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Report

Vale crude oil
- properties and behaviour at sea

Related to oil spill response

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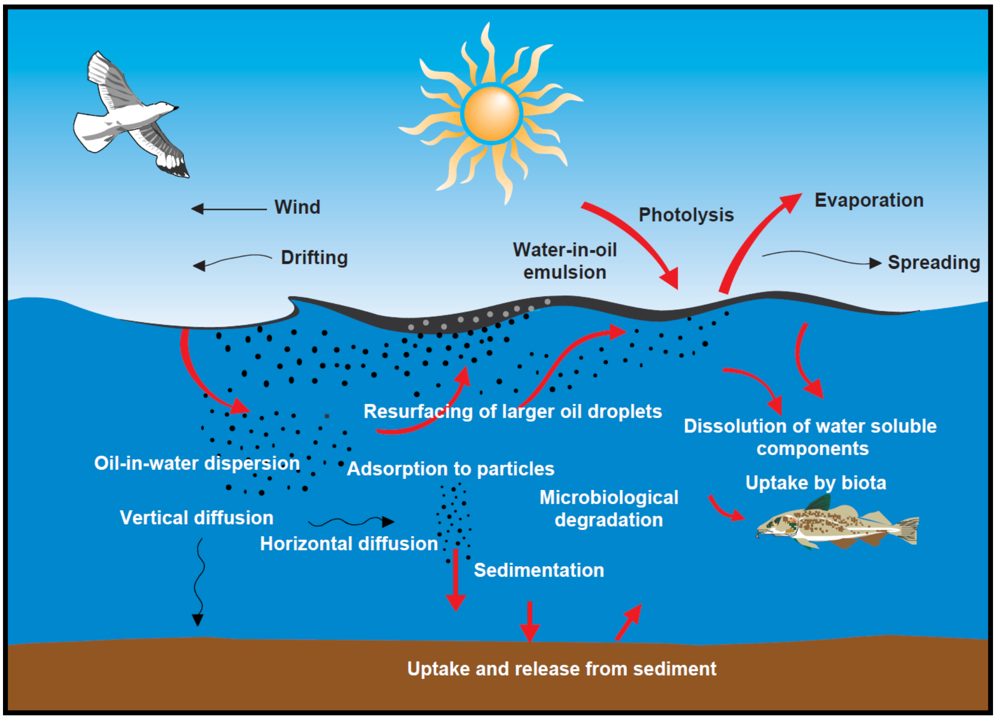

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Marine Environmental Technology
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Report

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- properties and behaviour at sea

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ABSTRACT

A small scale study of the weathering properties of Vale crude oil has been performed at 5°C and 13°C in SINTEFs laboratory. The data are used as input for SINTEF's Oil Weathering Model (OWM) to predict the properties and behaviour of Vale crude oil in a spill situation at sea. The weathering properties are discussed related to oil spill response; mechanical recovery and chemical dispersion.

The oil forms loose emulsions with the potential to form waxy lumps with increasing weathering. It is expected to have good potential for chemical dispersion under breaking wave conditions. Under very calm conditions the dispersant application should be followed by artificial turbulence 0.5-1 h after the treatment.

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1 Executive summary

When weathered on the sea surface, both oils and condensates will encounter changes that affect oil spill countermeasures in different ways, as a function of time and weather conditions. This summary gives a brief overview of changes to Vale crude oil on the sea surface and a summary of properties compared to previous studies.

Vale crude oil is a light paraffinic crude oil with density of 0.816 g/ml, an asphaltene content of 0.03 wt. % and a wax content of 3.3 wt. %. Compared to a previous study of Vale done in 2001 most parameters are fairly similar between the two studies, except from the asphaltene content, which is approximately 50% lower at present date (2013) than in 2001, and wax content, which is slightly lower now. Compared to some other oils of similar type (three light paraffinic oils and a heavy condensate) Vale has a more rapid water uptake and higher emulsion viscosities, but is similar in evaporative loss, flash point, and pour point.

The initial evaporative loss of Vale crude oil is high as 40 % will evaporate within 1 day at sea, even at low wind conditions and winter temperature. This evaporation causes a relative increase in wax content which may result in formation of waxy lumps in low quantity at later stages of weathering (after several days). However, in high sea states (15 m/s) the oil is predicted to have a short lifetime at sea and be naturally dispersed within 12 hours at winter temperatures.

Vale formed unstable w/o-emulsions which are prone to release water under static conditions. Additional stress to the emulsions promotes this water release and in a mechanical recovery situation the emulsion is expected to collapse in storage tank or during the recovery procedure. The risk of boom leakage in mechanical recovery operation is more pronounced for oils with low viscosities (<1000 mPas). As the emulsion viscosities of Vale emulsions are quite low this risk is relevant, especially at higher sea states. The best conditions for mechanical recovery would be calm sea states and slow moving recovery vessels. The Vale emulsions are predicted to remain beneath the viscosity limit of 1000 mPas for 12 hours during calm wind conditions and winter temperatures. It is worth mentioning that emulsion viscosities above 20,000 mPas will reduce skimmer efficiency but that Vale is not predicted to produce emulsions of this viscosity within the first 5 days after a spill.

Vale is expected to have good potential for chemical dispersion. The dispersibility of oil is related to emulsion viscosity and will be reduced when the emulsions reach 3000 mPas, but still chemically dispersible. If the emulsions reach 9000 mPas they are expected to be poorly dispersible. The window of opportunity for chemical dispersion of Vale is within 5 days at 10 m/s in winter temperatures. Calmer sea states and higher temperatures are predicted to prolong this window of opportunity. However, at very calm sea states it is important to apply additional energy after application of the dispersant, in order to soak the oil with dispersant. Such energy can be provided by the use of thrusters, Fire Fighting (Fi-Fi) systems or MOB (man over board) boats.

If oil is spilled on the sea surface it will be cooled to the ambient water temperature within a short period of time. The fire hazard will be greatest as long as the flash point of the oil remains below the sea temperature. For Vale crude oil, the flash point will be above the sea temperature within 1 hour after release, at both winter and summer temperatures.

Some recovery vessels have a flash point limit of 60°C for storage of liquids on board. At low wind speeds this limit will be reached after 8 hours in winter conditions, and faster in summer conditions. Higher wind speeds will cause this limit to be reached much sooner enabling more rapid recovery.

2 Introduction

New oil types (from heavy crude oil to light crude oils and condensates) are continuously coming into production worldwide. Due to large variations in different crude oils' physical and chemical properties, their behaviour and fate may vary greatly if spilled at sea. The "Braer" accident at the Shetlands (1993) and the "Sea Empress" accident in Wales (1996) have demonstrated how different the fate and behaviour of the oils can be when spilled on the sea surface. For that reason, having good knowledge about the expected behaviour of oil at sea in case of an accidental spill is highly valuable.

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

Vale is an oil field, located 16 kilometers north of the Heimdal platform, where the water depth is 115 m. It is a sub-surface construction connected to the Heimdal platform through a pipeline of 16.5 kilometer, where the oil/condensate is processed and for further export. The reservoir consists of sandstone from the Middle Jurassic ephoc, at a depth of approximately 3700 meters.

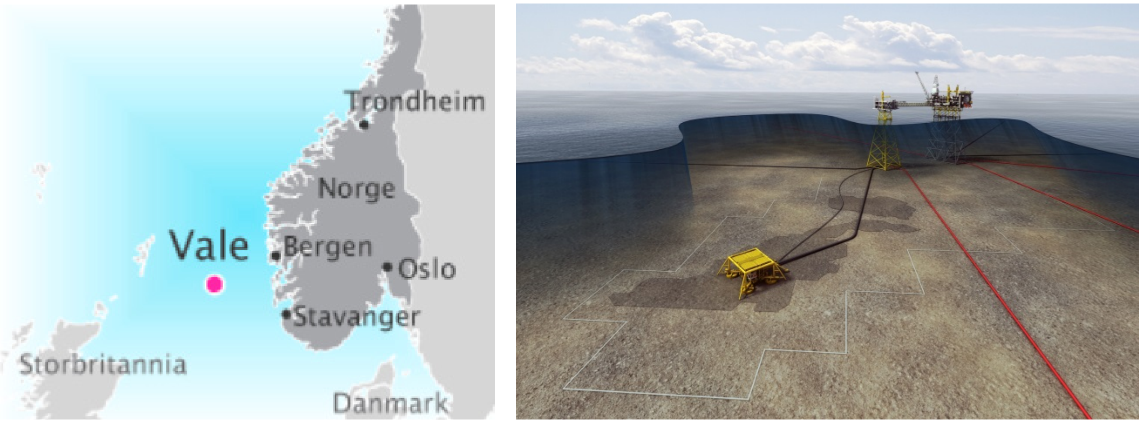


Figure 2-1: Location of the Vale oil fields in the North Sea (left) and the subsea installation (right), (Source: http://www.statoil.com/no/ouroperations/explorationprod/ncs/vale/pages/default.aspx)

According to the Norwegian Environment Agency and the Petroleum Safety Authority Norway (Ptil) regulations for petroleum activities, section 59 (Lovdata, 2012), 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.

Centrica Energi asked for a weathering study of Vale crude oil. The obtained data were used to predict Vales fate and behaviour when spilled at sea under different weathering conditions. The effects of weathering properties on oil spill response options are also discussed.

3 Experimental results

3.1 Small-scale laboratory testing results

The chemical and physical properties of Vale are shown in Figure 3-1 and in Figure 3-2. Appendix B shows the results of the chemical composition of the fresh oil on GC/MS.

The small-scale weathering results of Vale are compared with similar data of other Norwegian oils, listed in Table 3-1. The oils are primarily selected based on their variety in properties and behaviour.

Table 3-1: oils compared to Vale data in the report

Oil	SINTEF ID	Reference (SINTEF report)
Kvitebjørn	2009-0239	Sørheim and Altin, 2009
Trym	2011-0017	Sørheim and Andreassen, 2011
Gjøa	2010-0504	Sørheim et. al, 2011
Oselvar	2011-0602	Strøm, 2012

3.1.1 Chemical composition and physical properties

Gas chromatographic (GC/FID) characterization

The chemical composition of Vale, as characterized by gas chromatography (GC/FID), is shown in Figure 3-1. Gas chromatograms for fresh Vale crude in comparison with other Norwegian crude oils are shown in Figure 3-2. 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, shown as a broad and poorly defined bump below the sharp peaks, are often described as “Unseparated Complex Mixture” (UCM). Heavier compounds such as asphaltenes (> nC_{40}) are not possible to analyse with this technique.

The GC/FID characterization indicates that Vale is a light paraffinic crude oil. As can be seen from the chromatogram in Figure 3-1, Vale fresh oil consist mainly of paraffins in the form of lighter n-alkanes (in the left part of the chromatogram) and have a low UCM hump, which indicating low resin and naphtene content. Other analysis show low medium wax content and low levels of asphaltenes (see Table 3-3). This combined with an evaporative loss >50 % for the 250+ residue, qualifies Vale as a light oil but not qualified as a condensate as a low fraction of the components are above C_{35}.

The nC_{17}/Pristane and nC_{18}/Phytane ratios are important diagnostic ratios indicating the biodegradation of the oil, and are often used in to identification of oil spills. Oil degrading microbes have a natural preference for the n-alkane hydrocarbons (nC_{17} and nC_{18} in this case) compared to the isoprenoids Pristane and Phytane-. These ratios are also an indication of paraffinic content of the oil. These parameters for Vale and the other Norwegian oils are given in

Table *3-2*.

The changes seen in these ratios from 2001 may indicate a small shift in the paraffin content of Vale. Changes have been seen in the wax content as well. Despite these variations there is no significant change in the pour point of Vale.

Table 3-2: nC_{17}/Pristane and nC_{18}/Phytane ratios for Vale fresh oil compared to other Norwegian oil

Oil	nC_{17}/Pristane	nC_{18}/Phytane
Vale	1.7	3.0
Vale 2001	2.2	5.1
Kvitebjørn	1.8	2.4
Trym	1.4	4.0
Gjøa	0.9	1.4
Oselvar	3.8	4.2

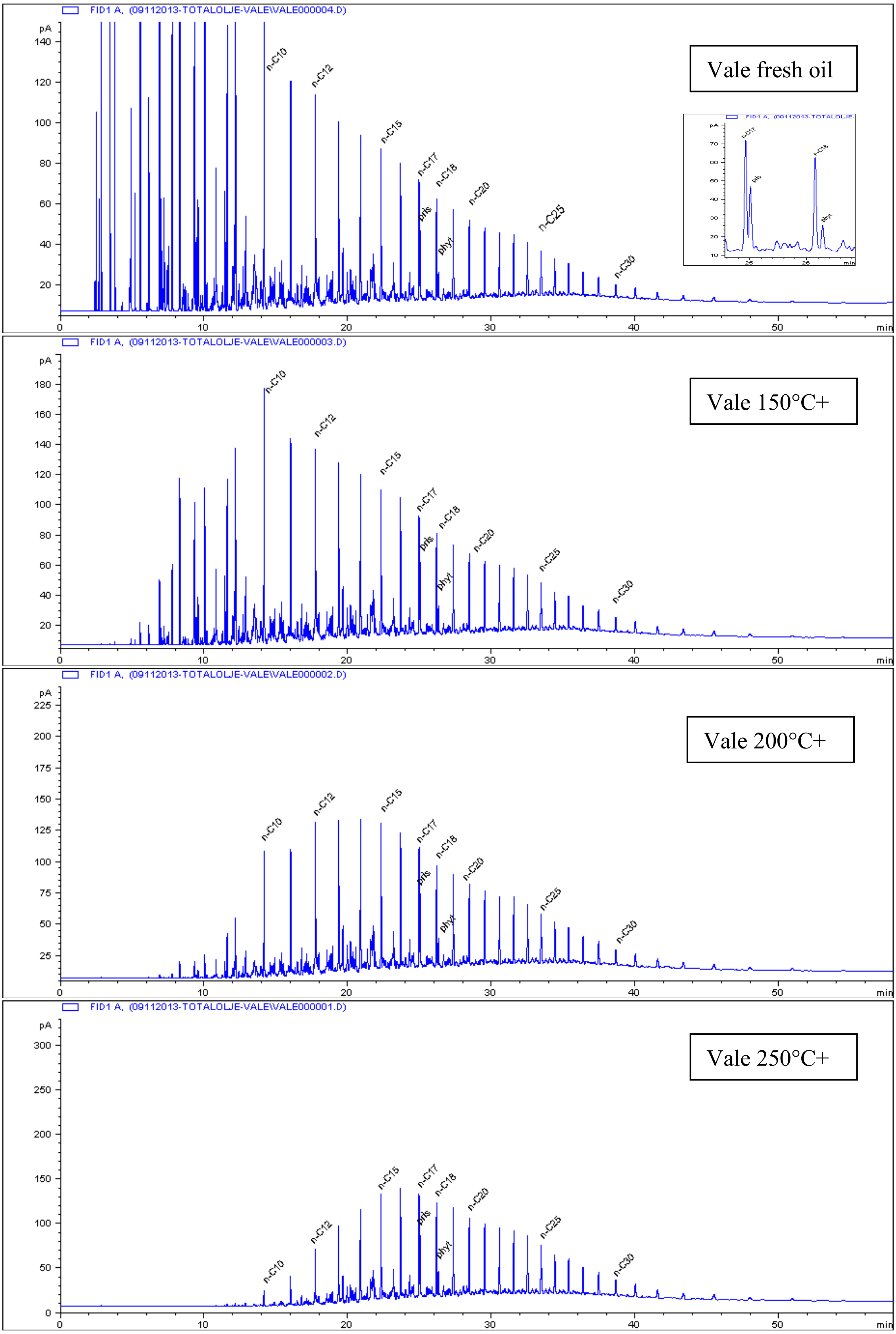
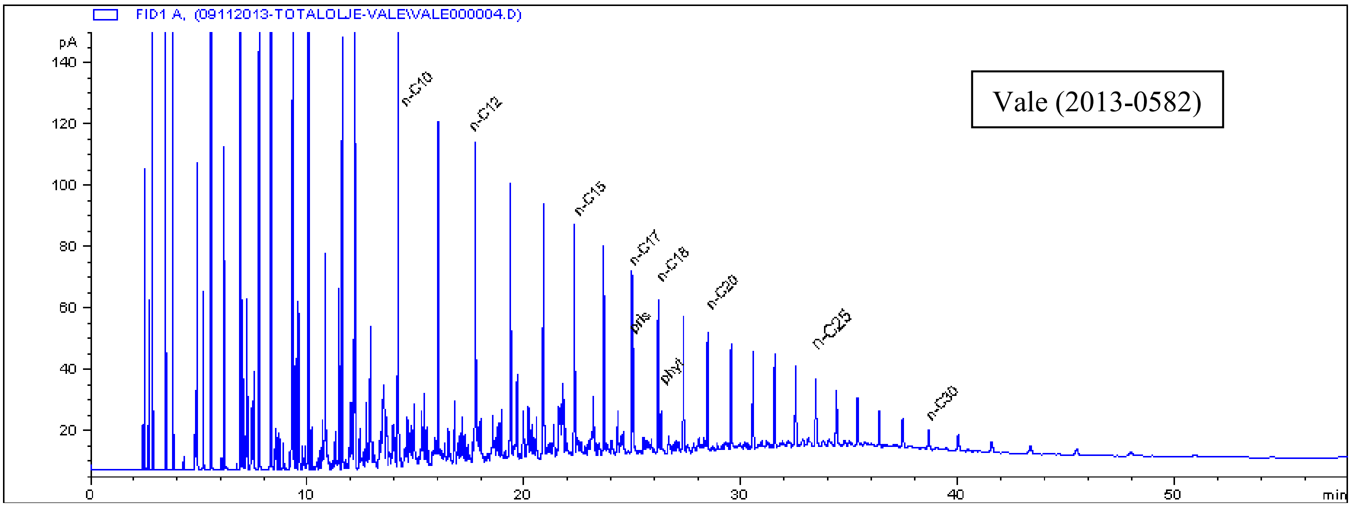
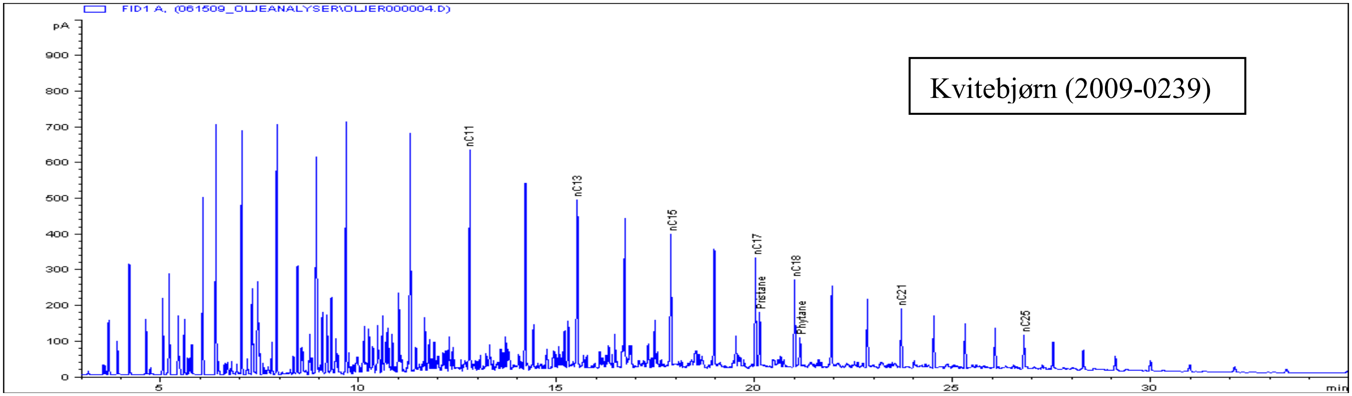
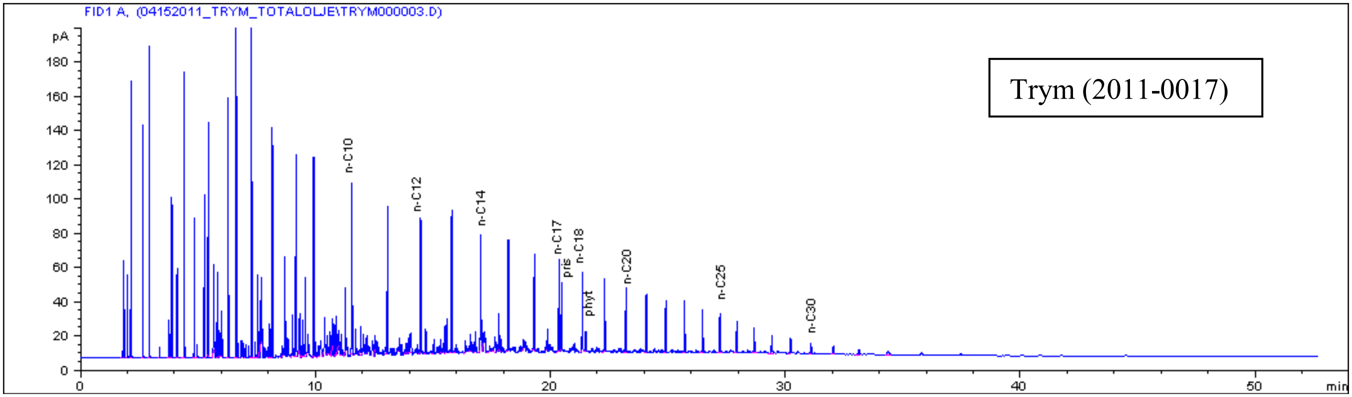
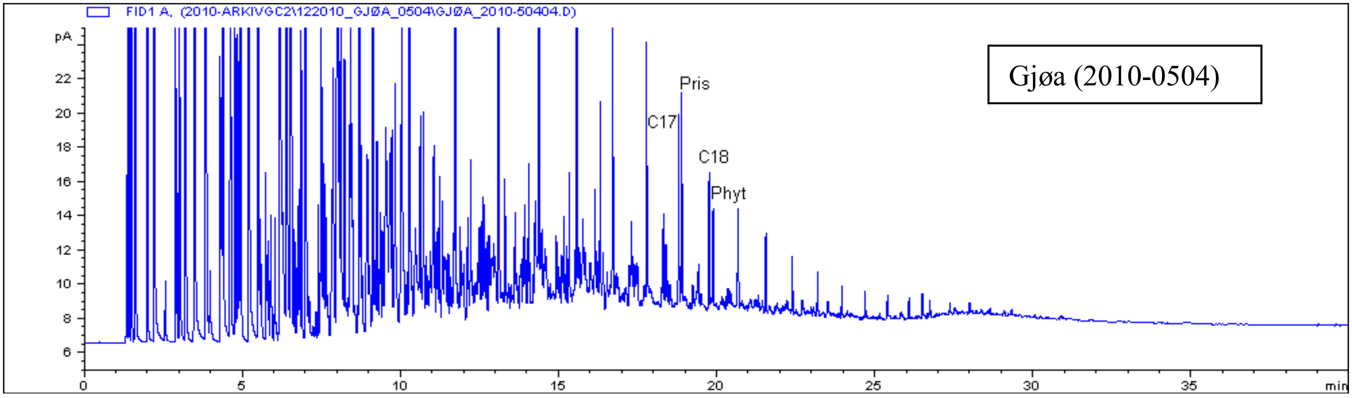


Figure 3-1: GC/FID chromatograms of the fresh and evaporated residues of Vale crude oil.


