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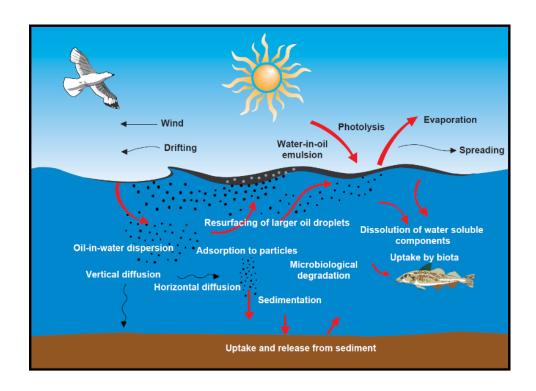
Report

Breidablikk – Weathering properties and behaviour at sea

In relation to oil spill response

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 REPORT NO.
 PROJECT NO.
 VERSION
 DATE

 2023:00459
 302007285
 1.0
 2023-04-17

KEYWORDS:

Breidablikk crude oil Weathering properties Oil spill response

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CLIENT(S)

Equinor ASA

CLIENT'S REF.NUMBER OF PAGES/APPENDICES:Kristin Øye72 incl. 4 Appendices

CLASSIFICATION CLASSIFICATION THIS PAGE ISBN

Open Open 978-82-14-07803-9

ABSTRACT

A standardized bench-scale weathering and dispersibility study has been conducted on Breidablikk crude oil at 5 and 13 °C. The dispersibility testing on Breidablikk was included to estimate the viscosity limits and time window for dispersant use. The laboratory data were used as input to the SINTEF Oil Weathering Model (OWM) for weathering and dispersibility predictions from a surface release of Breidablikk at sea at 5 and 15°C, reflecting winter and summer conditions. The weathering properties of Breidablikk are also discussed in relation to oil spill response.



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Document History

VERSION 0.1	DATE 2023-03-14	VERSION DESCRIPTION Draft version for review
1.0	2023-04-17	Final version



Table of Contents

1	Exec	cutive summary	5
2	Intro	oduction	8
3	Sma	ıll-scale laboratory testing of Breidablikk crude oil	9
	3.1	Gas chromatographic (GC-FID) characterization	9
	3.2	Asphaltenes and wax content	11
	3.3	Physical properties of the fresh and weathered residues	12
	3.4	Emulsifying properties	13
		3.4.1 Emulsification	13
		3.4.2 Kinetics of water uptake	14
		3.4.3 Efficiency of emulsion breaker and stability of emulsions	15
	3.5	Emulsion viscosities and yield stress	16
	3.6	Chemical dispersibility	18
		3.6.1 Screening testing of dispersants	18
		3.6.2 Dosage testing	18
		3.6.3 Systematic dispersant testing and dispersibility limits	19
4	Pred	dictions with SINTEF Oil Weathering Model (OWM)	22
	4.1	Description of SINTEF OWM	22
	5.2	Predictions of weathering properties of Breidablikk	23
6	Com	nparison of OWM predictions	34
	6.1	Evaporative loss	34
	6.2	Flash point	35
	6.3	Pour point	36
	6.4	Water uptake	37
	6.5	Emulsion viscosity	38
	6.6	Surface oil and emulsion	39
7	Wea	athering properties and response of Breidablikk (surface release)	40
	7.1	Oil properties	40
	7.2	Flash point – Fire/explosion hazard	40
	7.3	Solidification	41
	7.4	Emulsion formation	42
	7.5	Entrained oil and evaporation	42
	7.6	Film thickness from surface release	43
	7.6	Mechanical recovery by boom and skimmer	43
	7.7	Mechanical dispersion by high-capacity water flushing	44
	7.8	Chemical dispersion	45



8	8 Summary of response options of Breidablikk						
9	Cate	gorizatio	on of Breidablikk to other Norwegian oil (oil map)	48			
10	Refe	rences		50			
Α	The	behaviou	ur of oil on the sea surface	52			
	A.1	The ch	emical composition of crude oils and condensates	52			
	A.2	Main o	il categories related to weathering	53			
	A.3	Physica	al properties of crude oils	53			
		A.3.1	Rheological properties	54			
		A.3.2	Pour point	55			
		A.3.3	Distillation curve	55			
		A.3.4	Flash point	55			
	A.4	The be	haviour of crude oil spilled at sea	56			
		A.4.1	Evaporation	57			
		A.4.2	Spreading	57			
		A.4.3	Drift of an oil slick	58			
		A.4.4	Water-in-oil (w/o) emulsion	59			
		A.4.5	Oil-in-water (o/w) dispersion	61			
		A.4.6	Water solubility	61			
		A.4.7	Photo-oxidation	61			
		A.4.8	Biodegradation	61			
		A.4.9	Sedimentation	62			
		A.4.10	Deep water releases	62			
		A.4.11	Shallow releases	64			
В	Ехре	rimenta	l setup and HSE	66			
	B.1	Oil sam	nple and test temperature	66			
	B.2	Water	content	66			
	B.3	Small-s	scale laboratory testing	66			
	B.4	Evapor	ation	67			
	B.5	Physica	al and chemical analysis	67			
	B.6	Emulsi	fication properties	68			
	B.7	Chemic	cal dispersibility testing	68			
С	Inpu	t data to	SINTEF Oil Weathering Model (OWM)	70			
D	Cher	nical cha	racterization – OSCAR composition file	72			



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 reduced oil volumes of oil spills from the sea surface. Based on input from the experimental weathering data of the Breidablikk crude 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 Breidablikk oil when weathered on the sea surface.

Compared to many other Norwegian crude oils, this weathering study of Breidablikk shows the following properties relevant for the behaviour if spilled at sea with film thickness that is sufficient high to emulsify, i.e., typically higher than 0.1 mm.

- Breidablikk is a naphthenic heavy crude oil with a density of 0.913 g/mL with a relatively low volatile loss of 12.4 vol.% for the 250°C+ residue that cause a low degree of evaporation at sea. For example, after 12 hours, the evaporative loss is in the range of 10-13% at 10 m/s wind speed.
- The combination of wax content (1.8 wt.%), asphaltenes (0.77 wt.%) and density, Breidablikk forms stable water-in-oil emulsions with high viscosities and maximum water uptake to about 62 vol%. in winter conditions and about 73 vol. % in summer conditions.
- The emulsion formed are expected to have a high persistency on the sea surface, e.g., the predictions indicate a lifetime of 4-5 days at 15 m/s wind speed. In calmer weather conditions the lifetime is predicted to be >5 days.
- As much as 85-90 % of the oil can remain on the sea surface in very calm weather conditions (2 m/s wind speed) after 5 days.
- The overall volume of the spilled oil can increase 2-2.5 times relative to the volume due to emulsification.
- Breidablikk exbibits low pour points of -21 and -15 °C for the 150 and 250°C+ residues, respectively, and a potential residue at sea is therefore not expected to form semi-solid lumps that is typically for oils with high point, either in summer or winter conditions.

Comparation of Breidablikk vs. Grane

- Breidablikk (0.913 g/mL) and Grane (0.942 g/mL) are both heavy asphaltenic crude oils.
 - Breidablikk has asphaltene content of 0.77 wt% and Grane 1.4 wt.%
 - Grane is more biodegraded than Breidablikk.
- Both crude oils have low pour points both for the fresh oil and residue.
 - Pour point of Breidablikk fresh oil is -21 °C and -24 °C for Grane.
- Both crude oils show formation of stable and high emulsion viscosities.
 - The predicted viscosities as slightly higher for Grane than Breidablikk
- Maximum water of 73 % Breidablikk vs. 65 % for Grane at 15 °C, and a slower kinetics (water uptake rate) for Grane due to its higher oil viscosity
- Predicted mass balances show similarities in lifetime of remaining oil at sea for Breidablikk and Grane
- Breidablikk has a shorter predicted time window for dispersants use compared to Grane due to differences in dispersibility limits and water uptake from the laboratory studies.

Summary of oil spill response of Breidablikk

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 the flash point of the oil assumes to reach the ambient water temperature within a short time. The fire hazard, based on the evaporated volatiles from the oil, may be high if the flash point of the free -drifting oil is below the sea temperature.

 PROJECT NO.
 REPORT NO. 2023:00459
 VERSION
 Page 5 of 72

 302007285
 1.0



The flash points for Breidablikk are expected to surpass the sea temperature within a few minutes at 5 and 15 °C, predicted with the standardized surface release (80 m³/ h). However, for larger surface release rates, e.g., spill from a blowout, pipeline rupture, or incident due to tanker loading, 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. Breidablikk reaches this limit (60 °C) within few minutes after a spill at 5 and 15 °C. However, for oil recovery vessels (e.g., NOFO's ORO vessels) with A class certification for transport of liquids (Class I/II, flash point <60 °C), there should not be any risks in storing the recovered emulsion in such tanks. According to NOFO's "ORO (Oil Recovery Operation)-manual" the aeration tubes should be placed minimum 2.4 m above deck-levels, and aeration zones (ex-zones) will be established onboard, that will be manually controlled with explosimeters during a response operation.

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 always 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 of Breidablikk were stable but released about 68-75% of the incorporated water at winter conditions when adding concentrations 2000 ppm by weight of the emulsion breaker Aerosol OT-SE surfactant, and similar 84-91 % effectiveness at summer conditions. The highest concentration (2000 ppm) of emulsion breaker was shown to be more effective than a lower concentration of 500 ppm. Use of emulsion breaker may therefore 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.

Solidification of residue at sea:

Increased weathering may potentially increase the pour points to the point of solidification (elastic properties) at the sea surface and typically reduces the dispersibility. Solidification typically arises in calm sea conditions (i.e., non-breaking waves) when the pour point of the oil is 5-15 °C above the seawater temperature. For Breidablikk, the formation of solidified lumps is not likely due to its low pour points.

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. The predictions indicate that the emulsion viscosities of Breidablikk surpass 1000 mPa.s between 1.5-2 hours at 10 m/s wind speed at 5 and 15 °C, but the time may be stretched up to about 12 hours to 1-day for very low wind speed (2 m/s). Moreover, viscosities larger than 20 000 mPa.s are known to reduce the flowability of the oil/emulsion when using traditional weir skimmers. For example, Breidablikk has emulsion viscosities lower than this limit up to about 5 days weathering at 5 m/s wind speed, and 1.5-2.5 days at 10 m/s. Overall, Breidablikk is expected to have a wide window of opportunity for use of traditional weir-skimmer head.

Chemical dispersion (viscosity limits):

Breidablikk is expected to have a good potential for chemical dispersion with use of Dasic Slickgone NS (DOR; dispersant-to-oil ratio 1:25) for viscosities <7000 mPa.s based on the low-energy test (IFP), and poorly dispersible for viscosities >10 500 mPa.s based on the high-energy test (MNS). In the field, if the oil is reduced dispersible i.e., viscosities between 7000 -10 500 mPa.s, additional energy e.g., thrusters, Fire Fighting (Fi-Fi) systems, higher DOR by repeated dispersant application may increase the efficacy of the dispersant treatment.

High-capacity water flushing (mechanical dispersion):

The oil emulsion viscosity and oil film thickness are the limiting factors for this strategy. The predicted film thicknesses are >0.2-0.3 mm which is the estimated upper limit for effective use of water flushing. Water flushing should therefore not be a main response option for Breidablikk but could be a supplementary method



if there are areas on the sea surface with thin oil films e.g., metallic /rainbow appearance in very calm weather conditions.

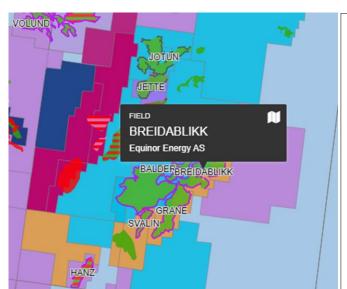
<u>Monitoring and remote sensing</u>: Monitoring and remote sensing should always be used a support in a response operations for Breidablikk.



2 Introduction

New oil types, from heavy crude oil to light crude oils and condensates, are continuously coming into production worldwide, as well as on the Norwegian continental shelf. 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 (NEA) 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 and dispersibility testing on Breidablikk crude oil at 5 and 13 °C. The obtained laboratory data have been used to predict the weathering properties of Breidablikk crude oil at 5 and 15 °C, reflecting winter and summer seawater temperatures in the North Sea, by use of the SINTEF Oil Weathering Model (OWM). Such documentation gives an important basis for oil spill contingency planning and decision making during an oil spill operation. Information about the Breidablikk field is given, below (Figure 2-1).



