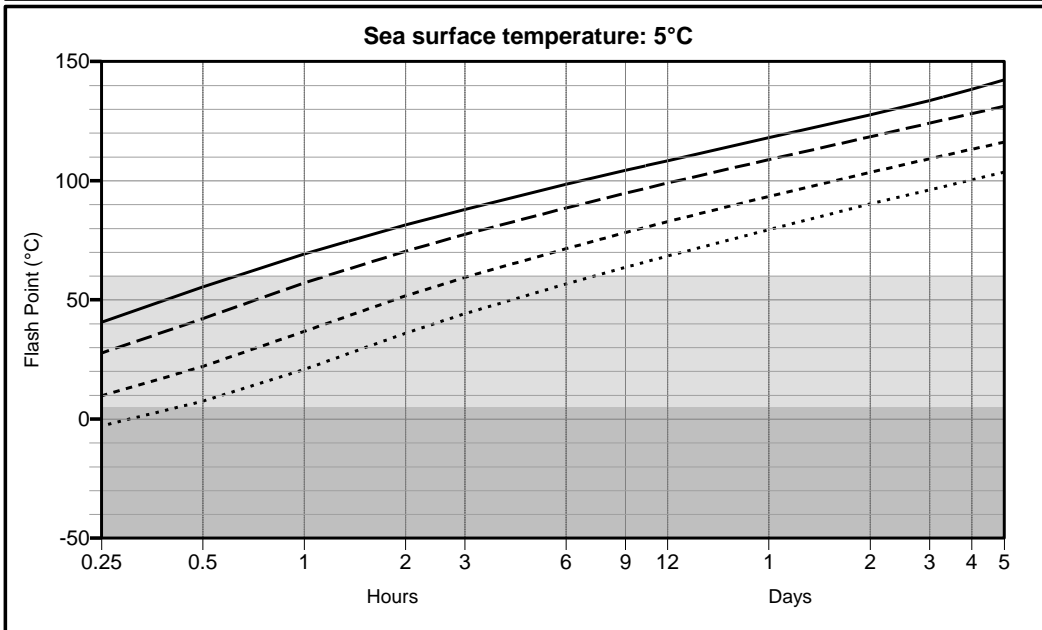Wind Speed (m/s): 2

No fire hazard
Fire hazard in tankage (<60 °C)
Fire hazard at sea surface (below sea temperature)
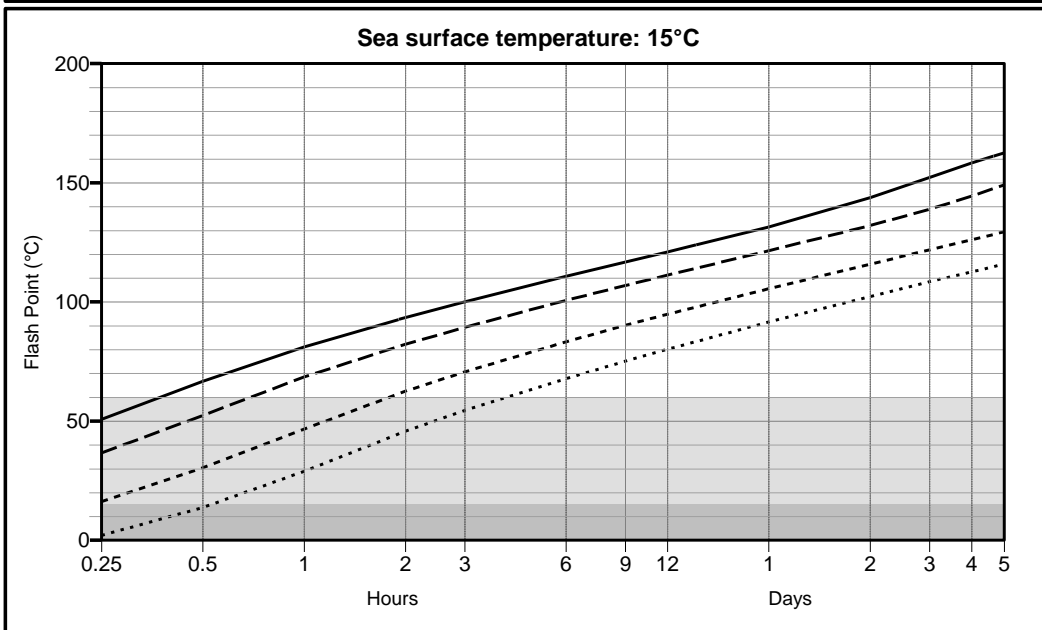
Figure 4-3   Flash point of Valhall 2021 predicted at sea temperatures of 5 and 15 °C.

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 23 of 65

Property: POUR POINT FOR WATER-FREE OIL	
Oil Type: VALHALL 2021	
Description:	OWModel© 13.0
Data Source: Sintef Ocean (2021), Weathering data used	

| Surface release | 2.0 |
| Amount/duration of oil spill : 20 metric tons 15.   )minute | Pred. date: Jul. 06, 2021 |

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

Figure 4-4   Pour point of Valhall 2021 predicted at sea temperatures of 5 and 15 °C.

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 24 of 65

Property: WATER CONTENT
Oil Type: VALHALL 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

SINTEF

OWModel© 13.0

Surface release
Amount/duration of oil spill : 20 metric tons 15.   minute

2.0
Pred. date: Jul. 06, 2021

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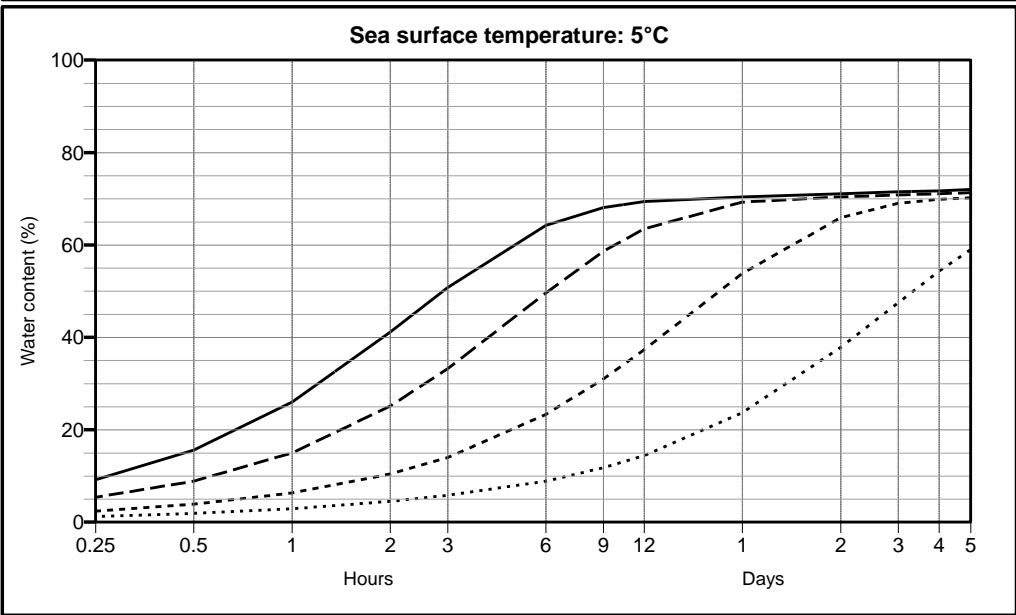······ Wind Speed (m/s): 2

Sea surface temperature: 5°C

Sea surface temperature: 15°C

Figure 4-5   Water content of Valhall 2021 predicted at sea temperatures of 5 and 15 °C, shear rate 10 s⁻¹.

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 25 of 65

Property: VISCOSITY OF EMULSION
Property: VISCOSITY OF EMULSION
Oil Type: VALHALL 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

SINTEF

OWModel© 13.0

Surface release
Amount/duration of oil spill : 20 metric tons 15.0   minute

2.0
Pred. date: Jul. 06, 2021

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

Chemically dispersible (<800 mPa•s)
Reduced chemical dispersibility
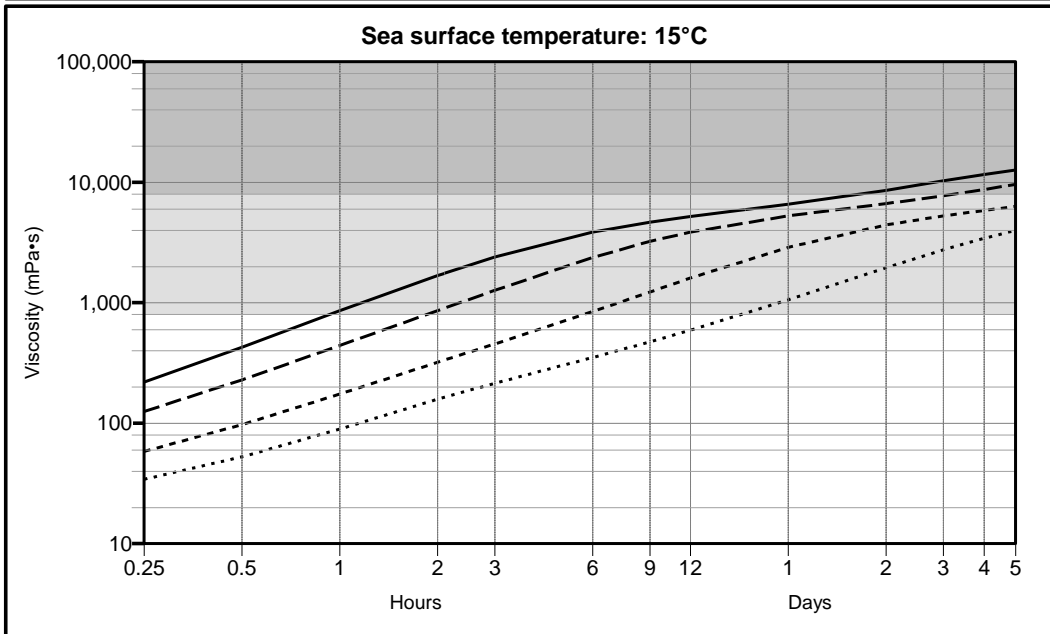Poorly / slowly chemically dispersible (>8,000 mPa•s)

Sea surface temperature: 5°C
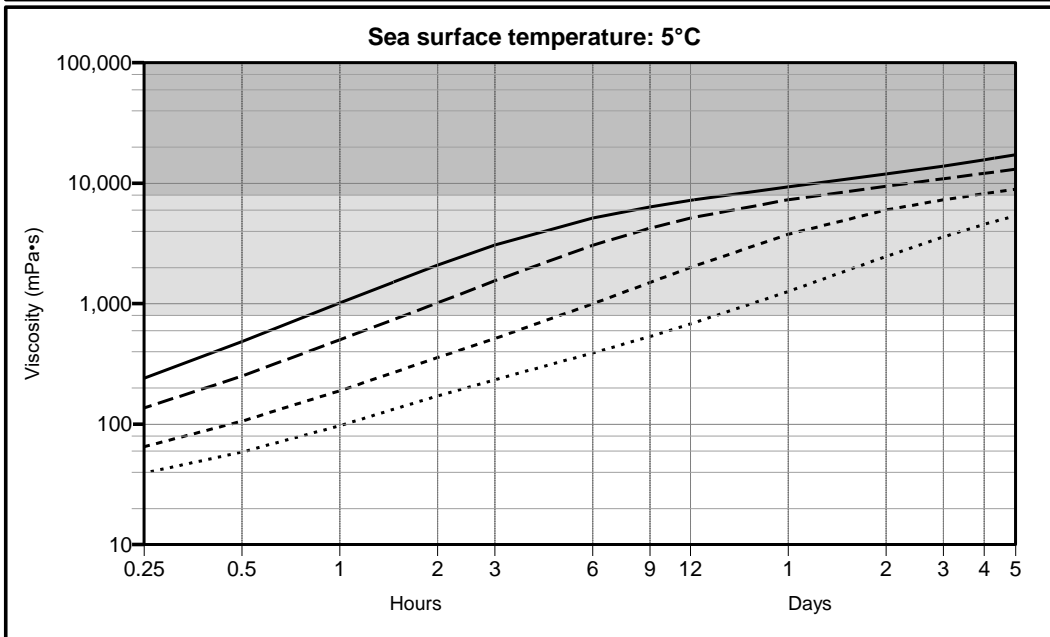
Sea surface temperature: 15°C

Figure 4-6   Viscosity of Valhall 2021 predicted at sea temperatures of 5 and 15 °C, shear rate 10 s⁻¹.

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 26 of 65

Property: MASS BALANCE Oil Type: VALHALL 2021 Description: Data Source: Sintef Ocean (2021), Weathering data used	SINTEF
	OWModel© 13.0
Surface release Release rate/duration: 1.33 metric tons/minute for 15 minute(s)	Pred. date: Jul. 06, 2021

Evaporated
Surface
Naturally dispersed   / Entrained oil

Figure 4-7   *Predicted mass balance of Valhall 2021predicted 5 °C, wind speeds of 2 and 5 m/s.*

Figure 4-8   Predicted mass balance of Valhall 2021 predicted 5 °C, wind speeds of 10 and 15 m/s.

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 28 of 65

Property: **MASS BALANCE**	**SINTEF**
Oil Type: **VALHALL 2021**	
Description:	
Data Source: **Sintef Ocean (2021), Weathering data used**	OWModel© 13.0

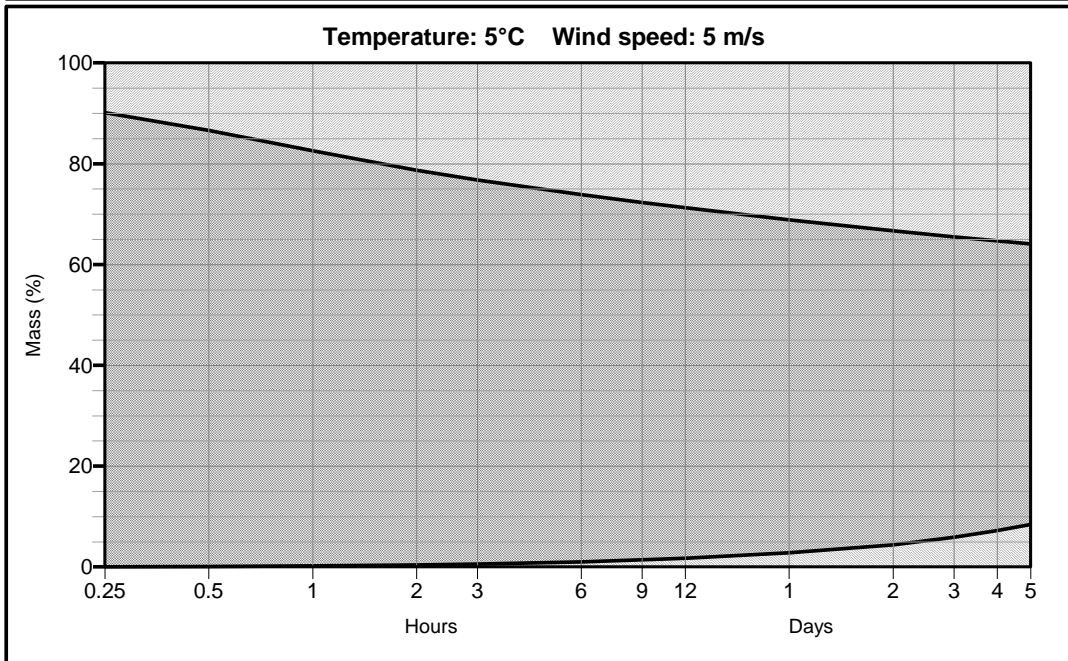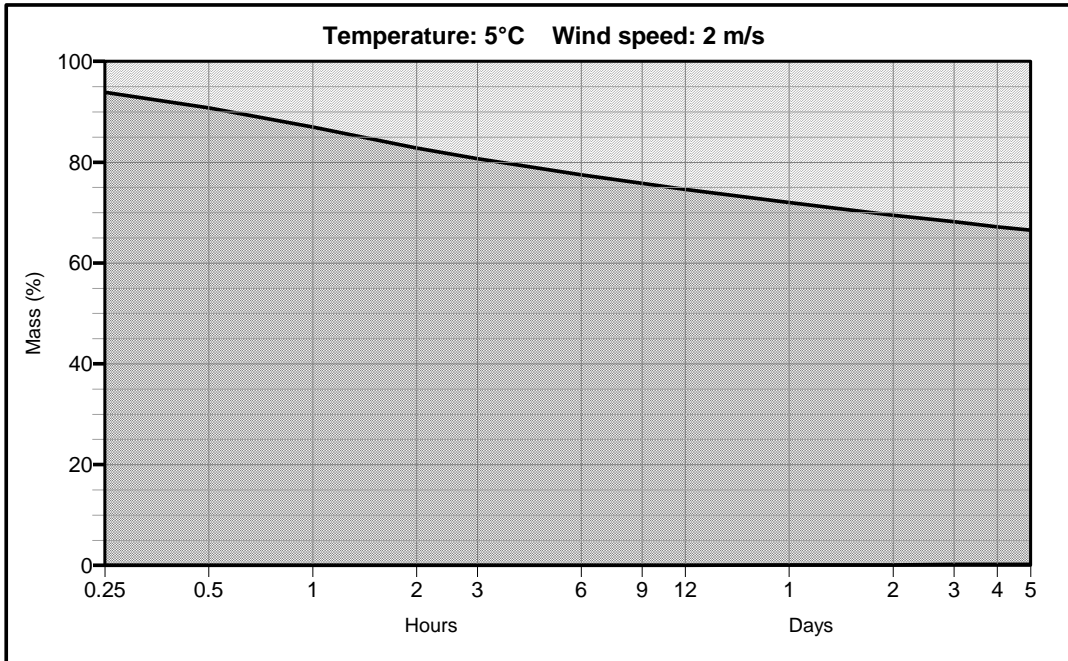| Surface release | |
| Release rate/duration: 1.33 metric tons/minute for 15 minute(s) | Pred. date: Jul. 06, 2021 |

Evaporated
Surface
Naturally dispersed / Entrained oil

Temperature: 15°C   Wind speed: 2 m/s

Temperature: 15°C   Wind speed: 5 m/s

Figure 4-9   Predicted mass balance of Valhall 2021 predicted 15 °C, wind speeds of 2 and 5 m/s.