FID1 A, (09112013-TOTALOLJE-VALE\VALE000004.D)
pA
140
120
100
80
60
40
20
0
10
20
30
40
50
min
n-C10
n-C12
n-C15
n-C17
pris
n-C18
phyt
n-C20
n-C25
n-C30
Vale (2013-0582)


FID1 A, (061509_OLJEANALYSER\OLJER000004.D)
pA
900
800
700
600
500
400
300
200
100
0
5
10
15
20
25
30
min
nC11
nC13
nC15
nC17
Pristane
nC18
Phytane
nC21
nC25
Kvitebjørn (2009-0239)


FID1 A, (04152011_TRYM_TOTALOLJE\TRYM000003.D)
pA
180
160
140
120
100
80
60
40
20
0
0
10
20
30
40
50
min
n-C10
n-C12
n-C14
n-C17
pris
n-C18
phyt
n-C20
n-C25
n-C30
Trym (2011-0017)


FID1 A, (2010-ARKIVGC2\122010_GJØA_0504\GJØA_2010-50404.D)
pA
22
20
18
16
14
12
10
8
6
0
5
10
15
20
25
30
35
min
Pris
C17
C18
Phyt
Gjøa (2010-0504)

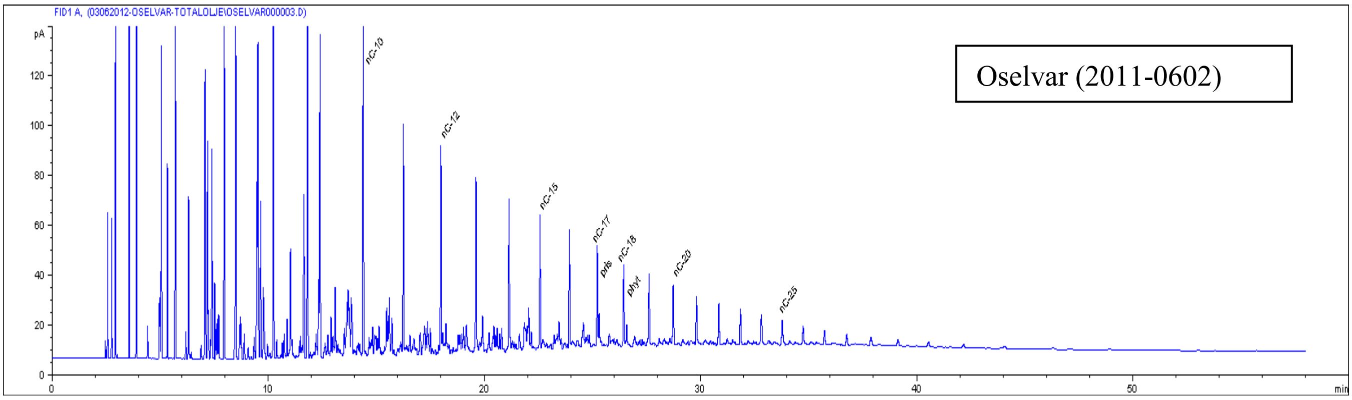


Figure 3-2: GC/FID chromatograms for fresh residues of Vale, Kvitebjørn, Trym, Gjøa and Oselvar, all marked with SINTEF ID.

Asphaltene and wax content

Table 3-3: Asphaltene ("hard") and wax content for different crude oils

Oil	Residue	Asphaltenes "hard" (wt%)	Wax (wt%)
Vale	**Fresh**	0.03	3.3
	150°C+	0.04	4.3
	200°C+	0.05	5.1
	250°C+	0.06	6.4
Vale 2001	**Fresh**	0.07	4.5
	150°C+	0.1	5.8
	200°C+	0.12	7.0
	250°C+	0.14	8.4
Kvitebjørn	**Fresh**	0.07	4.3
	150°C+	0.09	5.6
	200°C+	0.12	7.1
	250°C+	0.15	9.2
Trym	**Fresh**	0.02	3.8
	150°C+	0.02	5.4
	200°C+	0.03	6.7
	250°C+	0.03	8.6
Gjøa	**Fresh**	0.03	1.5
	150°C+	0.03	1.9
	200°C+	0.03	2.2
	250°C+	0.03	2.6
Oselvar	**Fresh**	0.10	4.2
	150°C+	0.20	5.8
	200°C+	0.20	7.3
	250°C+	0.20	9.2

-: No data available

Table 3-4: Physical parameters of Vale in comparison with other Norwegian crude oils

Oil type	Residue	Evap. (vol.%)	Residue (wt.%)	Density (g/ml)	Flash point (°C)	Pour point (°C)	Visc. (mPas) 13°C (10 s^{-1})	Visc. (mPas) 13°C (100 s^{-1})	Visc. (mPas) 5°C (10 s^{-1})	Visc. (mPas) 5°C (100 s^{-1})	IFT* (mN/m)
Vale	Fresh	0	100	0.816	-	-9	37	14	169	37	29
	150°C+	27	77	0.851	33	6	189	50	1183	233	29
	200°C+	40	64	0.866	69	18	1169	244	4105	818	24
	250°C+	53	51	0.879	108	27	5098	1024	15172	2302	-
Vale 2001	Fresh	0	100	0.821	-	-27	8	4	270	52	-
	150°C+	26.3	76.3	0.850	-	3	150	40	2180	310	-
	200°C+	39.6	63.7	0.866	-	18	1910	300	5710	850	-
	250°C+	50.5	52.8	0.877	-	21	6690	580	19200	2650	-
Kvitebjørn	Fresh	0	100	0.802	<-22	-9	5	-	26	-	-
	150°C+	25	77	0.827	37	-3	43	-	290	-	-
	200°C+	41	61	0.841	67	9	300	-	1740	-	-
	250°C+	53	47	0.853	105	24	4090	-	10090	-	-
Trym	Fresh	0	100	0.798	-	9	32	9	327	80	-
	150°C+	33	70	0.833	38	21	1336	171	6701	711	-
	200°C+	47	57	0.845	77	27	3851	447	10756	1253	-
	250°C+	59	44	0.852	107	30	6848	877	14292	1491	-
Gjøa	Fresh	0	100	0.836	-	<-36	5	5	-	-	-
	150°C+	25	78	0.866	40	-24	14	14	-	-	-
	200°C+	36	68	0.879	75	3	34	32	-	-	-
	250°C+	48	56	0.892	112	12	98	85	-	-	-
Oselvar	Fresh	0	100	0.791	-	<-36	3	-	-	-	17
	150°C+	31	72	0.827	35	-12	27	-	-	-	19
	200°C+	46	57	0.844	76	3	139	-	-	-	21
	250°C+	59	45	0.859	107	12	725	-	-	-	22

-: *No data available*

**IFT=Interfacial tension. Measured by the pendant drop method. It has been reported IFT measurement on 43 crude oils in a range of 9.9-31.5 mN/m (Donaldson et al, 1969). IFT is dependant of the properties of oil such as acid and base number, asphaltene content and pH of the sea water (Buckley and Tianguang, 2005).*

The physical and chemical properties of Vale have changed slightly since 2001. The densities, viscosities, pour points and evaporative losses are similar. Wax contents are slightly lower now than in 2001, as are the nC_{17}/Pristane and nC_{18}/Phytane ratios, while the asphaltene levels are halved compared to 2001.

Figure 3-3 demonstrates how Norwegian crude oils can be categorized based on whether they have naphtenic, paraffinic, asphaltenic or waxy properties. The oils chosen for comparison with Vale can be found in the map, as can Vale. The map categorizes Vale as a paraffinic oil with medium to low wax content.

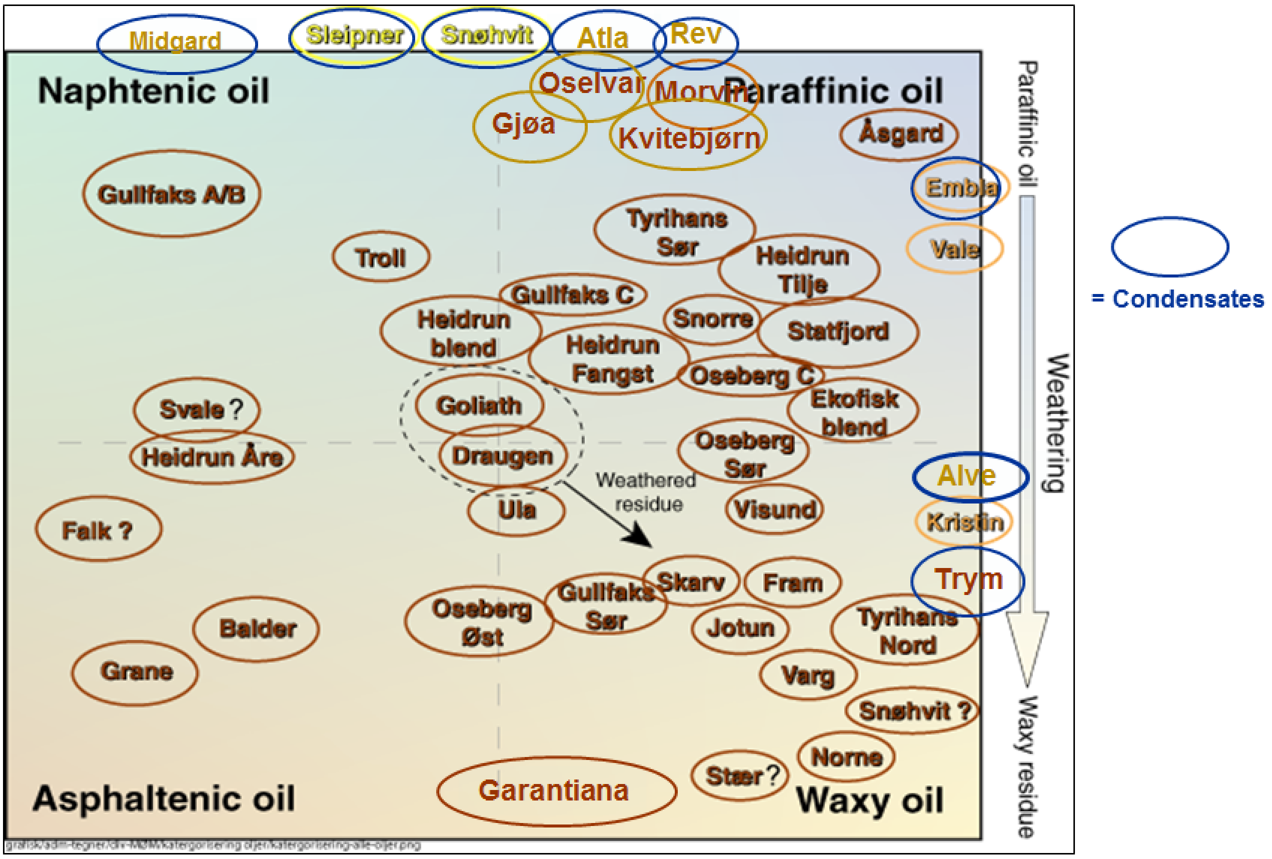
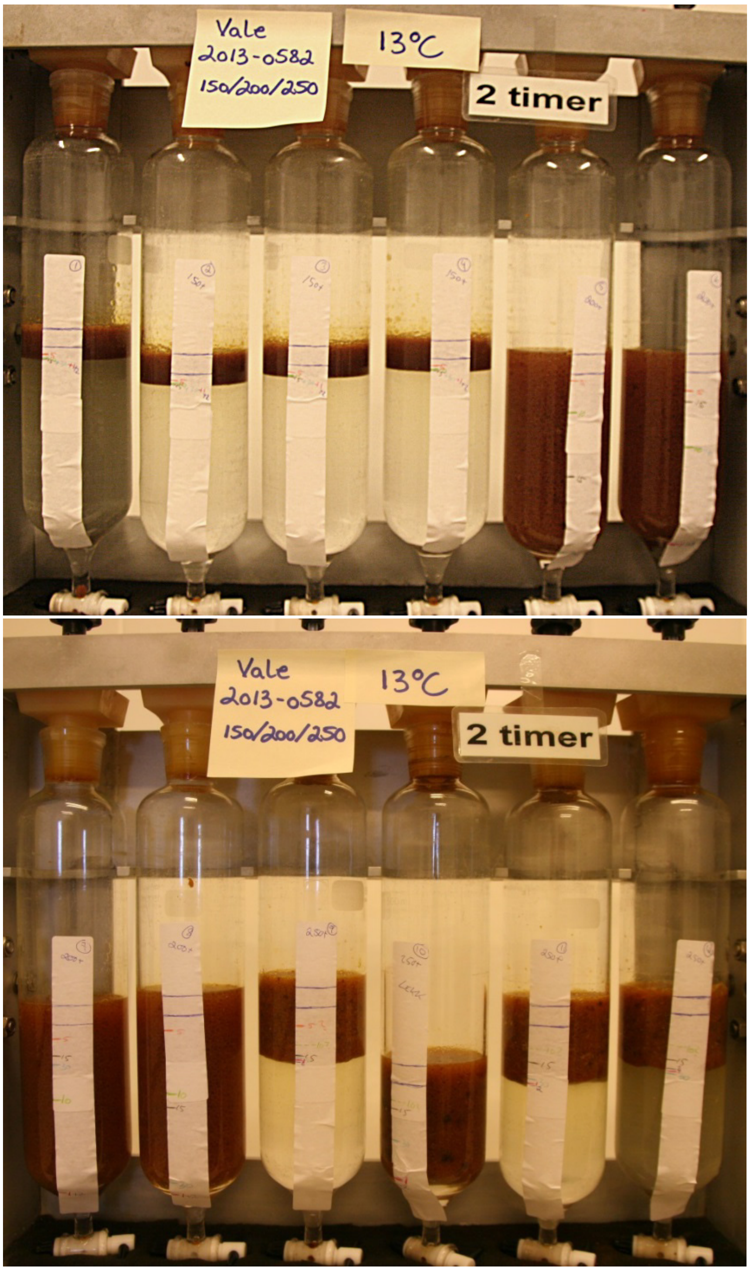


Figure 3-3: Categorisation of some crude oils and condensates based on previous studies at SINTEF. Blue circle indicate condensates, brown indicate crude oils.

3.1.2 Emulsifying properties of Vale

The emulsifying properties were studied by use of the rotation flasks (Hokstad et al 1993). Vale emulsions made from the three residues are demonstrated in Figure 3-4 and Figure 3-5 after two and four hours of rotations at 13°C and 5°C, respectively. Figure 3-6 display the effect of additional stress on an emulsion after 24 hours of rotation and 24 hours of settling.

Vale has a rapid water uptake of up to 70-85 % water. The emulsions that are formed are, however, loose and will release water when settled or if additional stress is applied. Unstable emulsions are a common trait among light oils and are caused by low content of wax and compounds with surface active properties.



Four flasks on the left: Emulsions formed at 13°C from the 150+ residue after two hours of rotation.

Two flasks on the right: Emulsions formed at 13°C from the 200+ residue after two hours of rotation. Demonstrate 90 % water content.

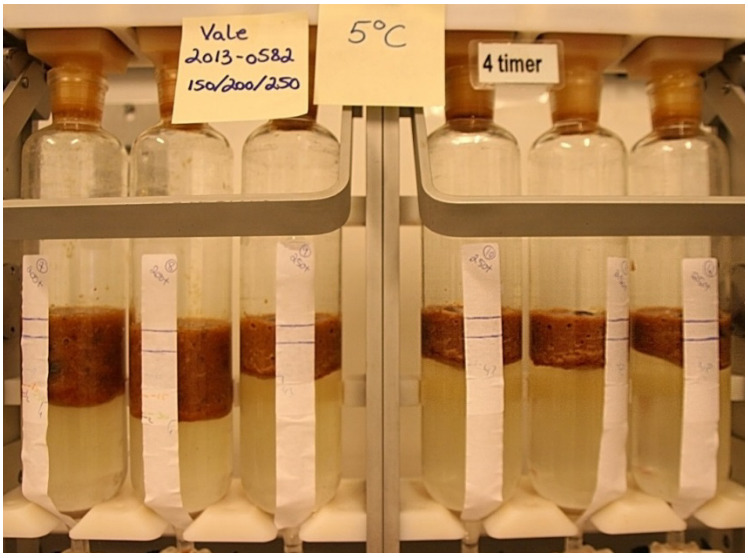
Two flasks on the left: Emulsions formed at 13°C from the 200+ residue after two hours of rotation. Demonstrate 90 % water content.

Four flasks on the right: Emulsions formed at 13°C from the 250+ residue after two hours of rotation.

Figure 3-4*: Emulsions formed after 2 hours at summer temperature (13°C).*

Four flasks on the left: Emulsions formed at 5°C from the 150+ residue after four hours of rotation. Demonstrate 91 % water content.

Two flasks on the right: Emulsions formed at 5°C from the 200+ residue after four hours of rotation.



Two flasks on the left: Emulsions formed at 5°C from the 200+ residue after four hours of rotation.

Four flasks on the right: Emulsions formed at 5°C from the 250+ residue after four hours of rotation.

Figure 3-5: ***Emulsions formed after 4 hours at winter temperature (5°C).***

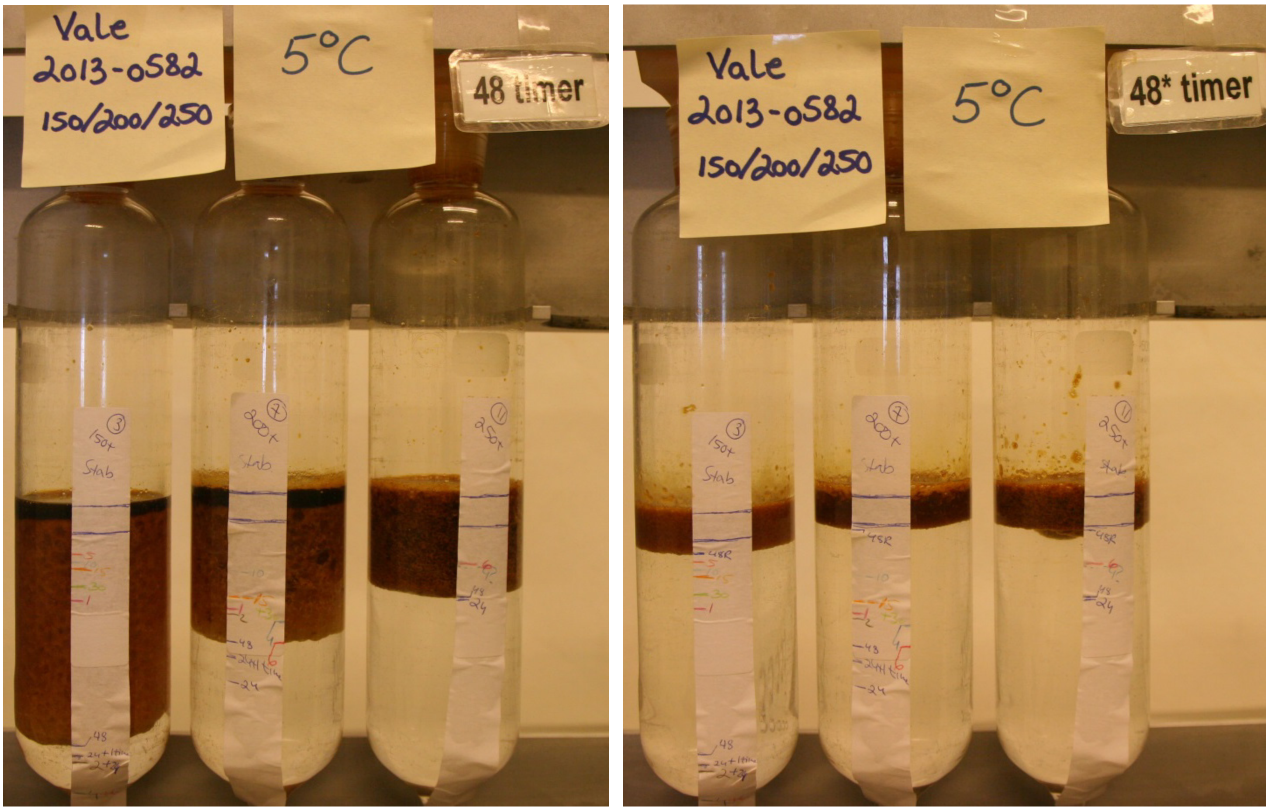


Figure 3-6: ***Picture is showing stability test of Vale crude oil emulsions formed on 5°C. On the left, from left to right: 150°C+, 200°C+ and 250°C+ residue left for 24 hours without rotation. On the right are the same flasks after ten rounds of rotation***.

Water uptake and maximum water content

The parameters for kinetics (rate of water uptake) and maximum water uptake were studied by use of the rotation flasks (Hokstad et al 1993). The emulsion water content as a function of time is shown in Table 3-5 and in Table 3-6. $T_{1/2}$, which is derived from the tabulated data, is defined as the consumed time (hours) needed to incorporate half the maximum water uptake, and is used as input to the Oil Weathering Model (OWM).

The results vary between the two temperatures (5°C and 13°) indicating that temperature is an important factor for the rate of water uptake. There are also some differences in the maximum water content at the different temperatures, e.g. the 150+ residue can reach a volume % of water of 91 % at 5°C but only 35 % at 13°C. The $T_{1/2}$ is lower at 13°C than at 5°C indicating more rapid water uptake at 13°C than at 5°C.

Table 3-5: Water uptake of the evaporated residues of Vale crude oil in rotating flasks at 5°C

Mixing time	**150°C+ (Vol.% water)**	**200°C+ (Vol.% water)**	**250°C+ (Vol.% water)**
Start	0	0	0
5 min	38	52	0
10min	51	69	0
15 min	57	77	0
30 min	69	79	3
1 hour	76	79	51
2 hours	87	80	58
4 hours	91*	81	57
6 hours	91*	83	66
24 hours	90*	87	71
$T_{1/2}$	0.16	0.07	1.10

**Super saturation of water, likely a result of the laboratory method and not likely to occur in field situations*

Table 3-6: Water uptake of the evaporated residues of Vale crude oil in rotating flasks at 13°C

Mixing time	**150°C+ (Vol.% water)**	**200°C+ (Vol.% water)**	**250°C+ (Vol.% water)**
Start	0	0	0
5 min	27	40	41
10 min	35	77	63
15 min	38	73	70
30 min	38	82	74
1 hour	38	90*	75
2 hours	38	90*	75
4 hours	36	90*	76
6 hours	36	90*	78
24 hours	35	73	77
$T_{1/2}$	0.04	0.05	0.07

**Super saturation of water, likely a result of the laboratory method and not likely to occur in field situations*

Emulsion stability and efficiency of emulsion breaker

Stability testing of emulsions formed from weathered residues of Vale crude oil, and the efficiency of the emulsion breaker (Alcopol O 60%), were evaluated. The results are shown in Table 3-7.

Vale crude oil forms emulsions at both temperatures (5°C and 13°) and has a relatively rapid water uptake with a potential water uptake of 70-85 %. The emulsions are not stable and will release water when settled under static conditions. After settling, there may remain an emulsion "skeleton" that will contain water, but this may collapse when additional stress is added, thus releasing even more water.
Such additional stress will occur during mechanical recovery operations at sea. These trends are demonstrated in Figure 3-6 and can also be seen in Table 3-7 and Table 3-8, reflected as the stability ratios.
Though the emulsion made from the 150°C+ residue does not release any water at 13°C, the very low volume percentage of water (35%) is not problematic for mechanical recovery.

At the 13°C, the 200°C+ residue emulsions almost reach super saturation (90 vol% water) after two hours of rotation. All emulsions are dehydrated after application of the emulsion breaker Alcopol and the effect is the same using the lower concentration (500 ppm) as using the higher concentration (2000 ppm). The results are also comparable for both temperatures.