Breidablikk is a field in the central part of the North Sea, ten kilometres northeast of the Grane field.

The water depth is 130 meters.

Breidablikk includes two discoveries (1992 and 2013): D-structure (25/8-4) and F-structure (25/11-27).

The plan for development and operation (PDO) was approved in June 2021.

The field is being developed with four subsea templates tied-back to the Grane platform.

The oil will be transported from Grane to the onshore terminal at Sture for storage and export.

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



3 Small-scale laboratory testing of Breidablikk crude oil

Description of the oil sample of Breidablikk for testing and the experimental setup for the small-scale and dispersibility methods are described in Appendix B. Physico-chemical parameters and weathering properties of Breidablikk are also compared with previous weathering studies of Grane and Balder from the neighbouring fields. The crude oils for comparison were selected in agreement with Equinor (Table 3-1).

Table 3-1 Crude oils compared with Breidablikk (SINTEF Id 2022-6485) in this report.

Oil name	SINTEF Id	SINTEF report no	Reference
Grane	1997-0253	STF66 F98038	Strøm and Daling, 1997
Balder	1999-0527	STF66 A01137	Moldestad og Schrader, 2002

3.1 Gas chromatographic (GC-FID) characterization

The hydrocarbon profile of Breidablikk 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 Breidablikk and the corresponding evaporated residues at three different degrees of evaporative loss of volatiles with boiling points 150, 200 and 250°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 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.

Breidablikk is an asphaltenic crude that is highly biodegraded up to nC_{13} (Figure 3-1). Figure 3-2 shows the GC/FID profile of Breidablikk in comparison with Grane and Balder. The three crude oils have similarities in their hydrocarbon profile, Breidablikk is more similar with Balder, and Grane is the most biodegraded oil. Moreover, 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 3-2 shows the ratios of Breidablikk in comparison with Grane and Balder.

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

Oil name	nC ₁₇ /Pristane	nC ₁₈ /Phytane
Breidablikk	1.2	2.2
Grane	1.1	1.6
Balder	1.5	2.2



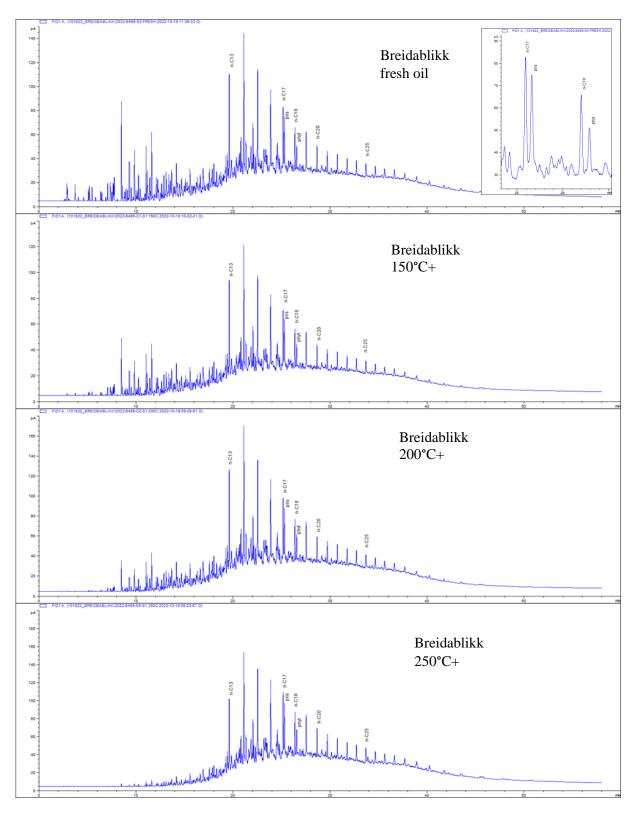


Figure 3-1 GC-FID chromatograms of fresh oil and evaporated residues of Breidablikk.



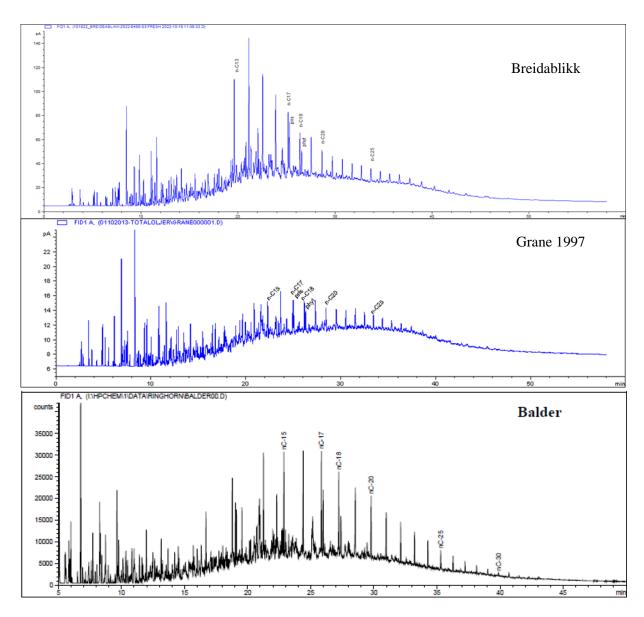


Figure 3-2 GC-FID chromatograms for fresh oils of Breidablikk in comparison with Grane and Balder. The retention times may differ between the chromatograms due to different temperature programs (relative comparison).

3.2 Asphaltenes and wax content

The content of asphaltenes and wax of Breidablikk in comparison with Grane and Balder are shown in Table 3-3. Breidablikk (fresh oil) has a low wax content of 1.81 wt.% and medium to high content of asphaltenes (0.77 wt.%) compared with many other Norwegian crude oils. Grane and Balder exhibit both a high asphaltene content of 1.4 and 1.1 wt% respectively, and relatively low contents of wax (3.5 and 2.1 wt.%).

 PROJECT NO.
 REPORT NO. 2023:00459
 VERSION
 Page 11 of 72

 1.0
 1.0
 1.0



Table 3-3 Asphaltene ("hard") and wax content of Breidablikk in comparison with Grane and Balder.

Oil type	Residue	Asph ¹⁾	Wax
		(wt. %)	(wt. %)
	Fresh	0.77	1.8
Breidablikk	150°C+	0.78	1.8
	200°C+	0.79	1.9
	250°C+	0.86	2.0
	Fresh	1.4	3.5
Grane	150°C+	1.4	3.9
	200°C+	1.4	4.3
	250°C+	1.5	4.8
	Fresh	1.1	2.1*
Balder	150°C+	1.2	2.2*
	200°C+	1.2	2.2*
	250°C+	1.3	2.4*

¹⁾ n-heptane (nC₇) precipitation *:Data from 1991

3.3 Physical properties of the fresh and weathered residues

The physical properties of Breidablikk are shown in Table 3-4 in comparison with Grane and Balder. The physical properties of Breidablikk have many similarities with Grane and Balder.

The fresh Breidablikk has a high density of 0.913 g/mL and is not similar with Balder (0.914 g/mL), whilst Grane has very high density of 0.942 g/mL. The evaporative loss of Breidablikk is 12 vol% for the 250°C+ residue most like Grane (13 vol.%) and slightly higher for Balder (17 vol.%).

Breidablikk has very low pour point (-21 °C) of the fresh oil, similar as for Grane (-24 °C) and Balder (-30 °C). The pour points of the residues are also very low for Breidablikk, Grane and Balder, typically for asphaltenic or biodegraded crude oils.

The viscosities of Breidablikk at shear rate 10s⁻¹ and 13 °C are 126 mPa.s of the fresh oil and in the range 152-447 mPa.s for of residues. The viscosities of Breidablikk are most similar with Balder, whilst the viscosities of Grane are significantly higher.

Table 3-4 Physical properties of Breidablikk in comparison with Grane and Balder.

Oil type	Residue	Evap.	Residue	Density	Flash	Pour	Visc.	Visc.	IFT
		(vol. %)	(wt. %)	(g/mL)	point	point	(mPa.s)	(mPa.s)	(mN/m),
					(°C)	(°C)	5°C	13°C	init.5 min)
							(10 s^{-1})	(10 s ⁻¹)	
	Fresh	0	100	0.913	-	-21	297	126	9.8
Breidablikk	150°C+	1.8	99	0.917	64	-21	351	152	9.5
	200°C+	4.3	96	0.920	78	-18	473	193	9.8
	250°C+	12	89	0.928	106	-15	1154	447	8.5
	Fresh	0	100	0.942	26	-24	1330*	638*	9**
Grane	150°C+	3	98	0.948	70	-18	1980*	962*	10**
	200°C+	5	96	0.950	92	-15	2830*	1084*	11**
	250°C+	13	89	0.960	139	-6	5970*	3229*	13**
	Fresh	0	100	0.914	-	-30	-	219	-
Balder	150°C+	7	94	0.924	77	-21	-	394	-
	200°C+	11	89	0.929	86	-21	-	985	-
	250°C+	17	85	0.936	115	0	-	1580	-

^{-:}No data

^{*:}Measured at 100 s-1 **: Measured with ASTM-method 971-82 (Du Noüy ring method)



The True Boiling Point curves (TBP) of Breidablikk in comparison with Grane and Balder are shown in Figure 3-3. Breidablikk exhibits a higher TBP from 250°C than the other oils, whilst Grane has the lowest TBP. The TBPs reflect the evaporative loss of the 150, 200 and 250°C+ residues (Table 3-4), indicating a low evaporative loss at sea for all the three oils.

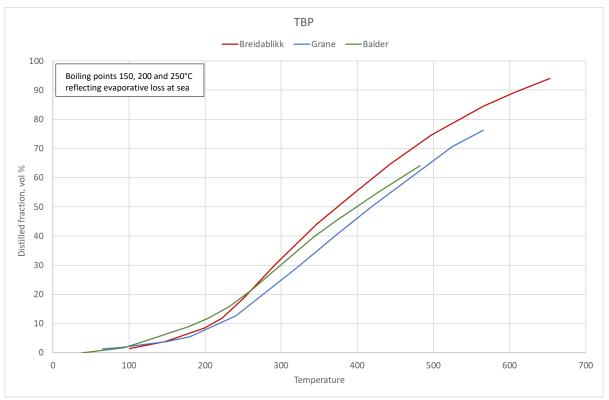


Figure 3-3 True boiling point curves of Breidablikk in comparison with Grane and Balder.

3.4 Emulsifying properties

In general, oil-in water (o/w) emulsification is the mixing of seawater droplets into spilled oil at the sea surface (water-in-oil emulsion). The rotating cylinder method (Mackay and Zagroski, 1982) was used to study the emulsifying properties of Breidablikk, and the procedure for maximum water uptake is described in Hokstad et al. 1993 (Appendix B).

3.4.1 Emulsification

Emulsification testing of Breidablikk were conducted on the residues of 150°C+, 200°C+ and 250°C+ to produce data for stability, viscosity, maximum water uptake, kinetics of water uptake, and the effectiveness of the emulsion breaker application. Emulsions of the maximum water content after 24 hours rotation are shown in Figure 3-4 and Figure 3-5 at 5 and 13 °C, below. The figures show from left to right four emulsions prepared from the residues of 150°C+, 200°C+ and 250°C+, respectively.

 PROJECT NO.
 VERSION
 Page 13 of 72

 302007285
 1.0





Figure 3-4 Rotating cylinders of water-in-oil (w/o) emulsions of Breidablikk after 24 hours at 5 °C.

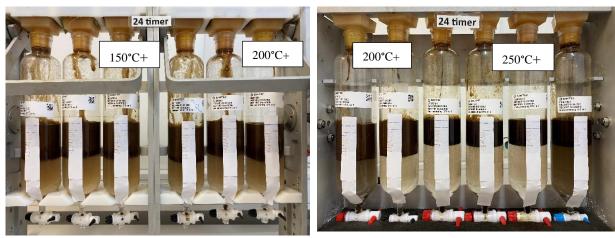


Figure 3-5 Rotating cylinders of water-in-oil (w/o) emulsions of Breidablikk after 24 hours at 13 °C.

3.4.2 Kinetics of 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).

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

Mixing time	150°C+ * (vol. % water)	200°C+ * (vol. % water)	250°C+ * (vol. % water)
Start	0	0	0
5 min	28	24	10
10 min	37	33	15
15 min	45	40	23
30 min	55	48	30
1 hour	61	56	34
2 hours	66	61	40
4 hours	71	67	47
6 hours	73	69	50
24 hours	77	75	61
t 1/2	0.21	0.27	0.76

^{*} 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.



Table 3-6 Kinetics $(t_{1/2})$ for the emulsified residues of Breidablikk at 13 °C.