Property: MASS BALANCE
Oil Type: VALHALL 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

SINTEF

OWModel© 13.0

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

Pred. date: Jul. 06, 2021
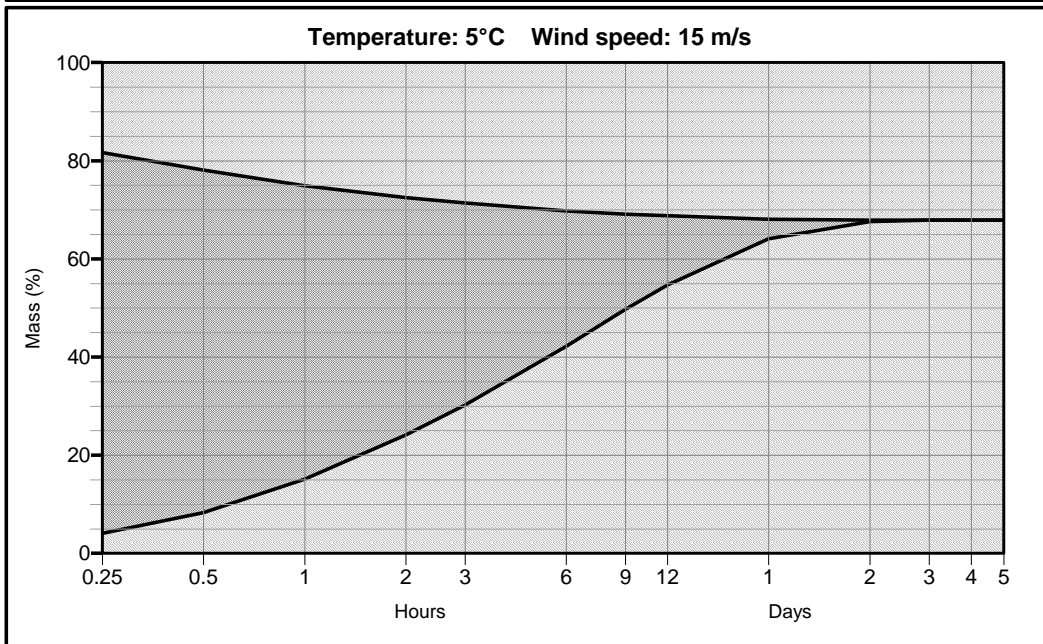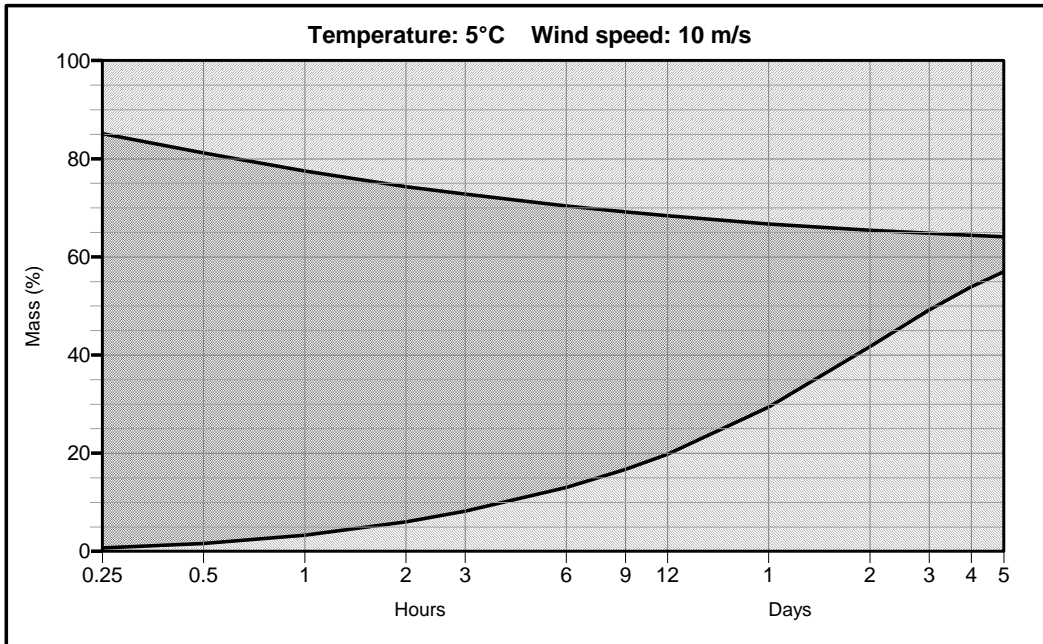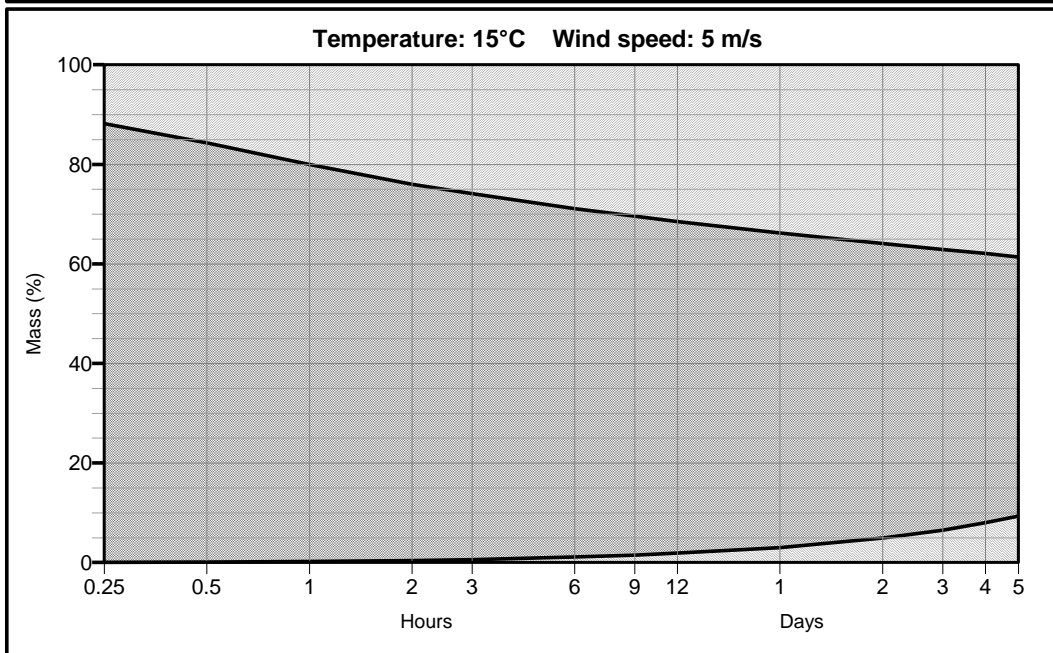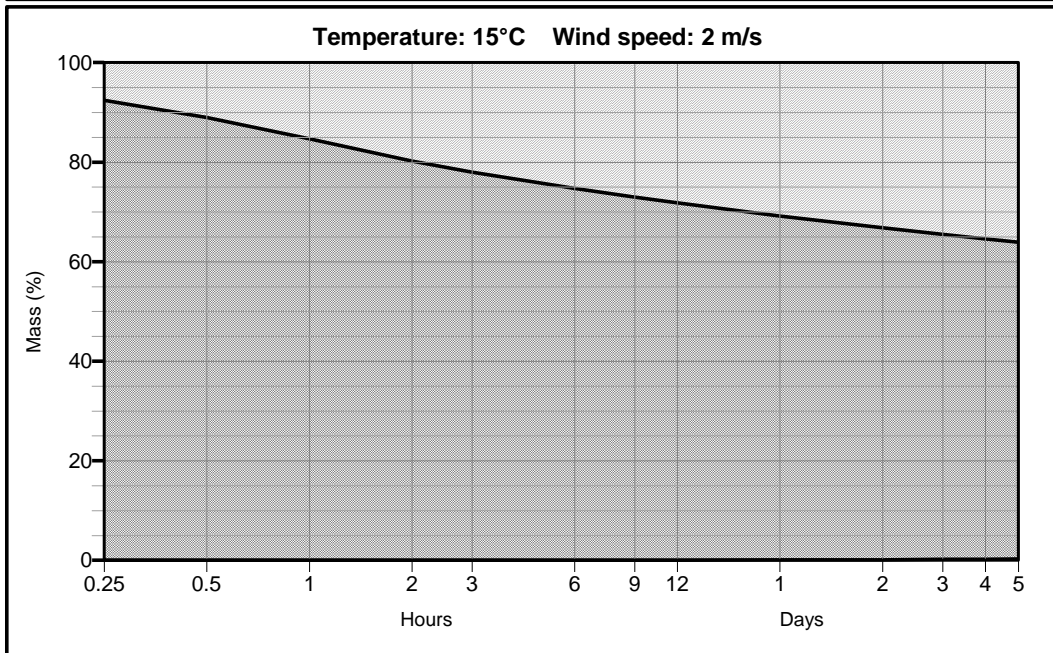
Evaporated
Surface
Naturally dispersed   / Entrained oil
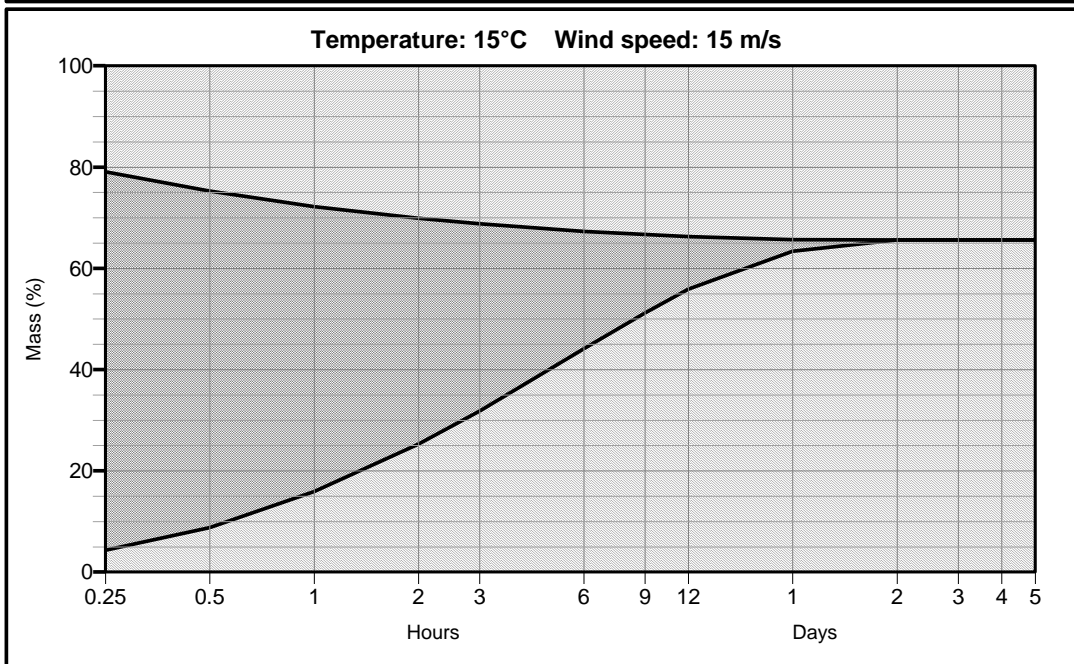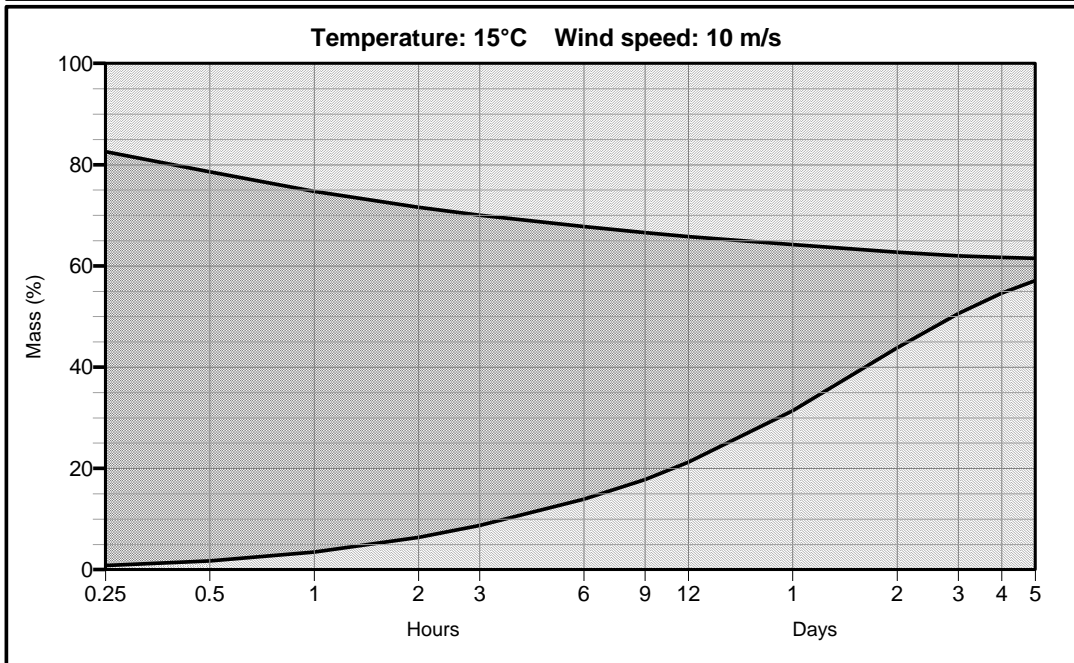
Figure 4-10   Predicted mass balance of Valhall 2021 predicted 15 °C, wind speeds of 10 and 15 m/s.

5 Comparison of OWM predictions

Weathering predictions from surface release of Valhall 2021 were compared with predictions of Valhall 2000. The predictions are based on sea temperature of 15 °C and wind speed of 10 m/s.