Table 3-7: Stability of Vale emulsions (no emulsion breaker) and efficiency of emulsion breaker at 5ºC

Residue	Emulsion breaker	Water-in-oil emulsion (vol.%) at 5°C				
		Reference	24 hours *	Stability ratio**	24 hours and 10 rotations ***	Stability ratio**
150ºC+	none	90	89	0.85	**35**	0.06
200ºC+	none	87	81	0.64	**19**	0.03
250ºC+	none	71	71	1	**14**	0.07
150ºC+	Alc. O 60 % 500 ppm	90	6	0.01	6	0.01
200ºC+	Alc. O 60 % 500 ppm	87	6	0.01	6	0.01
250ºC+	Alc. O 60 % 500 ppm	71	5	0.02	5	0.02
150ºC+	Alc. O 60 % 2000 ppm	90	2	0.00	2	0.00
200ºC+	Alc. O 60 % 2000 ppm	87	14	0.02	14	0.02
250ºC+	Alc. O 60 % 2000 ppm	71	0	0.00	0	0.00

ppm: parts per million
**: w/o emulsion after 24 hours rotation and 24 hours settling*
***: Stability ratio of 1 implies a totally stable emulsion during 24 h settling. A stability ratio of 0 (zero) implies a totally unstable emulsion: all the water is released from the emulsion during 24 h settling*
****: w/o emulsions after 24 hours rotation and 24 hours settling and 10 rounds of rotation is expected to be most reliable with respect to field operations.*

Table 3-8: Stability of Vale emulsions (no emulsion breaker) and efficiency of emulsion breaker at 13°C

Residue	Emulsion breaker	Water-in-oil emulsion (vol.%) at 13°C				
		Reference	24 hours *	Stability ratio**	24 hours + 10 rotations***	Stability ratio***
150ºC+	none	35	35	1	**35**	1
200ºC+	none	73	57	0.28	**17**	0.04
250ºC+	none	77	71	0.72	**3**	0.01
150ºC+	Alc. O 60 % 500 ppm	35	2	0.03	2	0.03
200ºC+	Alc. O 60 % 500 ppm	73	6	0.01	6	0.01
250ºC+	Alc. O 60 % 500 ppm	77	5	0.01	5	0.01
150ºC+	Alc. O 60 % 2000 ppm	35	0	0.00	0	0.00
200ºC+	Alc. O 60 % 2000 ppm	73	23	0.06	17	0.06
250ºC+	Alc. O 60 % 2000 ppm	77	0	0.00	0	0.00

ppm: parts per million
**: w/o emulsion after 24 hours rotation and 24 hours settling*
***: Stability ratio of 1 implies a totally stable emulsion during 24 h settling. A stability ratio of 0 (zero) implies a totally unstable emulsion: all the water is released from the emulsion during 24 h settling*
****: w/o emulsions and stability ratio after 24 hours rotation and 24 hours settling and 10 rounds of rotation is expected to be most reliable with respect to field operations.*

Viscosity of water free residues and emulsified residues

Table 3-9 and Table 3-10 show the measured viscosities of water free residues and residues after emulsification at respectively 5 and 13°C with 50%, 75% and maximum water content.

The fresh Vale crude oil is defined as a non-Newtonian fluid, thus the viscosity is dependent on its shear rate (this is more pronounced at 5 ºC compared with 13 ºC); the viscosity is higher at a shear rate of $10s^{-1}$ compared with a shear rate of $100s^{-1}$. The same also observed for the weathered residues mixed with water at both temperatures. This is probably due to the wax lattice structure being broken or disturbed when influenced by mechanical stress.

In general the results from the viscosity measurements on Vale crude oil indicate higher viscosity with higher degree of residue evaporation (and similar water content).

Some formation of waxy lumps in the emulsions made from heavier residues (250°C+) were seen at both temperatures but was more prominent at 5°C than at 13° C.
As the wax components aggregates in lumps they are effectively removed from the emulsion. Consequently, the emulsion viscosities may have been influenced by this "removal" of waxy compounds, and this can explain the fairly low viscosities seen for emulsions of higher degree of weathering (both evaporation and water content).

Most of the emulsions made from Vale crude oil residues also contained visible water droplets, and the emulsions broke easily when mechanical stress was applied, as is demonstrated in Figure 3-6. Water droplets and waxy lumps are visible in Figure 3-7.

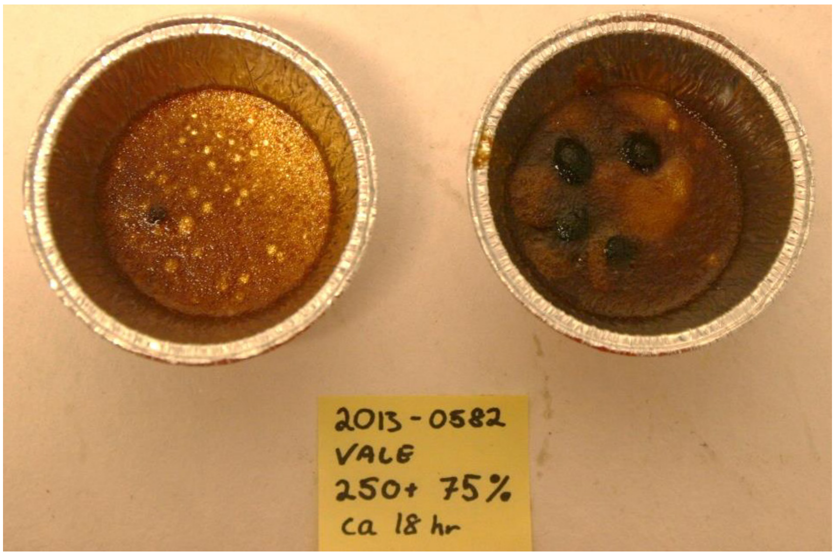


Figure 3-7: Show a 75 % emulsion made of 250+ residue of Vale crude oil. The emulsion contains visible water droplets and small waxy lumps.

Table 3-9: Viscosity of Vale water free residues and emulsified residues at 5ºC.

Residue	**Water content (vol.%)**	**Viscosity (mPas)**	
		10 s^{-1}	**100 s^{-1}**
Fresh	0	169	37
150°C+	0	1183	233
200°C+	0	4105	818
250°C+	0	15172	2302
150°C+	50	510	164
200°C+	50	1205	471
250°C+	50	4436	1529
150°C+	75	265	81
200°C+	75	623	238
250°C+	75	-*	-*
150°C+	88	144	52
200°C+	79	527	187
250°C+	68	3190	613

**The 250+ residue did not form 75 % emulsion at 5°C, max. water uptake was 68 %*

Table 3-10: Viscosity of Vale water free residues and emulsified residues at 13ºC

Residue	Water content (vol.%)	Viscosity (mPas)	
		10 s^{-1}	100 s^{-1}
Fresh	0	37	14
150°C+	0	189	50
200°C+	0	1169	244
250°C+	0	5098	1024
150°C+	50	342	126
200°C+	50	643	211
250°C+	50	2100	806
150°C+	75	244	56
200°C+	75	331	70
250°C+	75	1210	245
150°C+	32	351	86
200°C+	62	969	288
250°C+	81	1680	336

3.1.3 Chemical dispersibility

The dispersibility testing included:

- Screening of five different dispersants to find the best and relevant dispersant for the Vale oil.
- Dosage testing of the best dispersant.
- Systematic dispersant study with the best dispersant at the optimal dosage rate (Dispersant to Oil Ratio, DOR), to determine the time window for effective dispersant use on the Vale oil in a spill scenario.

Screening study of dispersants

The screening study was performed using the IFP test to find the most suitable dispersant. The study was performed using a 200°C+ residue emulsified with 50 vol. % water and a DOR of 1:25 at a temperature of 13ºC.

The results revealed that Dasic NS and Corexit 9500 had the best effectiveness of 63 wt.% and 52 wt.%. Dasic NS was chosen for further tests as it is the dispersant agent in NOFO's stock and was the most effective dispersant.

Results from the screening study are listed in Table 3-11.

Table 3-11: Screening test of dispersants on Vale crude oil at 13ºC using the IFP test.

Dispersant (DOR 1:25)	Efficiency dispersant 200°C+ /50%	Viscosity (mPas) shear rate 10 s^{-1}, 13ºC
Dasic NS	63	643
Corexit 9500	52	643
Gamlen OD 4000	27	643
Superdispersant 25	17	643
Finasol OSR 62	10	643

Dosage rate study of dispersants

The dosage rate study was performed using Dasic NS, being one of the most efficient dispersants for the Vale crude oil. Both the MNS and IFP test method were used. The study was performed using a 200°C+ residue emulsified with 50 vol. % water at a test temperature at 13 ºC.

Results from the dosage rate study are listed in Table 3-12.

Table 3-12: Dosage rate testing of Dasic NS on Vale crude oil at 13ºC.

Test method	Dispersant (dosage rate)	Efficiency dispersant 200°C+ / 50%	Viscosity (mPas) 10 s^{-1} , 13ºC
IFP	Dasic NS (1:25)	63	643
	Dasic NS (1:50)	29	597
	Dasic NS (1:100)	18	597
	Dasic NS (1:200)	6	597
MNS	Dasic NS (1:25)	91	643
	Dasic NS (1:50)	90	597
	Dasic NS (1:100)	90	597
	Dasic NS (1:200)	86	597

Window of opportunity for use of dispersant on Vale crude oil

Based on the screening study, Dasic NS, at a dosage rate of 1:25 (4 wt.%), was chosen for the continued testing of Vale to define the time window for dispersant use. A dosage rate of 1:25 (4 wt.%) is usually considered as the operational target when applying dispersant on a marine oil spill (vessel or air application).

Results from the systematic dispersibility study at 5°C and 13°C are listed in Table 3-13 and in Table 3-14.

Table 3-13: Efficiency of Dasic NS on Vale crude oil weathered oil at 5°C

Residue	Water content (vol.%)	Viscosity (mPas) 10 s^{-1}	IFP Efficiency (%)	MNS Efficiency (%)
150°C+	0	1183	2	100
200°C+	0	4105	1	61
250°C+	0	15172	2	2
150°C+	50	510	14	85
200°C+	50	1205	21	97
250°C+	50	4436	5	89
150°C+	75	265	17	86
200°C+	75	623	14	86
250°C+	75	-	-	-
150°C+	88	144	39	79
200°C+	79	527	17	100
250°C+	68	3190	14	61

- Not analysed

Table 3-14: Efficiency of Dasic NS on Vale crude oil weathered oil at 13°C

Residue	Water content (vol.%)	Viscosity (mPas) 10 s^{-1}	IFP Efficiency (%)	MNS Efficiency (%)
150°C+	0	189	11	88
200°C+	0	1169	3	90
250°C+	0	5098	1	11
150°C+	50	342	25	88
200°C+	50	643	63	91
250°C+	50	2100	28	91
150°C+	75	244	24	81
200°C+	75	331	14	79
250°C+	75	1210	31	87
150°C+	32	351	29	92
200°C+	62	969	21	91
250°C+	81	1680	19	73

The efficiency criteria for use of chemical dispersants, as well as the dispersibility limits (expressed as viscosity) for Vale crude oil, are listed in Table 3-15. The dispersibility limits are estimated based on the efficiency of Dasic NS on emulsions of Vale Crude oil, shown in Figure 3-8. This figure demonstrates the effectiveness of the dispersant relative to the viscosities of the Vale emulsions. The viscosities are measured by a rotary viscometer where a rotating spindle measures shear rate and shear stress, and the ratio of these gives the viscosity. The figure expresses the viscosity measured at a shear rate of 10 s^{-1}, which is ten rotations per second.

The MNS test had an effectiveness ranging from 60 wt% to 100 wt% while the IFP test results typically ranged from 5 wt% to 40 wt% excepting one result of 63 wt%.

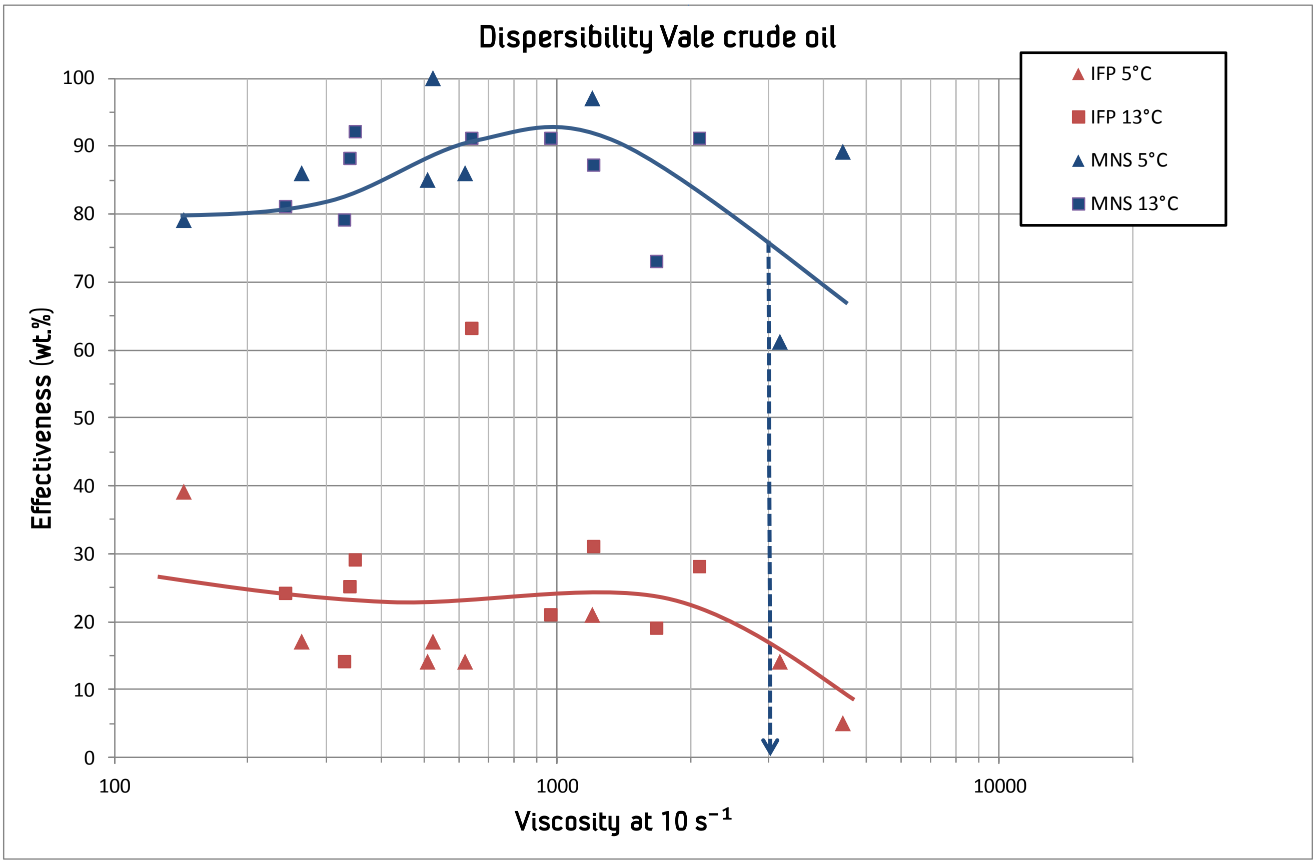


Figure 3-8: Dispersant efficiency on the weathered residues of Vale

The experimental results do not reveal a dispersibility limit where the emulsions are not chemically dispersible. This limit has been estimated based on the available data.

Table 3-15: Criteria for definition of time window for effective use of dispersant for Vale

Dispersibility*	Criteria (wt.%)	Dispersibility limit based on oil viscosity (mPas = cP)
Chemically dispersable	MNS efficiency > 75%	3000
Not chemically dispersible	MNS efficiency <5%	est. 9000

**The limit for chemical dispersibility is presented with values only from the MNS test (high energy test) after an evaluation of the results (Figure 3-8). The IFP results for the lower limit of dispersability, were too low (<50%) to be included in the definition of time window for effective use of dispersant.*

As can be seen from Figure 3-8 the dispersant efficiency vary greatly between the two test methods (IFP and MNS), demonstrating the artificial energy in addition to dispersants in calm sea conditions order to reach the high efficiency of the MNS test.

The fairly high pour point of the Vale Crude oil residues can contribute to the relatively low efficiency at low energy input (i.e. IFP-test) as the effect of dispersants are reduced in scenarios where the sea temperature is 10-15°C (or more) lower than the pour point of a residue.

In a case of solidification of oil or residue the dispersants will lie on top of the slick without soaking into it, and without this mixing the effect of the dispersant is absent. Emulsions made from residues with high pour point may express this same trend.

4 Predictions with SINTEF Oil Weathering Model (OWM)

4.1 Description of SINTEF OWM

A laboratory study of the weathering properties of Vale at 5°C and 13°C has been conducted. The data are used as input to the SINTEF OWM (version 4.0 beta). The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, sea state and sea temperature) and predicts the change rate of the oil's properties and behaviour on the sea surface. The SINTEF OWM is schematically shown in Figure 4-1.

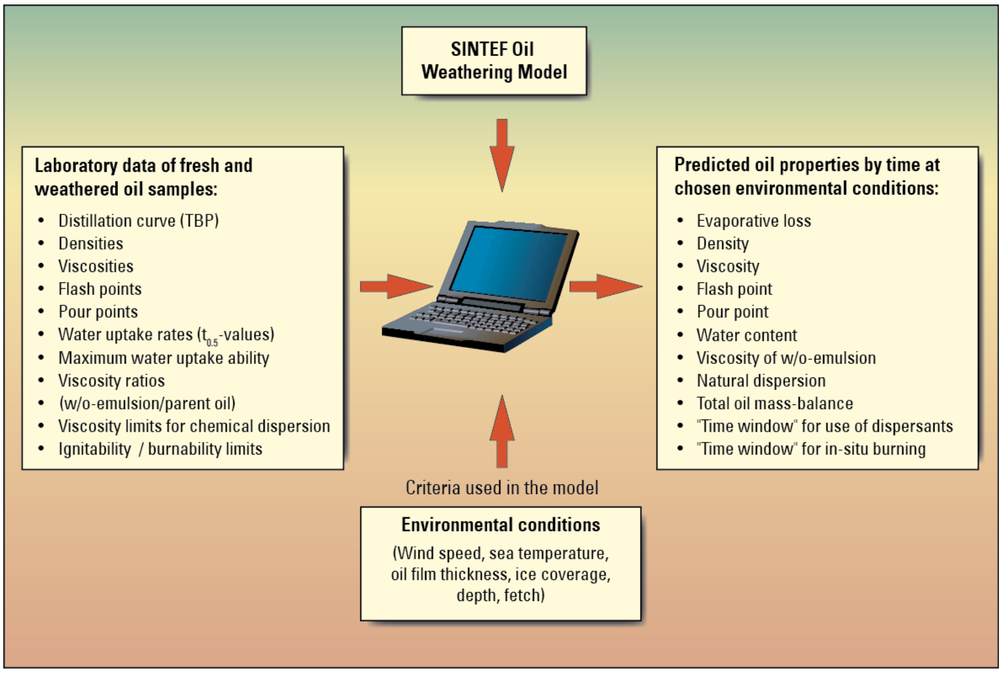


Figure 4-1: Schematic input data to the SINTEF OWM and the predicted output oil properties

The predictions obtained from the SINTEF OWM are useful tools in Environmental Impact Assessment studies and for determining the most effective response. In this report, the presented predictions span a time period from 15 minutes to 5 days after an oil spill has occurred. This covers potential spill situations in which the response time is short (e.g. close to a terminal) to offshore spills in which the response time can be several days. The SINTEF OWM is described in more detail in Johansen (1991) and in the user's guide for the model.

In laboratory testing, a systematic stepwise procedure developed at SINTEF (Daling *et al.*, 1990) is used to isolate and map the various weathering processes that take place when oil is spilled on the sea surface. The experimental design for the study of Vale is described in Appendix B, and the results are presented in detail in Chapter 3. The input data to the SINTEF OWM is given in Appendix A. The experimental weathering data are processed and used as input for the SINTEF OWM. The following physical and emulsification properties obtained in the testing are used in the model:

- Density
- Pour point
- Flash point
- Viscosities of fresh and the water-free residues (150°C+, 200°C+ and 250°C+)
- Viscosities of the 50% and 75% w/o emulsions
- Water uptake (maximum water content, stability and emulsification rate)

Spill scenario

In this project, a surface release at a standard rate of 1.33 metric tonnes per minute was chosen as the spill scenario. This number is derived from a model spill situation of a total of 20 metric tonnes over 15 minutes, which is used as a standard in the model predictions. These numbers correspond to a release rate of 2,000m^3/day. These standard settings are chosen in order to ease the comparison between different oils.

Oil film thickness

In the SINTEF OWM, the oils are categorized into condensate, emulsifying crude, low emulsifying crude, heavy bunker fuel or refined distillate based on experimental results obtained in small-scale testing. The terminal film thickness varies among these categories based on experimental field experience. Vale is categorized as an emulsifying crude oil.

Sea temperature

The prevailing weather conditions greatly influence the weathering rate of oil on the sea surface. Two sets of predictions are given in this report, one for average summer temperatures and one for average winter temperatures. The temperatures chosen for Vale are 5°C and 15°C.

Wind speed

The relationship between the wind speed and significant wave heights used in the prediction charts obtained from the SINTEF OWM are shown in Table 4-1.

Table 4-1: Relationship between wind speed and significant wave height used in the SINTEF OWM

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

4.2 Input to SINTEF OWM

Oil type:	Crude
Geographical area:	North Sea
Terminal oil film thickness:	1 mm
Release rate:	1.33 metric tonnes/minute for 15 minutes, a total of 20 metric tonnes
Sea temperature:	5°C and 15°C
Wind speed:	2 m/s, 5 m/s, 10 m/s and 15 m/s

The data used as input to SINTEF OWM for Vale are given in Appendix C.

4.3 Predictions of Vale weathering properties

The prediction charts are shown in the figures below.

How to use the prediction charts: an example

If Vale has drifted on the sea surface for 12 hours after a release, the following prediction charts can be used to determine the remaining oil/emulsion's chemical, physical and emulsifying properties.