Mixing time	150°C+ * (vol. % water)	200°C+ * (vol. % water)	250°C+ * (vol. % water)
Start	0	0	0
5 min	27	28	26
10 min	41	41	36
15 min	50	49	41
30 min	59	56	46
1 hour	65	64	51
2 hours	70	69	56
4 hours	75	72	60
6 hours	77	75	64
24 hours	81	81	71
t 1/2	0.20	0.20	0.24

^{*} 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.

3.4.3 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 Breidablikk at 5 and 13 °C. The choice of emulsion breaker was selected in agreement with Equinor.

The results show that the emulsified oil volume decreased after treatment with the emulsion breaker, as water was released from the emulsion as shown in Table 3-7 at 5°C and Table 3-8 at 13 °C. Overall, adding 2000 ppm (0.2 wt.%) of the emulsion breaker relative to the oil was shown to be more efficient (68-75% at 5°C and 84-91% at 13°C) 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. Overall, Breidablikk formed stable w/o-emulsions of the 150, 200 and 250°C+ residues, as shown in the first main row of and Table 3-7 and Table 3-8. The emulsions released only a small amount of water after settling time, with stability ratios in the range of 0.97-1.00 at 5 and 13 °C.

Table 3-7 Stability of emulsion and the effectiveness of emulsion breaker at 5 °C of Breidablikk.

Residue Breida- blikk	Emulsion breaker		nulsion (vol. %) 3 °C	Stability ratio**	% Effect. (Released water)
		Reference	24 hours settling *		
150°C+	None	77	77	0.99	1
200°C+	None	75	75	0.97	3
250°C+	None	61	61	1.00	0
150°C+	Aerosol OT-SE 500 ppm	77	59	0.43	57
200°C+	Aerosol OT-SE 500 ppm	75	59	0.49	51
250°C+	Aerosol OT-SE 500 ppm	61	49	0.63	37
150°C+	Aerosol OT-SE 2000 ppm	77	45	0.25	75
200°C+	Aerosol OT-SE 2000 ppm	75	45	0.28	72
250°C+	Aerosol OT-SE 2000 ppm	61	33	0.32	68

^{*} Reference: w/o emulsion after 24 hours rotation

PROJECT NO. 302007285 REPORT NO. 2023:00459 VERSION Page 15 of 72

^{*:} 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.



Table 3-8 Stability of emulsion and the effectiveness of emulsion breaker at 13 °C of Breidablikk.

Residue Breida- blikk	Emulsion breaker		nulsion (vol. %) 3 °C	Stability ratio**	% Effect. (Released water)
		Reference	24 hours settling *		
150°C+	None	81	81	1.00	0
200°C+	None	81	81	0.98	2
250°C+	None	71	71	1.00	0
150°C+	Aerosol OT-SE 500 ppm	81	74	0.65	35
200°C+	Aerosol OT-SE 500 ppm	81	71	0.60	40
250°C+	Aerosol OT-SE 500 ppm	71	56	0.51	49
150°C+	Aerosol OT-SE 2000 ppm	81	36	0.13	87
200°C+	Aerosol OT-SE 2000 ppm	81	27	0.09	91
250°C+	Aerosol OT-SE 2000 ppm	71	29	0.16	84

^{*} Reference: w/o emulsion after 24 hours rotation

3.5 Emulsion viscosities and yield stress

The viscosities of emulsified residues of Breidablikk at 5 and 13 °C are given in Table 3-9 and Table 3-10 (including fresh oil and waterfree residues). 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). This decrease in viscosity with increasing shear rate is due to the shear thinning property of emulsion with increased mechanical force.

Yield stress is defined as the force that must be overcome so that an oil can spread / flow like a liquid on the sea (also known as the flow limit). This force is called the fluids "yield stress" or flow limit and is given the unit Pascal (Pa). Yield stress is measured with Physica MRC 300 rheometer. Many crude oils (particularly weathered residues and emulsions) are so-called *Bingham-plastic* fluids at sea temperature. This means that applied force must be exerted to the fluid to make it flow and spread and is mainly pronounced for *non-Newtonian* oils where the viscosities vary with the shear rate. The oil /emulsions of Breidablikk have low yield stress (Table 3-9 and Table 3-10), compared with typically paraffinic waxy crude oil with high pour points.

^{*:} 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.



Table 3-9 Viscosities waterfree residues and emulsions of Breidablikk at 5 °C.

Breidablikk	Water content (vol. %)	Viscosity 5 °C (mPa.s) 10 s ⁻¹	Viscosity 5 °C (mPa.s) 100 s ⁻¹	Yield stress Pa
Fresh	0	297	272	nd
150°C+	0	351	337	nd
200°C+	0	473	440	nd
250°C+	0	1154	1012	nd
150°C+	50	1986	1188	nd
200°C+	50	2485	1441	nd
250°C+	50	5659	2627	nd
150°C+	75	7984	1200	3.9
200°C+	75	9975	1119	6.5
250°C+	75	-	-	-
150°C+	77	9547	923	8.3
200°C+	73	8290	1084	nd
250°C+	62	8870	1250	nd

nd: not detected. -: Emulsion of 75% not obtained in the laboratory.

Table 3-10 Viscosities waterfree residues and emulsions of Breidablikk at 13 °C.

Breidablikk	Water content (vol. %)	Viscosity 13 °C (mPa.s) 10 s ⁻¹	Viscosity 13 °C (mPa.s) 100 s ⁻¹	Yield stress Pa
Fresh	0	126	122	nd
150°C+	0	152	149	nd
200°C+	0	193	190	nd
250°C+	0	447	438	nd
150°C+	50	1062	705	nd
200°C+	50	1285	827	nd
250°C+	50	2562	1474	nd
150°C+	75	4523	1711	nd
200°C+	75	5830	1974	2.3
250°C+	75	10669	932	5.9
150°C+	82	17344	1103	44
200°C+	80	12647	1347	20
250°C+	72	8856	1059	nd

nd: not detected.



3.6 Chemical dispersibility

The dispersibility testing of Breidablikk included:

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

3.6.1 Screening testing of dispersants

The screening testing was performed using the low-energy IFP test (Institute Français du Pétrole), reflecting non-breaking waves (<5 m/s wind speed), in combination with the high-energy MNS test (Mackay-Nadeau-Szeto), reflecting breaking waves conditions (>5 m/s wind speeds). Dispersants tested were Dasic Slickgone NS, Corexit 9500A, Finasol OSR-52, and Gamlen OD 4000. The screening testing was performed at 5 and 13 °C using the 200°C+ residue emulsified with 50 vol. % seawater. The results are presented in Table 3-11.

The IFP test showed dispersant effectiveness in the range 66-74%, where Dasic Slickgone NS and Corexit 9500A were most efficient dispersants (74%). Dispersant efficiency >50% for the low-energy test (IFP) is considered as good dispersion. Dispersant efficiency >75% for the high-energy MNS test is considered as good dispersion, and all the dispersants tested showed dispersibility of 100%. However, Dasic Slickgone NS and Corexit 9500A visually seemed to promote smaller oil droplets. DOR=Dispersant to oil ratio /DER=Dispersant to emulsion ratio.

Table 3-11 Screening testing on Breidablikk using the IFP-test and MNS-test at standard temperature of 13 °C.

Dispersant (DOR/DER =1:25)	Efficiency dispersant (200°C+/50 vol. % emulsion)* IFP	Efficiency dispersant (200°C+/50 vol. % emulsion)* MNS
Dasic NS	74	100
Corexit 9500A	74	100
Finasol OSR 52	66	100
Gamlen OD 4000	69	100

^{*} Emulsion viscosity: 1285 mPa.s (10s-1)

3.6.2 Dosage testing

The dosage test helps to identify optimal design conditions for dispersant use and was performed with DOR/DER of 1:25, 1:50, 1:100 and 1:200, and with no dispersant added. Dosage testing at 13 °C was performed using Dasic Slickgone NS on Breidablikk emulsion (200°C+ / 50 vol. %). Dasic Slickgone NS is the main dispersant agent in NOFO's stockpile today. Results from the dosage testing are presented in Table 3-12. Examples (images) from the dosage testing (MNS test) on Breidablikk are given in Figure 3-12.

The tests show a clear dosage dependant effect for the low-energy test (IFP). The DOR/DER 1:25 showed the highest effect of 74% and was reduced to 37% with DOR/DER 1:50 and showed almost no effect (8%) with DOR/DER 1:200. The MNS test gave high dispersion effectiveness for alle the dosage tested, but dosage of 1:25 and 1:50 clearly produced smaller oil droplets compared to the lower dosages of 1:100 and 1:200. With no dispersant added to the emulsion, the wave declined, and the oil was spread out as a thin layer on the water surface. It was therefore and not possible to take good samples for testing. Images from the MNS testing are shown in Figure 3-6.

PROJECT NO. 302007285 REPORT NO. 2023:00459 1.0 VERSION Page 18 of 72



Table 3-12 Dosage testing on 200°C+/50% emulsion of Breidablikk at 13 °C.

Dispersant (dispersant-to- emulsion ratio)	% Effectiveness 200 °C+/ 50%* IFP	% Effectiveness 200 °C+/ 50%* MNS	
Dasic NS (1:25)	74	100	
Dasic NS (1:50)	37	100	
Dasic NS (1:100)	15	100	
Dasic NS (1:200)	8	85	

^{*} Emulsion viscosity: 1285-1287 mPa.s (10s-1)







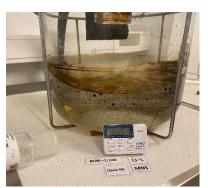


Figure 3-6 Example MNS high energy test on 200°C+ 50% emulsion (Breidablikk). Upper Left to right: After adding DOR/DER 1:25, 1:50 and 1:100 of Dasic Slickgone NS. Below: After adding DOR/DER 1:200 of Dasic Slickgone and no dispersant added on the emulsion (the wave energy stopped, and the oil was spread as a layer on the water surface).

3.6.3 Systematic dispersant testing and dispersibility limits

A dispersant-to oil-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 5 and 13 °C are shown in Figure 3-7 and tabulated in Table 3-13.



Table 3-13 Systematic testing and effectiveness of Dasic Slickgone NS on Breidablikk at 5°C.

Breidablikk	Water content (vol. %)	Viscosity 5 °C (mPa.s) 10 s ⁻¹	Effectiveness (%) IFP	Effectiveness (%) MNS
150°C+	0	351	72	100
200°C+	0	473	76	100
250°C+	0	1154	68	100
150°C+	50	1986	72	100
200°C+	50	2485	74	100
250°C+	50	5659	72	56
150°C+	75	7984	26	30
200°C+	75	9975	31	5
250°C+	75	-	-	-
150°C+	77	9547	21	6
200°C+	73	8290	54	47
250°C+	62	8870	61	46

^{-:}No data

Table 3-14 Systematic testing and effectiveness of Dasic Slickgone NS on Breidablikk at 13 °C.

Breidablikk Water content		Viscosity 13 °C (mPa.s)	Effectiveness (%) IFP	Effectiveness (%) MNS	
	(vol. %)	10 s ⁻¹			
150°C+	0	152	63	100	
200°C+	0	193	68	100	
250°C+	0	447	57	100	
150°C+	50	1062	70	100	
200°C+	50	1285	74	100	
250°C+	50	2562	68	100	
150°C+	75	4523	50	42	
200°C+	75	5830	48	26	
250°C+	75	10669	14	5	
150°C+	82	17344	6	5	
200°C+	80	12647	11	5	
250°C+	72	8856	36	16	



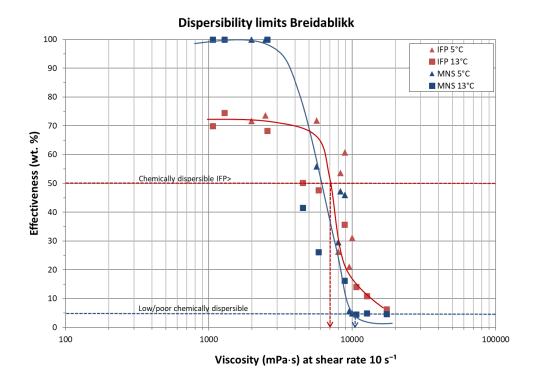


Figure 3-7 Dispersant effectiveness limits of Breidablikk.

Breidablikk was estimated to be good chemically dispersible for viscosities lower than 7000 mPa.s (IFP test) and found not or poor chemically dispersible >10500 mPa.s based on the high energy MNS-test, reflecting breaking waves conditions (>5 m/s wind speeds). Breidablikk is expected to be reduced dispersible with viscosities between 7000 and 10500 mPa.s, this means that the oil is still dispersible but may require additional energy and/or higher dispersant dosage or multiple applications to enhance effective dispersion. The dispersibility limits are also summarised in Table 3-15.