5.1 Evaporative loss

Evaporation is one of the natural process that helps removing spilled oil from the sea surface. Valhall 2021 has about 2-5 % higher predicted evaporative loss compared with Valhall 2000 (Figure 5-1). The predicted evaporative loss is within expected range for medium paraffinic crude oils.
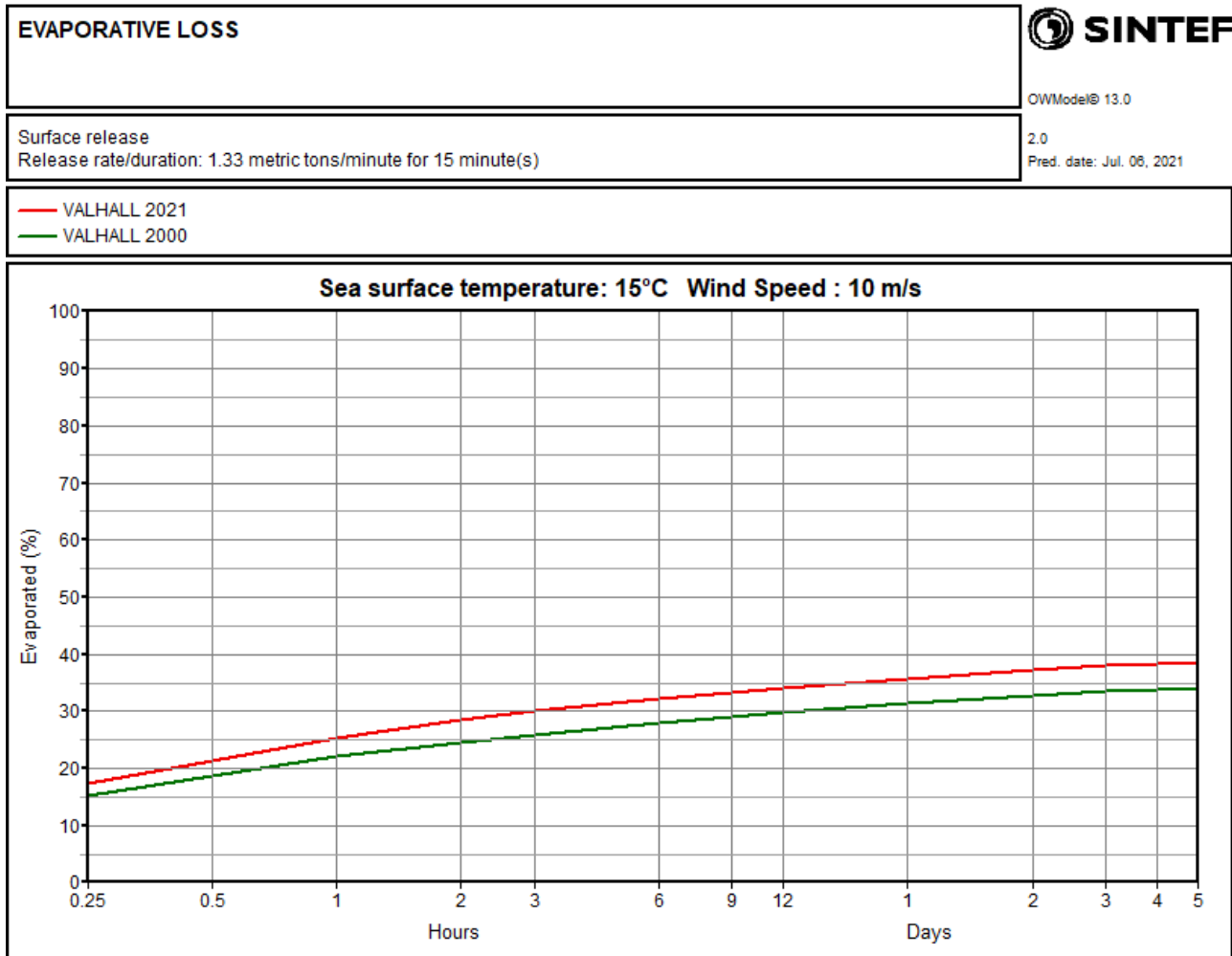
Figure 5-1   Predicted evaporative loss at 15 °C and 10 m/s for Valhall 2021 and Valhall 2000.

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 31 of 65

5.2 Pour point

The pour point Valhall 2021 and Valhall 2000 are given in Figure 5-2. Valhall 2021 has higher pour points by time than Valhall 2000.
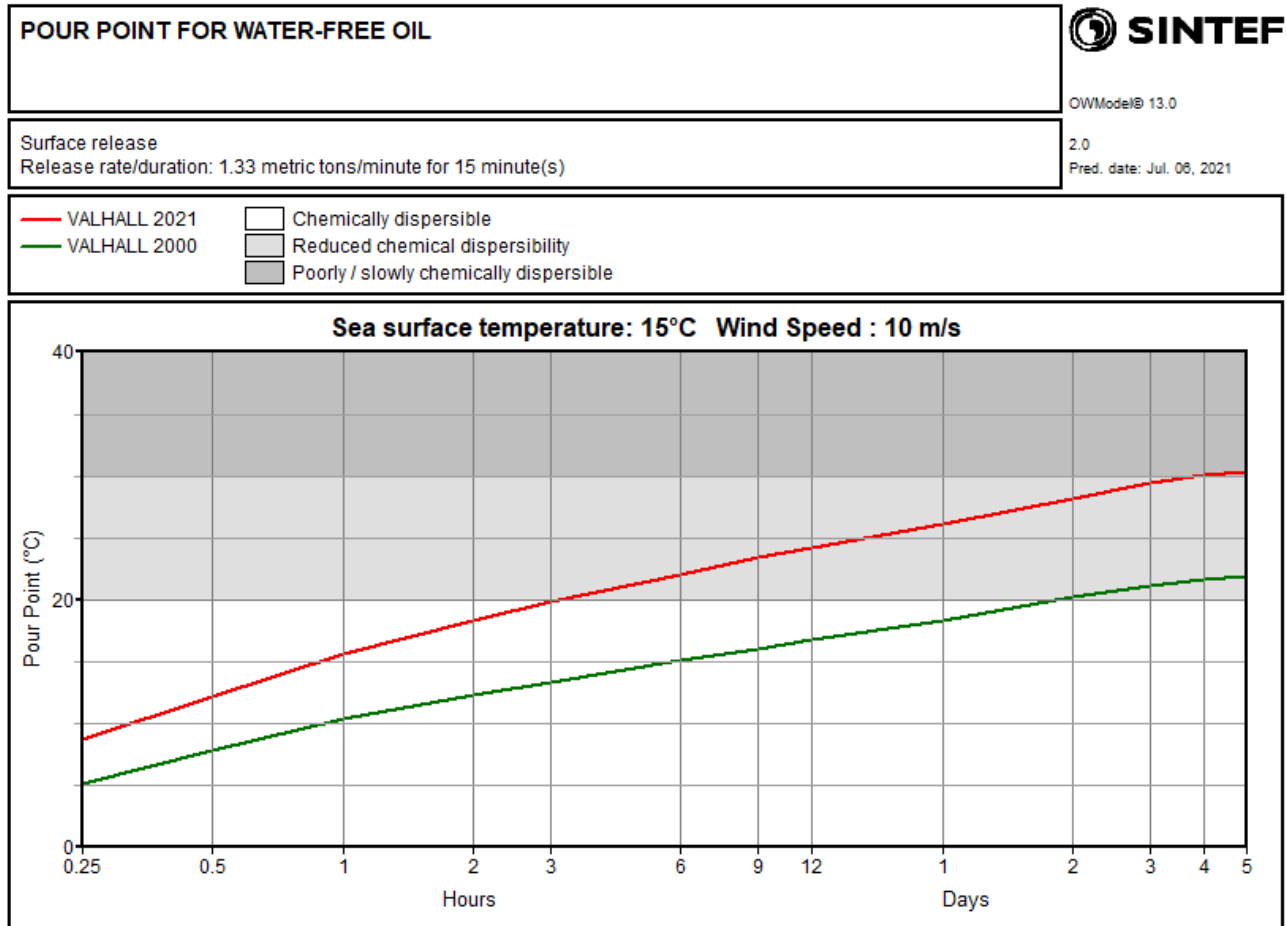
Figure 5-2   Predicted pour point at 15 °C and 5 m/s for Valhall 2021 and Valhall 2000.

5.3 Water uptake

The water uptakes of the Valhall 2021 and Valhall 2000 are shown in Figure 5-3. Valhall 2021 has a slower rate of water uptake, and reach a slightly lower water uptake 75 vol% than Valhall 2000 (80 vol. %).
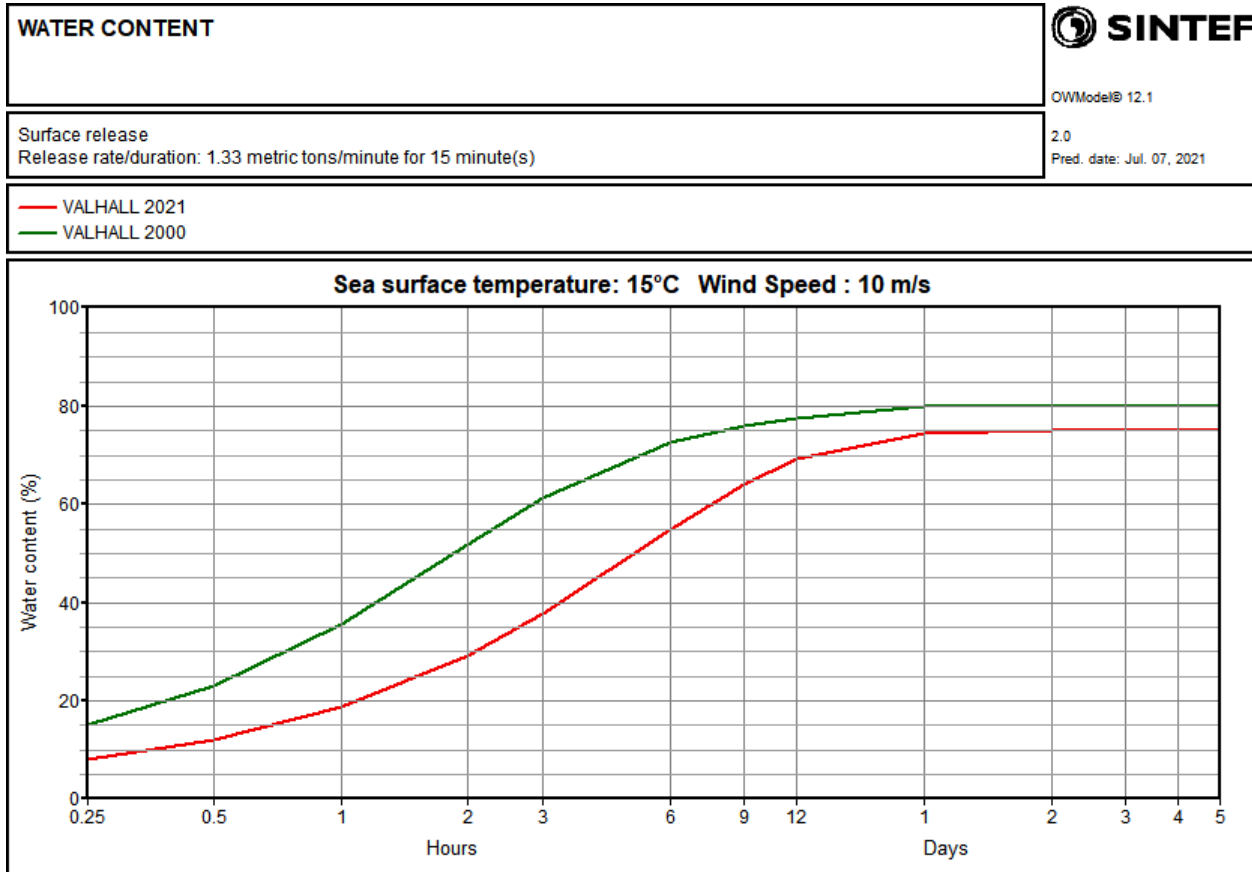
Figure 5-3   Predicted water uptake at 15 °C and 5 m/s for Valhall 2021 and Valhall 2000.

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 33 of 65

5.4 Viscosity

Figure 5-4 shows the predicted (emulsion) viscosities of Valhall 2021 and Valhall 2000. Valhall 2021 has lower initial viscosity than Valhall 2000 but increases to reach higher viscosities after 4-5 hours. Valhall 2021 may reach viscosity > 8000 mPa.s whilst Valhall about 6000 mPa.s for this scenario. The viscosities of Valhall oils are within the expected range for medium paraffinic crude oils.

VISCOSITY OF EMULSION	SINTEF
	OWModel® 13.0
Surface release Release rate/duration: 1.33 metric tons/minute for 15 minute(s)	2.0 Pred. date: Jul. 06, 2021

— VALHALL 2021
— VALHALL 2000

Sea surface temperature: 15°C   Wind Speed : 10 m/s
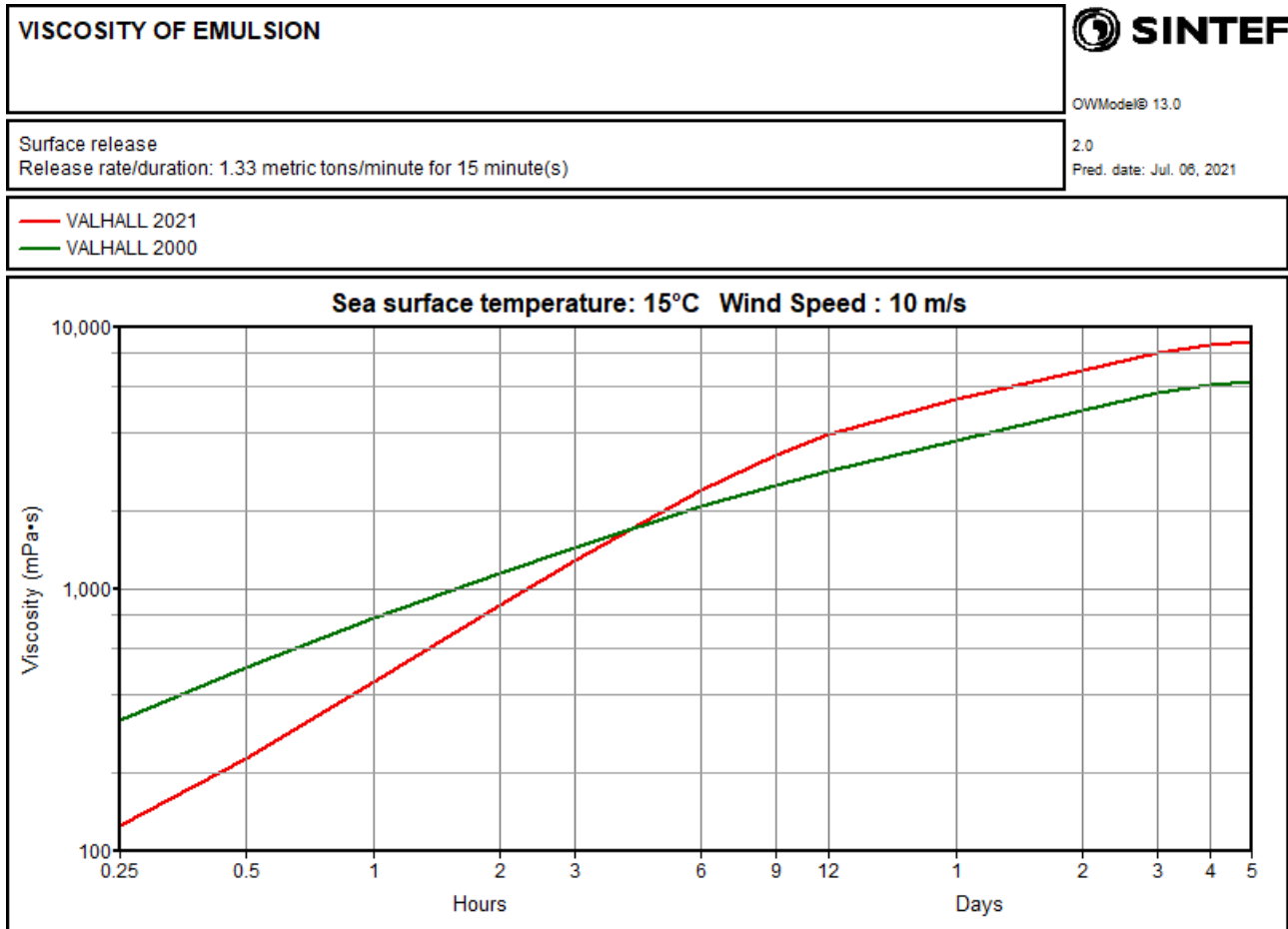
Figure 5-4   Predicted (emulsion) viscosity at 15 °C and 5 m/s for Valhall 2021 and Valhall 2000.