Table 4-2 gives an example for the following scenario:

- Drift time: 12 hours
- Sea temperature: 5°C/15°C
- Wind speed: 10 m/s

Table 4-2: Weathering properties for Vale obtained from the prediction charts after 12 hours of weathering

Property	**Winter temperature (5°C, 10 m/s)**	**Summer temperature (15°C, 10 m/s)**
Evaporation, vol.%	46	50
Pour point, °C	25	28
Water content, vol.%	67	75
Viscosity of the emulsion, mPas	3200	1900

mPas = cP (mPas: SI-standard/cP: Industrial denotation)

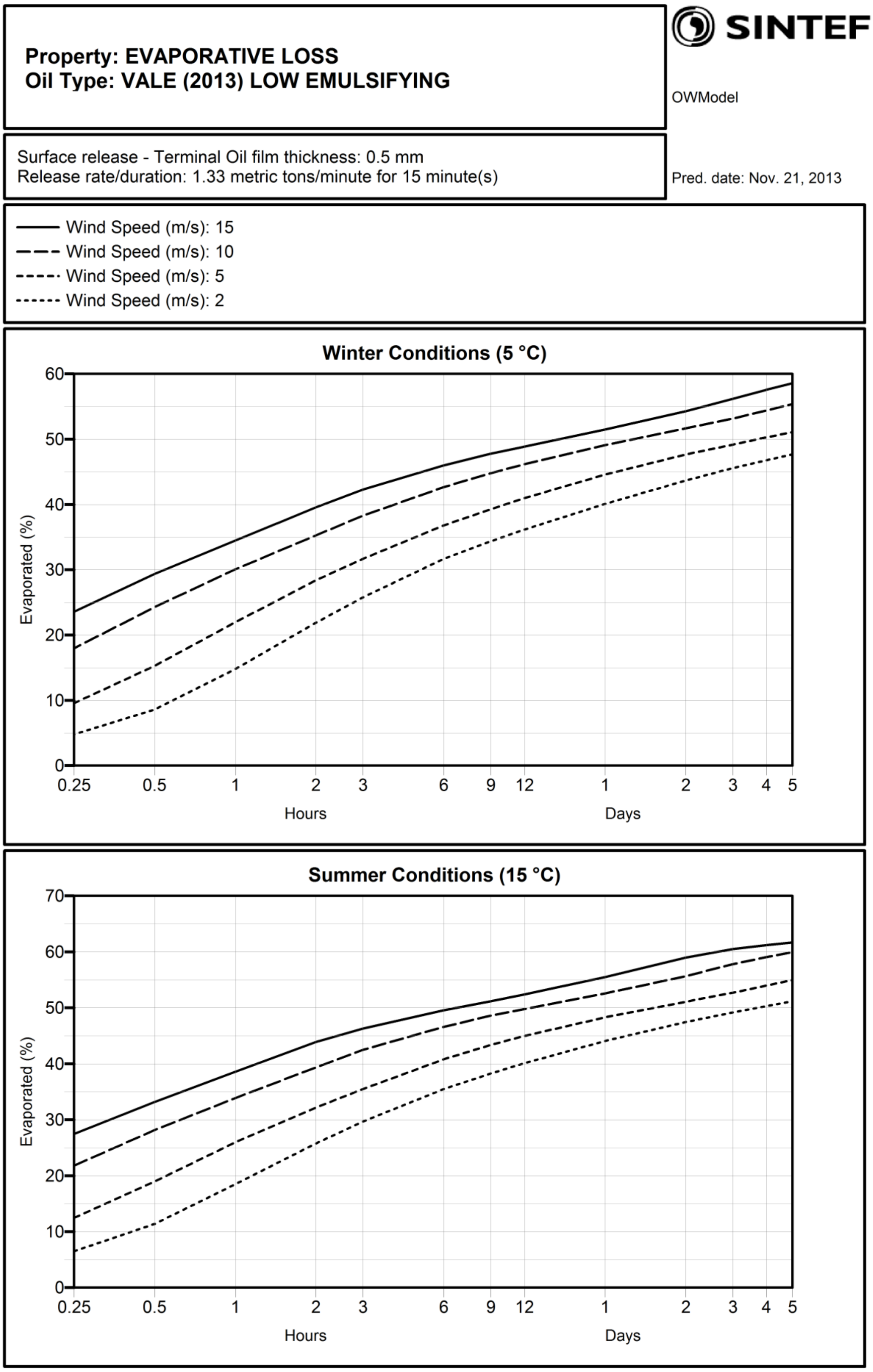


Figure 4-2: Evaporative loss of Vale predicted at sea temperatures of 5°C and 15°C

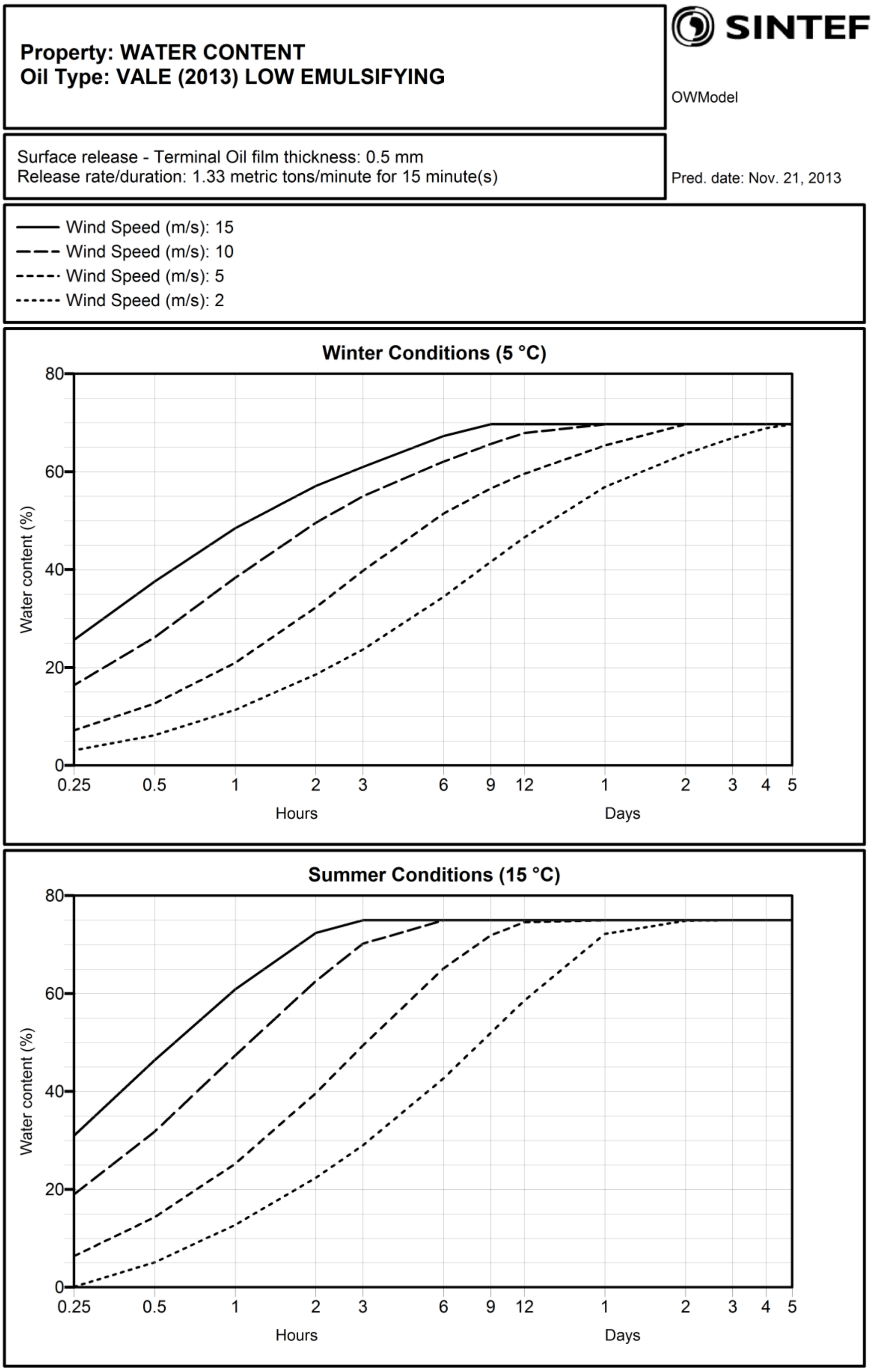


Figure 4-3: Water content for the Vale emulsions predicted at 5°C and 15°C

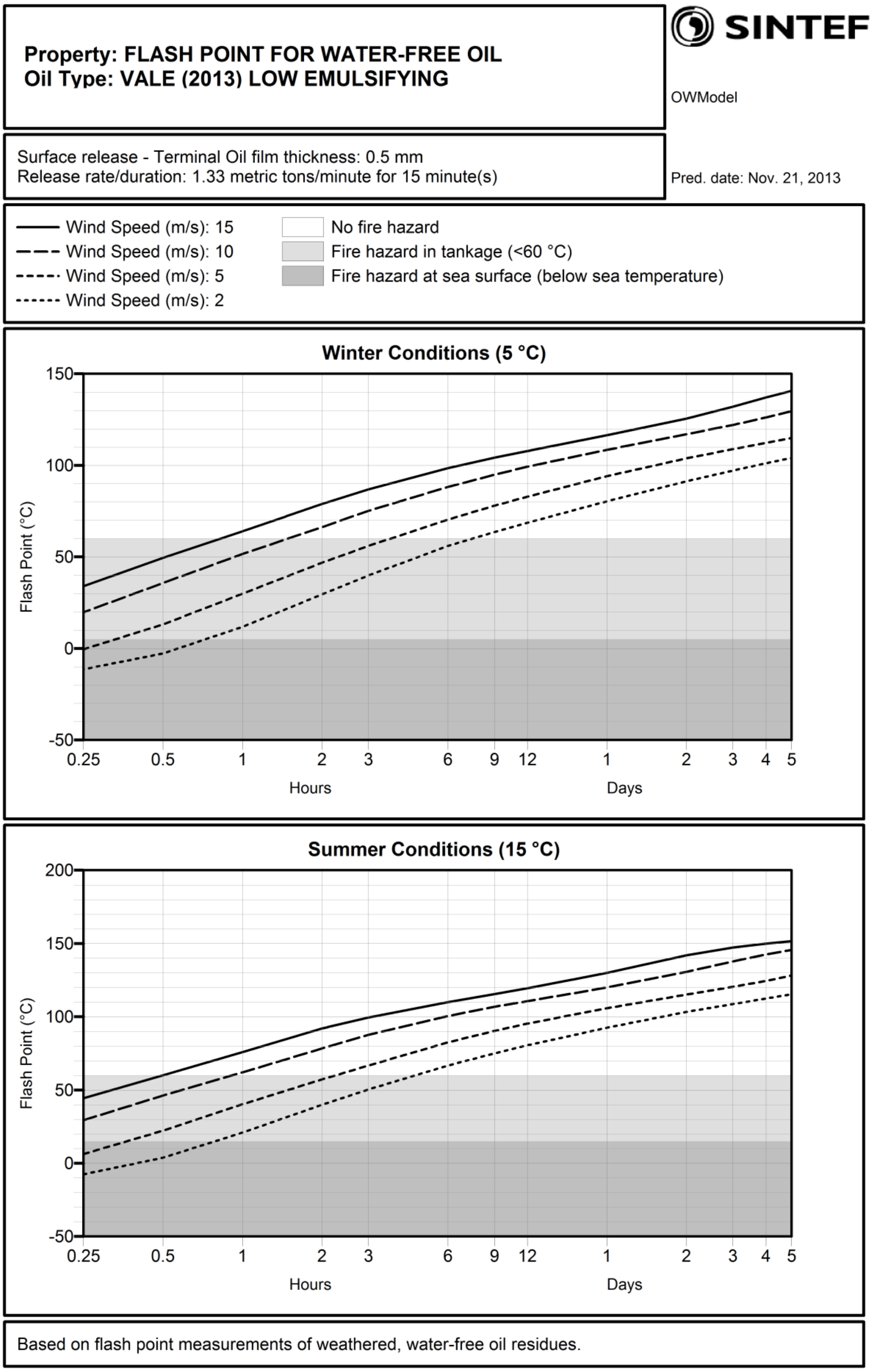


Figure 4-4: Flash point of Vale predicted at sea temperatures of 5°C and 15°C

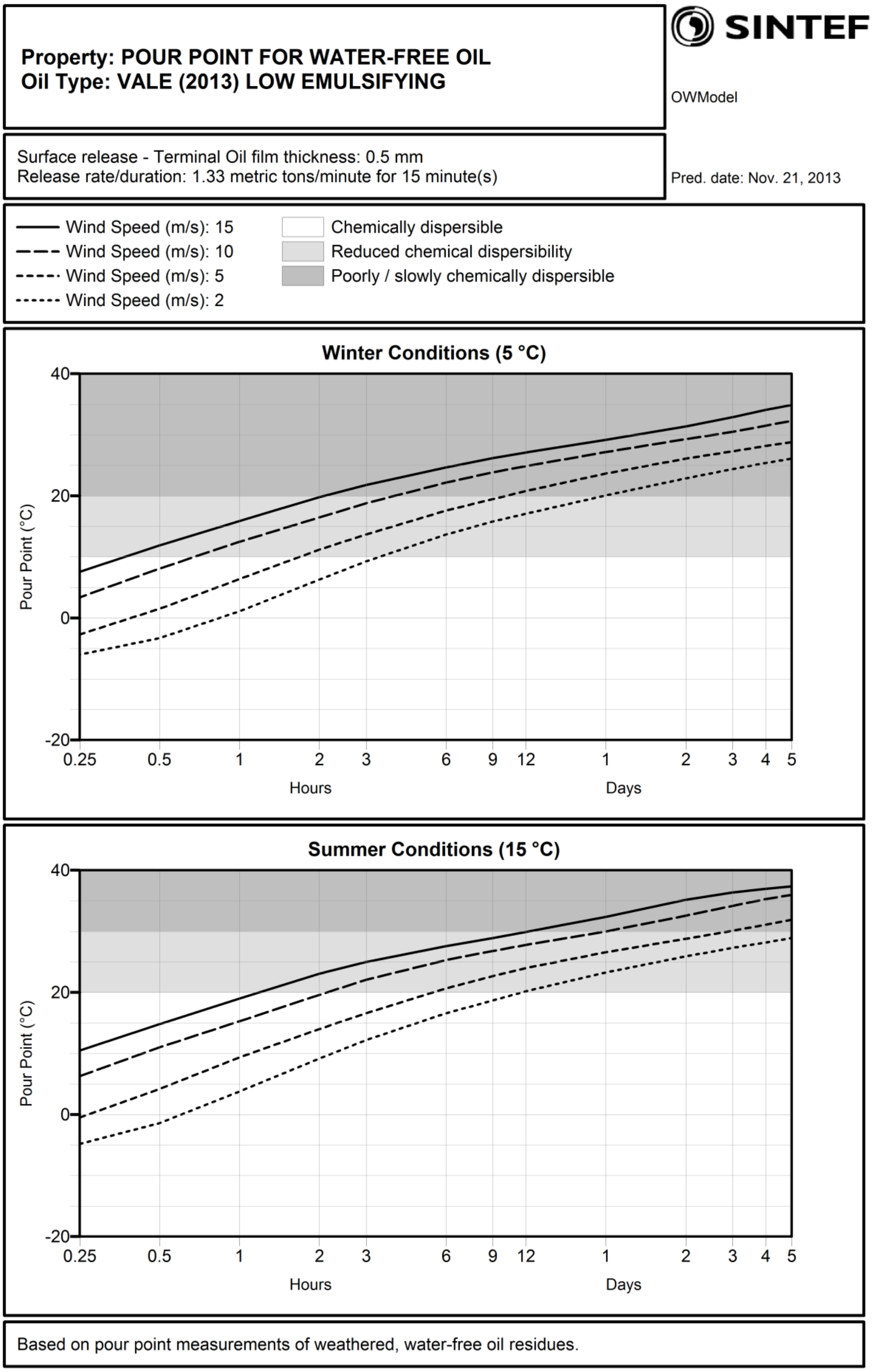
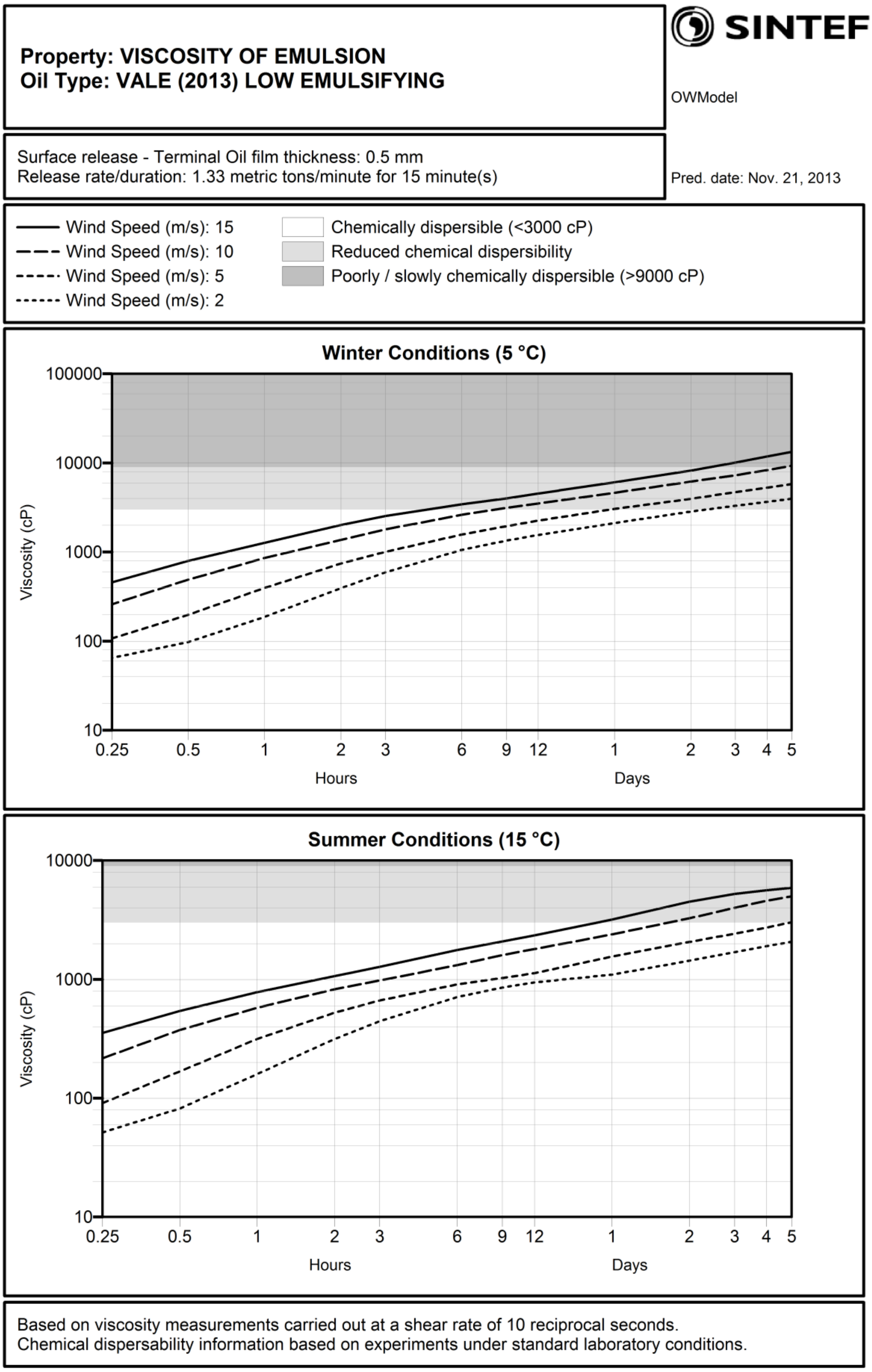


Figure 4-5: Pour point of Vale predicted at sea temperatures of 5°C and 15°C



Property: VISCOSITY OF EMULSION
Oil Type: VALE (2013) LOW EMULSIFYING

OWModel

Surface release - Terminal Oil film thickness: 0.5 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Nov. 21, 2013

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

Figure 4-6: Viscosity of Vale emulsion at sea temperatures of 5°C and 15°C. Viscosity is predicted based on measurements performed at a shear rate of 10 s^{-1}.

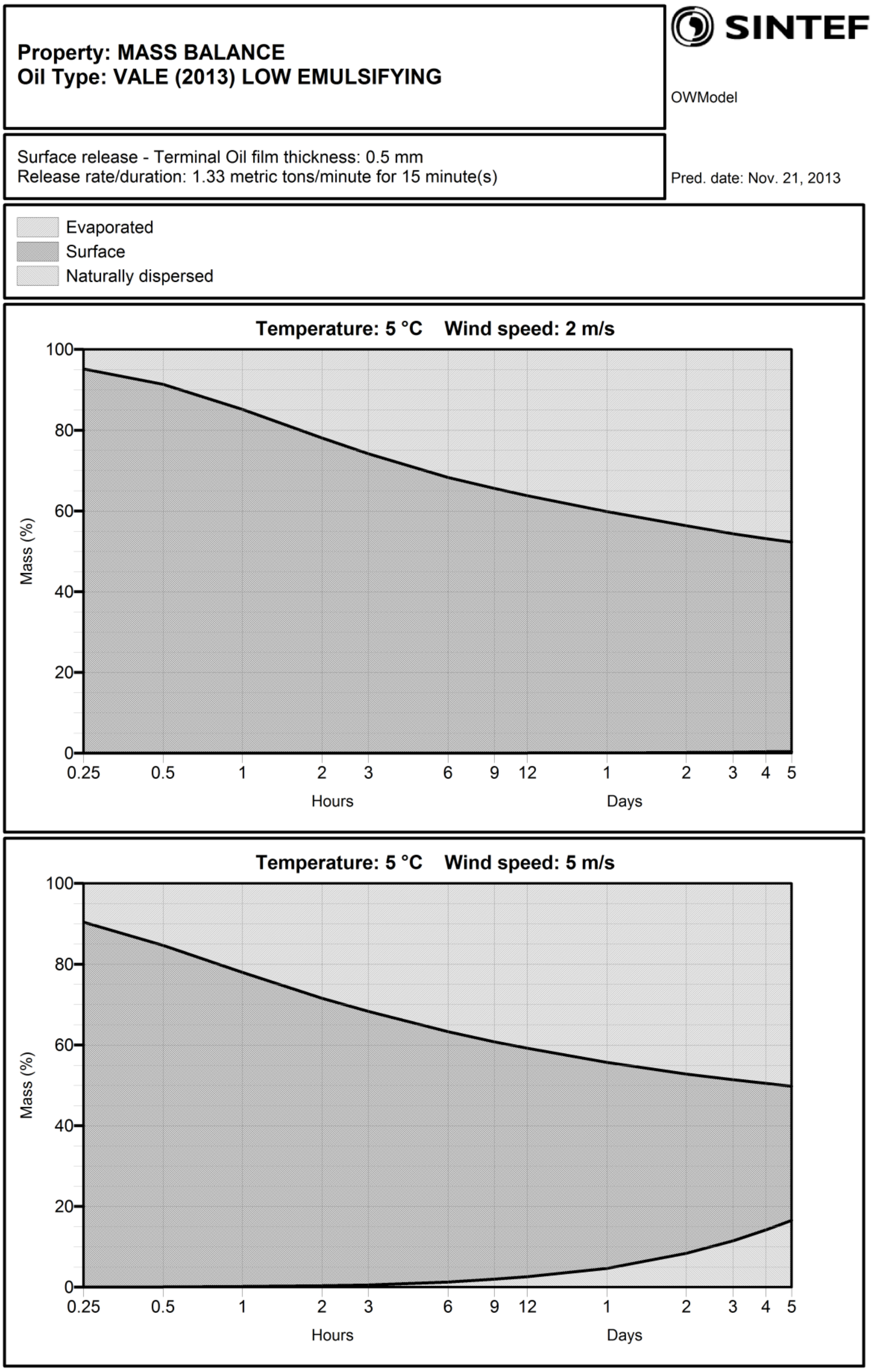


Figure 4-7: Predicted mass balance for Vale at 5°C and wind speeds of 2 and 5 m/s