<u>Table 3-15</u> Estimated viscosity limits for Breidablikk for use of dispersant and definition of time window.

Dispersibility	Criteria for effectiveness (wt. %)	Dispersibility limits based on emulsion viscosity (mPa.s)
Good chemically dispersible	IPF >50%	7000
Not/poor chemically dispersible	MNS < 5 %	10500

 PROJECT NO.
 REPORT NO. 2023:00459
 VERSION
 Page 21 of 72

 1.0
 1.0
 1.0



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 Breidablikk was conducted at 5 and 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 Breidablikk 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.

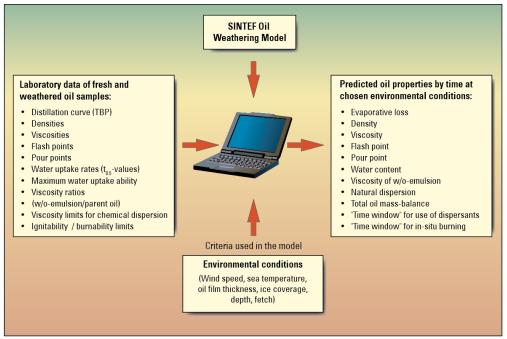


Figure 4-1 Schematic input data to the SINTEF OWM and the predicted output oil properties.

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. Breidablikk is categorized as an emulsifying oil in OWM with 1 mm terminal film thickness.

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 seawater temperatures chosen for Breidablikk predictions was 5 and 15 °C, reflecting typically winter and summer conditions.

PROJECT NO. 302007285 REPORT NO. 2023:00459 1.0 VERSION Page 22 of 72



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

5.2 Predictions of weathering properties of Breidablikk

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 m³/hour or 1900 m³/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 5-2 and Table 5-3 gives an example of predicted weathering properties for Breidablikk.



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

Weathering properties	12 hours 5 °C 2 m/s	12 hours 5 °C 5 m/s	12 hours 5 °C 10 m/s	12 hours 5 °C 15 m/s
Evaporation, wt. %	6	8	10	12
Flash point, °C	84	92	104	112
Pour Point, °C	-18	-17	-15	-14
Water content, vol.%	13	41	61	62
Viscosity, mPa.s *	840	2690	9890	13290
Mass balance / Oil on surface wt.%	94	91	74	37

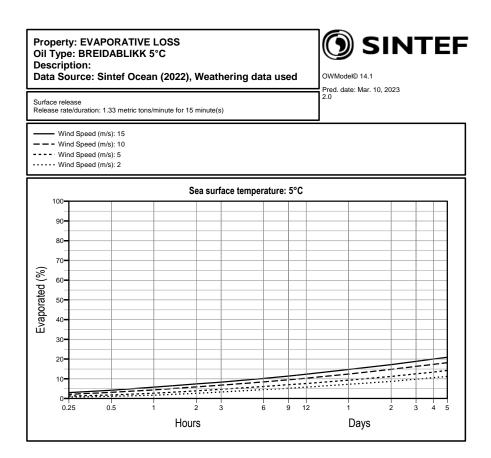
^{*}mPa.s = cP (mPa.s: SI-standard / cP: Industrial denotation)

Table 4-3 Example of weathering properties of Breidablikk obtained from the OWM predictions after 12 hours of weathering at 2, 5 and 10 m/s at 15 °C.

Weathering properties	12 hours 15 °C	12 hours 15 °C	12 hours 15 °C	12 hours 15 °C
	2 m/s	5 m/s	10 m/s	15 m/s
Evaporation, wt. %	7	10	13	16
Flash point, °C	90	100	116	127
Pour Point, °C	-17	-16	-14	-127
Water content, vol.%	29	64	72	73
Viscosity, mPa.s *	580	4330	12180	16560
Mass balance / Oil on surface wt.%	93	89	73	37

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





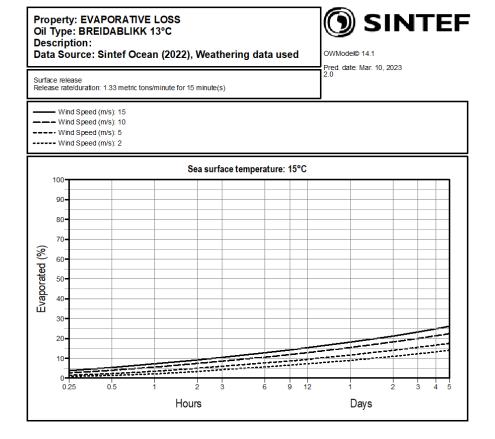


Figure 5-2 Evaporative loss of Breidablikk predicted at sea temperatures of 5 and 15 °C.

 PROJECT NO.
 VERSION
 Page 25 of 72

 302007285
 1.0



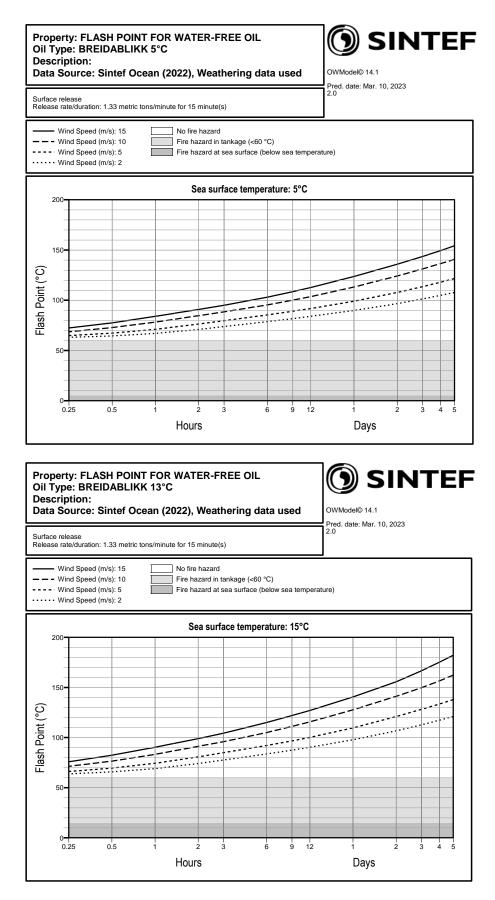


Figure 5-3 Flash point of water-free Breidablikk predicted at sea temperatures of 5 and 15 °C.



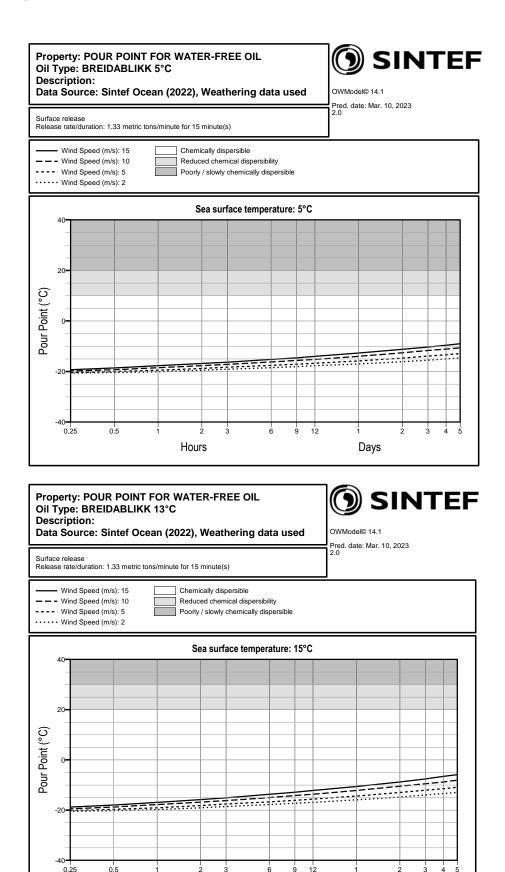


Figure 5-4 Pour point of water-free Breidablikk predicted at sea temperatures of 5 and 15 °C.

Hours

Days



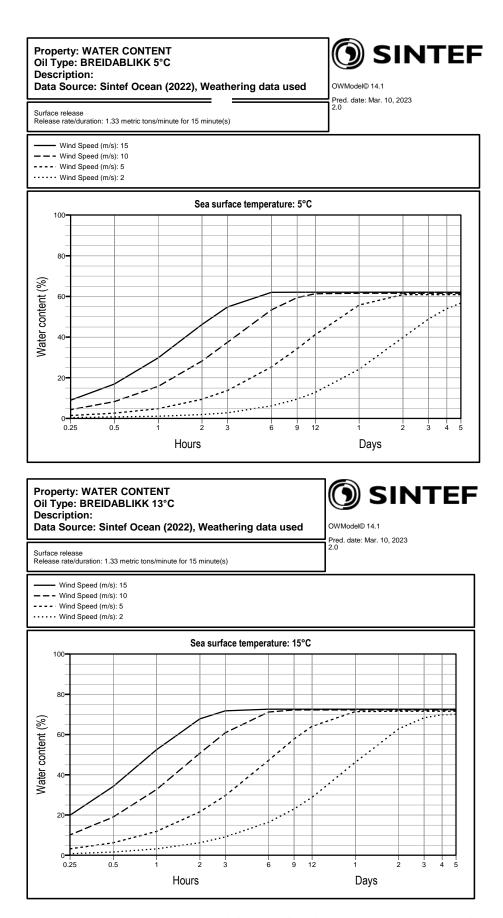


Figure 5-5 Water content of Breidablikk predicted at sea temperatures of 5 and 15 °C.



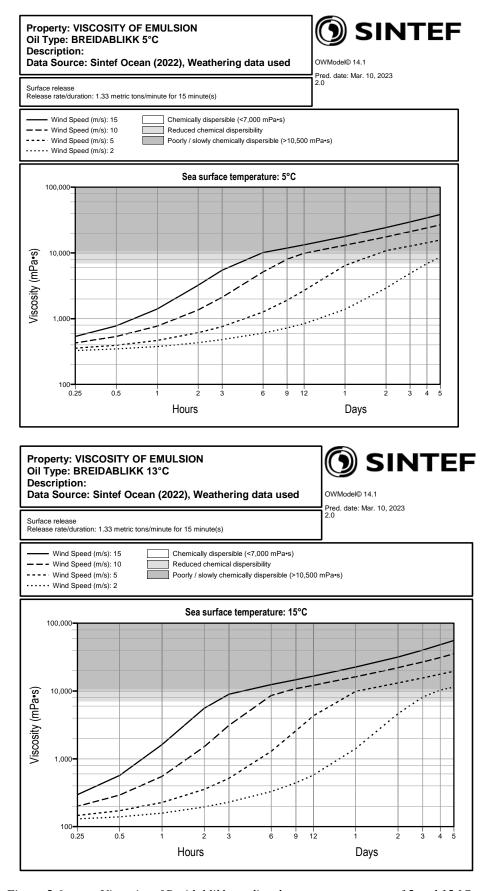


Figure 5-6 Viscosity of Breidablikk predicted at sea temperatures of 5 and 15 °C.



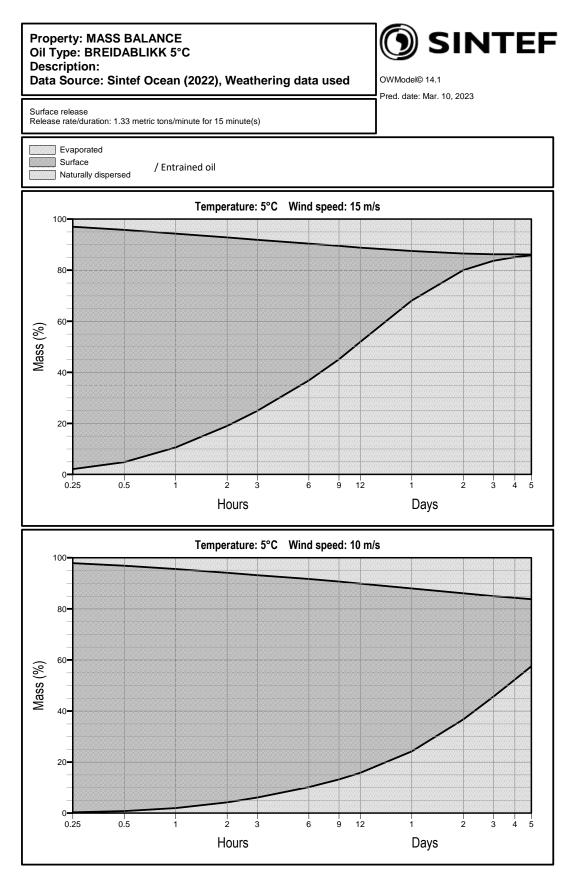


Figure 5-7 Predicted mass balance of Breidablikk predicted 5 °C, wind speeds of 2 and 5 m/s.