5.5 Surface oil and emulsion

The predicted surface oil is based on the evaporative loss, natural dispersion/entrainment, whilst surface emulsion also includes emulsification that may increase the oil volume subsequently. Figure 5- (above) shows the predicted mass balance of remaining surface oil as a function of weathering for Valhall 2021 and Valhall 2000, while Figure 5-5 (below) shows the remaining surface emulsion of both oils. Both oils are persistent on the sea surface with predicted lifetime >5 days for this scenario, however Valhall 2000 may increase the oil volume about 1.5 time than Valhall 2021.

Figure 5-5 *Above: Predicted remaining surface oil at 15 °C and 10 m/s for Valhall 2021 and Valhall 2000. Below: Predicted remaining surface emulsion at 15 °C and 10 m/s for Valhall 2021 and Valhall 2000.*

6 Weathering properties and response of Valhall

The relative content of heavy oil components within a spilled oil increases due to evaporation , and the physical and chemical properties of the oil will change over time. Knowledge about how the oils properties change during weathering is therefore important in the management of oil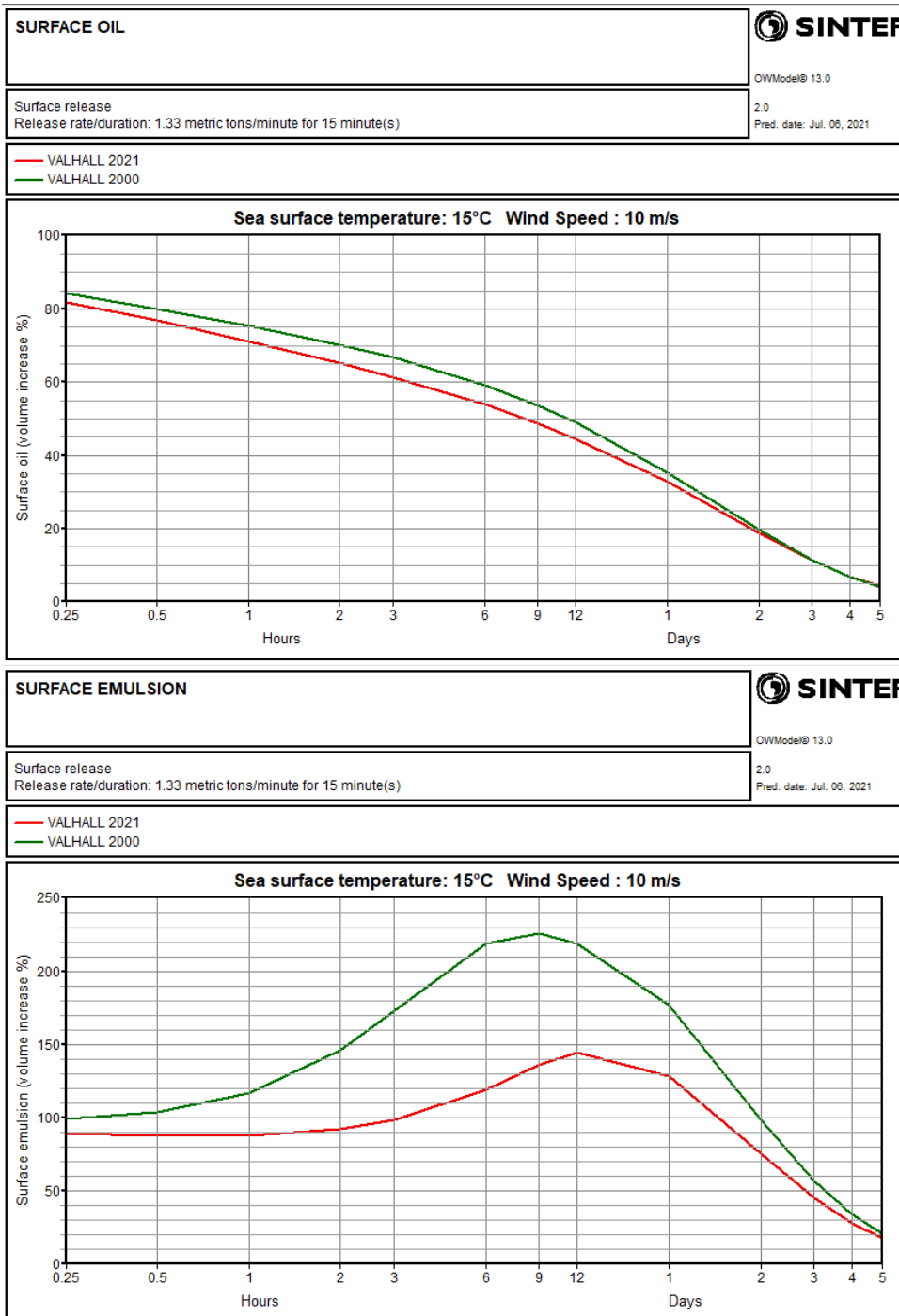 spill response. Currently, mechanical recovery and the use of oil spill dispersants are the main oil spill response options at sea in the Norwegian sector, today. The potential of using water-flushing (artificial energy) to disperse thin oil films and low viscous oils is also discussed in this report.

6.1 Oil properties

The specific physico-chemical parameters of Valhall 2021 are input to SINTEF OWM. The physico-chemical analysis of the fresh and topped residues show that Valhall 2021 is a paraffinic crude oil with a density of 0.842 g/mL with a low content of asphaltenes (0.04 wt. %) and a medium wax content of 4.99 wt. %. Valhall has a moderate evaporate loss of 42 vol. % of the 250°C+ residue. The fresh oil has a viscosity of 21 mPa.s at shear rate $10s^{-1}$ (13 °C) and increases by evaporation to 2859 mPa.s ($10s^{-1}$) for the waterfree 250°C+ residue. The fresh oil has a low pour point of -6 °C, that increases significantly to +21 and to +24 °C upon evaporation (200 to 250 °C+). Moreover, Valhall forms stable water-in-oil emulsions with moderate to high viscosities that partly or totally breaks with application of emulsion breaker (Aerosol OT-SE surfactant).

6.2 Flash point – Fire/explosion hazard

Flash point refers to the lowest temperature at which a fuel or oil can vaporize to form an ignitable mixture in the air. In case of an oil spill on the sea surface, the (heated) oil rapidly will be cooled to the ambient seawater temperature within a short period of time. The potential for fire/explosion hazard will be at its greatest if the flash point of the spilled oil is <u>below</u> the seawater temperature.

The flash points for Valhall are expected to surpass the sea temperature within a few minutes at 5 and 15 °C, at wind speeds of 10 and 15 m/s predicted with the standardized surface release as shown in Figure 4-3 and Figure 6-1. In calmer weather conditions (2 and 5 m/s), care should be taken during the first 0.5 hour and use of explosimeter is recommended. Less than 1-hour delay time can be predicted related to fire/explosion hazard related to the flash point of the drifting oil itself.

However, the release rate may influence on the rate of evaporation, and for considerably larger (batch) release rates e.g.100 times higher (8000 m³/h), the rate of evaporative loss is thus reduced particularly for the first hours after the release. Such high batch release can be e.g. an incident scenario in connection to loading on vessels. For Valhall 2021, the time when the flash point has surpassed the sea temperature has now increased to 1-2 hours at 2 and 5 m/wind speed (Figure 6-2).

Moreover, some vessels/storage tanks engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C, e.g. towing vessels, smaller cargo, or other vessels available in the emergency. This means that fuels or oils with the flash point less than 60 °C, are for those type of vessels not permitted as cargo. However, this limit is not considered as relevant for oil recovery vessels with A-class certification for transport of liquids (Class I/II, flashpoints < 60 °C), according to NFPA classification of Flammable and Combustible Liquids (http://www.thetankshop.ca). Refers to the flash point predictions in Figure 4-3 and Figure 6-1.

As a general recommendation after an acute oil spill involving free gas (e.g. from a oil/gas blowout), a "safety" zone typically 1-2 km from the source should be established early on and downwind from the spill site before response actions are initiated in open seawaters. Prior to the initiation of spill response operations, an evaluation of fire/explosion hazard must always be conducted at the site. Explosimeters should be utilized continuously, and one should be aware of the possibility for varying release rates if "free" gas is involved.

Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: VALHALL 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

OWModel© 13.0

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

2.0
Pred. date: Jul. 06, 2021

- 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

Sea surface temperature: 15°C

Figure 6-1   *Predicted flash points for Valhall 2021 at 15 °C (80 m³/h)*

Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: VALHALL 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

OWModel© 13.0

Surface release
Amount/duration of oil spill : 2,000 metric tons 15.000000minute

2.0
Pred. date: Jul. 06, 2021

- 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

Sea surface temperature: 15°C

Figure 6-2   *Predicted flash points for Valhall 2021 at 15 °C (8000 m³/h)*

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 37 of 65

6.3 Solidification

Pour point depends on the oil's wax content and the amounts of light components that can keep the wax components dissolved in the oil phase. In addition, contents of asphaltenes may prevent or reduce precipitation and lattice formation and hence lowers the pour point. High pour points may prevent the dispersant to soak into the oil slick and influence the dispersant effectiveness and may also reduce the potential for flowability towards weir skimmers. In cases when high viscosities are not a limiting factor, high pour points may cause solidification (elastic properties) of semi-solid patches when oil is spilled on the sea surface. High pour point may therefore imply solidification on the sea surface immediately after the release, and this is pronounced when the pour point is typically 5-15 °C above sea temperature and in cold temperatures.

If the oil is mixed with the seawater by waves, the wax lattice in the oil will likely be weakened and may break up. This is accordance with the emulsifying properties of oils from the laboratory experiments. Valhall 2021 has high pour points of its residues, and a remaining residue at sea may therefore have a potential to solidify, particularly in winter condition as shown for the pour point prediction in Figure 4-4.

6.4 Submerged oil 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). Submerged oil (natural dispersion) and evaporation are the main weathering processes that remove an oil spill from the sea surface. The remaining surface oil after a release depends on the wind speeds and typically oils are more persistent on the sea surface with lower wind.

Figure 6-3 shows the predicted remaining surface oil over time for different wind speeds and temperatures for Valhall 2021. Only minor difference in lifetime between 5 and 15 °C for this crude oil. At high wind speeds of 15 m/s, no oil is predicted to remain on the sea surface after 2 days of weathering.
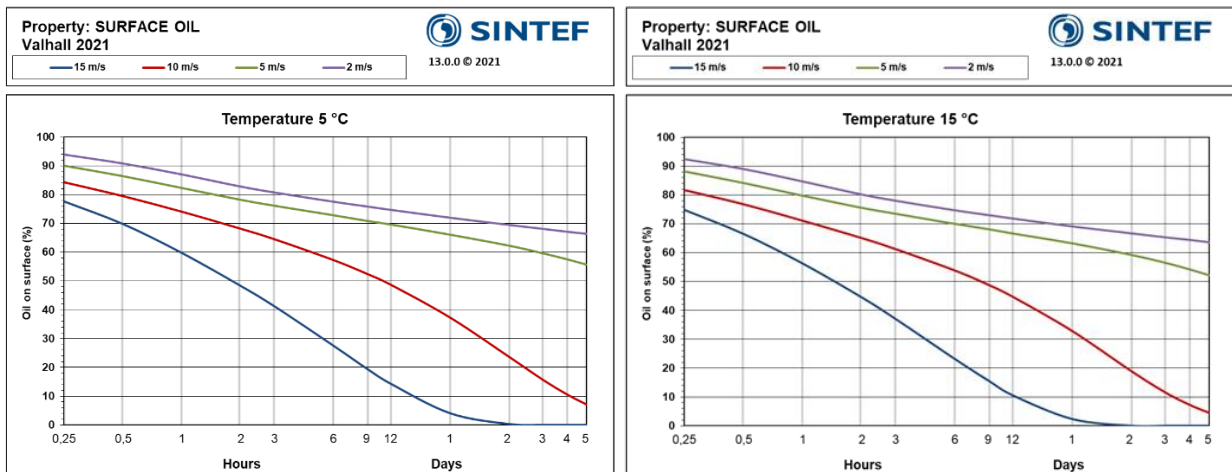

Figure 6-3   Predicted remaining surface oil for Valhall 2021 at 5 and 15 °C.

6.5 Film thickness from surface release

In general, mechanical recovery requires normal minimum film thicknesses >0.1-0.2 mm. Film thicknesses > 0.05-0.1 mm are considered for application of oil spill dispersants. Lower film thicknesses are likely to disperse naturally under breaking waves conditions and can be enhanced in non-breaking waves by mechanical dispersion (chapter 6.8). Figure 6-4 shows the predicted film thickness of Valhall for a surface release. The increase in film thickness after 1.2 hours is due to emulsification. Other factors than film thickness should also be considered when evaluate response options, as described in the next chapters.
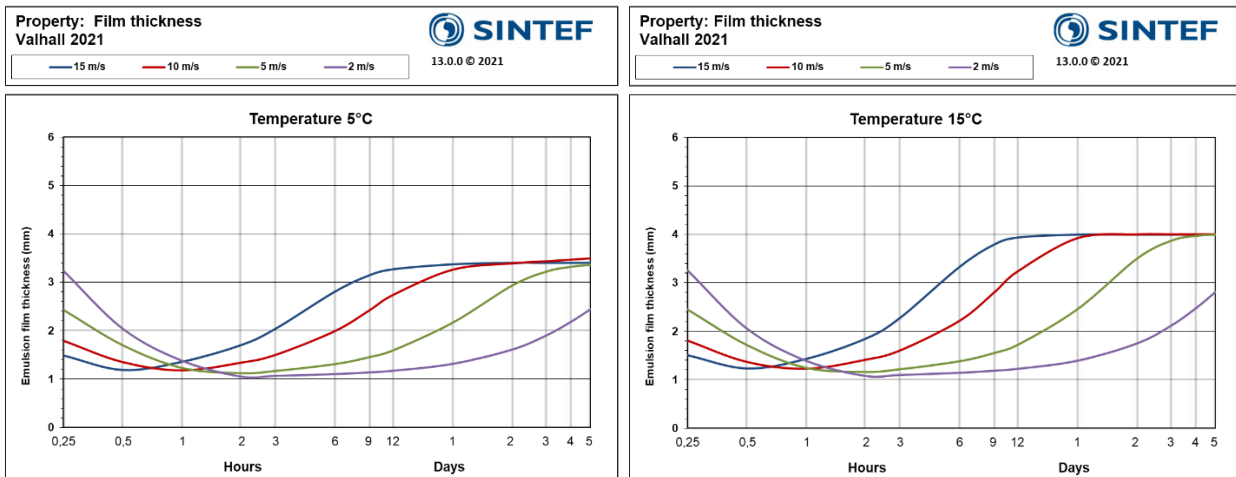

Figure 6-4   *Predicted film thickness of Valhall 2021 from a surface (batch) release at 5 and 15 °C.*

6.6 Mechanical recovery by boom and skimmer

Experiences from Norwegian field trials with booms have demonstrated that the effectiveness of various mechanical clean-up operations may be reduced due to the high degree of leakage of the confined oil or emulsion from the oil spill boom. Boom leakage is particularly pronounced if the viscosity of the oil or the w/o-emulsion is lower than 1000 mPa.s (Nordvik et al., 1992). The lower viscosity limit for an optimal mechanical clean-up operation has therefore been estimated to 1000 mPa.s. However, other factors like the operational speed of recovery vessel and current weather conditions will also influence on the risk of boom leakage.

Weir skimmers may reduce recovery rates (m³/h) when skimming oils with viscosities in the range 15-20 000 mPa.s (Leirvik et al., 2001). NOFO is operating with viscosity limits for skimmer efficiency as followed: primary use of weir skimmers (< 20 000 mPa.s), combination of weir and high-visc. skimmers (20-50 000 mPa.s), and primary high visc. skimmer (> 50 000 mPa.s).