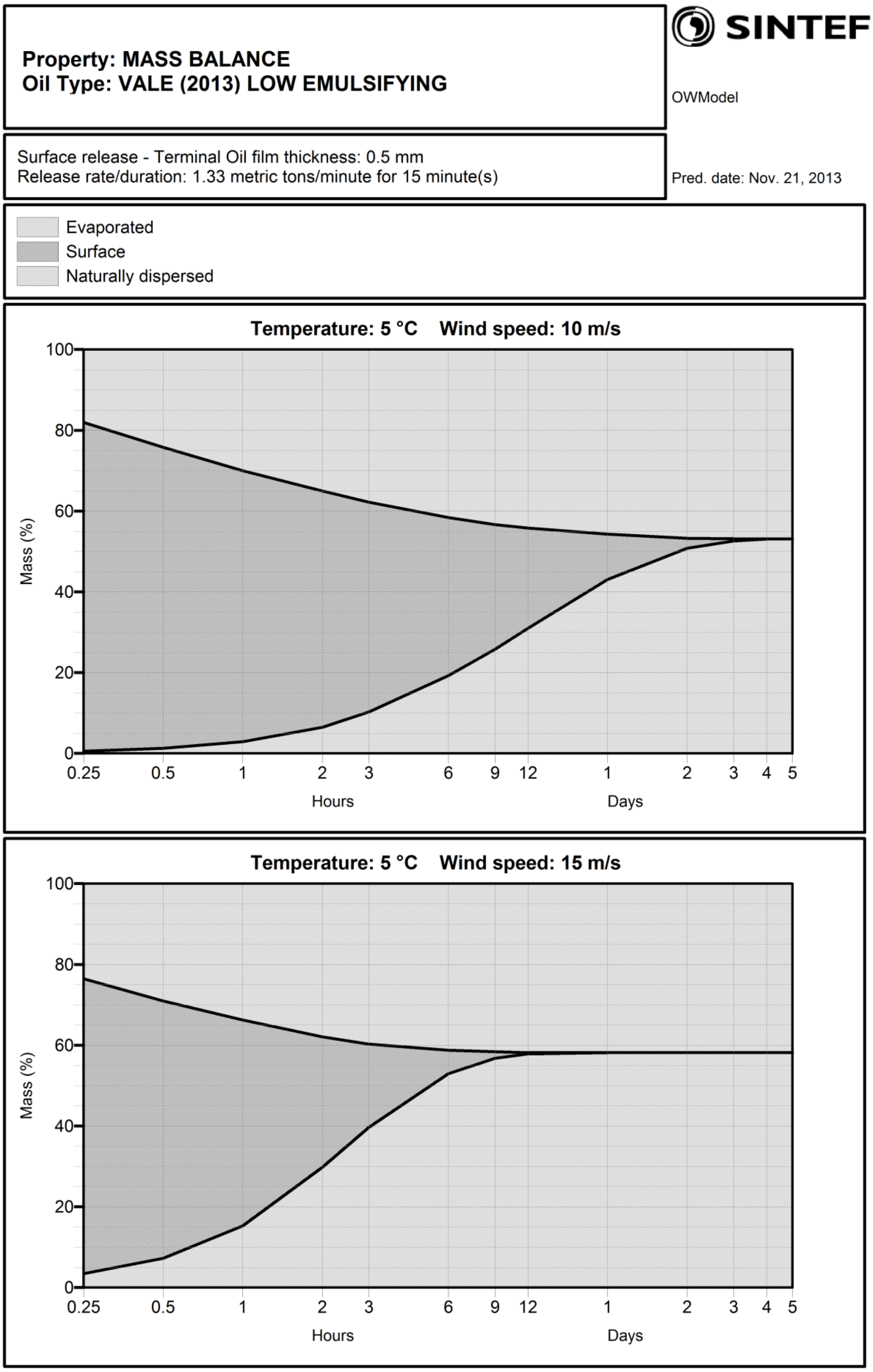


Figure 4-8: Predicted mass balance for Vale at 5°C and wind speeds of 10 and 15 m/s

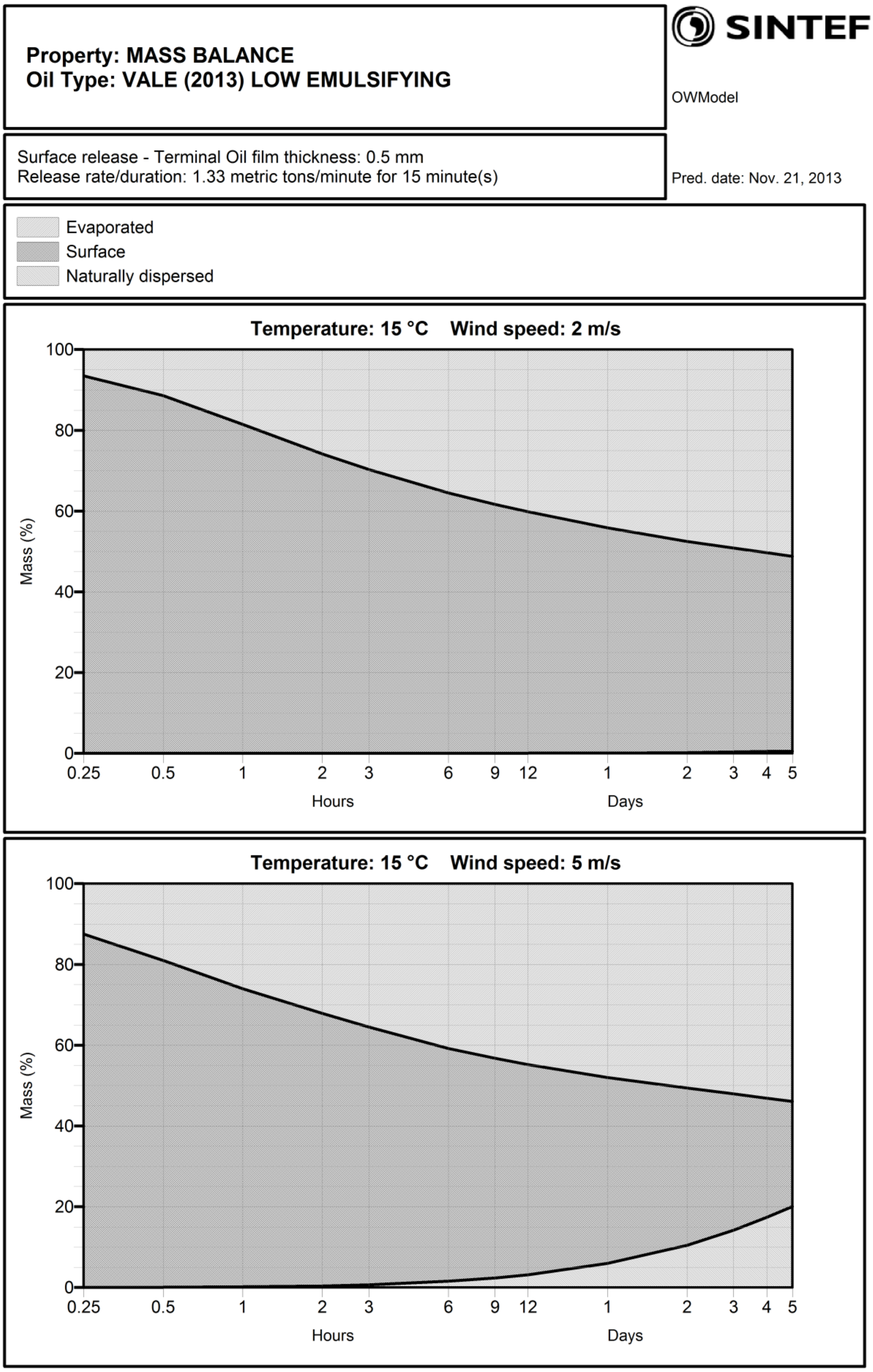


Figure 4-9: Predicted mass balance for Vale at 15°C and wind speeds of 2 and 5 m/s

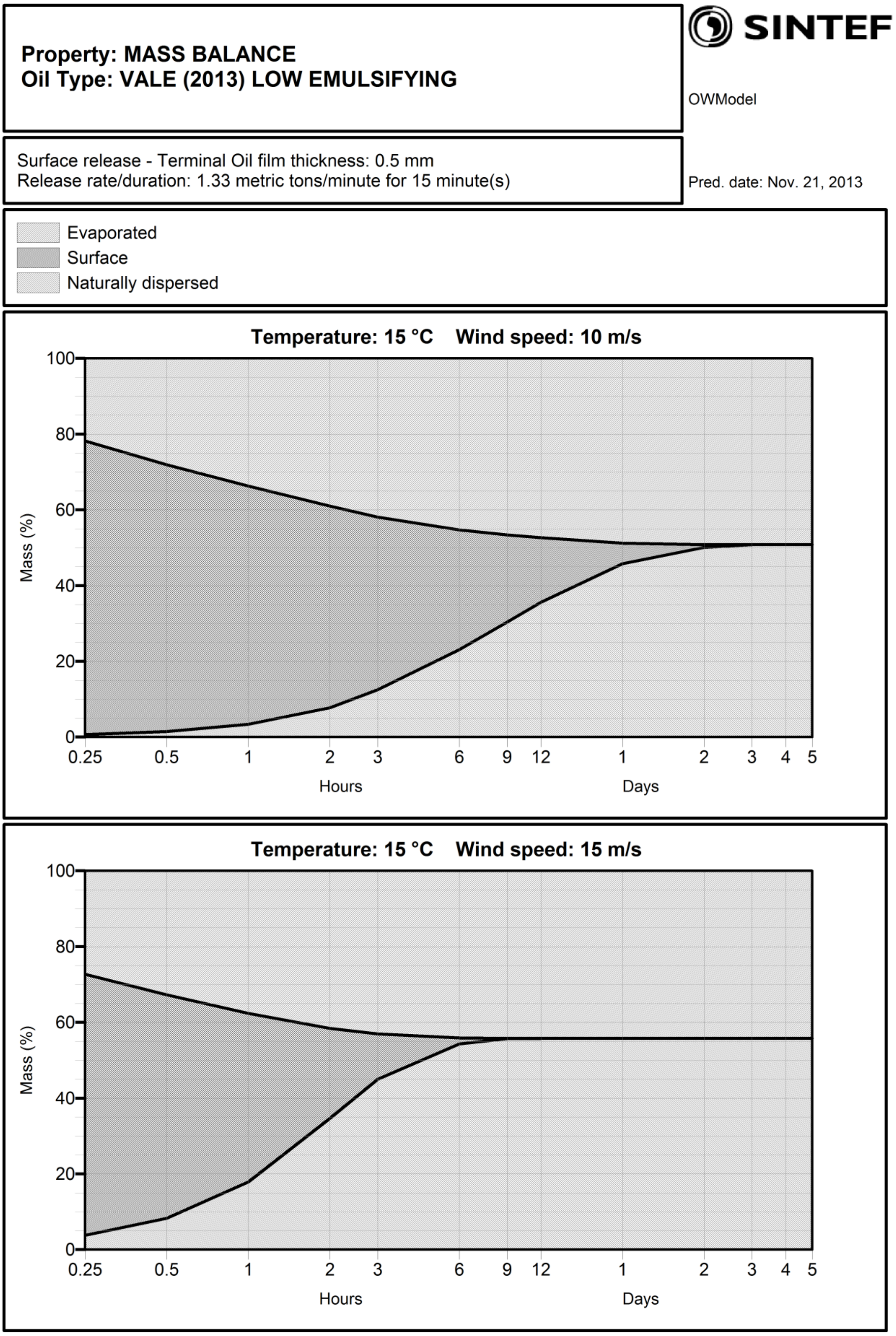


Figure 4-10: Predicted mass balance for Vale at 15°C and wind speeds of 10 and 15 m/s

4.4 Comparison with other oils

The weathering predictions of Vale are compared to Kvitebjørn, Trym, Gjøa and Oselvar crude oil at 15°C and 10 m/s in the figures below. These condition parameters are chosen as an example, and as data of all oils are available for these parameters.

Evaporative loss

Figure 4-11 shows that Vale has an average evaporative loss compared to the other oils, similar to both Oselvar and Kvitebjørn. After five days 60 vol % are predicted lost through evaporation.

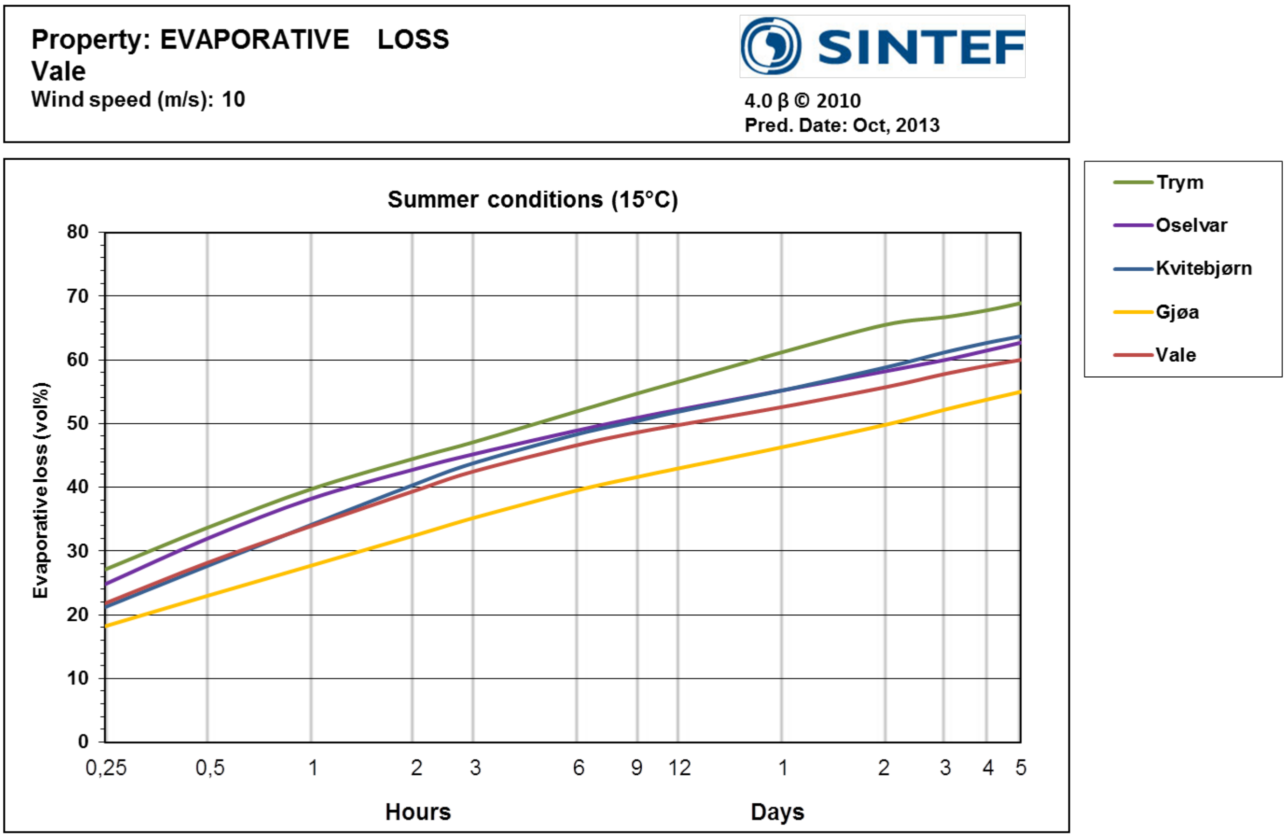


Figure 4-11: Predicted evaporative loss at 15°C and 10 m/s for Vale compared to other oils

Flash point

As oil is spilled on the sea surface, the temperature of the oil will be cooled to the ambient water temperature within a short period of time. The fire hazard will be at its greatest as long as the flash point of the oil is below the sea temperature.

As shown in Figure 4-12 Vale has similar flash point as Trym and Gjøa, and initially also similar to Kvitebjørn and Oselvar. It is also seen that there is no predicted fire hazard for any of the oils at the presented weather scenario, 15 °C and 10 m/s wind. An explosion hazard only exist for the very few first minutes at sea, before the oil is cooled to sea temperature.

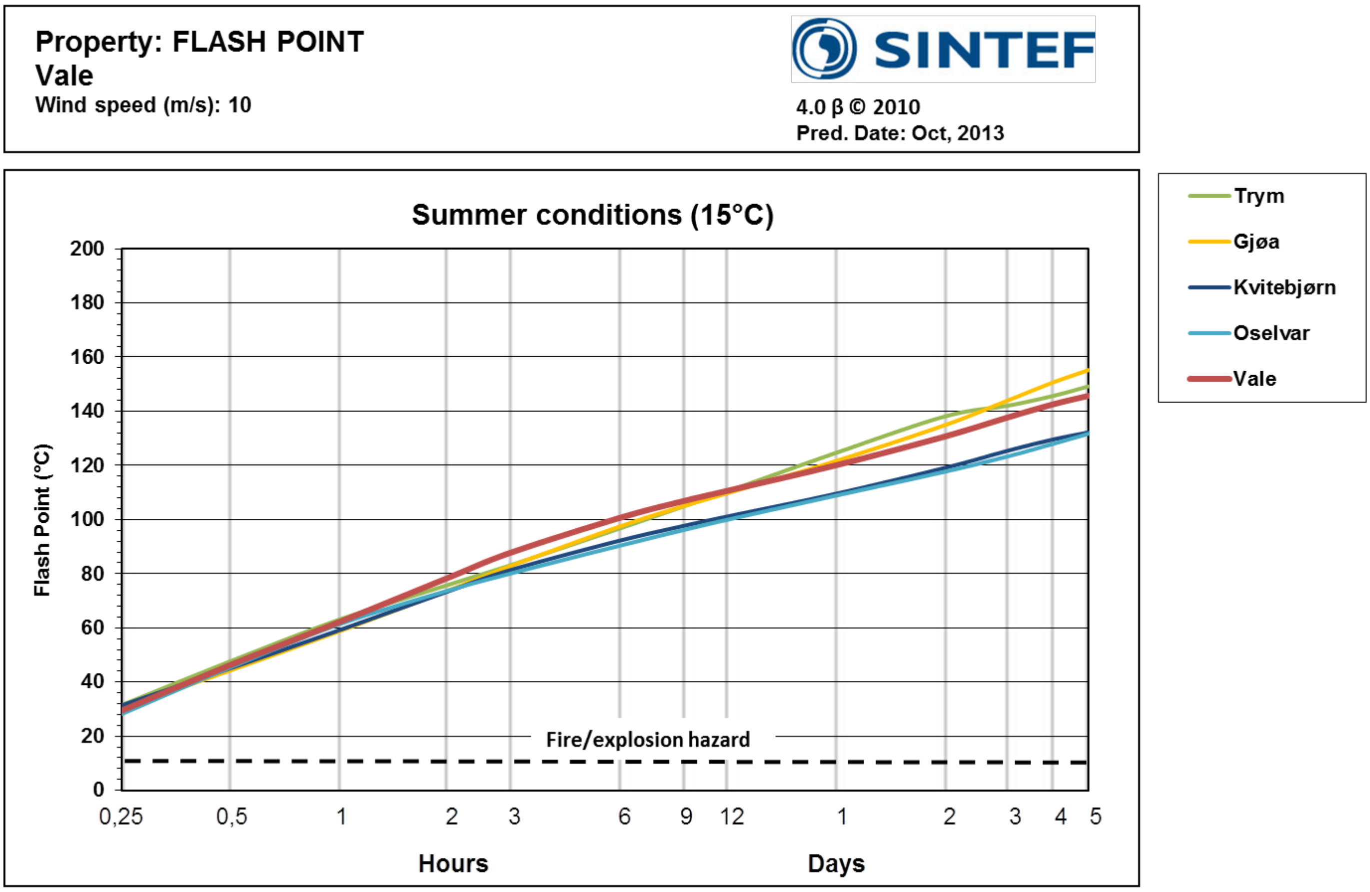


Figure 4-12: Predicted flash point at 15°C and 10 m/s for Vale compared to other oils

Pour point

Pour point depends on the oil's wax content and the amount of light components that are able to keep the waxes dissolved in the oil.

The oils chosen for the comparison all have a medium wax content (1.5-4.31 % in fresh oil) but have different compositions of lighter components. Gjøa and Oselvar express similarities in their predicted pour points while Vale demonstrates a predicted pour point intermediate of Trym and Kvitebjørn.

The predicted pour point for Vale implies solidification on the sea surface after only approx. three hours of weathering in summer conditions and 10 m/s wind speed. Solidification arises at 10-15 °C above the sea temperature, shown as a dotted line in Figure 4-13.

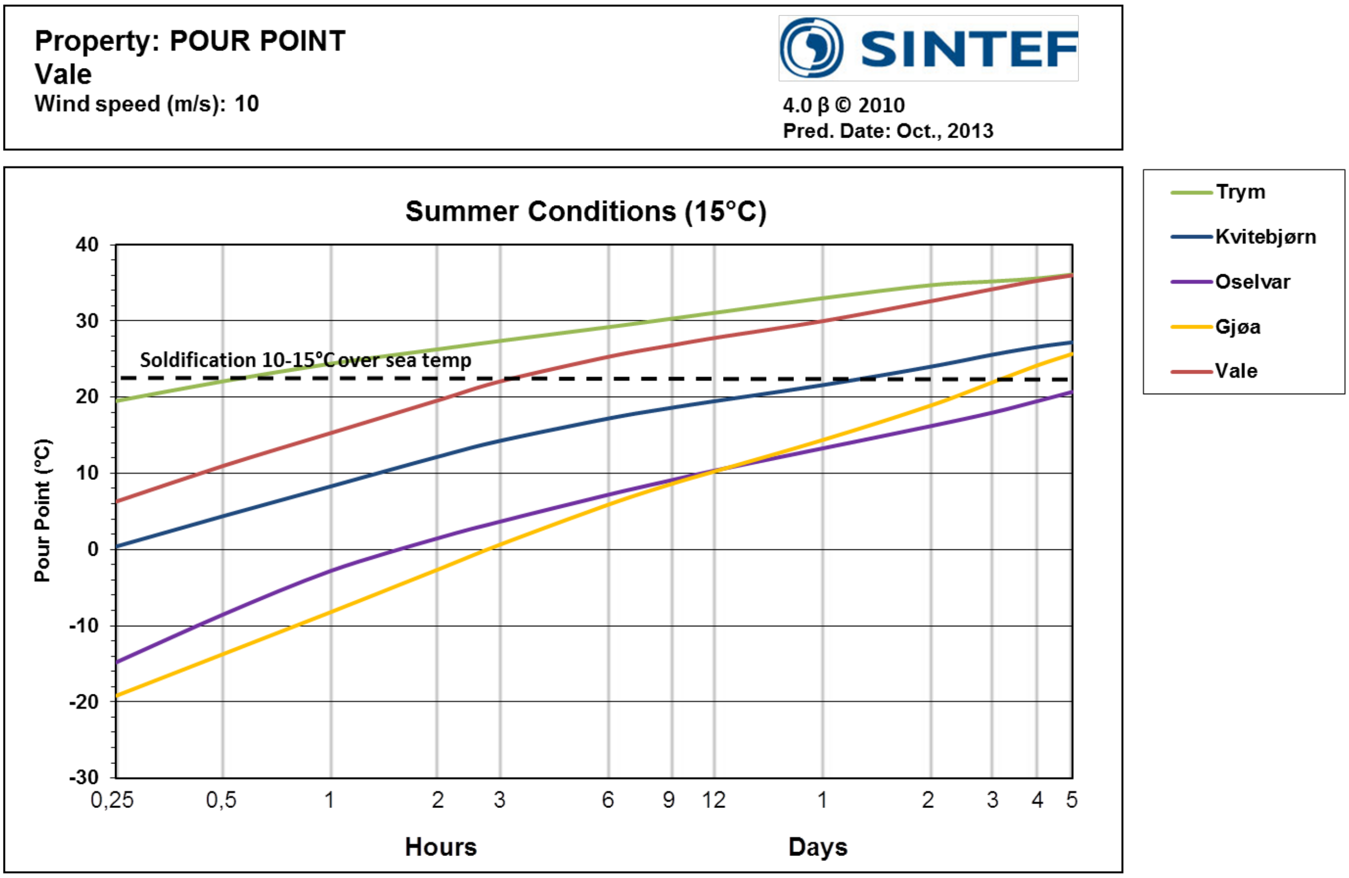


Figure 4-13: Predicted pour point at 15°C and 10 m/s for Vale compared to the other oils. Dotted line at predicted solidification point (10-15°C above sea temperature).

Water content

Vale is predicted to have a rapid and high water uptake, reaching a maximum water level of 75 vol.% after approx. 6 hours of weathering at 15 °C and 10 m/s wind speed. As Figure 4-14 express, Vale has the most rapid water uptake of the chosen oils and only Oselvar reaches the same water content, though after four days.