PROJECT NO. 302007285



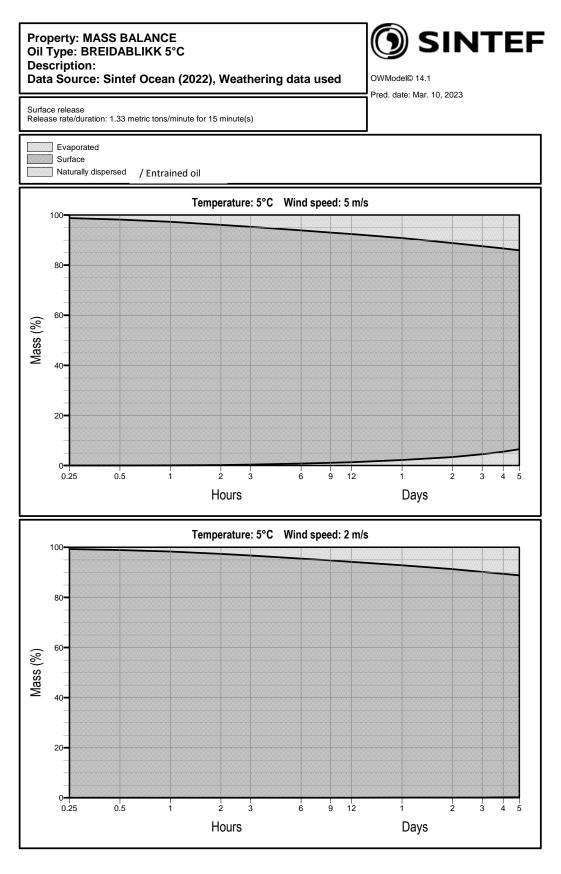


Figure 5-8 Predicted mass balance of Breidablikk predicted 5 °C, wind speeds of 10 and 15 m/s.

PROJECT NO. 302007285

REPORT NO. 2023:00459



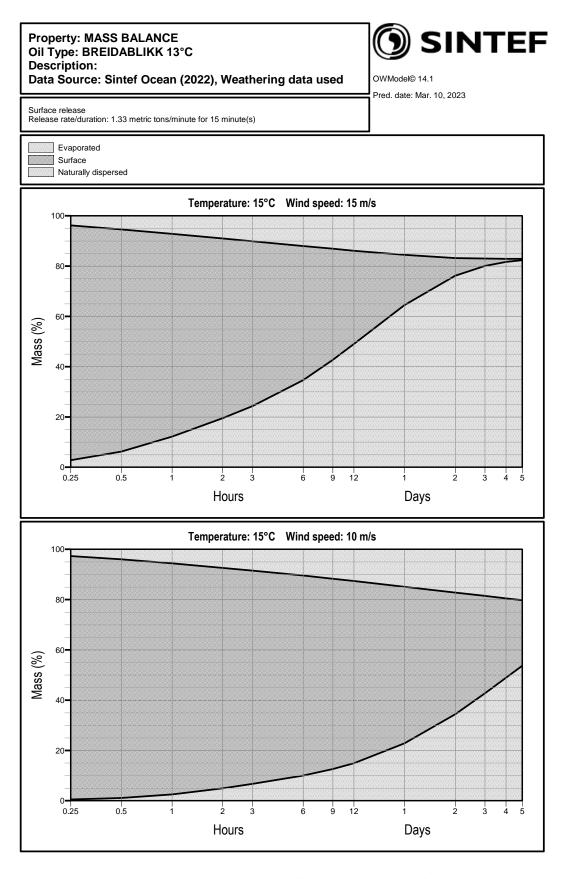


Figure 5-9 Predicted mass balance of Breidablikk predicted 15 °C, wind speeds of 2 and 5 m/s.

 PROJECT NO.
 REPORT NO. 2023:00459
 VERSION
 Page 32 of 72

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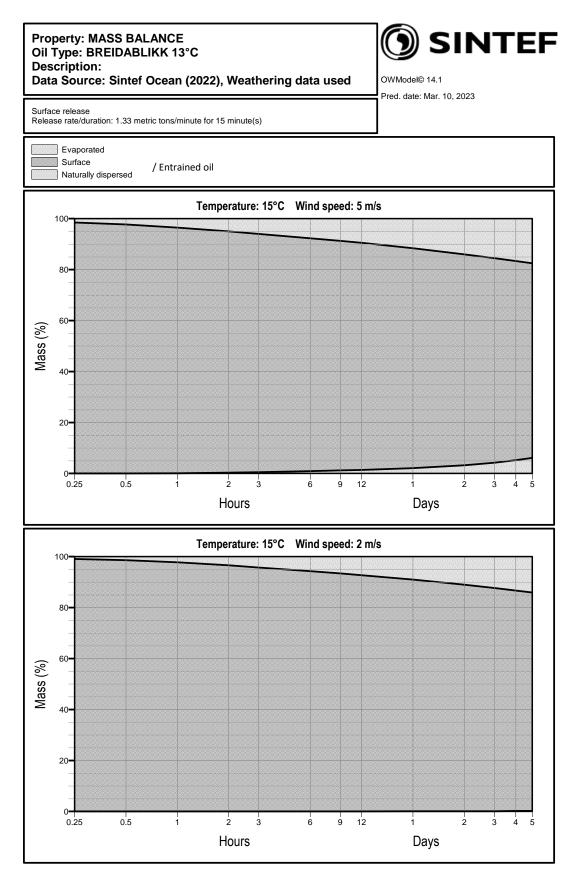


Figure 5-10 Predicted mass balance of Breidablikk predicted 15 °C, wind speeds of 10 and 15 m/s.

PROJECT NO. 302007285



6 Comparison of OWM predictions

Weathering predictions from surface release of Breidablikk were compared with predictions of Grane and Balder. The prediction scenario for comparison is based on sea temperature of 15 °C and wind speed of 10 m/s.

6.1 Evaporative loss

Evaporation is one of the natural processes that helps reducing the surface oil volume if the oil is spilled at sea. The evaporative loss of Breidablikk show similarities with Grane and Balder, and most similar to Balder (Figure 6-1).

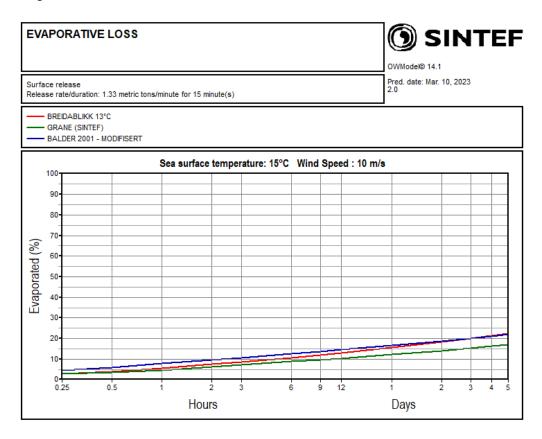


Figure 6-1 Predicted evaporative loss at 15 °C and 10 m/s for Breidablikk in comparison with Grane and Balder.



6.2 Flash point

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

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

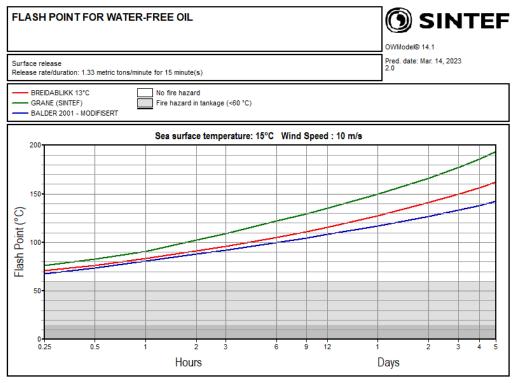


Figure 6-2 Predicted flash point at 15 °C and 10 m/s for Breidablikk in comparison with Grane and Balder.



6.3 Pour point

The pour points of the asphaltenic crude oils of Breidablikk, Grane and Balder show very low pour points of the waterfree residues (Figure 6-3). Breidablikk exhibits lower pour pints after some days weathering at sea predictions compared with Grane and Balder. Solidification at sea is not likely for these crude oils if spilled at sea

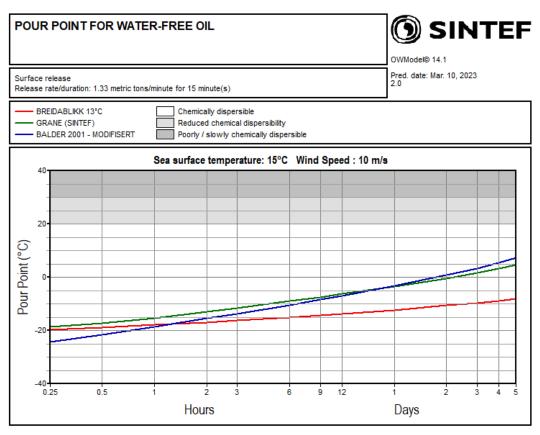


Figure 6-3 Predicted pour point at 15 °C and 10 m/s for Breidablikk in comparison with Grane and Balder.



6.4 Water uptake

The water uptake of Breidablikk compared with Grane and Balder is shown in Figure 6-4. Breidablikk and Balder reaches a maximum water uptake of about 73-75vol.% and follow very similar kinetics (rate of the water uptake). Grane reaches a lower maximum water uptake of 65vol.%, but the kinetics is very similar during the first hours.

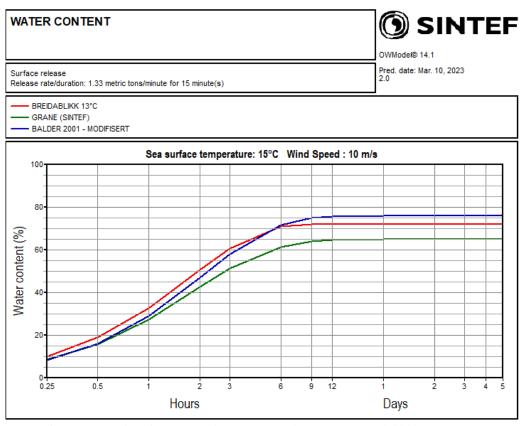


Figure 6-4 Predicted water uptake at 15 °C and 10 m/s for Breidablikk in comparison Grane and Balder.



6.5 Emulsion viscosity

Figure 6-5 shows the predicted (emulsion) viscosities of Breidablikk, Grane and Balder. The viscosity of Breidablikk is somewhat lower than Grane and Balder during the first 6 hours, but then increases and reach a very similar viscosity as Grane and Balder within 5 days of weathering at sea.

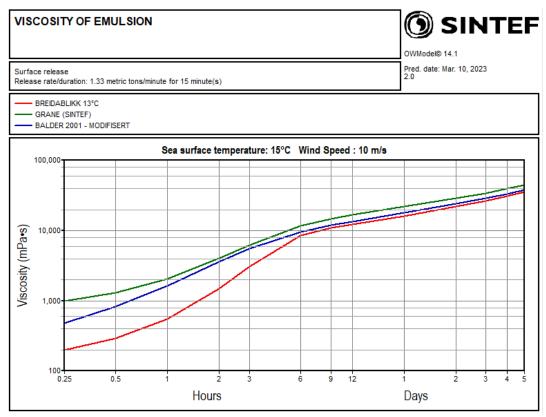


Figure 6-5 Predicted (emulsion) viscosity at 15 °C and 10 m/s for Breidablikk in comparison Grane and Balder.



6.6 Surface oil and emulsion

The predicted surface oil volume is based on the evaporative loss, natural dispersion/entrainment, whilst surface emulsion also includes emulsification that may increase the oil volume subsequently. Figure 6-6 shows the predicted mass balance of remaining surface oil and surface emulsion as a function of weathering of the oils in comparison. The mass balance (surface oil) of Breidablikk is most like Balder, similar for surface emulsion due to emulsification (water uptake). Moreover, the oils in comparison are all persistent on the sea surface with a predicted lifetime >5 days.