The emulsion viscosities of Valhall are shown in Figure 6-5 at 5 and 5 and 15 °C. For example, the emulsion viscosity exceeds 1000 mPa.s after 2 hours at 10 m/s wind speed but may be stretched to about 24 hours in calm wind conditions (2 m/s), at both temperatures. Overall, Valhall 2021 has a wide window of opportunity for traditional weir-skimmer head due to viscosities < 20 000 mPa.s after 5 days of weathering at summer and winter conditions.
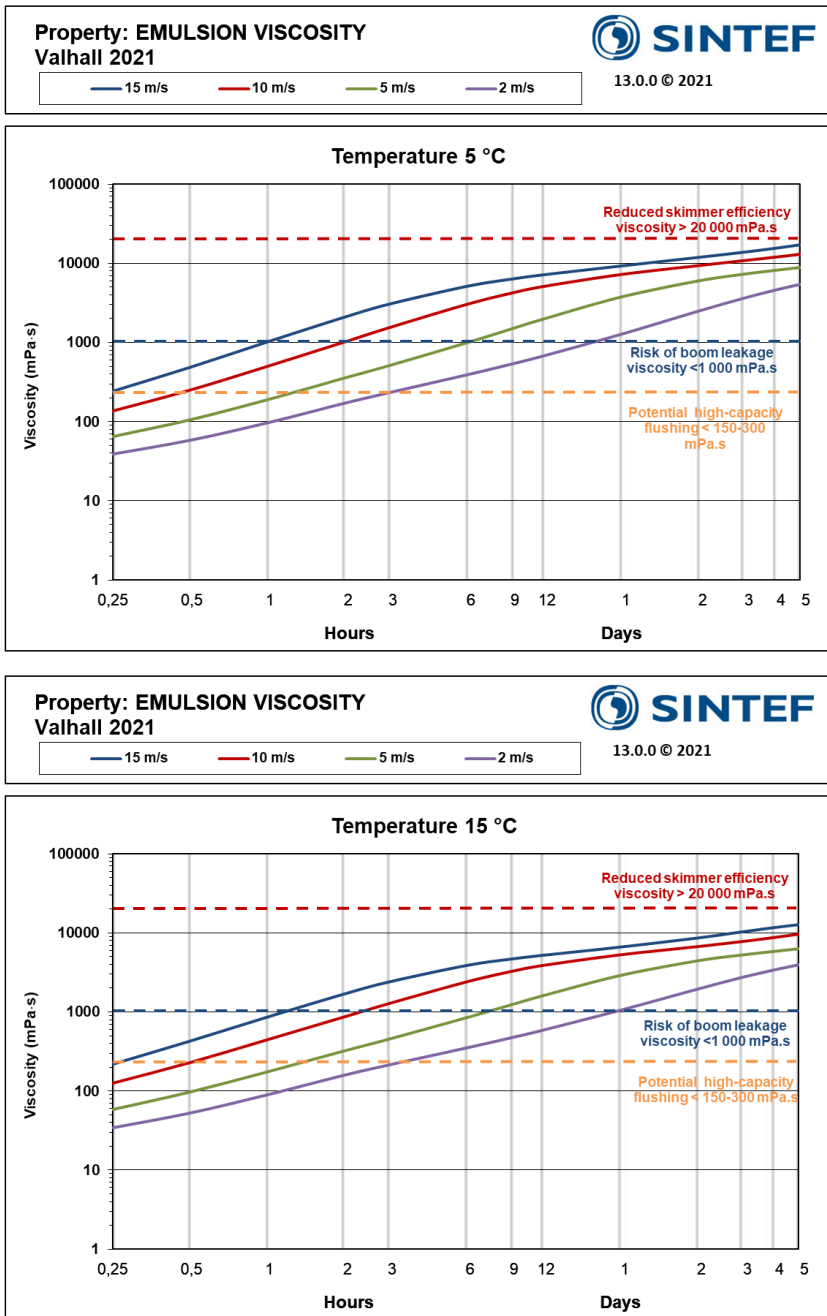
Figure 6-5   *Expected time window for effective use of booms and skimmers and high-capacity water flushing (see chapter 6.8) as a function of emulsion viscosity of Valhall at 5 and 15 ºC.*

6.7 Mechanical dispersion by high-capacity water flushing

In general, mechanical dispersion by high-capacity water flushing without using dispersants could have a potential for oil spill with thin (initial) film thickness up to 0.2-0.3 mm and viscosities <150-300 mPa.s. In such cases, water flushing from high-capacity water flush boom and/or firefighting (Fi-Fi) systems could possibly break up the oil/residue into smaller droplets and enhance the dispersion into the water column. Moreover, water flushing could also be used in combination with application of dispersant in calm weather condition to enhance dispersant efficiency with use of artificial energy some minutes after the dispersant treatment. This technology was tested in a full-scale trial (NOFO Oil-on-Water trial) in 2016 and described by Daling et al., 2017 and Sørheim et al., 2017.

However, for Valhall crude oil mechanical dispersion by water flushing is not considered as a strategy in oil spill response due to the formation of high emulsion film thicknesses (Figure 6-4) by emulsification, even the oil has low emulsion viscosities in the very early stage after an oil spill, as shown in Figure 6-5. The rapidly emulsification of Valhall 2021 is the limiting factor for this strategy. However, use of water-flushing can be a supplementary method in areas with thin oil films, e.g. metallic /rainbow appearance.

6.8 Chemical dispersion

Valhall 2021 has a potential for use of oil spill dispersant from aircraft and /or vessel but seems to require energy to obtain efficient dispersion.

The viscosity limit for effective dispersant use was estimated to 800 mPa.s in the laboratory (low energy IFP-test). The viscosity limit for when the emulsified oil is not considered to be dispersible by use of the high energy MNS-test was estimated to 8000 mPa.s. Valhall 2021 has thus reduced dispersibility for viscosities between 800-8000 mPa.s. In cases were the oil (emulsion) is expected to be reduced dispersible, additional energy or use of a higher dispersant dosage and/or repeated dispersant application is recommended to possible enhance the dispersant efficiency. Providing additional energy through use of Fi-Fi systems, thrusters or MOB boats after dispersant application may increase the dispersion rate in calm weather condition.

The window of opportunity for use of dispersant Dasic Slickgone NS is presented in Figure 6-6. The oil-emulsion is e.g. predicted to be (reduced) dispersible up to 2-4 days at summer conditions, and 1-2 days in winter conditions with wind speeds 10-15 m/s, and longer time-window in calmer wind speeds.

High pour points could reduce the dispersant effectiveness, where the dispersant droplets have a reduced ability to diffuse into the oil and may appear as droplets on the surface of the solidified wax and be washed of by wave activity. In certain weather conditions, low emulsification rate may enhance formation of solidified lumps, particularly at 5 °C. In a spill situation, the use of a simplified dispersibility testing kit is therefore recommended to assess the potential for chemical dispersion.

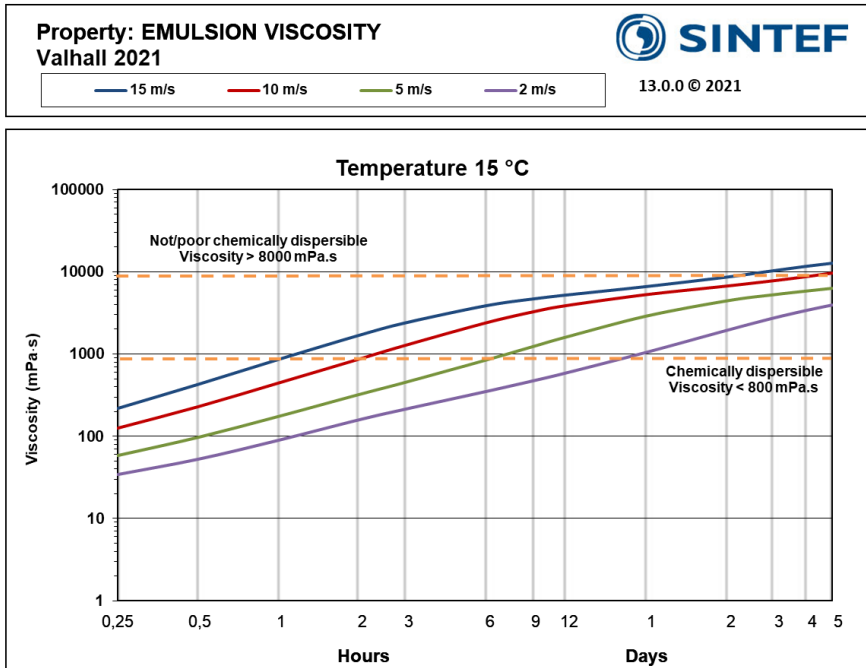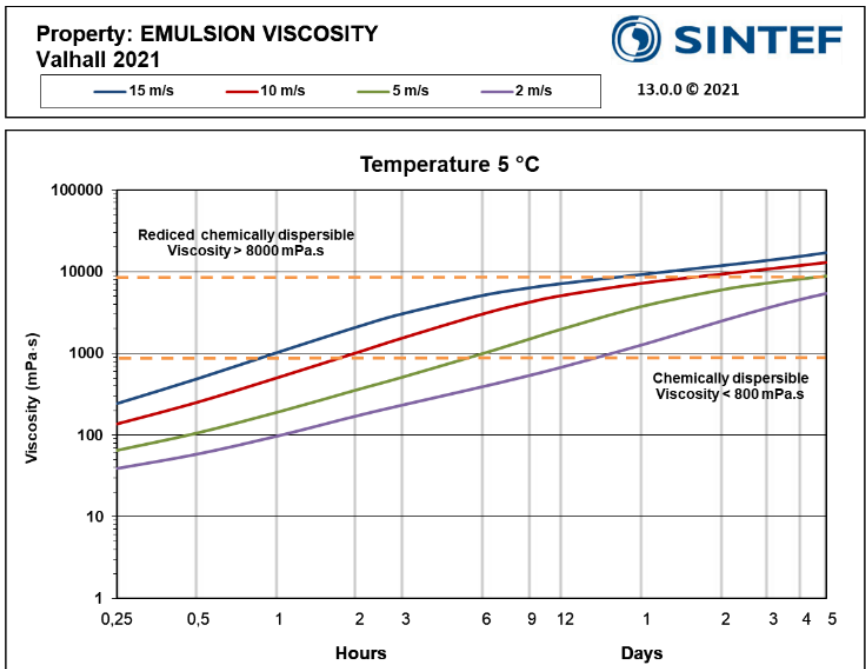*Figure 6-6   Expected time window for effective use of dispersants as a function of emulsion viscosity of Valhall at 5 and 15 ℃.*

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 42 of 65

7 Summary of response options

Valhall is a medium density paraffinic crude oil that forms stable water-in-oil (w/o) emulsion in scenarios where the (initial) film thickness > 0.1 mm, typically from surface releases. Certain scenarios from underwater releases depending on the water depth, gas to oil ratio (GOR), release rate etc. may also produce initial film thicknesses > 0.1 mm of surfaced oil, otherwise thinner initial oil films can be expected, however this has not been evaluated for Valhall. The high pour point of surface residue may cause solidification at sea, particularly in low temperature. High pour points typically prevent or reduce the dispersant efficiency.

Mechanical recovery:
- Valhall has a wide window of opportunity for mechanical recovery with use of skimmers, such as the Transrec equipped with traditional weir-skimmer head for emulsion viscosities < 20 000 mPa.s
- Boom leakage and reduced recovery is expected for viscosities < 1000 mPa.s

Use of chemical dispersants:
- Valhall is found to be dispersible with use of Dasic Slickgone NS for viscosities < 800 mPa.s (DOR 1:25), and not (poorly) dispersible for viscosities > 8000 mPa.s.
- In the field, additional energy or higher DOR and/or repeated dispersant application may increase the dispersant effectiveness when viscosities are between 800 mPa.s and 8000 mPa.s.

High-capacity water flushing (mechanical dispersion):
- The emulsification is the limiting factor for this strategy.
- The predicted film thickness is > 0.2-0.3 mm which is the estimated upper limit for effective use of water flushing.
- Water flushing is therefore not considered as a main response option for emulsions of Valhall. Mechanical dispersion be used a supplementary /secondary method on areas of thin oil films e.g. metallic/rainbow appearance in calm weather conditions.

Monitoring and remote sensing:
- Monitoring and remote sensing should be used a support in a response operations for Valhall.

Mechanical recovery should still be the main response strategy for Valhall followed by dispersant use. Use of dispersants requires breaking waves /artificial energy in very calm sea conditions for being efficient.

8 References

Brakstad, O.G., and Faksness, L.-G., (2000). Biodegradation of water-accommodated fractions and dispersed oil in the seawater column. Proceedings for the International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Stavanger, 26-28 June 2000

Brakstad, O-G and A.G.G Lødeng 2005. Microbial diversity during micro biodegradation of crude oil in seawater from the North Sea. Microbial Ecology 49:94-104

Bridié, A.L., Wanders, T. H., Zegweld, W. V. and den Heijde, H. B., 1980. Formation, Prevention and Breaking of Seawater in Crude Oil Emulsions, Chocolate Mousse. Marine Poll. Bull., vol. 11, pp. 343-348. Commission Internationale De L'Eclairage (CIE), No. 85, ISBN No. 3 900 734 22 4, 1989.

Daling, P. S., Brandvik, P. J., Mackay, D. and Johansen, Ø. (1990): "Characterisation of crude oils for environmental purposes." Oil & Chemical Pollution 7, 1990, pp. 199-224.

Daling, P.S., Lewis, A., Sørheim, K.R., Gjesteland, I. 2017. Full-scale field testing of thin oil films from releases of light crude oil at sea. NOFO Oil-on-Water field trial in 2016. SINTEF report 2017:00030 Unrestricted. ISBN:978-82-21-40670-8.

Hokstad, J. N., Daling, P. S., Lewis, A. and Strøm-Kristiansen, T. 1993: "Methodology for testing water-in-oil emulsions and demulsifiers. Description of laboratory procedures." Proceedings Workshop on Formation and Breaking of W/O Emulsions. MSRC, Alberta June 14-15, 24 p.

Johansen, Ø. 1991. "Numerical modelling of physical properties of weathered North Sea crude oils." DIWO-report no. 15. IKU-report 02.0786.00/15/91. Open.

Leirvik, F., Moldestad, M. and Johansen, Ø., 2001. Kartlegging av voksrike råoljers tilflytsevne til skimmere

McAuliffe, C.D. (1987). Organism exposure to volatile/soluble hydrocarbons from crude oil spills - a field and laboratory comparison. In: Proc. 1987 Oil Spill Conference. Washington, D.C., American Petroleum Institute. pp. 555-566.

Mackay, D. and Zagorski, W. 1982. "Studies of W/o Emulsions". Report EE-34: Environment Canada, Ottawa, Ontario.

Mackay, D. and Szeto, F. 1980. "Effectiveness of oil spill dispersants - development of a laboratory method and results for selected commercial products." Institute of Environmental Studies, University of Toronto, Publ. no. EE-16.

McDonagh, M., Hokstad, J. N. and Nordvik, A. B. 1995. "Standard procedure for viscosity measurement of water-in-oil emulsions". Marine Spill Response Corporation, Washington, D.C. MRSC Technical Report Series 95-030, 36 p.

Moldestad, M.Ø., Leirvik, F., Faksness, L-G., Singsaas, I., Ditlevsen, M.K., Melbye, A. 2001. Ekofiskoljene, Gyda og Valhall. Egenskaper og forvitring på sjøen, karakterisering av vannløselige komponenter relatert til beredskap. Rapport: STF66 F01090. ISBN:82-14-02288-6.

Nordvik, A. B., Daling, P. and Engelhardt, F. R. 1992. "Problems in the interpretation of spill response technology studies." In: Proceedings of the 15th AMOP Technical Seminar, June 10-12, Edmonton, Alberta, Canada, pp. 211-217.