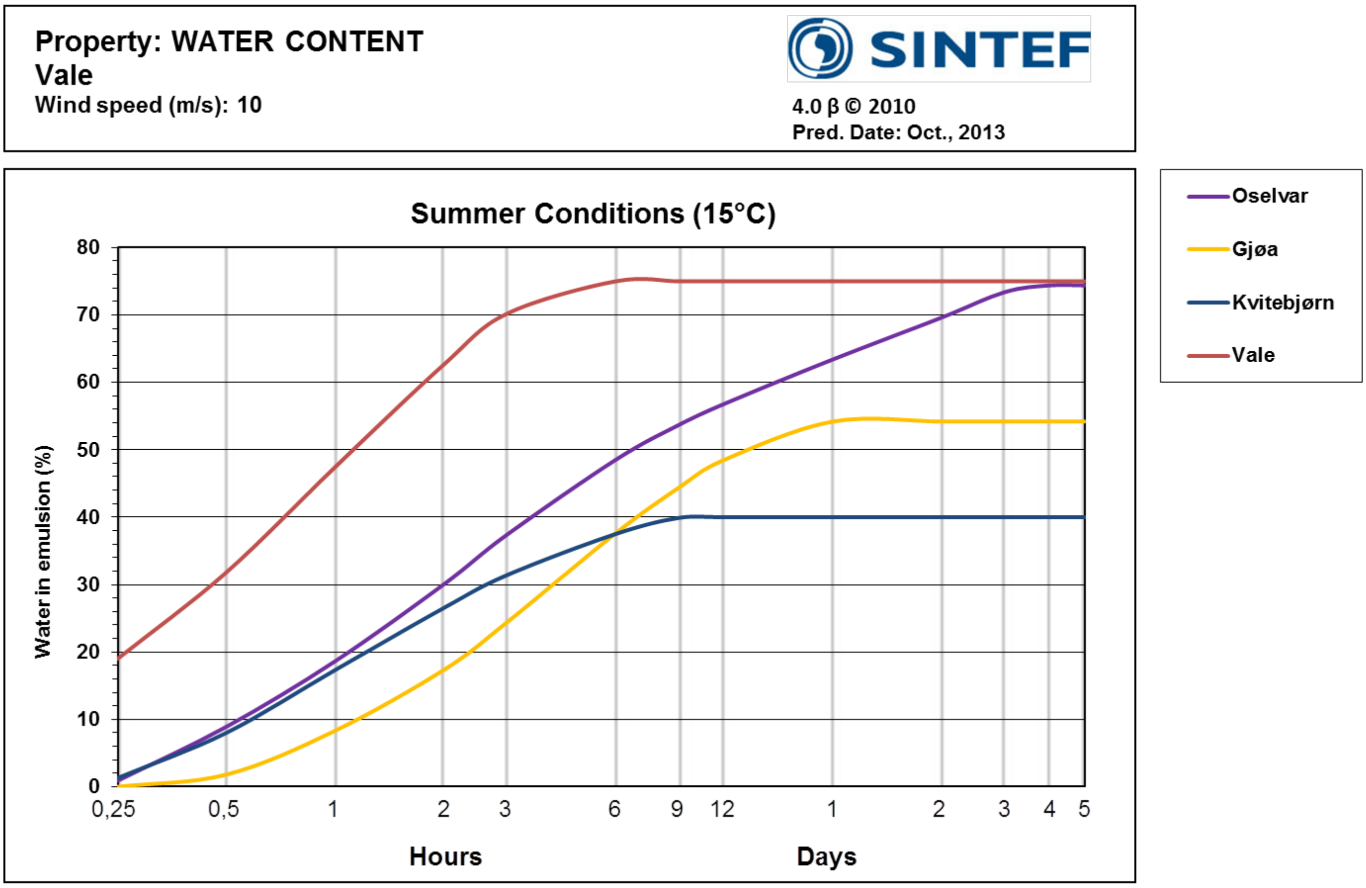


Figure 4-14: Predicted water content at 15°C and 10 m/s for Vale, compared to the other oils

Emulsion viscosity

Vale forms loose emulsions that are prone to lose water when mixing energy is removed. As Figure 4-15 shows, the Vale emulsion has a relatively high viscosity compared to the other oils.

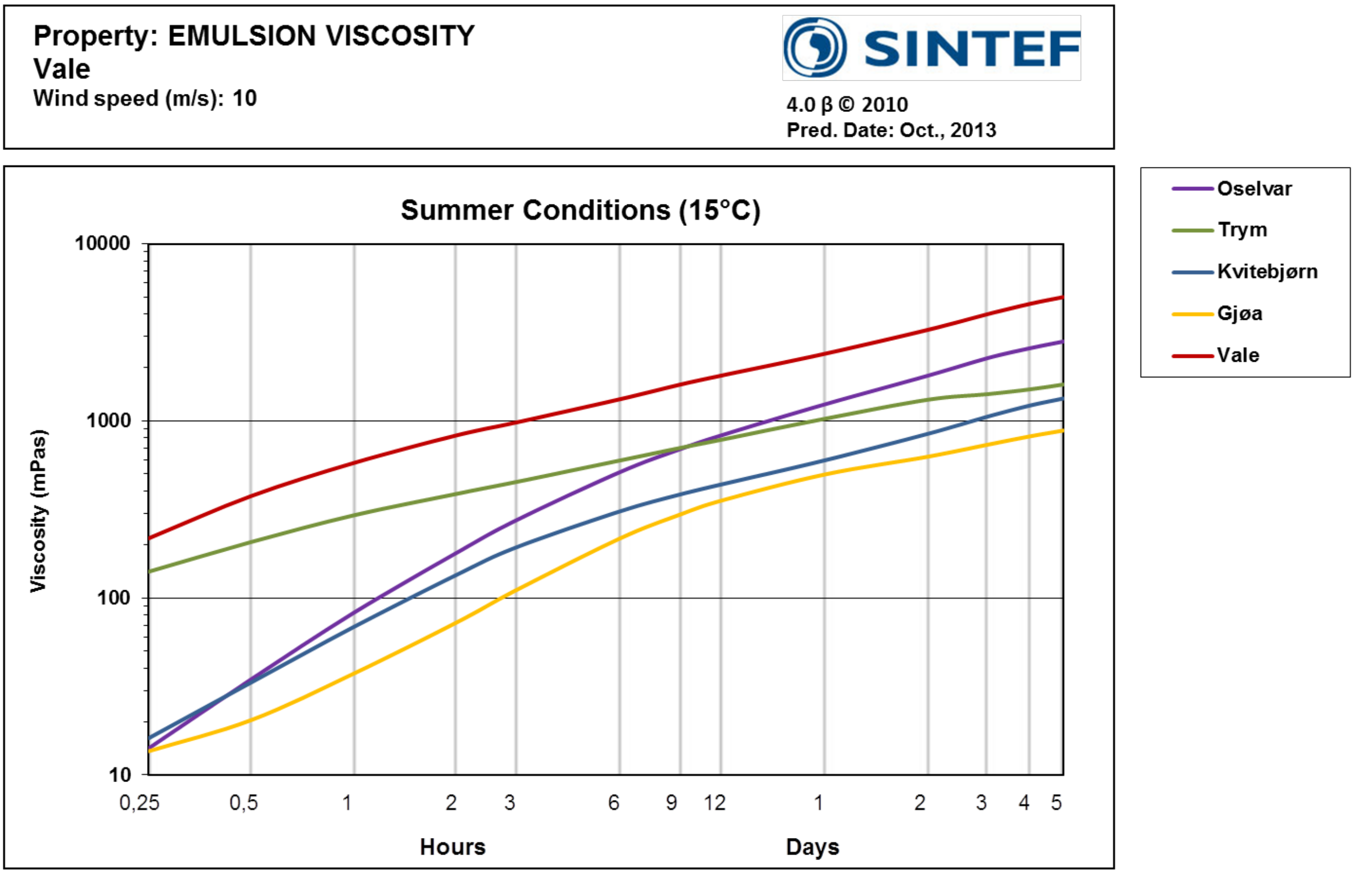


Figure 4-15: Predicted viscosity of the emulsions for Vale compared with the other oils at 15°C and 10 m/s.

Mass balance of surface oil

Figure 4-16 shows the remaining oil on the sea surface after evaporative loss and natural dispersion. Vale is predicted to be removed from sea surface in the course of five days, similar to Oselvar.

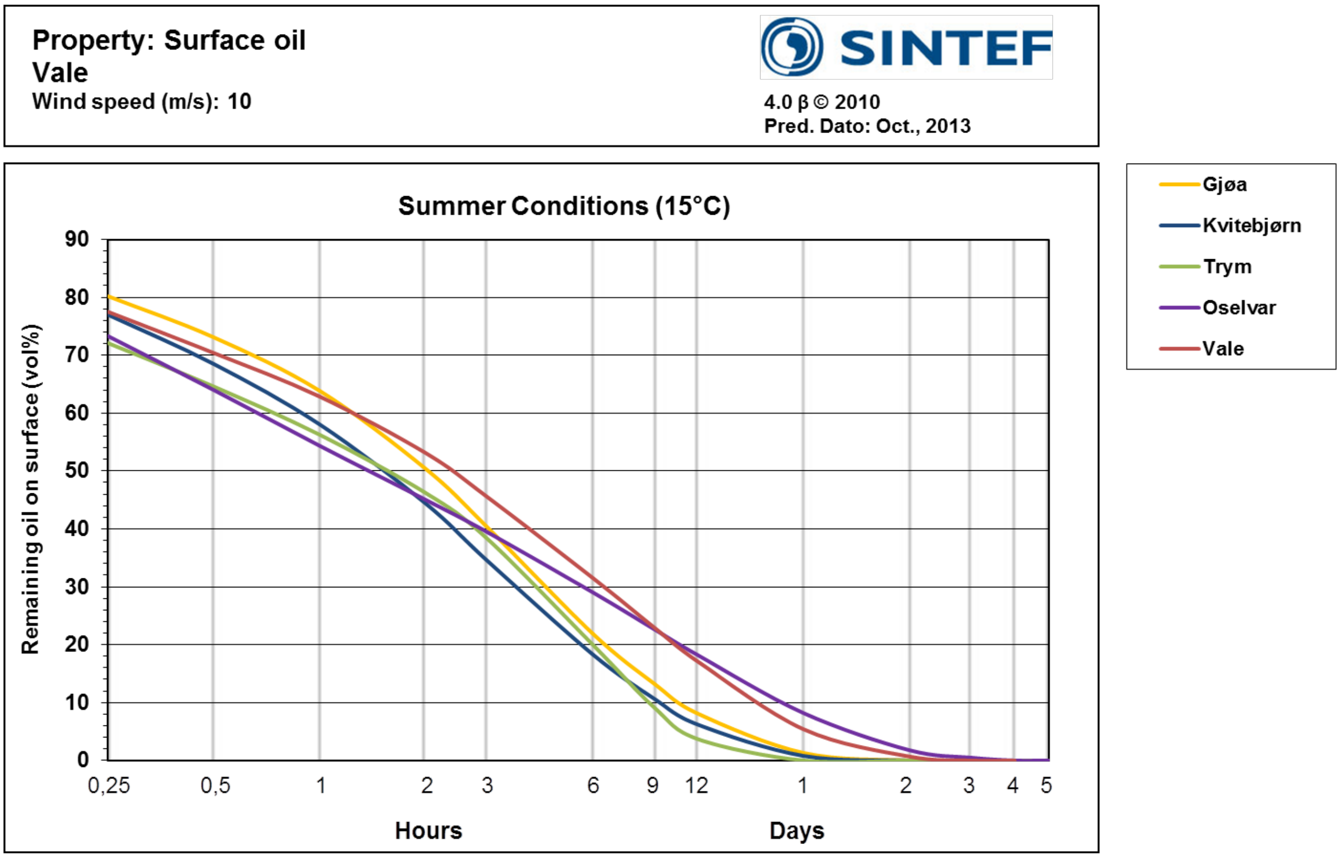


Figure 4-16: Predicted surface oil at 15°C and 10 m/s for Vale compared to the other oils

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

5.1 Oil properties

Vale has a medium wax content and low content of asphaltenes (0.06 %), and is defined as paraffinic light oil. Due to the high content of lighter components initial evaporation after a spill will be relatively high. This loss will shift the relative content of wax and asphalthenes.

Since the relative concentration of heavy end components increases with the degree of weathering, the physical properties of the oil will change. Knowledge about how the oil properties change during weathering is important in an oil spill response.

5.2 Flash point - fire/explosion hazard

The fire or explosion hazard after an oil spill is greatest at the very beginning, before the oil has cooled to ambient water temperatures. The fire/explosion hazard prevails as long as the oil's flash point is below the sea temperature. For Vale, the flash point will be above the sea temperature within an hour at low wind speed (2 m/s) and at both temperatures.

Vessels involved in oil recovery often have a flash point limit of 60 °C for the liquids stored on board. For Vale this limit is predicted to be reached after eight hours of low wind speed (2 m/s) in winter conditions. In summer conditions the same limit is reached after five hours. Higher wind speeds will cause the tank storage limit to be reached considerably faster.

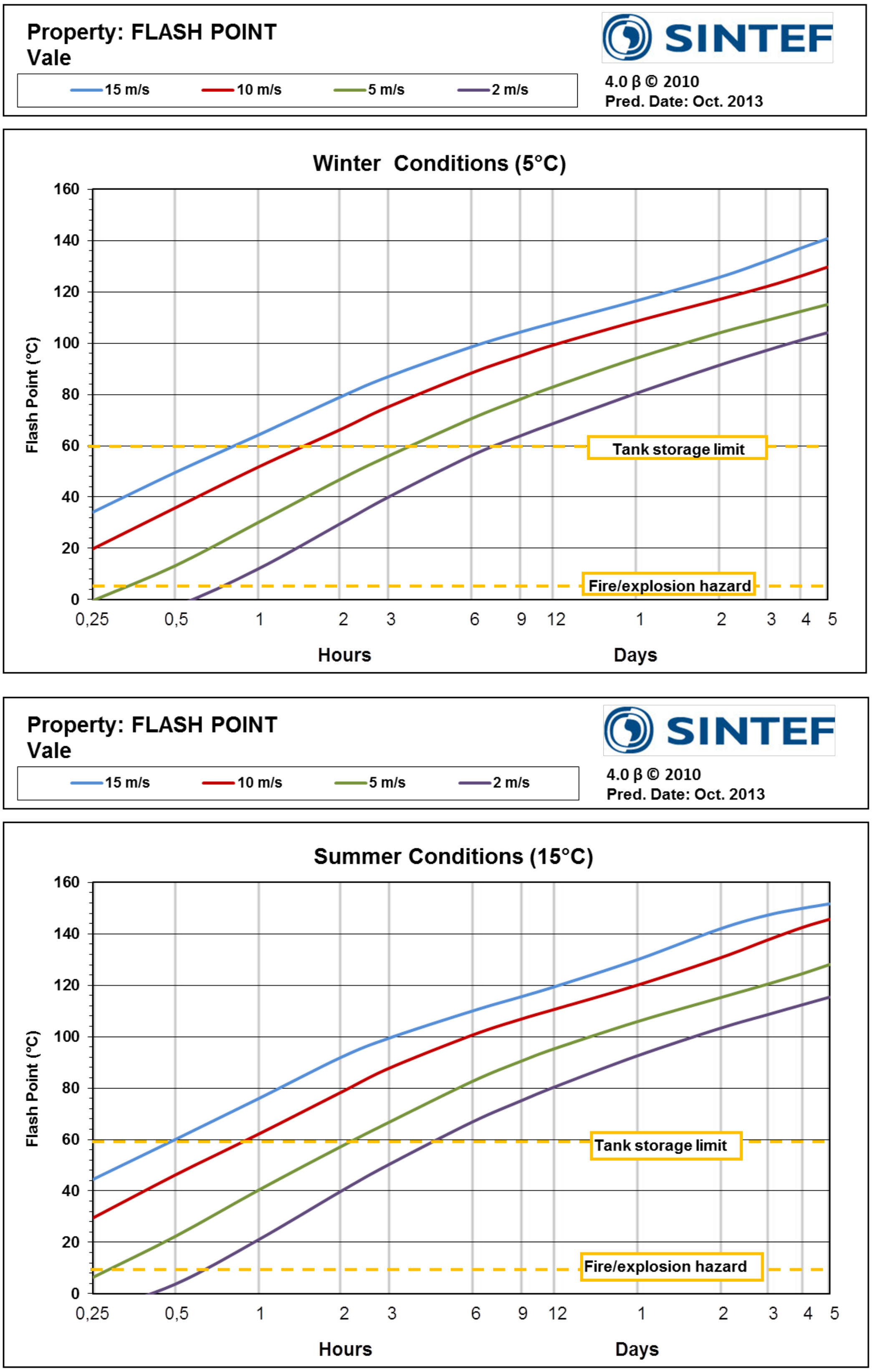


Figure 5-1: Flash point for different sea states of Vale crude oil at 5ºC and 15ºC

5.3 Emulsion formation

The total amount of oil on the sea surface is reduced due to evaporation and natural dispersion in the initial stages of weathering. However, the water mixed into the oil increases the volume considerably, as illustrated in Figure 5-2. Due to Vales rapid water uptake, emulsions with high water content are formed quickly on the sea surface under both winter and summer conditions.

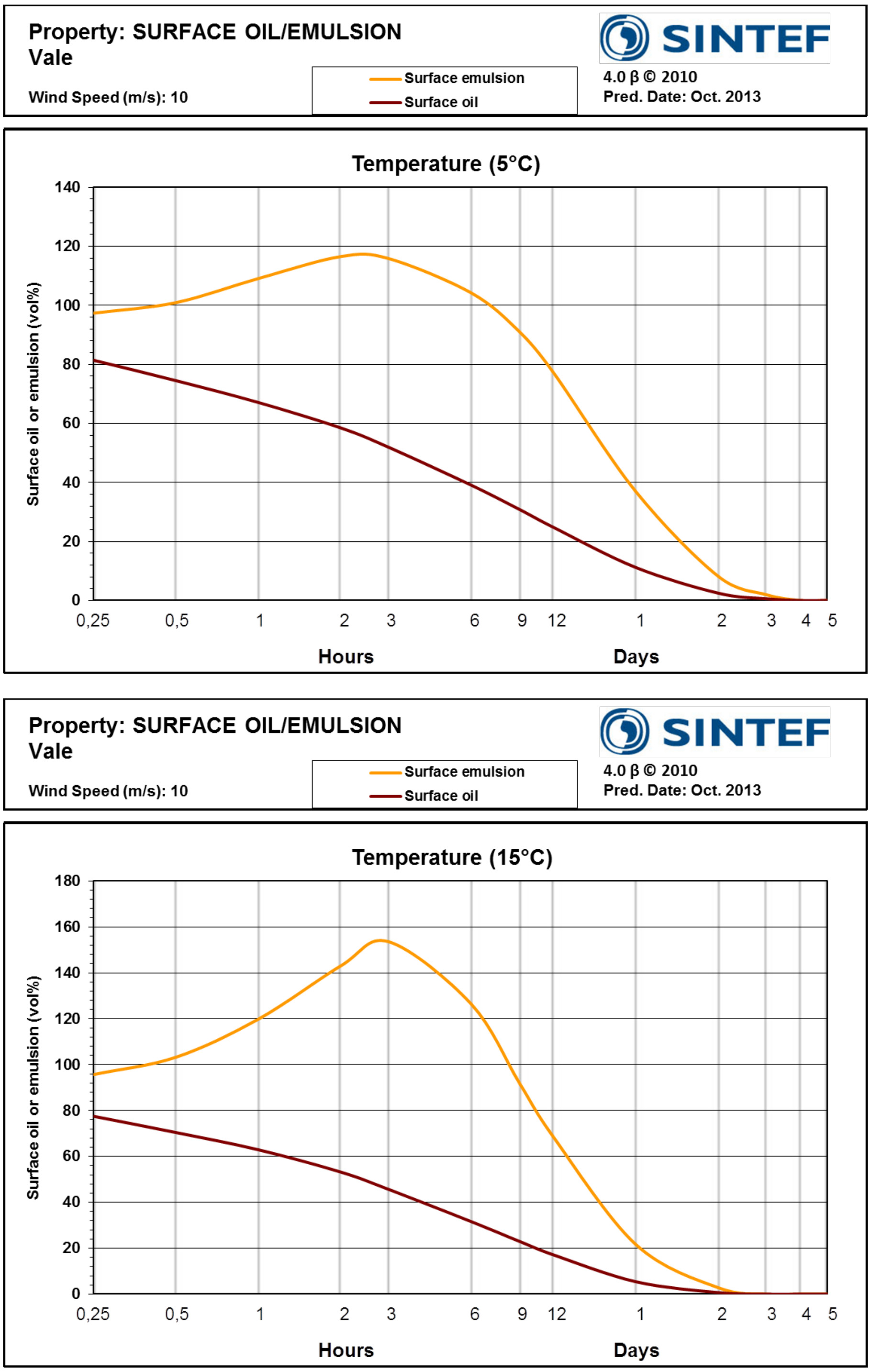


Figure 5-2: Difference in the total slick volume due to emulsification compared to non-emulsified oil. Decrease in total volume due to evaporation and natural dispersion predicted at 10 m/s wind speed at temperatures of 5ºC and 15ºC

5.4 Breaking of emulsion with addition of emulsion breaker

Figure 5-3 illustrates the relative volumetric composition of water-in-oil emulsion and free water, approximately one week after a spill of Vale oil at 5°C and 13°C, both with and without the addition of emulsion breaker (Alcopol O 60%).

Vale forms loose emulsions which will release water when placed for settling. The application of emulsion breaker was very effective, releasing almost all the water in the emulsions even at the lowest concentration (500 ppm). The results were similar for both 5 °C and 13°C.

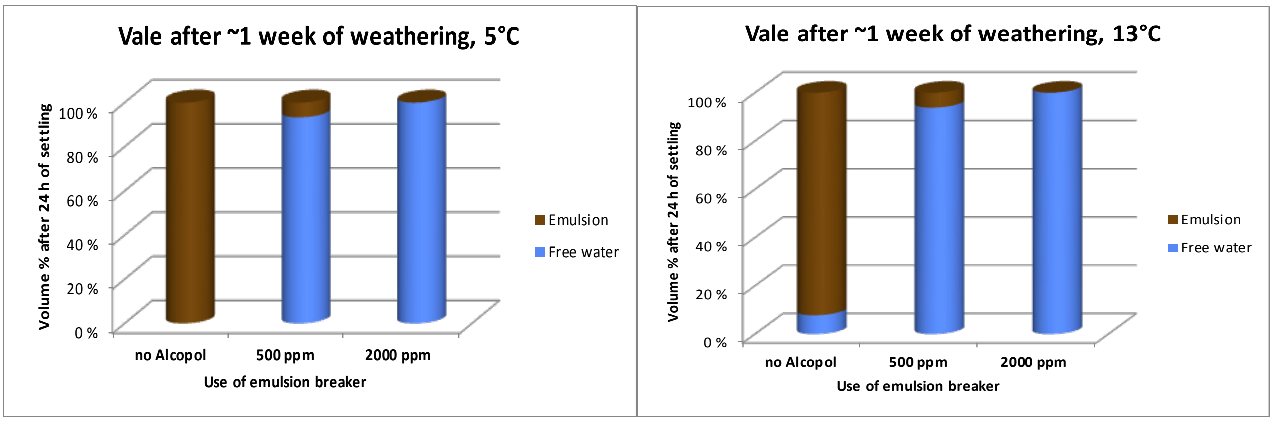


Figure 5-3: Emulsion stability of Vale oil both with and without treatment of emulsion breaker approximately one week of weathering (250°C+ residue) on the sea surface at 5°C and 13°C.

5.5 Lifetime at sea - natural dispersion and evaporation

The lifetime of an oil spill at sea depends on the oil's composition, the release conditions (e.g. on the surface, underwater) and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the surface.

Figure 5-4 shows the remaining surface oil as a function of time for different sea states under summer and winter conditions for Vale crude oil.

Considerably larger spills (>1 000 m^3) are expected to produce longer lifetimes. Individual modelling for such spills is needed.