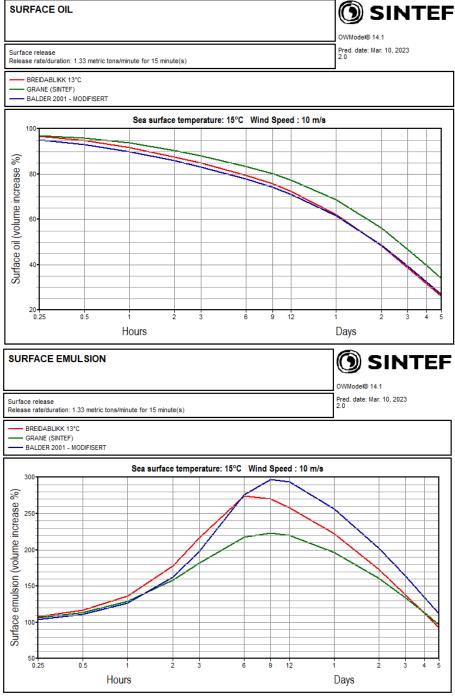


Figure 6-6 Predicted remaining surface oil (above) and surface emulsion (below) at 15 °C and 10 m/s for Breidablikk in comparison with Grane and Balder.



7 Weathering properties and response of Breidablikk (surface release)

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. 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 is also discussed in this chapter.

7.1 Oil properties

The specific physico-chemical parameters of Breidablikk are input to SINTEF OWM for oil weathering predictions. The physico-chemical analysis of the fresh and topped residues show that Breidablikk is a heavy asphaltenic crude oil with a density of 0.913 g/mL, with a low contents of wax (1.81 wt.%) and a medium to high content of asphaltenes (0.77 wt. %). Breidablikk has a low evaporative loss of 12 vol.% for the 250°C+ residue. The fresh oil has a viscosity of 126 mPa.s at 13°C (10s⁻¹) that increases by evaporation to 447 mPa.s for the 250°C+ residue. The fresh oil has a low pour point of -21 °C and low pour points of its waterfree residues -15 °C of the 250°C+.

7.2 Flash point - Fire/explosion hazard

Flash point refers to the lowest temperature at which an oil can vaporize to form an ignitable mixture in the air. In case of an oil release on the sea surface, the 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.

Due to the low content of volatiles in the Breidablikk crude, the flash points for Breidablikk are high compared to many other crude oils. Already within 15 minutes after a standardized surface release (80 m³/ h) prediction at 5 and 15 °C, at wind speeds of 2-15 m/s, the predicted flash points are higher than 60°C (Figure 5-3 and Figure 7-1). However, care should be taken during the first hours, and use of an explosimeter is recommended. The release rate may influence the rate of evaporation. For a considerably larger (batch) release rates e.g.,100 times higher (8000 m³/h), the rate of evaporative loss can be reduced particularly for the first hours after the release due to thicker oil layer, and such high batch releases could be for example incident scenarios in connection to blowouts, pipeline ruptures or tanker loadings. However, for Breidablikk the higher release showed very similar predictions as for the standardized batch release as shown in Figure 7-1.

Moreover, some vessels/storage tanks engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60°C, e.g., towing vessels, smaller cargo, or other vessels available in an emergency. However, for oil recovery vessels (e.g., NOFO's ORO vessels) with A class certification for transport of liquids (Class I/II, flash point <60 °C), there should not be any risks in storing the recovered emulsion in such tanks. According to NOFO's "ORO-manual" the aeration tubes should be place minimum 2.4 m above deck-levels, and aeration Zones (ex-zones) will be established onboard, that will be manually controlled with explosimeters during a response operation.

As a general recommendation after an acute oil spill involving free gas (e.g., from an 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.



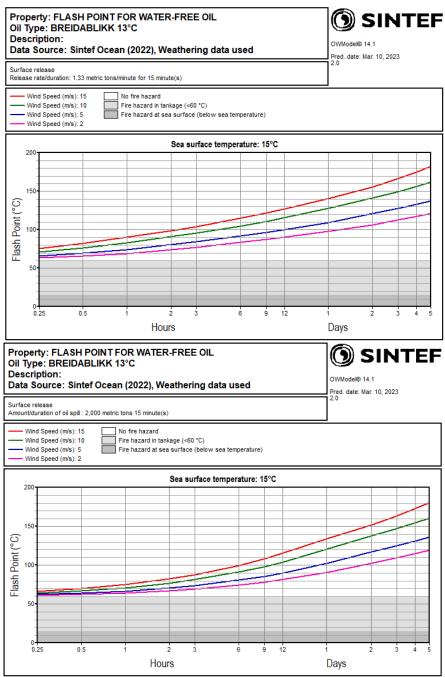


Figure 7-1 Predicted flash points for Breidablikk at 15°C (upper) with a release rate of $80m^3/h$, and below) with release rate $8000 m^3/h$.

7.3 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. However, Breidablikk has low high pour points of its residues (-21 to -15 °C), and possible remaining water-free residue

 PROJECT NO.
 REPORT NO. 2023:00459
 VERSION
 Page 41 of 72

 1.0
 1.0
 1.0



is therefore not likely to solidify at sea either in summer or winter conditions as shown for the pour point prediction in Figure 5-4.

7.4 Emulsion formation

The total amount of oil on the sea is reduced due to evaporation and natural dispersion in the early stages of weathering. However, as water is mixed into the oil and emulsions are formed, the total volume will increase. Figure 7-2 shows an example of the predicted mass balance of remaining surface emulsion and surface oil as a function of weathering of Breidablikk at 10 m/s windspeed at 5 and 15 °C. The figure shows an increase in the volume of emulsion relative to the volume og released oil with a factor of approximately 2-2.5.

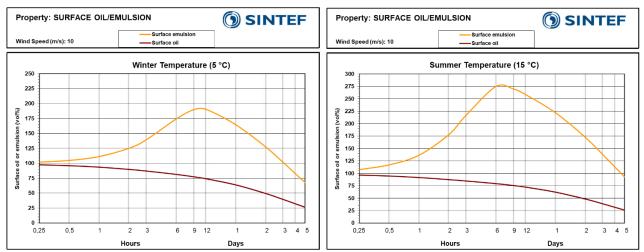


Figure 7-2 Difference in the total slick volume due to emulsification compared to non-emulsified oil of Breidablikk. Decrease in total volume due to evaporation and natural dispersion at 10 m/s wind speed at temperatures of 5 °C and 15 °C.

7.5 Entrained 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). Entrained oil and evaporation are the main weathering processes that reduce the surface oil volume from a spill. 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 7-3 shows the predicted remaining surface oil over time for different wind speeds at 5 and 15 °C for Breidablikk. There is only some minor difference in lifetime between 5 and 15 °C for Breidablikk. At high wind speeds of 15 m/s, no oil is predicted to remain on the sea surface after 4-5 days of weathering at 5 and 15 °C. Lower wind speeds will not provide sufficient energy to remove Breidablikk entirely from the surface within the first 5 days. For the lowest wind speed (2 m/s), the prediction indicates about 85-89 % of the spilled oil remains on the sea surface after 5 days at summer and winter conditions. Considerably larger spills are expected to produce longer lifetimes, and specific modelling may be necessary.

PROJECT NO. 302007285 REPORT NO. **2023:00459** UVERSION Page 42 of 72



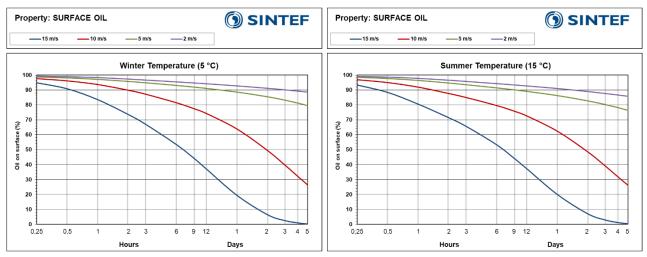


Figure 7-3 Remaining surface oil under different sea states for Breidablikk at 5 °C and 15 °C. Release rate 80m³/h.

7.6 Film thickness from surface release

In general, mechanical recovery requires normal minimum film thickness >0.1-0.2 mm. Film thickness >0.05-0.1 mm is considered for application of oil spill dispersants. Lower film thicknesses are likely to disperse naturally under breaking waves conditions and may be enhanced in non-breaking waves by mechanical dispersion (chapter 7.7). Figure 7-4 shows the predicted film thickness of Breidablikk for a surface release at 5 and 15 °C with an initial surface release of 80 m³/h, if the initial film thickness of the oil is sufficient high to emulsify, i.e., typically >0.1 mm. The increase in film thickness after few hours is due to emulsification that is most pronounced at 15 °C (summer conditions) than at 5 °C (winter conditions). Other factors than film thickness should also be considered when evaluate response options, as described in the next chapters.

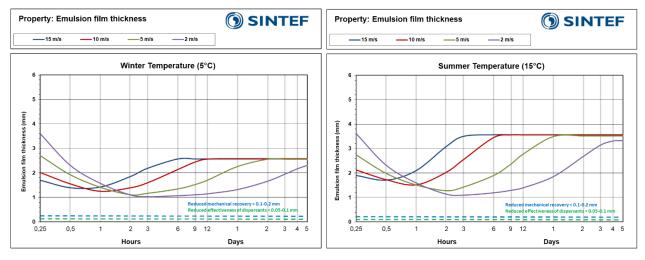


Figure 7-4 Predicted film thickness of Breidablikk emulsion from a surface (batch) release at 5 and 15 °C with terminal film thickness of 1 mm water-free oil (80 m^3/h).

7.6 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

PROJECT NO. 302007285 REPORT NO. 2023:00459 L.0 VERSION Page 43 of 72



operational speed of recovery vessel and current weather conditions will also influence on the risk of boom leakage.

Generally, for many oils, 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 HiVisc. skimmers (20-50 000 mPa.s), and primary HiVisc. skimmer (>50 000 mPa.s).

The emulsion viscosities of Breidablikk are shown in Figure 7-5 at 5 and 15 °C. For boom leakage of confined oil, the emulsion viscosity exceeds 1000 mPa.s between 1.5-2 hours at 10 m/s wind speed, but the time may be stretched up to about 12 hours to 1-day for very low wind speed (2 m/s). Overall, Breidablikk has a wide window of opportunity for use of traditional weir-skimmer head for viscosities <20 000 mPa.s, e.g., 2-3 days at 10 m/s wind speed.

Moreover, Breidablikk 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).

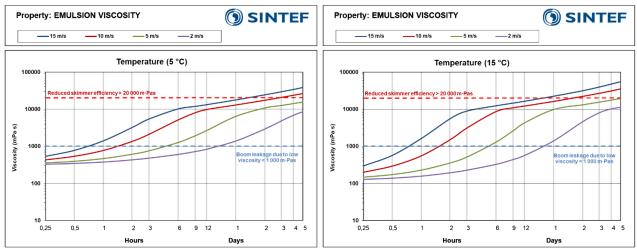


Figure 7-5 Predicted emulsion viscosity for Breidablikk at 5 ° C (left) and 15 °C (right) included expected viscosity limits for boom leakage and poor flow to weir skimmers.

7.7 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 (FiFi) 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 Breidablikk mechanical dispersion by water flushing only is not considered as a main strategy in oil spill response due to the formation of high emulsion film thicknesses (Figure 7-4) by emulsification, even the oil has low emulsion viscosities in the very early stage after an oil spill, as shown in Figure 7-5. The rapidly emulsification of Breidablikk is the limiting factor for this strategy. However, use of water-flushing can be a supplementary method in "peripheral" areas with thin oil films, e.g., metallic /rainbow appearance.

 PROJECT NO.
 REPORT NO. 2023:00459
 VERSION
 Page 44 of 72

 1.0
 1.0



7.8 Chemical dispersion

The viscosity limit for effective dispersant use was estimated to 7000 mPa.s and the viscosity limit for when the emulsified oil is not or poorly dispersible was estimated to 10500 mPa.s. The viscosity limits were based the high energy MNS-test on Breidablikk reflecting breaking waves >5 m/s wind. This means that Breidablikk requires breaking waves to break up a chemically treated slick. In cases where the oil (emulsion) is expected to be reduced dispersible, additional energy or use of a higher dispersant dosage by repeated dispersant application is recommended to possibly enhance the dispersant efficiency. Providing additional energy through use of FiFi systems or thrusters after dispersant application may increase the dispersion effectiveness in calm weather conditions.

The window of opportunity for use of dispersant Dasic Slickgone NS is presented in Figure 7-7 at 5 and 15 °C. The oil-emulsion is e.g., predicted to be (reduced) dispersible up to about 9 hours in winter conditions and about 6 hours in summer conditions, and longer time-windows in calmer wind speeds (2-5 m/s wind speeds). The time window for use of dispersants is somewhat longer at 5 °C then 15 °C due to a more rapid and higher degree of emulsification at summer conditions.