Perry JJ (1984). Microbial metabolism of cyclic alkanes: Atlas RM (Ed) Petroleum Microbiology Macmillan Publ Co New York pp 61-98

Ramstad S., Sørheim K.R., Daling, P.S. 2017. Thin Oil Films – Properties and behaviour at sea. Laboratory studies and oil weathering predictions. SINTEF report OC2017 A-207. ISBN: 978-82-7174-321-3

Reed M., and C. Turner, 1991: Field Tests of Satellite tracked buoys to simulate oil drift. In Proceeding of the IOSC, SanDiego, CA. US., pp. 619 – 628

Reed, M., Turner, C. and Odulo, A. 1994. "The role of wind and emulsification in modelling oil spill and surface drifter trajectories." Spill Science and Technology, Pergamon Press (2): .143-157.

Singsaas, I., Daling, P.S., Moldestad M. Ø and Jensen, H. 2000.Samle rapport: Effektivitet av Foxtail skimmer på IF-30 bunkersolje og forvitret Ula, Balder, Jotun og Troll råoljer. SINTEF report. STF66 A00082

Stiver, W. and Mackay. D. 1984. "Evaporation rate of spills of hydrocarbons and petroleum mixtures." Environ, Sci. Technol., vol. 18 (11), pp. 834-840.

Singsaas, I., Sørheim, K. R. and Daling, P.S., 2017. Project recommendations for response to oil spills from condensates and light crude oils. SINTEF report no.: OC2017A-205. ISBN: 9788271743208.

Sørheim, K.R., Daling, P.S., and F., Leirvik., 2017: "Mekanisk dispergering av tynne oljefilmer. Oljevern 2015". WP048. SINTEF rapport: OC2017 A-125, ISBN: 978-82-7174-300-0.

A The behaviour of oil on the sea surface

A.1 The chemical composition of crude oils and condensates

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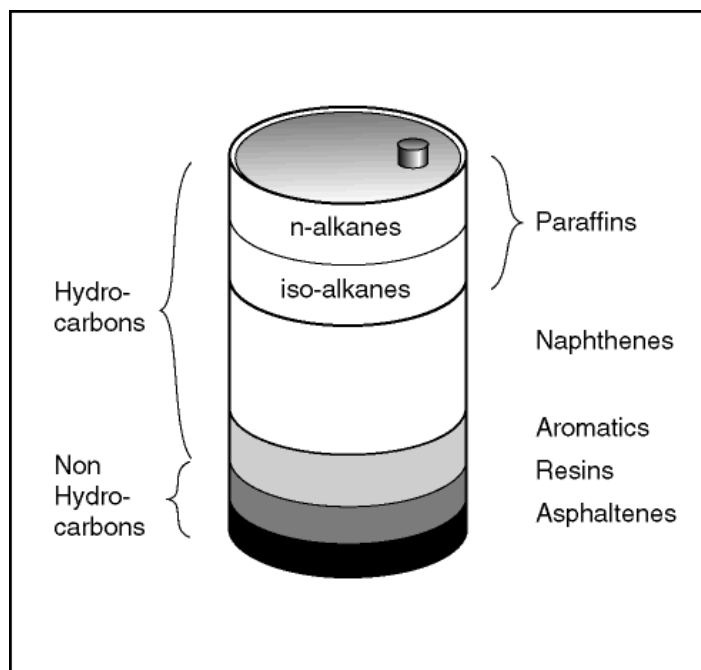

Figure A-1   The chemical composition of crude oils.

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

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

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

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

Non-hydrocarbons

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

Resins

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

Asphaltenes

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

A.2 Main oil categories related to weathering

Different oil types can have extremely different compositions, which impact their physical properties and effect their behaviour after a spill at sea.
Oils that are subject to weathering can roughly be divided into 3 main categories:

- Crude oils
- Light oils
- Condensates

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

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

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

A.3 Physical properties of crude oils

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

Density

The density of a crude oil is dependent on the density of all of its components. The density of hydrocarbons increases with increasing molecular weight. Furthermore, paraffinic oils have lower density than those containing larger amounts of high molecular weight aromatics, such as naphthenic and asphaltenic oils. Specific gravity is defined as the oil density at 60°F (15.5°C) divided by water density at 60°F. In American literature, the density of the oil is often expressed as °API, where:

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

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** also known as dynamic viscosity) is a measure of internal resistance. In the SI system, absolute viscosity has units of N s/m^2, Pa s or kg/(m s), where 1 Pa s = 1 N s/m^2 = 1 kg/(m s). Absolute viscosity can also be expressed in the metric CGS (centimeter-gram-second) system as g/ (cm s), dyne s/cm^2 or Poise, where 1 Poise = 1 dyne s/cm^2 = 1 g/(cm s) = 1/10 Pa s = 1/10 N s/m^2. https://www.engineeringtoolbox.com/dynamic-absolute-kinematic-viscosity-d_412.htmlThe industry often uses centipoise, as the *Poise* is normally too large, 1 Poise = 100 cP and 1 cP = 0.001 N s/m^2. The viscosity of fresh crude oils can vary from less than 1 to more than 2000 mPa.s (cP) at ambient sea temperature. In comparison, water has an "absolute" viscosity of 1 cP and syrup's is 120 000 cP at 20°C.

Kinematic viscosity is absolute viscosity divided by density. 1 centistoke (cSt) = 1 cP / density. Because the density of weathered oils and emulsion are typically 0.9 – 1 g/mL, the units cSt and cP will often have similar values. Viscosity is temperature dependent. For liquids, the viscosity decreases with increasing temperatures. Viscous and waxy crude oils can exhibit non-Newtonian behaviour (viscosity varies with shear rate), especially close to, or below, their pour point. Water-in-oil (w/o) emulsions exhibits this non-Newtonian behaviour with shear thinning. In an oil spill situation, an emulsion may be liquid under turbulent conditions at sea, but can become much more viscous, or even semi-solid in calmer water conditions, or on beaches. Thus, the measurements of the viscosity of w/o-emulsions must be carried out under strictly controlled conditions (defined shear rates and thermal and mechanical history of the sample). At SINTEF, a shear rate of 10 s^{-1} is routinely used for expressing viscosity data on w/o-emulsions.

The viscosity of an oil increases with evaporation since the heavier, more viscous components remain in the residue (Mackay et al., 1982). The difference in viscosity for crude oils is approximately 3 to 2000 mPa.s for fresh crude oils and several hundred/thousand mPa.s for their residues. Water-in-oil (w/o) emulsions are generally more viscous than the parent crude oil; this is illustrated in Figure A-2.
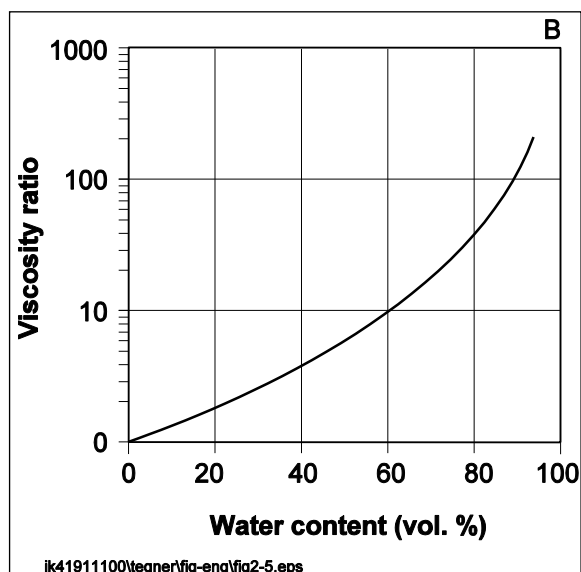
PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 48 of 65

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

A.3.2 Pour point

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

A.3.3 Distillation curve

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

A.3.4 Flash point

The flash point is the lowest temperature at which the gas or vapour generated by the heating of oil will form an ignitable mixture in air. The flash point depends on the proportion of low molecular weight components. Fresh crude oils normally have a low flash point (from -40°C to 30°C).From a safety point of view, flash points are most significant at, or slightly above, the maximum temperature that may be encountered in storage or transport. The flash point is an approximate indicator of the relative fire and explosion hazard of oil.

Rule of thumb:

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

Natural weathering processes such as evaporation and emulsion formation contribute to reducing the potential hazard by increasing the flash point. Thus, it will be a relatively short fire and/or explosion danger in the initial stages of oil spill. In the laboratory, the flash point is measured in a closed system with the components in the oil and gas equilibrated. In the field, however, the weather situation will influence the flammability of the air above the slick. The gas concentration will be high just above the oil film in calm weather and high temperatures, whereas the concentration will be low in cold and windy weather due to dilution and transport and a lower degree of evaporation.

A.4 The behaviour of crude oil spilled at sea

This chapter gives a general description of the main weathering processes when oil is spilled at sea. There are many natural processes take place that change the volume and chemical properties of the oil. These natural processes are evaporation, water-in-oil (w/o) emulsification, oil-in-water (o/w) dispersion, spreading, sedimentation, oxidation and biodegradation. A common term for all these natural processes is weathering. The relative contribution of each process varies during the duration of the spill. The weathering of oil depends on the oil type (chemical and physical properties), the weather conditions (wind, waves, temperature and sunlight) and the properties of the seawater (salinity, temperature, bacterial flora, etc.). Figure A-3 illustrates the various weathering processes, and Figure A-4 shows their relative importance over time.
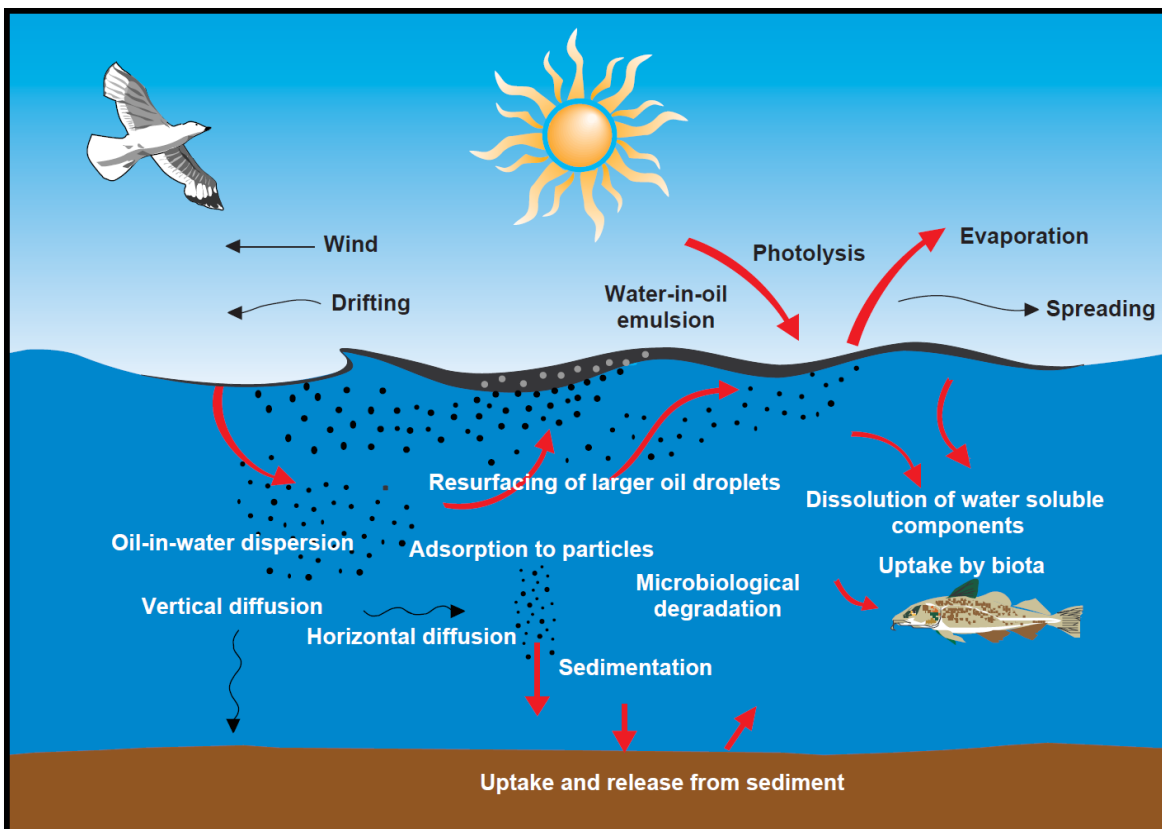

Figure A-3   Illustrating the weathering processes that take place when oil is spilled on the sea surface.
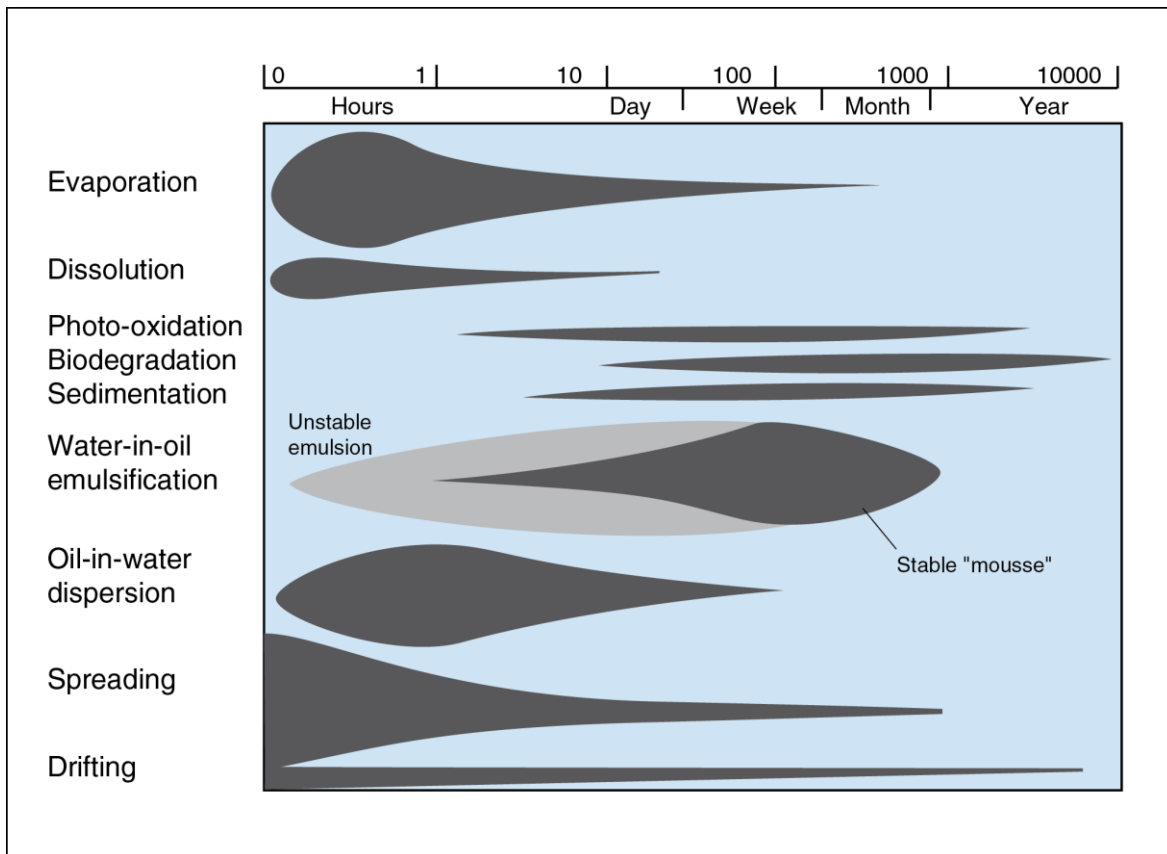
Figure A-4   Weathering processes' relative importance over time. Note: logarithmic scale.

A.4.1 Evaporation

Evaporation is one of the natural processes that support the removal of spilled oil from the sea surface. The evaporation process starts immediately after the oil is spilled, and the evaporation rate decreases exponentially throughout the duration of the oil spill. The evaporated amount depends on the chemical composition of the oil in addition to the prevailing weather conditions, sea temperature and oil film thickness.

The rate of evaporation varies for different oil types. Light refinery products (e.g. gasoline and kerosene) may completely evaporate after a few hours/days on the sea surface. Condensates and lighter crude oils can lose 50% or more of their original volume during the first days after an oil spill. The most significant difference caused by evaporation is the loss of volatile and semi-volatile compounds, which increases the relative amounts of higher molecular weight compounds. With evaporations, the chemical and physical properties of the remaining oil will change. The density, viscosity, pour point and wax and asphaltene content, will all increase with increased evaporation.