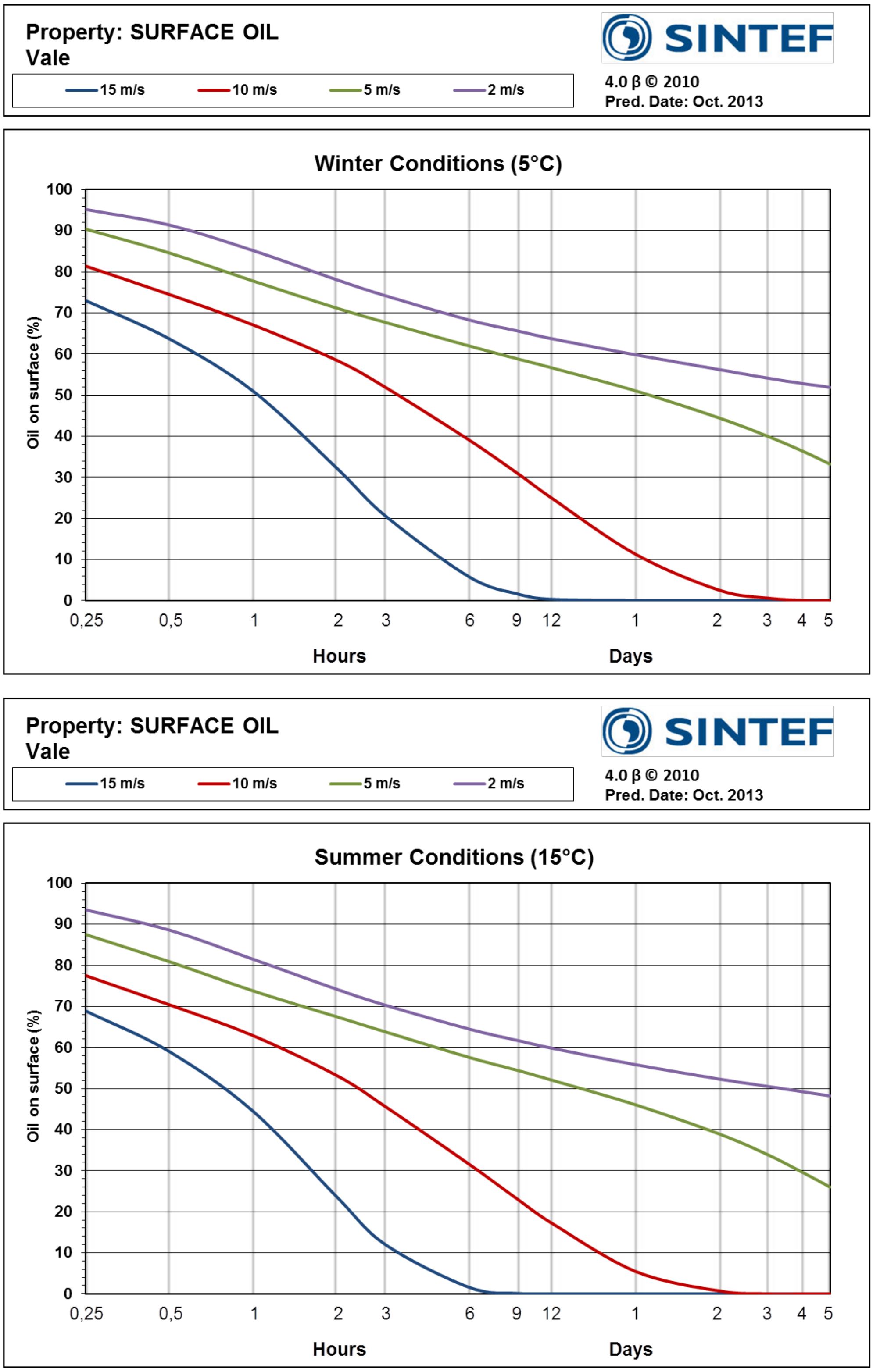


Figure 5-4: Remaining surface oil under different sea states for Vale at 5°C and 15°C. Predictions for an instant surface release of 20 tonnes.

5.6 Oil spill response

Mechanical recovery

Experiences from Norwegian field trials have demonstrated that the effectiveness of various mechanical clean-up operations is reduced due to the high degree of leakage of the confined oil or w/o emulsion from the oil spill boom. This leakage is particularly pronounced if the viscosity of the oil or the w/o emulsion is lower than 1000 mPas (Nordvik et al., 1992). The lower viscosity limit for an optimal mechanical clean-up operation has therefore been set at 1000 mPas. However, if conditions are calm successful recovery of emulsions with lower viscosities is possible.

As can be seen in Figure 5-5 Vale will remain beneath this 1000 mPa limit for 12 hours under low wind and summer conditions. During winter conditions and low wind speed the time limit before Vale reaches 1000 mPas is six hours. The limit will be reached faster at higher wind speeds.

Previous studies at SINTEF have shown that both weir skimmers operated by NOFO (Transrec) and adsorption skimmers (e.g. Foxtail) may have reduced recovery effectiveness at viscosities above 15,000-20,000 mPas (Leirvik at al., 2001). The viscosities of Vale emulsions are not predicted to reach such levels under any wind or temperature conditions. This gives a wide window of opportunity for mechanical recovery using the Transrec with traditional weir-skimmer head.

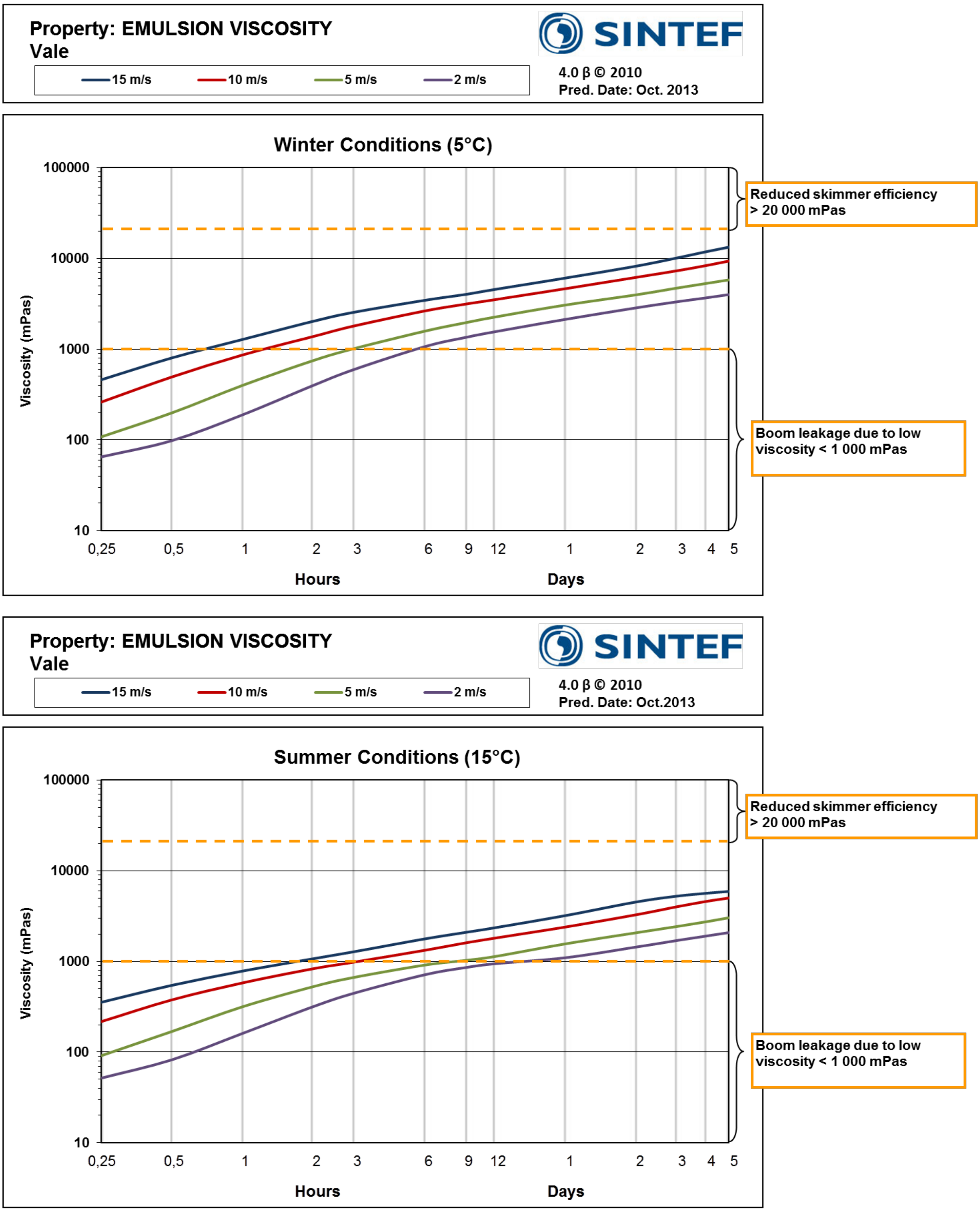


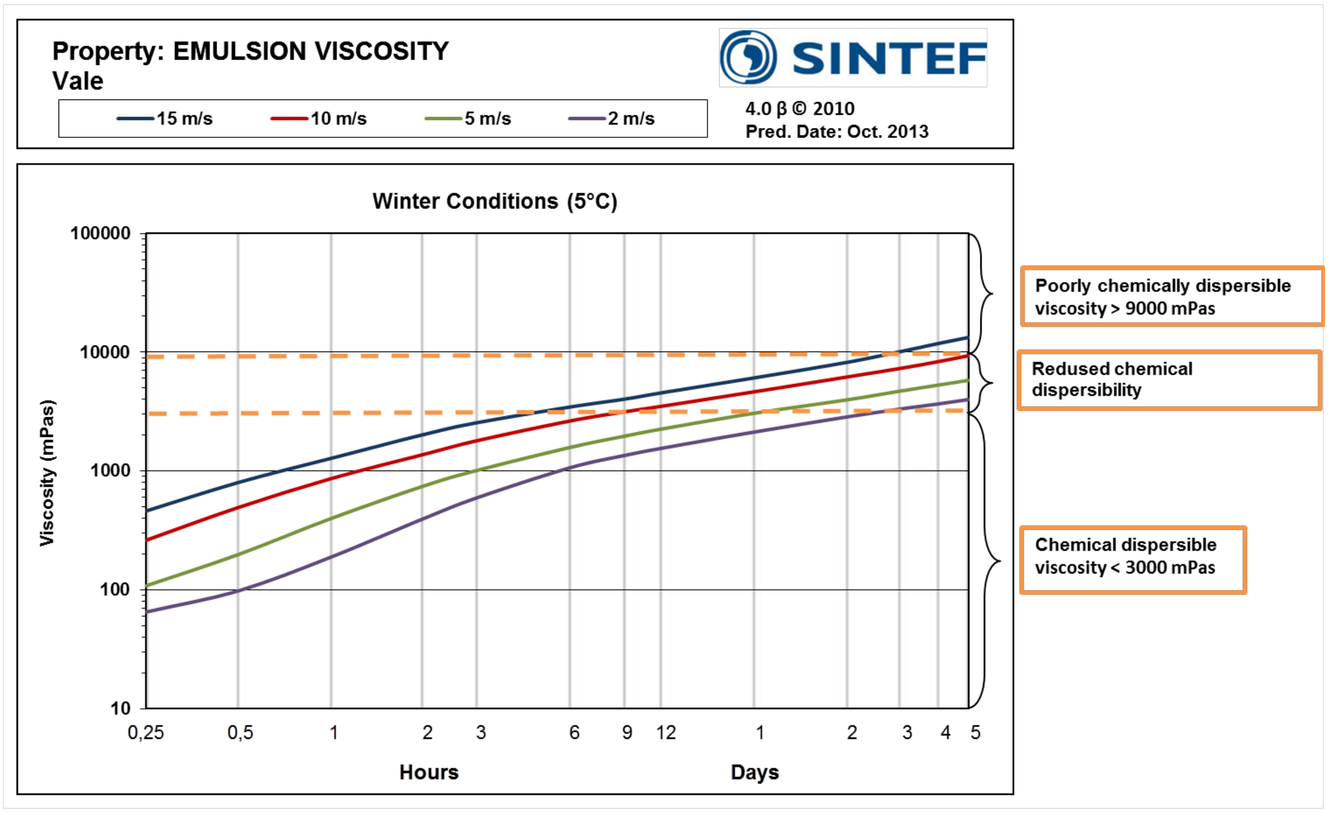
Figure 5-5: Predicted emulsion viscosity for Vale at 15°C and 5°C compared with expected viscosity limits for extensive boom leakage and poor flow to weir skimmers

Use of chemical dispersants

Vale is expected to have good potential for successful chemical dispersion as long as certain criteria are met. As previously mentioned, chemical dispersants worked well on emulsions under high energy conditions. This is demonstrated by the clear differences seen in the two dispersibility tests (IFP and MNS) in Figure 3-8 on page 26.

In high energy conditions such as during high wind speeds, the oil and emulsions will be more fluid than in calmer weather due to Vale's non-Newtonian properties. This will result in a higher degree of mixing between chemical dispersant and oil/emulsion, thus increasing the effectiveness of the dispersants.

As Vale is expected to have reduced dispersibility in calm weather, applying additional energy by use of e.g. thrusters, Fire Fighting (Fi-Fi) systems or MOB (Man over board) boats 10-30 minutes after treatment may in such situations increase the dispersant effectiveness.



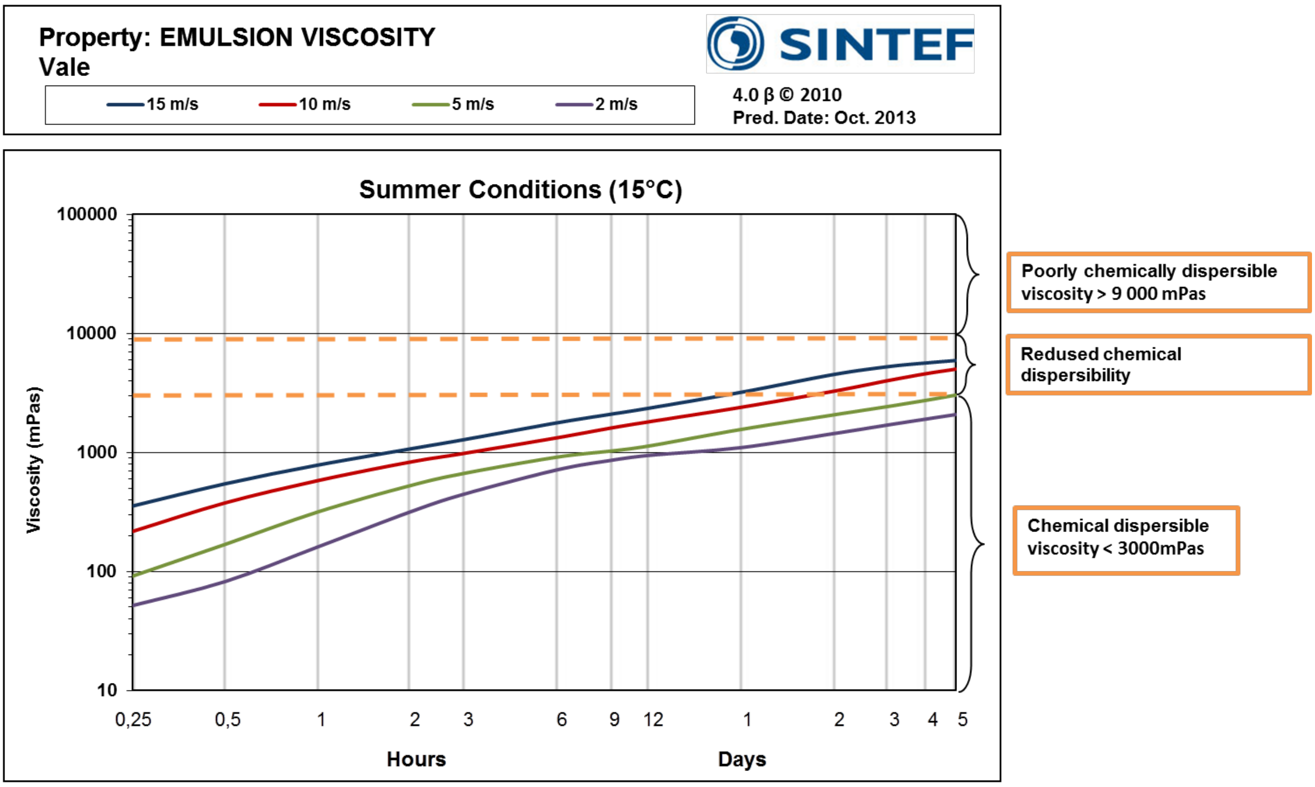


Figure 5-6: Time window for use of chemical dispersants as a function of viscosity for Vale at 5ºC and 15ºC.

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A - The behaviour of crude oil on the sea surface (in general)

A.1 The chemical composition of crude oils

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

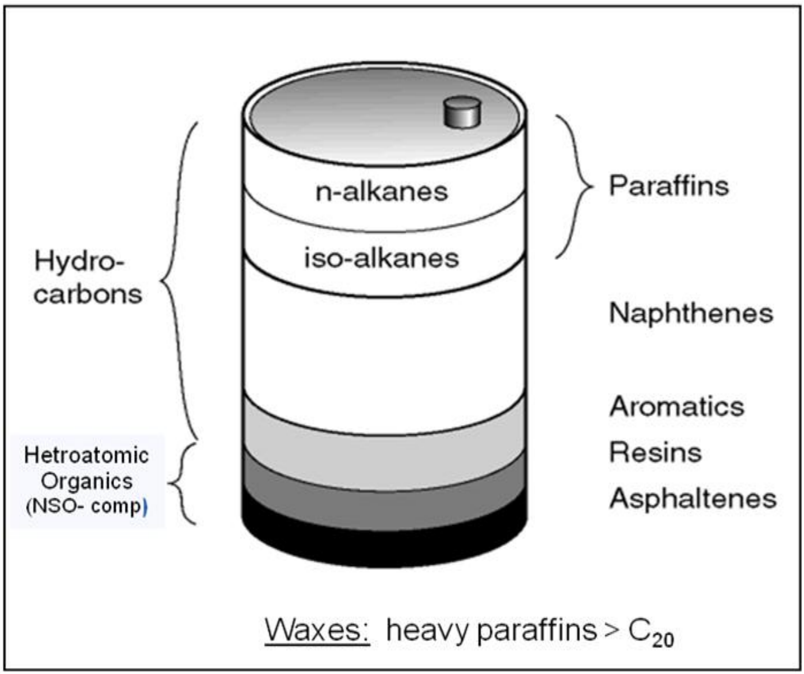


Figure A 1: The chemical composition of crude oils

A.1.1 Hydrocarbons

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

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

Paraffins

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

Naphthenes

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

Aromatics

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

A.1.2 Heteroatomic organics

In addition to pure hydrocarbons, some organic compounds in crude oils also contain small amounts of oxygen, nitrogen or sulphur, as well as some trace metals such as vanadium and nickel. The two most important groups of heteroatomic organic compounds are resins and asphaltenes.

Resins

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

Asphaltenes

This is a complex group of poorly characterized chemical compounds that consist of condensed polycyclic aromatic compounds. They are large molecules with 6-20 aromatic rings and side chains (molecular weight 1000-10000). Asphaltenes may be classified as "hard" or "soft" on the basis of the method of determination. Crude oils may contain up to 6 wt.% "hard" and 10 wt.% "soft" asphaltenes.

A.2 Main oil categories - related to weathering

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

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

- Crude oils
- Light oils
- Condensates

Crude oils contain relatively more heavier components than the other two categories, and the 250˚C+ residue (corresponds to 0.5 to 1 week after a spill at sea) evaporates less than 50 vol.%. The heavier components make possible formation of stable water-in-oil (w/o) emulsions, which reduces the oil spreading at the sea surface. The final (terminal) film thickness of a crude oil depends on the emulsion's physical properties, and will be in the order of 1 mm.

Light oils and crude oils are not differentiated in the reservoir terminology. However, related to weathering studies, it is suitable to deal with the light oils as a separate category. Light oils have a high content of light components, and the 250˚C+ residue evaporates less than 50 - 70 vol.%. In contrast to condensates light oils also contain heavier components. The content of these heavier, emulsion-stabilizing components cause that light crudes may emulsify water. These w/o emulsions are, however, very unstable. A light oil will spread less than a condensate, and a final film thickness of 0.5 mm is estimated.

Condensates evaporates typically more than 70 vol.% for the 250˚C+ residue. Condensates will not contain components as asphaltenes and heavier waxes, and will not emulsify significantly amounts of water. The spreading is vast, with a final film thickness in the order of 0.05 mm.

A.3 Physical properties of crude oils

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

Density

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

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

$$\boxed{°\text{API} = \frac{141{,}5}{Secific\ gravity} - 131{,}5}$$

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

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

A.3.1 Rheological properties

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

Absolute viscosity is: *force distance/area speed* and has the unit: $\text{dyn}\cdot\text{sec/cm}^2$ = 1 Poise. The industry is often using the unit mPas = centipoise (cP). The viscosity of fresh crude oils can vary from less than 1 to more than 2000 mPas (cP) at ambient sea temperature. In comparison water has an “absolute” viscosity of 1 cP and syrup 120 000 cP at 20°C.

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

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

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

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

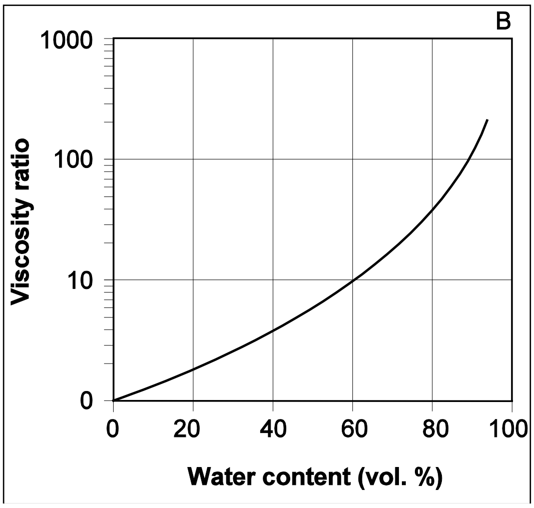


Figure A 2: Example of viscosity ratio as a function of water content

A.3.2 Pour point

The temperature at which oil ceases to flow when cooled without disturbance under standardized conditions in the laboratory is defined as the oil's pour point (ASTM-D97). The method accurately determines the temperature at which the oil become semi-solid under the specified laboratory conditions. Due to the movement at the sea surface, the oil may remain a liquid at sea at temperatures as low as *10 to 15°C lower* than the pour point of the oil. The pour point of oil with high wax content will increase dramatically with evaporation as the lower weight molecules, which contribute to keeping the wax in solution, evaporate. The pour point for oils with high wax contents can reach 30°C, while low viscous naphthenic oils may have pour points as low as - 40°C.