In a spill situation, the use of a simplified dispersibility testing kit is recommended to assess the potential for chemical dispersion.

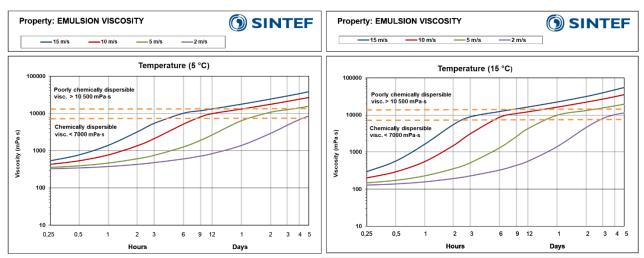


Figure 7-7 Predicted emulsion viscosity for Breidablikk at 5 °C (left) and 15 °C (right) included the dispersibility limits stated in chapter 3.



8 Summary of response options of Breidablikk

Breidablikk is a high density asphaltenic crude oil that forms stable water-in-oil (w/o) emulsion in scenarios where the (initial) film thickness >0.1 mm. An evaluation of a potential subsurface release has not been evaluated for Breidablikk. However, certain scenarios from underwater releases depending on the water depth, gas to oil ratio (GOR), release rate, release rupture diameter etc. may also produce initial film thicknesses >0.1 mm of surfaced oil, otherwise thinner initial oil films can be expected for sub-surface gas/oil releases of e.g., high GORs in shallow waters.

Explosion hazard / flash point:

• Due to the low content of volatiles in the Breidablikk crude, the flash points for Breidablikk are high compared to many other crude oils. Already within 15 minutes after a standardized surface release (80 m³/h) the predicted flash points are higher than 60°C.

Mechanical recovery:

- Breidablikk 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.
- Emulsion breaker (recommended dosage: 2000 ppm relative to the oil) may effectively be used during an oil spill operation to remove or reduce water from the recovered oil/emulsion which minimizes the storage volume.

Use of chemical dispersants:

- Emulsions of Breidablikk is found to be good dispersible with use of Dasic Slickgone NS for viscosities <7000 mPa.s (DOR 1:25) in non-breaking waves (<5m/s wind speeds), and not/poorly dispersible for viscosities >10 500 mPa.s assuming breaking waves conditions (>5m/s wind speeds).
- In the field, additional energy or higher DOR by repeated dispersant application may increase the
 dispersant effectiveness when the oil is reduced dispersible for viscosities in the range of 7000 -10 500
 mPa.s.

Bench-scale dispersant effectiveness of sub-surface dispersant injection (SSDI) has not been included in this study. On-going projects to improve OSCAR's ability to predict the effect of SSDI both environmentally and operationally is presently taking place at SINTEF.

High-capacity water flushing (mechanical dispersion):

- 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 and is therefore not considered as a main response option for emulsions of Breidablikk.
- Mechanical dispersion be used as a supplementary /secondary method on e.g., peripherical areas of thin oil films of metallic/rainbow appearances in calm weather conditions.
- Mechanical dispersion can be used after dispersant treatment under calm sea conditions.

Monitoring and remote sensing:

• Monitoring and remote sensing should be used a support in a response operations for Breidablikk.

This study of the weathering and dispersibility properties of the Breidablikk crude oil has shown many similarities to the Grane crude, i.e.:

- Low evaporative loss
- High flash points
- Low pour points
- Viscosity of emulsion when weathered at sea is slightly higher for Grane than for Breidablikk, resulting to a slower natural dispersion (longer "life-time") of the Grane crude at sea.



• A slightly higher and rapid water uptake rate, and lower viscosity limits for the chemical dispersibility, gives however, some shorter operative "time windows" for effectiveness use of dispersants for Breidablikk compared to Grane.

In spite for these minor differences in weathering and behaviour when spilled at sea between Breidablikk and Grane, the oil spill contingency dimensioned for the Grane oil field should be considered sufficient also for Breidablikk.



9 Categorization of Breidablikk to other Norwegian oil (oil map)

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

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

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

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

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

The categorization of a selection of Norwegian crude oils including Breidablikk is given in Figure 9-1.



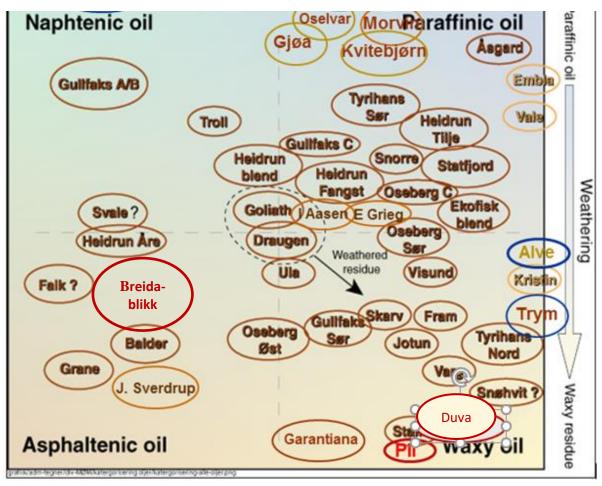


Figure 9-1 Categorization of a selection of Norwegian crude oils from previous studies including Breidablikk, Grane and Balder.



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 PROJECT NO.
 REPORT NO. 2023:00459
 VERSION
 Page 50 of 72

 1.0



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 PROJECT NO.
 VERSION
 Page 51 of 72

 302007285
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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

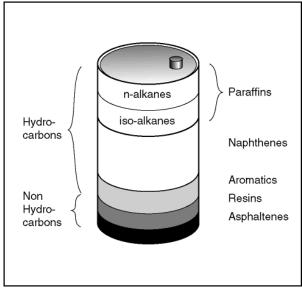


Figure A-1 The chemical composition of crude oils.

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.2Main 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.3Physical 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:

$$^{\circ}$$
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/m², Pa s or kg/(m s), where 1 Pa s = 1 N s/m² = 1 kg/(m s). Absolute viscosity can also be expressed in the metric CGS (centimeter-gram-second) system as g/ (cm s), dyne s/cm² or Poise, where 1 Poise = 1 dyne s/cm² = 1 g/(cm s) = $1/10 \text{ Pa s} = 1/10 \text{ N s/m}^2$. https://www.engineeringtoolbox.com/dynamic-absolute-kinematic-viscosity-d_412.html The industry often uses centipoise, as the *Poise* is normally too large, 1 Poise = 100 cP and 1 cP = 0.001 N s/m^2 . The viscosity of fresh crude oils can vary from less than 1 to more than 2000 mPa.s (cP) at ambient sea temperature. In comparison, water has an "absolute" viscosity of 1 cP and syrup's is 120 000 cP at 20° C.

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

The viscosity of an oil increases with evaporation since the heavier, more viscous components remain in the residue (Mackay et al., 1982). The difference in viscosity for crude oils is approximately 3 to 2000 mPa.s for fresh crude oils and several hundred/thousand mPa.s for their residues. Water-in-oil (w/o) emulsions are generally more viscous than the parent crude oil; this is illustrated in Figure A-2.



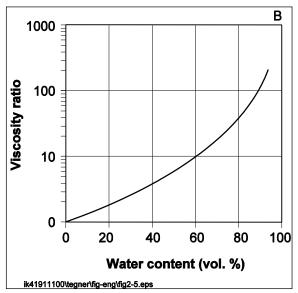


Figure A-2 Example of viscosity ratio as a function of water content.

A.3.2 Pour point

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

A.3.3 Distillation curve

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.4The 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.

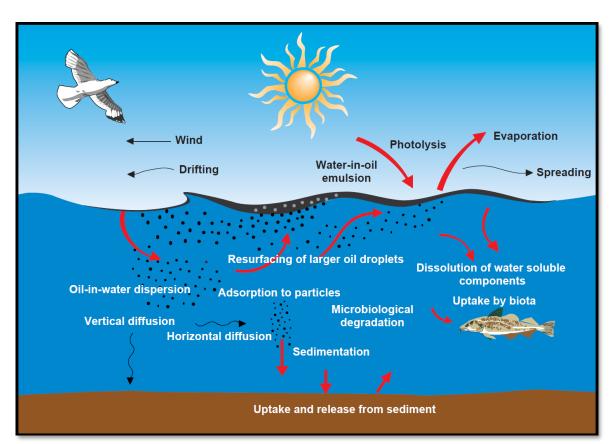


Figure A-3 Illustrating the weathering processes that take place when oil is spilled on the sea surface.



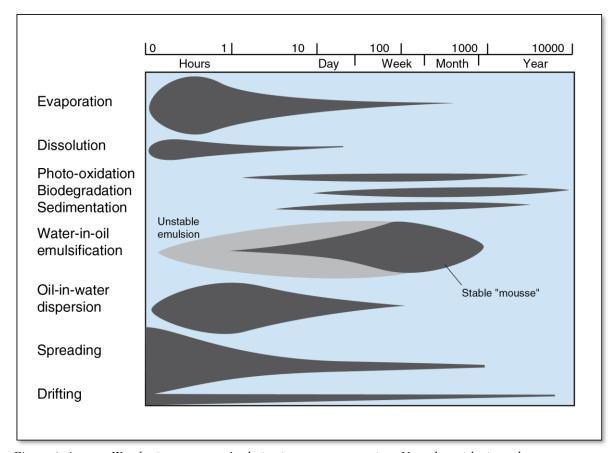


Figure A-4 Weathering processes' relative importance over time. Note: logarithmic scale.

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 ($<1 \mu m$ oil thickness) that only contains 10% of the oil volume. Most of the oil

PROJECT NO. 302007285 REPORT NO. 2023:00459 1.0 VERSION Page 57 of 72



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.

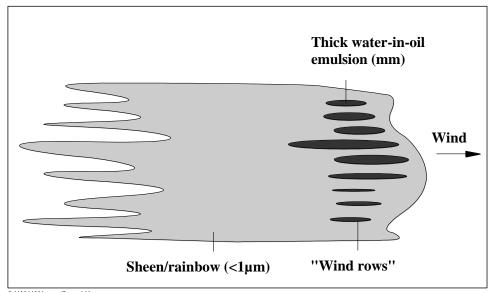


Figure A-5 The spreading of oil spilled on the sea surface and the distribution within the oil slick.

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.

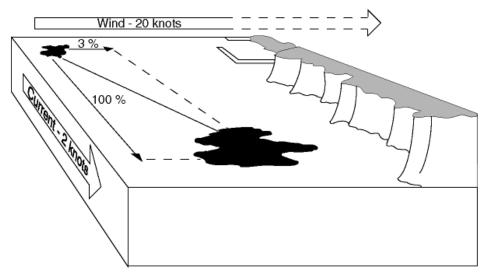


Figure A-6 An illustration showing how wind and current can influence the drifting of an oil slick.



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.

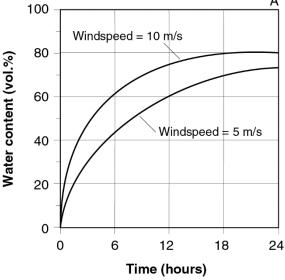


Figure A-7 Example of how weather conditions influence the w/o emulsion formation for typical oils.

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 μ m, yielding a more stable emulsion.

PROJECT NO. 302007285 REPORT NO. **2023:00459** UVERSION Page 59 of 72 1.0



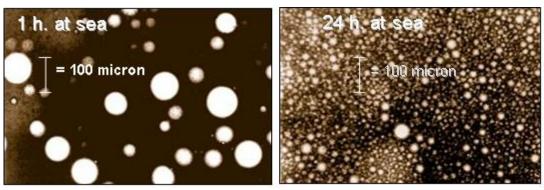


Figure A-8 Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder.

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.

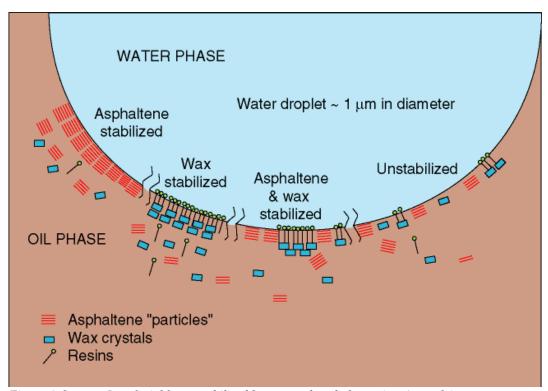


Figure A-9 Interfacial layer stabilized by wax and asphaltenes in w/o emulsion.

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.