A.4.2 Spreading

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

Oceanographic conditions (e.g. wind, waves and currents) affect the spreading process. The oil slick will be broken into "wind rows" aligned in the direction of the wind, see Figure A-5. The thickness of the oil slick varies, often differing by a factor of several thousand. Experience has shown that most of the total oil slick area consists of a thin film (<1 μm oil thickness) that only contains 10% of the oil volume. Most of the oil

volume (~90%) is in small patches of w/o emulsions with a film thickness of 1 to 5 mm, which often constitutes less than 10% of the total oil slick area.
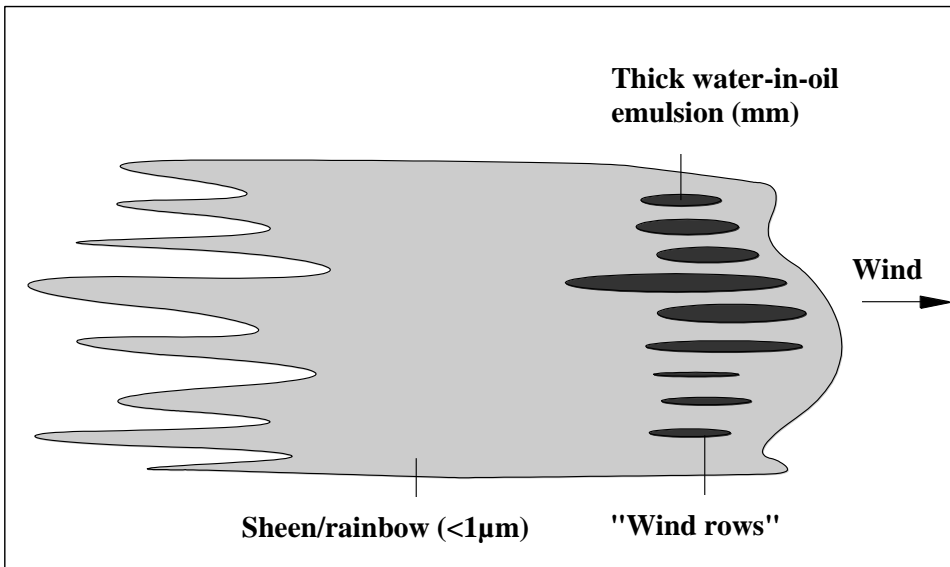

Figure A-5   The spreading of oil spilled on the sea surface and the distribution within the oil slick.

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-6. Waves and wind create a current in the mass of water which amounts to approximately 3% of the wind speed at the sea surface. The influence of the wind decreases rapidly with the depth of the water below the surface. At 1 to 2 meters the current reduces to approximately 1% of the wind speed. This means that oil on the surface of the open sea, will move faster than the water below (e.g. Reed and Turner, 1991; Reed et al., 1994). In the absence of wind, the oil drift is governed by the prevailing (background) current.
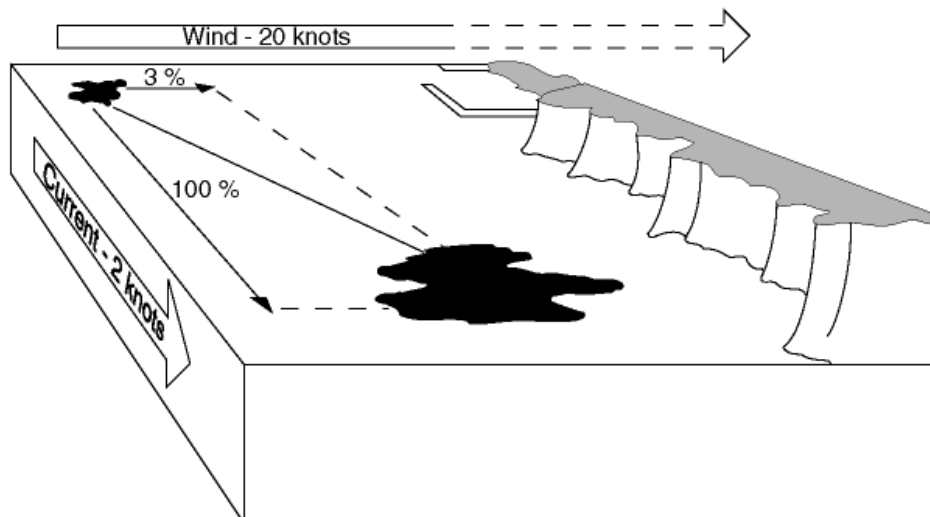

Figure A-6   An illustration showing how wind and current can influence the drifting of an oil slick.

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

The formation of water-in-oil emulsions significantly affects the behaviour and clean-up of oil spilled at sea. Because of emulsification, the total emulsion volume may increase to as much as six times the original spilled oil volume depending on the properties of the oil. The formation of w/o emulsions also contributes to keeping oil on the sea surface. A w/o emulsion normally has a higher viscosity than the parent crude oil, so the emulsification process will therefore retard/delay evaporation and the natural dispersion process. The minimum criterion for the formation of w/o emulsions is the presence of breaking waves (i.e. a wind speed of >5 m/s). Nonetheless, a slow water uptake can also take place during calmer weather. Figure A-7 shows how wind speed influences the w/o formation rate.

Surface active compounds present in crude oil will promote the formation of w/o emulsions and contribute to stabilizing the emulsion. These components contain both hydrophilic and hydrophobic groups. The maximum water uptake will vary for different crude oils. Tests performed at SINTEF have revealed that the maximum water uptake is independent of the prevailing weather conditions if the lower energy barrier for the formation of w/o emulsions is exceeded. The rate, however, depends highly on the weather conditions. In the laboratory, the $t_{1/2}$-value is determined, which is the time in hours it takes before the oil has emulsified half of its maximum water content. The w/o emulsion formation rate depends on the oil's chemical composition, which varies for different oil types.
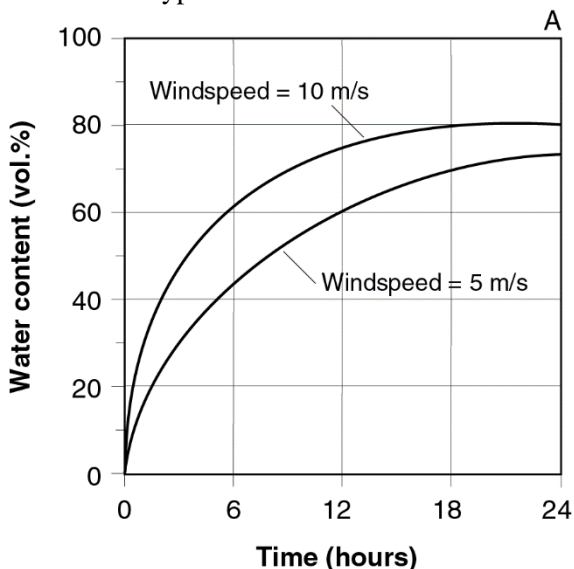
Figure A-7   Example of how weather conditions influence the w/o emulsion formation for typical oils.

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

Figure A-8   Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder.

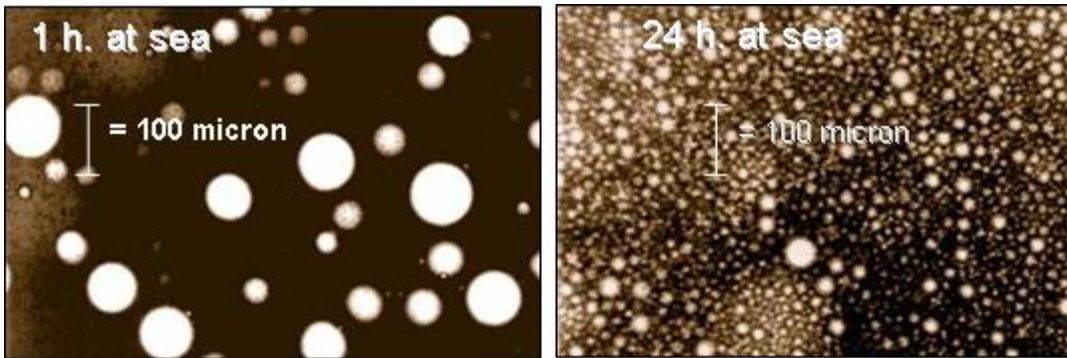Thus, the formation of emulsions is the result of water retention by oil as an effect of both viscous and interfacial forces. The interfacial forces are the most important, and asphaltenes are largely responsible for this. Resins are similar compounds to asphaltenes and can stabilize an emulsion, but 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-9.
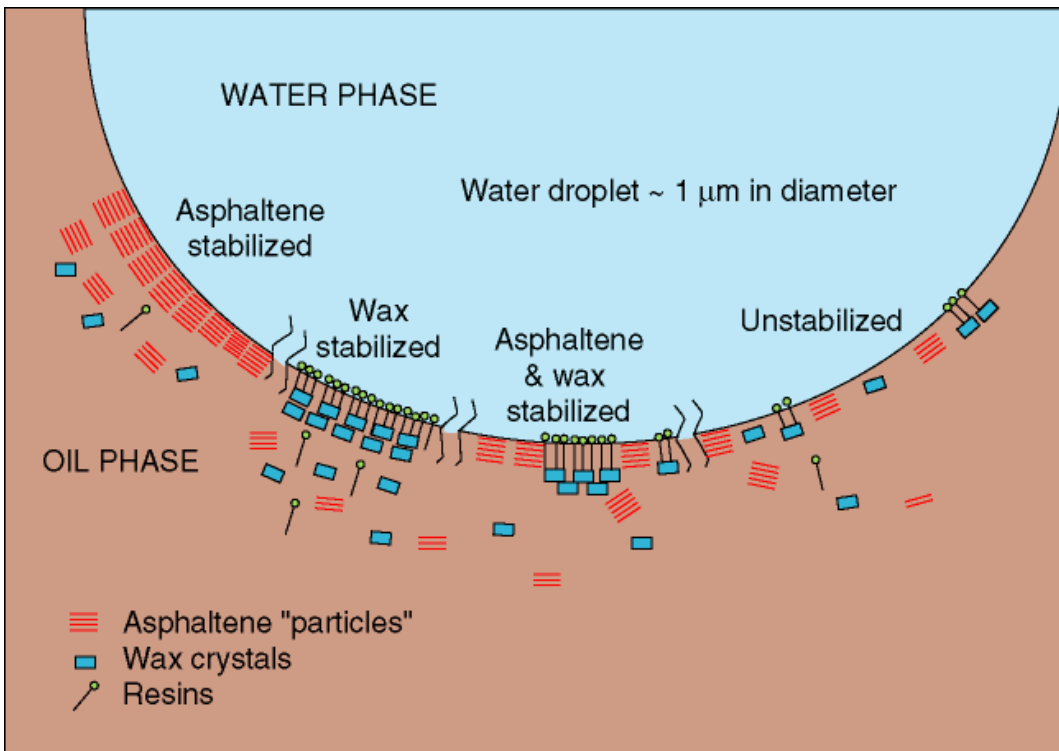
Figure A-9   Interfacial layer stabilized by wax and asphaltenes in w/o emulsion.

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

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

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

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

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

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

A.4.6 Water solubility

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

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

A.4.7 Photo-oxidation

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

A.4.8 Biodegradation

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

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 55 of 65

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

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

A.4.9 Sedimentation

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

A.4.10 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-10. This was observed both during the "DeepSpill" experiments in 2000 (Figure A-11) and the DWH oil spill in 2010 (Figure A-12). This emulsification will be dependent on oil properties and environmental conditions, such as temperature and sea state.
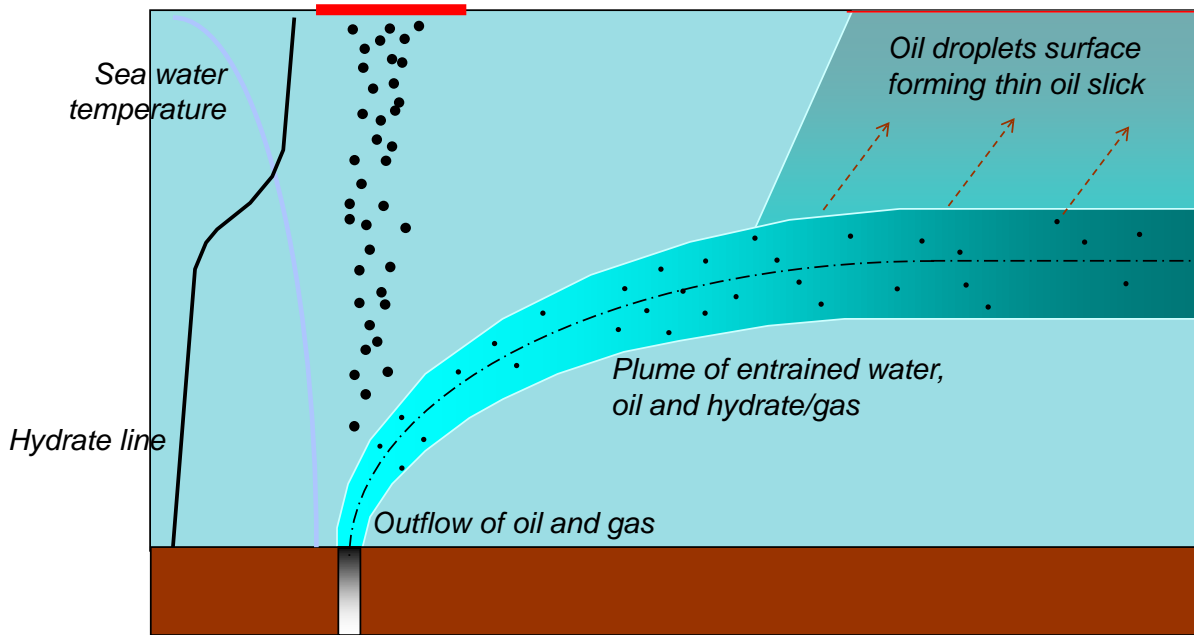
Thick surface oil slick

Sea water temperature

Oil droplets surface forming thin oil slick

Plume of entrained water, oil and hydrate/gas

Hydrate line

Outflow of oil and gas

Figure A-10   Illustration of possible creation of thick surface oil slick (> 200 µm) from deep-water release of oil.