PROJECT NO. 302007285 REPORT NO. 2023:00459 Seport No. 2023:00459 REPORT NO. 2023:00459 Seport No. 2023:00459



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 μ m - 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 μ m). 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 $100~\mu m$. 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 C₇) 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.
 VERSION
 Page 61 of 72

 302007285
 1.0



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

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

A.4.9 Sedimentation

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

A.4.10 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

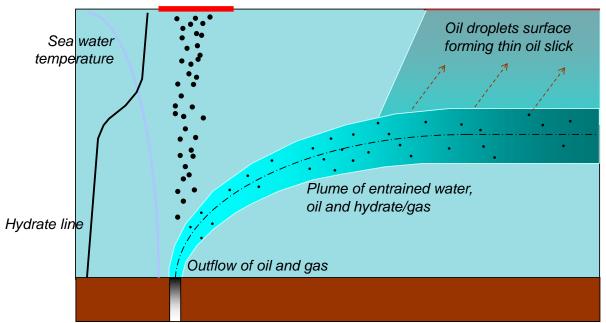


Figure A-10 Illustration of possible creation of thick surface oil slick (> 200 μ m) from deep-water release of oil.

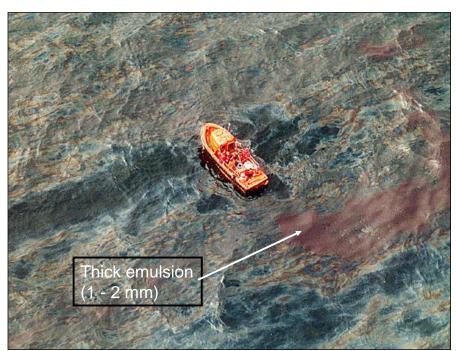


Figure A-11 Surface oil slick (initial thickness > 200 μ m) from the experimental deep-water release "DeepSpill" in 2000. Surface oil is emulsifying like an oil slick from a surface batch release (from Leirvik et al., 2011).



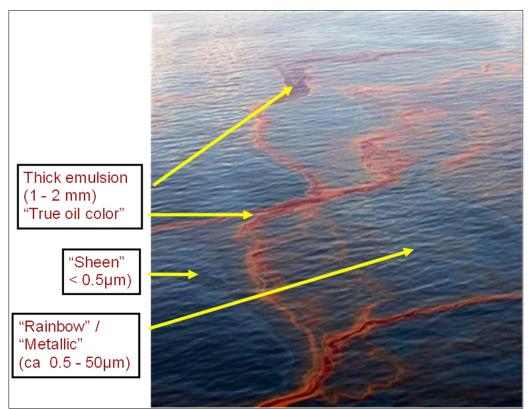


Figure A-12 Surface oil slick (initial thickness > 200 μ m) from the DWH deep-water release. Surface oil is emulsifying like an oil slick from a surface batch release.

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.



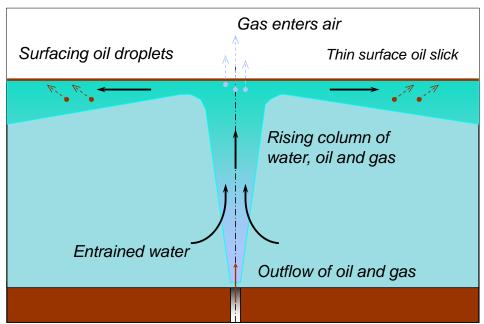


Figure A-13 Illustration of possible creation of thin surface oil slick ($< 200 \, \mu m$) from a shallow subsurface release ($< 500 \, m$).

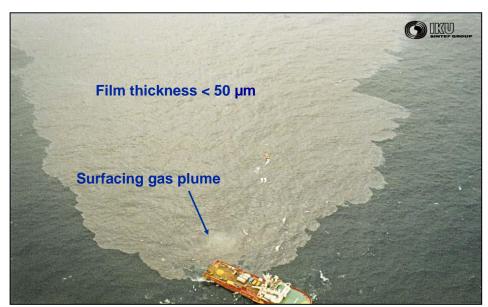


Figure A-14 Surface oil slick ($< 50 \,\mu m$) from experimental subsurface release at 106 m in 1996. The surface oil did not emulsify and had a very limited lifetime (hours) due to the low film thickness and high rate of natural dispersion (even at $< 10 \, m/s$ wind).



B Experimental setup and HSE

B.10il sample and test temperature

SINTEF Ocean received 1x 25litre steel drums of Breidablikk crude oil on 08.09.2022. The sample info: Well 25/11 K-4H from the D-structure. The oil sample were registered in LIMS and given SINTEF ID: 2022-6485.

The weathering dispersibility study (small-scale) were performed at 5 and 13 °C. The oil sample was prehandled, heated to about 50 °C and homogenised before distillation and further analysis.



Figure B-1 Breidablikk crude oil 1x25L. Well: 25/11 K-4 H (D-structure).

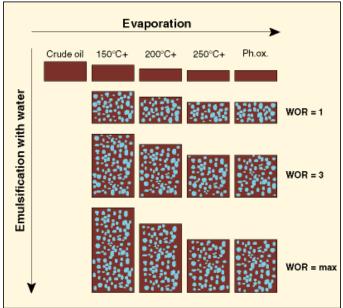
B.2 Water content

Water content in the oil phase was quantified by use Karl Fisher titration for HSE and risk assessment prior to the topping/distillation step to simulate evaporative loss at sea by topping/distillation. The water content was well below the HSE limit < 2 vol. %, and no extra precautions were needed for Breidablikk prior to topping.

B.3Small-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.4Evaporation

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.5Physical 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 (nC₅-nC₄₀) 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 (C₀-C₄) were completed using an Agilent 6890 Gas Chromatograph coupled with 5973 MSD detector (GC-MS) operating in SIM mode (Selected Ion Monitoring)

The volatile components were in the range of nC₅-nC₁₀ 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.6Emulsification 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.

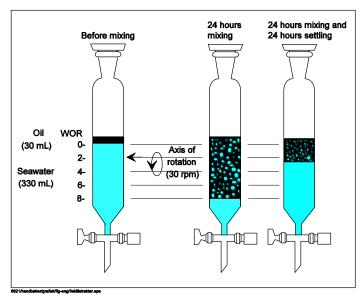


Figure B-3 Principle of the rotating cylinder method

B.7Chemical 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.

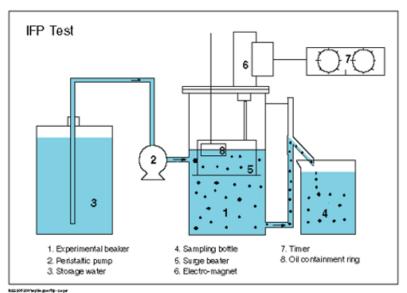
MNS (Mackay-Nadeau-Szeto test, Mackay and Szeto, 1980) is estimated to correspond to a medium to high sea state condition. The energy input in this system, applied by streaming air across the oil/water surface,

 PROJECT NO.
 VERSION
 Page 68 of 72

 302007285
 1.0



produce a circular wave motion. The sample of the oily water is taken under dynamic conditions after a mixing period of 5 min.



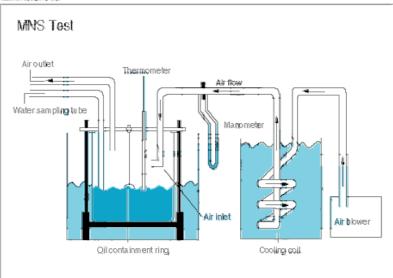


Figure B-4 Laboratory apparatus for effectiveness testing of dispersants.



C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Breidablikk are given from Table C-1 to Table C-4. The oil weathering predictions at 5 and 15 °C were based on the laboratory data at 5 and 13 °C, respectively.

Table C-1 Physical and chemical properties Breidablikk

Properties of fresh oil	Breidablikk
Density (g/mL)	0.913
Pour point (°C)	-21
Reference temperature (°C)	5/13
Viscosity at ref. temp. (mPa·s = cP) *	272 /122
Flash point (°C)	-
Asphaltenes (wt. %)	0.77
Wax Content (wt. %)	1.81
Dispersible for visc. <	7000
Not dispersible for visc. >	10500

^{*} Measured at shear rate 100 s⁻¹-: Not analyzed /no data

Table C-2 True boiling point (TBP) curve of Breidablikk TBP based on results from Intertek Sunbury UK. Report no: 4698596.

Temp. °C	Breidablikk vol. %	Breidablikk, wt%
101	1.4	1
148	3.8	3
199	8.5	7
222	11.9	10
250	18.5	16
293	30.4	27
347	44.2	40
395	54.5	50
443	64.7	60
497	74.6	70
565	84.4	80
606	89.2	85
653	94.0	90
711	98.7	95
739	100.6	97



Table C-3 Lab weathering data for Breidablikk, 5 °C.

Properties	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	242	262	299
Vol. Topped (%)	0	1.8	4.3	12.4
Weight Residue (wt. %)	100	98.6	96.4	89.0
Density (g/mL)	0.9134	0.9167	0.9197	0.9280
Pour point (°C)	-21	-21	-18	-15
Flash Point (°C)	-	63.5	78.0	106
*Viscosity of water-free residue (mPa.s =cP)	297	351	473	1154
Viscosity of 50% emulsion (mPa.s = cP)*	-	1986	2485	5659
Viscosity of 75% emulsion (mPa.s = cP)*	-	7984	9975	-
Viscosity of max water (mPa.s = cP)**	-	9547	8290	8870
Max. water cont. (vol. %)	-	77.3	72.5	62.0
(T1/2) Halftime for water uptake (hrs)	-	0.21	0.27	0.76
Stability ratio	-	0.99	0.97	1

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

Table C-4 Lab weathering data for Breidablikk, 13 °C

Properties	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	242	262	299
Vol. Topped (%)	0	1.8	4.3	12.4
Weight Residue (wt. %)	100	98.6	96.4	89.0
Density (g/mL)	0.9134	0.9167	0.9197	0.9280
Pour point (°C)	-21	-21	-18	-15
Flash Point (°C)	-	63.5	78.0	106
*Viscosity of water-free residue (mPa.s =cP)	126	152	193	447
Viscosity of 50% emulsion (mPa.s = cP)**	-	1062	1285	2562
Viscosity of 75% emulsion (mPa.s = cP)**	-	4523	5830	10669
Viscosity of max water (mPa.s = cP)**	-	17344	12647	8856
Max. water cont. (vol. %)	-	81.8	80.0	72.2
(T1/2) Halftime for water uptake (hrs)	-	0.20	0.20	0.24
Stability ratio	-	1	0.98	1

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



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.

<u>Table D-1</u> Chemical characterization of Breidablikk (fresh oil) from GC-MS analysis and TBP oil fraction

Tuble D-1	Chemic	ai characierization of Bretaablikk (fresh oil) from GC-MS analysis and TBL oil fraction
0.100	1	C1-C4 gasses (dissolved in oil)
0.100	2	C5-saturates (n-/iso-/cyclo)
0.292	3	C6-saturates (n-/iso-/cyclo)
0.008	4	Benzene
0.500	5	C7-saturates (n-/iso-/cyclo)
0.063	6	C1-Benzene (Toluene) et. B
1.937	7	C8-saturates (n-/iso-/cyclo)
0.217	8	C2-Benzene (xylenes; using O-xylene)
1.594	9	C9-saturates (n-/iso-/cyclo)
0.189	10	C3-Benzene
1.000	11	C10-saturates (n-/iso-/cyclo)
0.018	12	C4 and C4 Benzenes
3.982	13	C11-C12 (total sat + aro)
0.000	14	Phenols (C0-C4 alkylated)
0.118	15	Naphthalenes 1 (C0-C1-alkylated)
7.882	16	C13-C14 (total sat + aro)
0.235	18	Naphthalenes 2 (C2-C3-alkylated)
7.765	19	C15-C16 (total sat + aro)
0.226	20	PAH 1 (Medium soluble polyaromatic hydrocarbons (3 rings-non-alkyltd;<4 rings)
7.774	21	C17-C18 (total sat + aro)
7.000	22	C19-C20 (total sat + aro)
9.581	23	C21-C25 (total sat + aro)
0.419	24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)
49.000	25	C25+ (total)

The SINTEF OSCAR model is a 3-dimensional Oil Spill Contingency And Response model system that calculates and records the distribution (as mass and concentrations) of contaminants on the water surface, on shore, in the water column and in sediments. The model allows multiple release sites, each with a specified beginning and end to the release. This allows time-variable releases at a given location, as well as throughout the study area. The model computes surface spreading, 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.