Thick emulsion (1 - 2 mm)
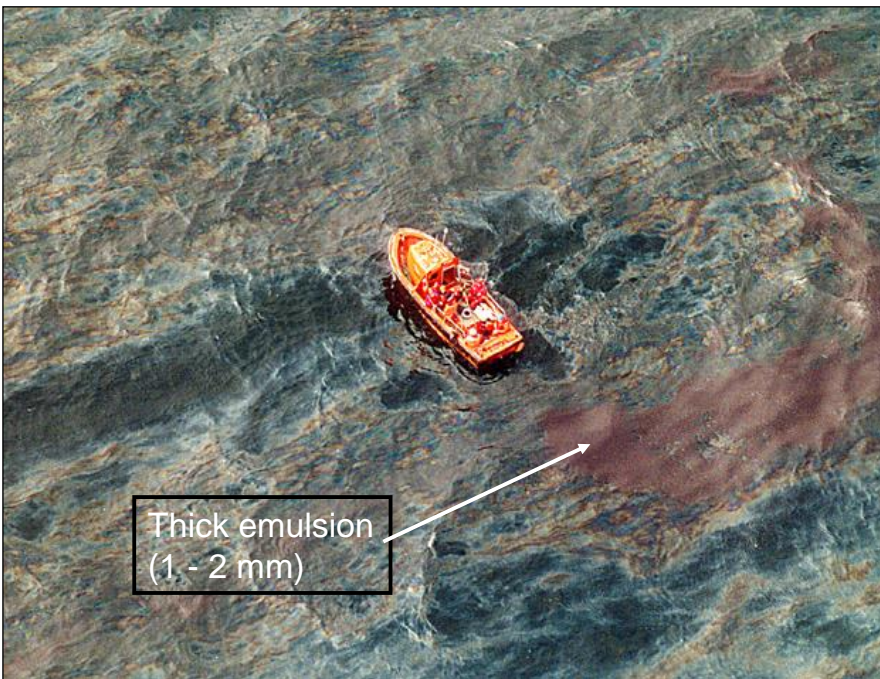
Figure A-11   Surface oil slick (initial thickness > 200 µm) from the experimental deep-water release "DeepSpill" in 2000. Surface oil is emulsifying like an oil slick from a surface batch release (from Leirvik et al., 2011).
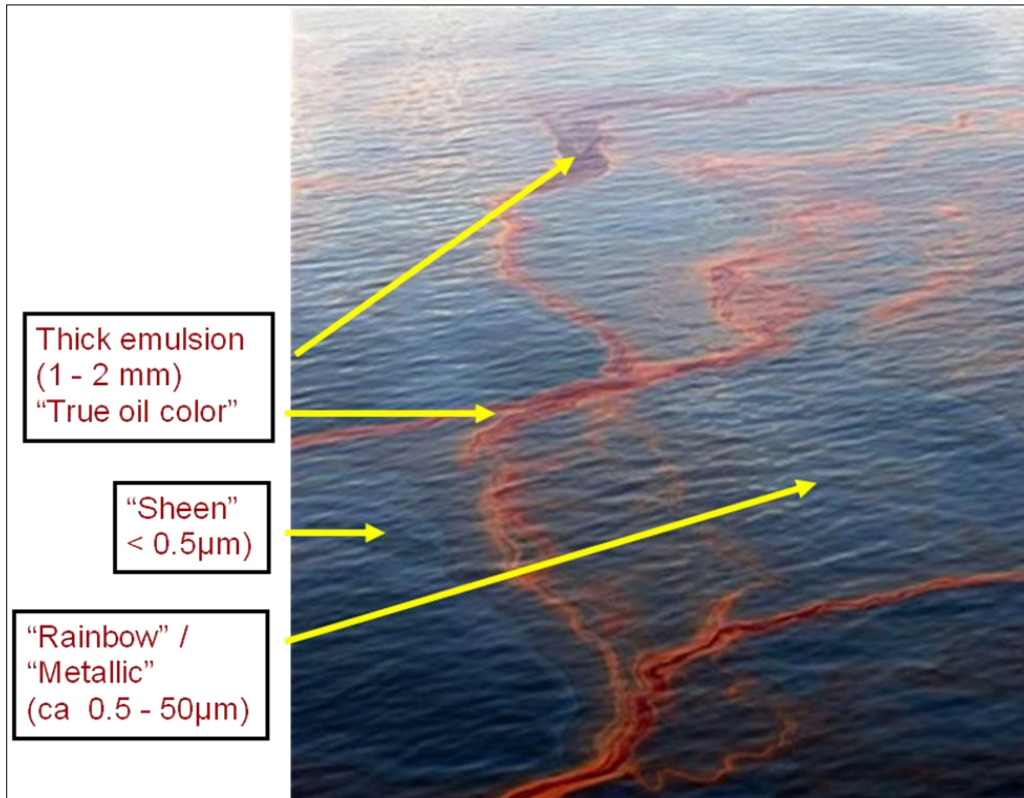
Figure A-12   Surface oil slick (initial thickness > 200 µm) from the DWH deep-water release. Surface oil is emulsifying like an oil slick from a surface batch release.

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-13 and Figure A-14, Rye et al., 1997). This surface oil slick could be too thin to emulsify (< 200 microns), and evaporation and natural dispersion will be the predominant weathering processes.
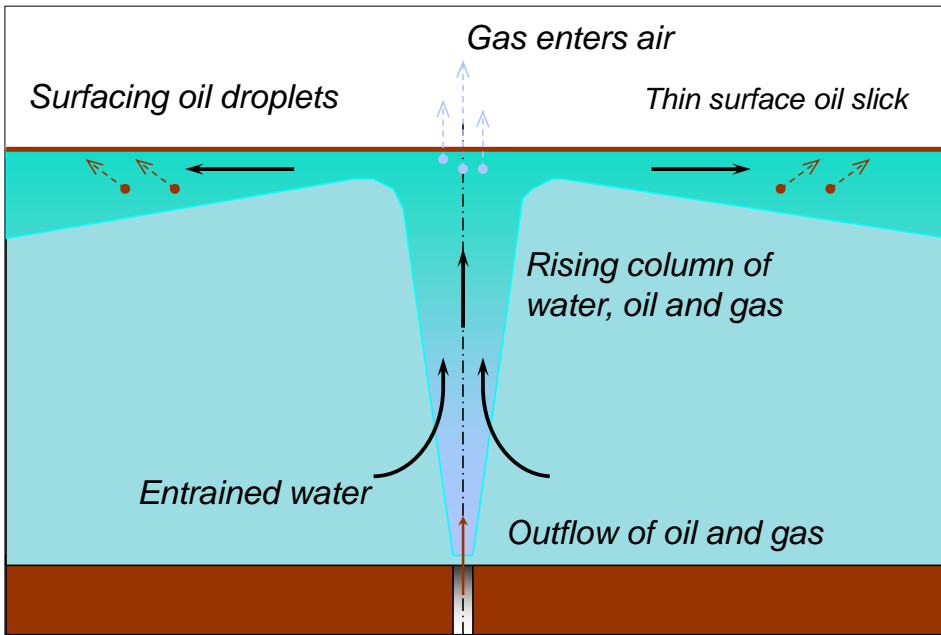
Figure A-13   *Illustration of possible creation of thin surface oil slick (< 200 µm) from a shallow subsurface release (<500 m).*
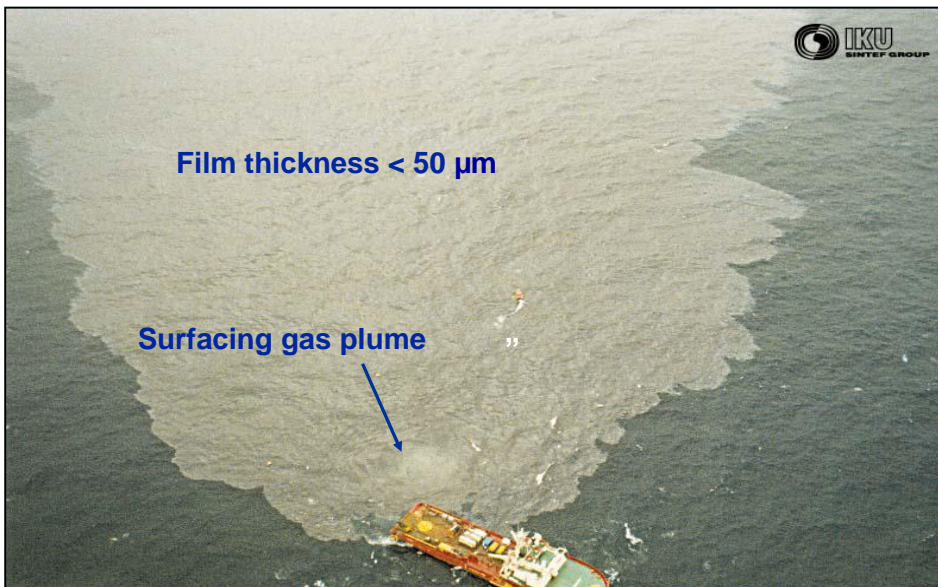

Figure A-14   *Surface oil slick (< 50 µm) from experimental subsurface release at 106 m in 1996. The surface oil did not emulsify and had a very limited lifetime (hours) due to the low film thickness and high rate of natural dispersion (even at < 10 m/s wind).*

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 59 of 65

B Experimental setup

B.1 Oil samples and test temperature

SINTEF Ocean received 3x10 litres steel cans of Valhall 19 February 2021. The oil samples were registered in LIMS and given SINTEF ID: 2021-880. Check of free-water in the cans and water content in the oil phase (Karl Fisher titration). Important for HSE and risk assessment for the topping/distillation step (limit < 2 vol. %). Approx. 200 ml free-water and minor water in the oil phase (2 of 3 cans). Homogenization of the oil prior to simulate evaporative loss at sea by topping/distillation.

The weathering study (small-scale) were performed at 13 °C.

Figure B-1   Valhall crude oil (3 x 10 litres).

B.2 Small-scale laboratory testing

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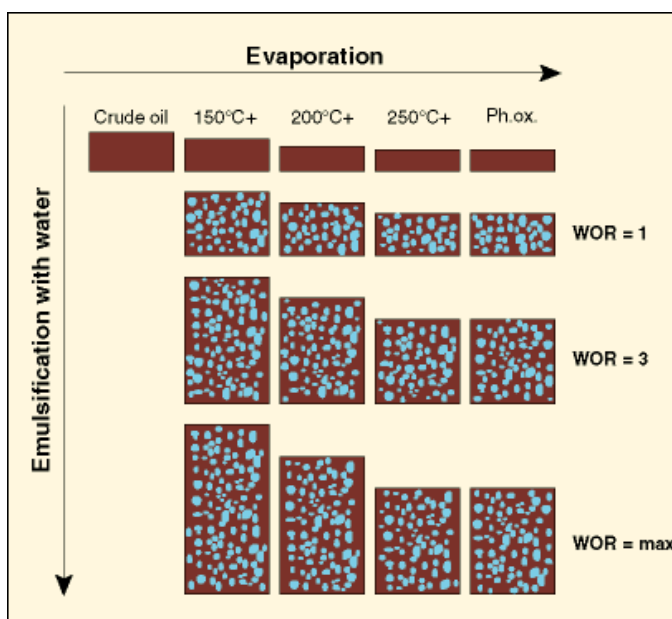

WOR: Water to Oil Ratio

WOR=1: 50 vol.% water

WOR=3: 75 vol.% water

WOR=max: the maximum water content

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

B.3 Evaporation

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.4 Physical and chemical analysis

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

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

Physical property	Analytical method	Instrument
Viscosity	McDonagh et al, 1995	Physica MCR 300
Density	ASTM method D4052-81	Anton Paar, DMA 4500
Pour point	ASTM method D97	-
Flash point	ASTM D 56-82	Pensky-Martens, PMP1, SUR

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

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

Chemical characterization by GC-FID and GC-MS

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

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

B.5 Emulsification properties

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

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

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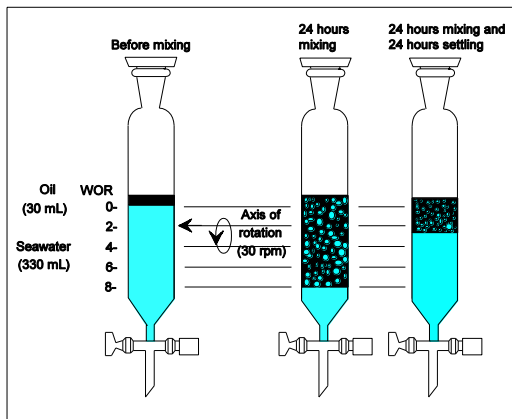
Figure B-3   Principle of the rotating cylinder method

B.6 Chemical dispersibility testing

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 and MNS test apparatus are shown in Figure B-4.

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

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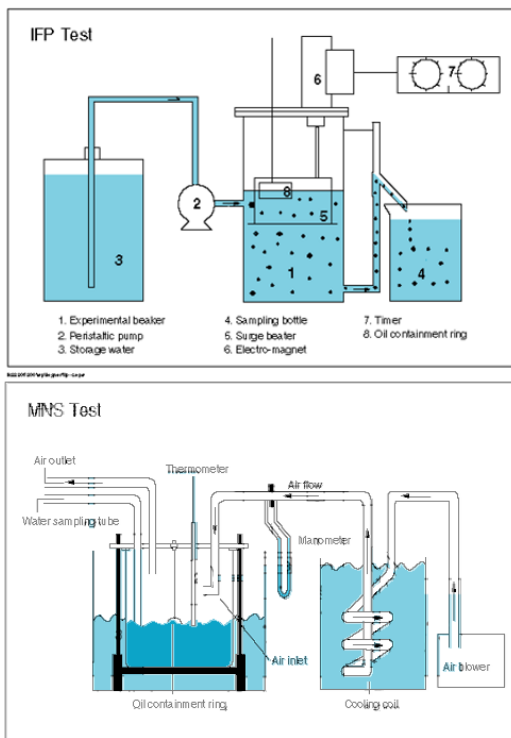

Figure B-4   Laboratory apparatus for effectiveness testing of dispersants.

PROJECT NO.
302006208

REPORT NO.
OC2021 A-063

VERSION
2.0

Page 62 of 65

C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Valhall 2021 are given in Table C-1 to Table C-3. The oil weathering predictions were based on the laboratory data at 13 °C.

Table C-1   Physical and chemical properties Valhall 2021

Properties of fresh oil	Valhall
Density (g/mL)	0.842
Pour point (°C)	-6
Reference temperature (°C)	13
Viscosity at ref. temp. (mPa·s = cP) *	15
Flash point (°C)	-
Asphaltenes (wt. %)	0.04
Wax Content (wt. %)	4.99
Dispersible for visc. <	800
Not dispersible for visc. >	8000
Max. water uptake vol.%	75

* Measured at shear rate 100 s^{-1}
-: Not analyzed or tested

Table C-2   True boiling point (TBP) curve of Valhall 2021
*TBP based on Simdist. Intertek Sunbury, UK. 2021-SUNB-4140856.

Temp. °C	Valhall* Vol. %
28	3.2
90	12.0
144	22.4
204	34.1
264	44.3
317	54.2
379	63.8
441	73.2
510	82.4
606	91.3
674	95.7
742	98.5

Table C-3   Lab weathering data for Valhall, 13 ℃

Properties	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	190.3	265.3	316.7
Vol. Topped (%)	0	20.9	33.3	41.6
Weight Residue (wt. %)	100	82.6	71.0	62.7
Density (g/mL)	0.842	0.878	0.896	0.909
Pour point (°C)	-6	9	21	24
Flash Point (°C)	-	36.5	84.5	121
*Viscosity of water-free residue (mPa.s =cP)	15	91	301	949
Viscosity of 50% emulsion (mPa.s = cP)**	-	528	1720	3890
Viscosity of 75% emulsion (mPa.s = cP)**	-	578	3011	-
Viscosity of max water (mPa.s = cP)**	-	588	1654	5480
Max. water cont. (vol. %)	-	61	81	70
(T1/2) Halftime for water uptake (hrs)	-	0.26	0.85	0.57
Stability ratio	-	1	0.98	0.98

Measured at shear rate 100 s^{-1}

Measured at shear rate 10 s^{-}

- No data – not measured

D   Chemical characterization – OSCAR composition file

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

Table D-1   Chemical characterization of Valhall (fresh oil) from GC-MS analysis and TBP oil fraction

Wt.%	Comp. group no.	Valhall SINTEF ID 2021-880
3.200	1	C1-C4 gasses (dissolved in oil)
3.500	2	C5-saturates (n-/iso-/cyclo)
1.852	3	C6-saturates (n-/iso-/cyclo)
0.248	4	Benzene
3.000	5	C7-saturates (n-/iso-/cyclo)
0.622	6	C1-Benzene (Toluene) et. B
6.878	7	C8-saturates (n-/iso-/cyclo)
0.698	8	C2-Benzene (xylenes; using O-xylene)
3.878	9	C9-saturates (n-/iso-/cyclo)
0.524	10	C3-Benzene
3.200	11	C10-saturates (n-/iso-/cyclo)
0.044	12	C4 and C4 Benzenes
4.956	13	C11-C12 (total sat + aro)
0.000	14	Phenols (C0-C4 alkylated)
0.273	15	Naphthalenes 1 (C0-C1-alkylated)
6.427	16	C13-C14 (total sat + aro)
0.000	17	Unresolved Chromatographic Materials (UCM: C10 to C36) 0 0 0
0.000	37	metabolite 1
0.000	38	metabolite 2
0.367	18	Naphthalenes 2 (C2-C3-alkylated)
5.333	19	C15-C16 (total sat + aro)
0.179	20	PAH 1 (Medium soluble polyaromatic hydrocrbns (3 rings-non-alkyltd;<4 rings)
5.321	21	C17-C18 (total sat + aro)
4.800	22	C19-C20 (total sat + aro)
7.929	23	C21-C25 (total sat + aro)
0.171	24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)
36.600	25	C25+ (total)

The SINTEF OSCAR model is a 3-dimensional O̲il S̲pill C̲ontingency A̲nd R̲esponse 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.