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

A.3.3 Distillation curve (True Boiling Point curve-TBP)

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

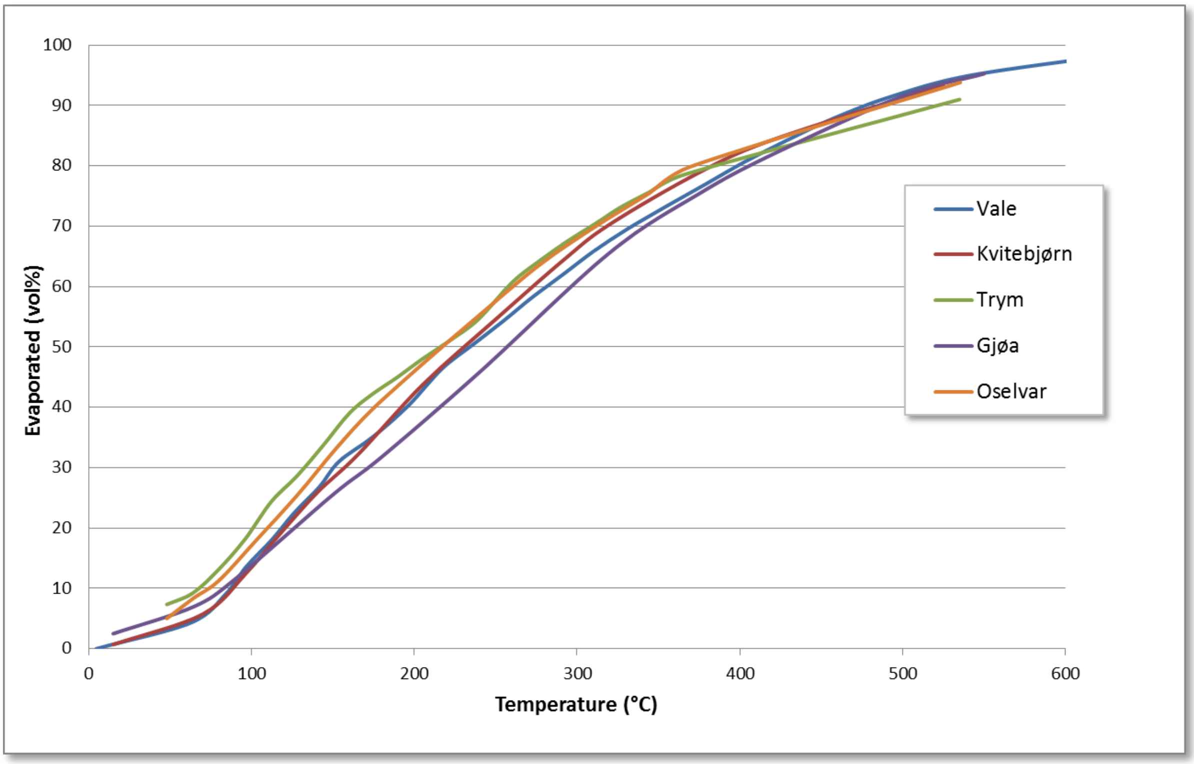


Figure A 3: Distillation curves for Vale crude in comparison with other Norwegian crude oils

A.3.4 Flash point

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

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

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

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

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

A.4 The behaviour of crude oil spilled at sea

When crude oil is spilled at sea, a number of natural processes take place that change the volume and chemical properties of the oil. These natural processes are evaporation, water-in-oil (w/o) emulsification, oil-in-water (o/w) dispersion and the release of oil components into the water column, spreading, sedimentation, oxidation and biodegradation. A collective term for all these natural processes is weathering. The relative contribution of each process varies during the duration of the spill.

The weathering of oil depends on the oil type (chemical and physical properties), the weather conditions (wind, waves, temperature and sunlight) and the properties of the seawater (salinity, temperature, bacterial flora, etc.).

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

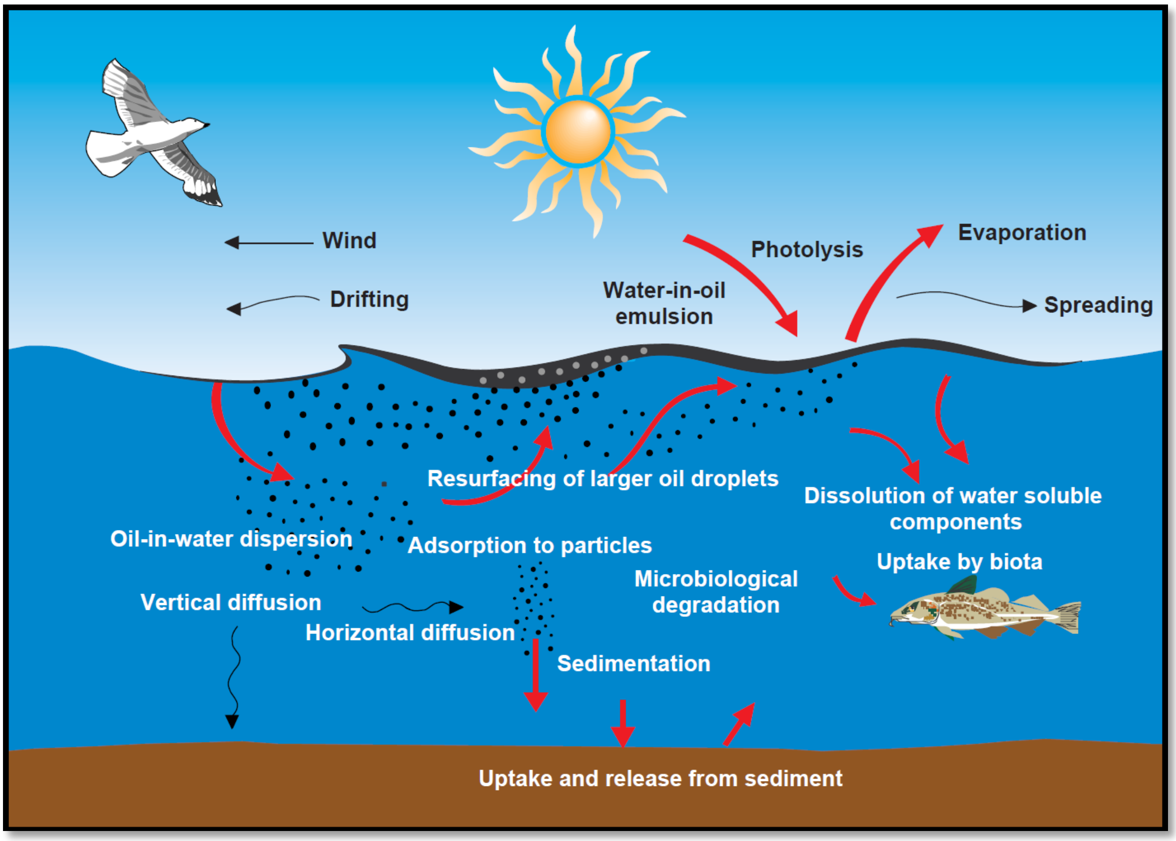


Figure A 4: Illustrating the weathering processes that take place when oil is spilled on the sea surface

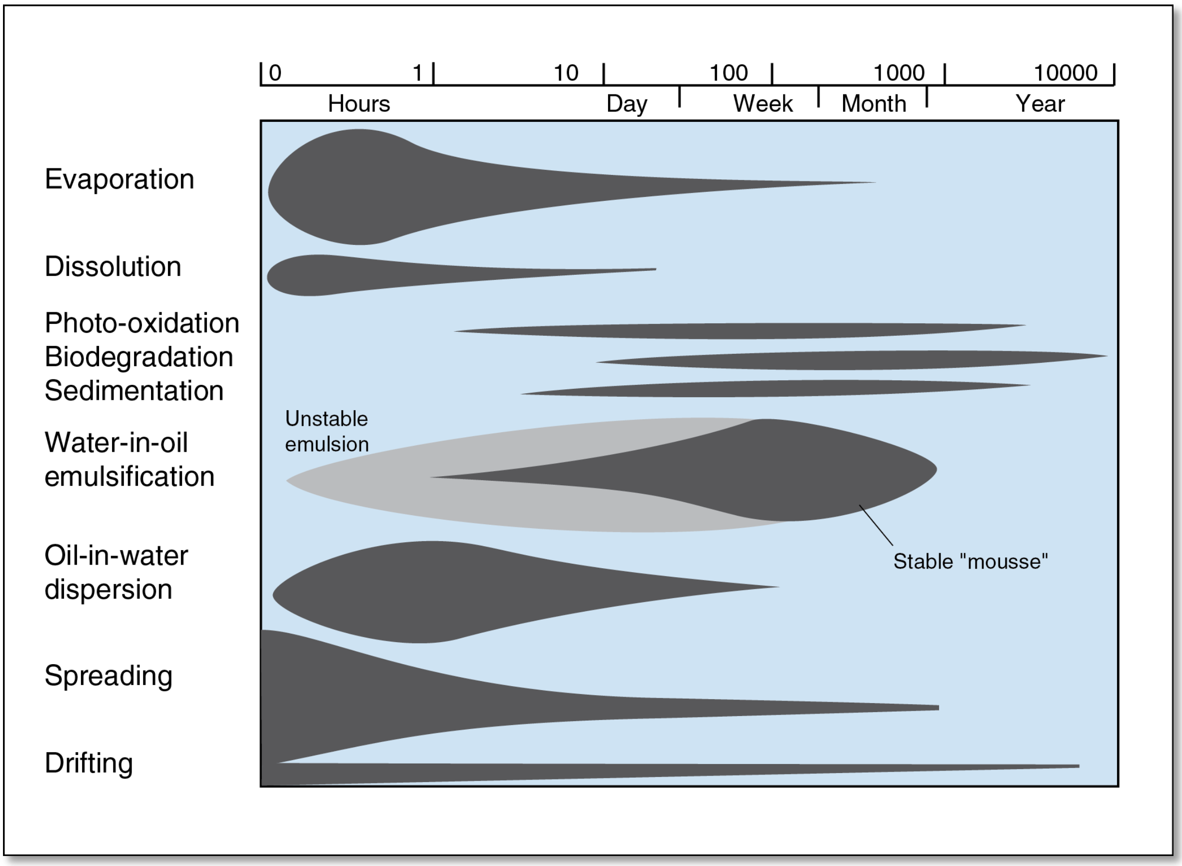


Figure A 5: Weathering processes' relative importance over time. Note: logarithmic scale.

A.4.1 Evaporation

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

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

The rate of evaporation varies for different oil types. Light refinery products (e.g. gasoline and kerosene) may completely evaporate after a few hours/days on the sea surface. Condensates and lighter crude oils can lose 50% or more of their original volume during the first days after an oil spill.

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

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

A.4.2 Spreading

Oil spilled at sea will spread on the sea surface. Spreading is often the dominant process in the initial stages of an oil spill, and decreases as the viscosity and density of the remaining oil increases. The spreading process is also retarded if the oil's pour point is 10-15°C below the sea temperature.

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

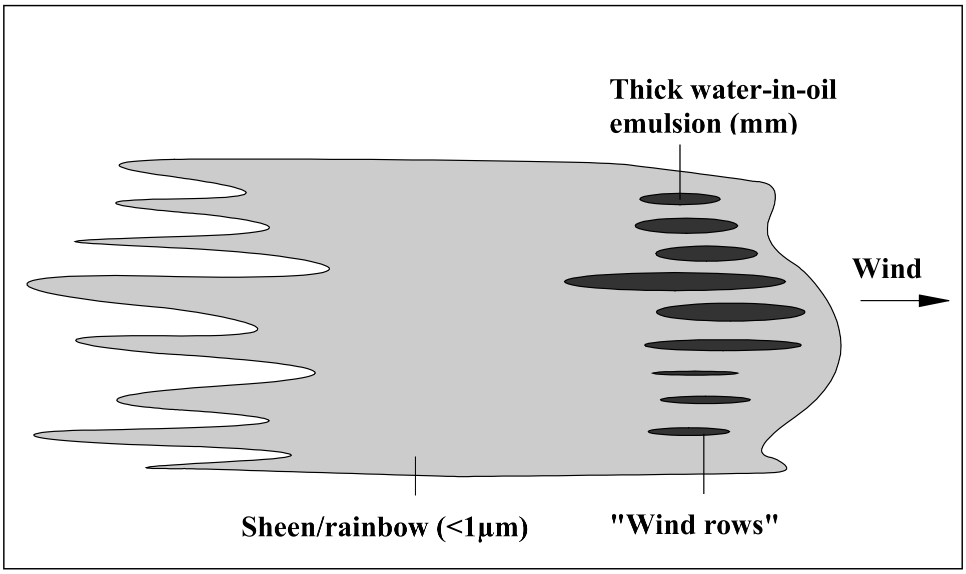


Figure A 6*:* ***The spreading of oil spilled on the sea surface and the distribution within the oil slick***

A.4.3 Drift of an oil slick

The oil slick will drift as the weathering processes continue. The wind and current conditions cause the oil slick to drift, as illustrated in **Error! Reference source not found.**. 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, 1993). In the absence of wind, the oil drift is governed by the prevailing (background) current.

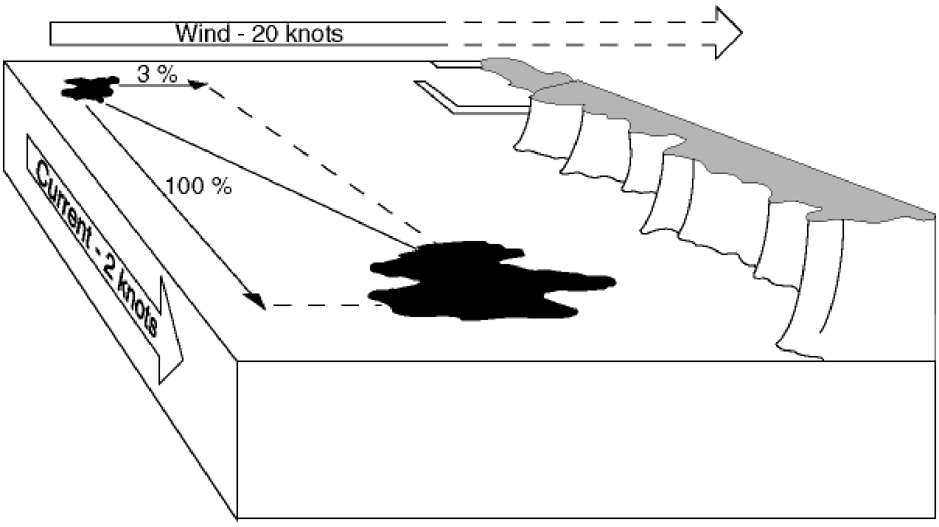


Figure A 7: An illustration showing how wind and current can influence the drifting of an oil slick

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

The formation of water-in-oil emulsions significantly affects the behaviour and clean-up of oil spilled at sea. As a result of emulsification, the total emulsion volume may increase to as much as six times the original spilled oil volume depending on the properties of the oil. The formation of w/o emulsions also contributes to keeping oil on the sea surface. A w/o emulsion normally has a higher viscosity than the parent crude oil, so the emulsification process will therefore retard/delay evaporation and the natural dispersion process.

A minimum criterion for the formation of w/o emulsions is often 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. **Error! Reference source not found.** shows how wind speed influences the w/o formation rate.

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

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

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

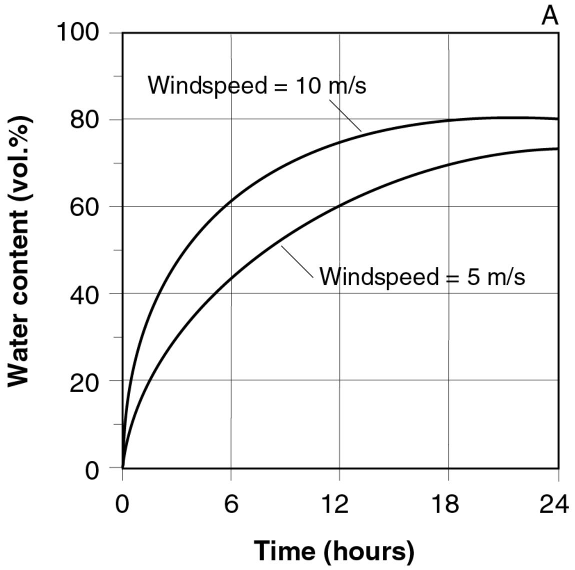


Figure A 8: Example of how weather conditions influence the w/o emulsion formation for typical oils

The formation of emulsion 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 asphaltic compounds in the oil 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 **Error! Reference source not found.**.

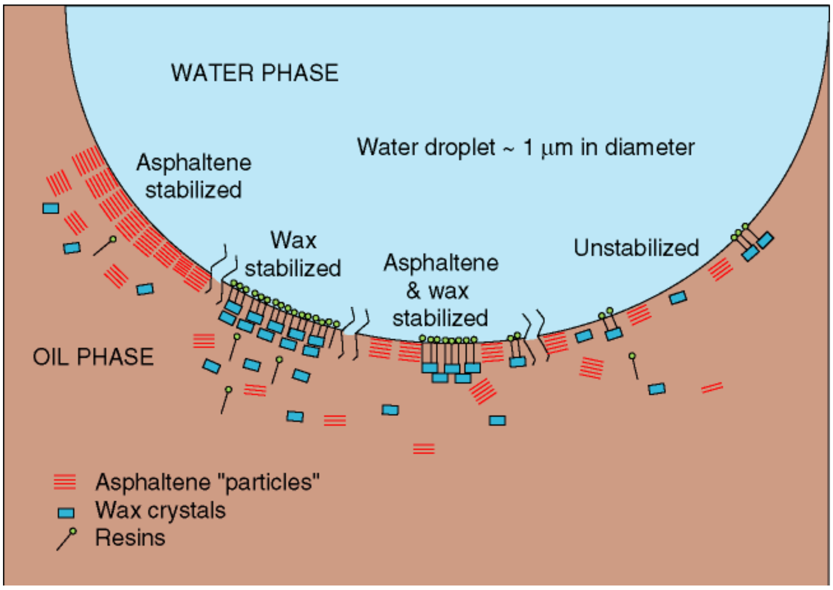


Figure A 9: Interfacial layer stabilized by wax and asphaltenes in w/o emulsion

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.

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

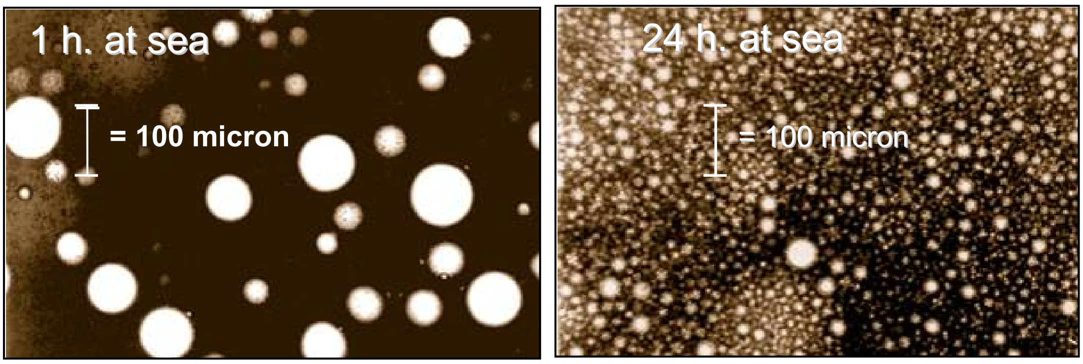


Figure A 10: Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder

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

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

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

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

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

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

A.4.6 Water solubility

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

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

A.4.7 Photo-oxidation

Under the influence of sunlight, some of the oil components will slowly oxidize to resins and finally asphaltenes. This contributes to the stability of w/o emulsions (chapter A.4.4), therefore exerting a large influence on the oil's persistence on the sea surface. The photo-oxidized components will stabilize the w/o emulsions. After a long period of weathering at sea, tar balls, mainly consisting of asphaltenes, may be formed and can break down very slowly, both at sea and on beaches.

A.4.8 Biodegradation

Seawater contains an abundance of micro-organisms that can break down all types of oil components. The various micro-organisms prefer specific oil components as their energy source. Bacteria can only degrade oil in contact with water and depend on the water/oil interface area. The interface area increases as the oil is spread over the sea surface in a thin layer or by chemical or natural dispersion of oil in the water mass.

Important factors influencing the biodegradation rate are temperature, the nutrient supply that contain nitrogen and phosphorus, the oxygen supply, oil type and the degree of weathering. Low molecular compounds are degraded more rapidly than the heavier compounds in the oil, thus giving the following order for biodegradation: straight-chain *n*-alkanes > branched isoalkanes > cyclic alkanes > cyclic naphthenes > aromatics> resins > asphaltenes (Perry, 1984). PAHs dissolved in water can be degraded within a few days (Brakstad and Faksness, 2000). Degradation of oil in contact with seawater depends highly on the water/oil interface area. The interfacial area increases as the oil is spread over the sea surface as a thin layer or by chemical or natural dispersion of oil into the water column.

At sea, the formation of oil droplets by natural or chemical enhanced dispersion will increase the biodegradation rate in the water mass by10 to >100 times compared to surface oil due to increased water/oil interfacial area, and it has been shown that n-alkanes are biodegraded within 2-4 weeks at North Sea conditions (Brakstad and Lødeng, 2005). Other higher molecular-weight oil compounds are biodegraded more slowly and some very high molecular-weight compounds (equivalent to the heavy residues in crude oil that are used to make bitumen) may not biodegrade to any significant degree.

A.4.9 Sedimentation

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

B Experimental setup

B.1 Oil samples and test temperature

The cans were marked as follows:

Vale, DS-2401
Ref. 500 515 649
Sendt av Statoil, fra 1760 Heimdal A Platform
Merket MD-637
Sendt 25.6.13

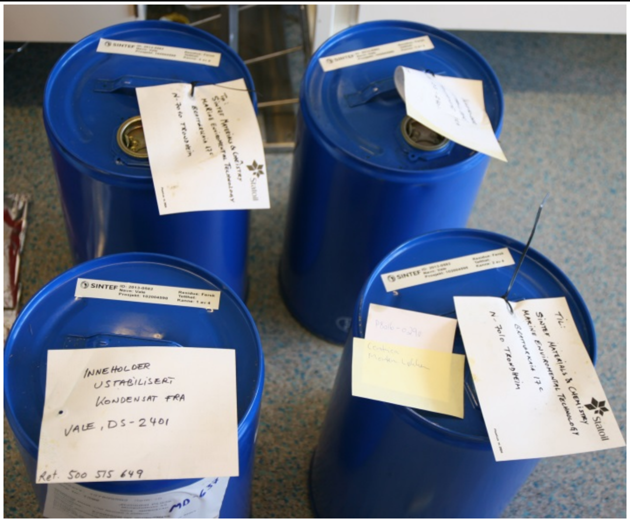


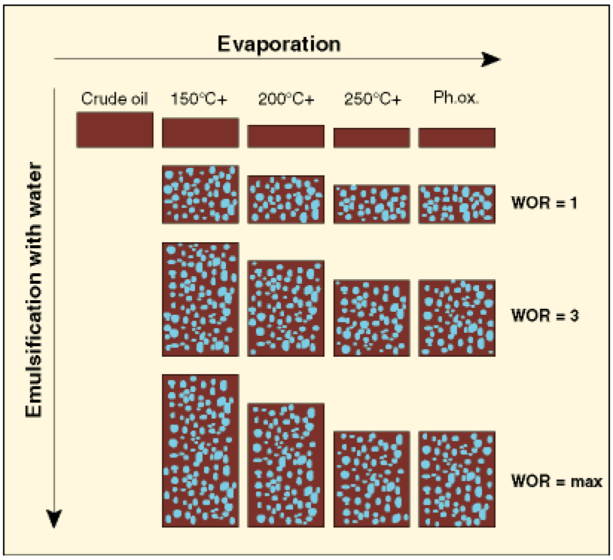
Figure B 1: Picture of the cans with Vale crude oil

Vale was given the unique SINTEF ID: **2013 - 0582**

The testing of the weathering properties was performed at 5°C and 13°C, which are regarded as typical winter and summer North Sea temperatures.

B.2 Small-scale laboratory testing

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



WOR: Water to Oil Ratio

WOR=1: 50 vol.% water

WOR=3: 75 vol.% water

WOR=max: the maximum water content

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

B.2.1 Evaporation

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

B.2.2 Physical and chemical analysis

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

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

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

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

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

Chemical characterization by GC/FID and GC/MS

- The distribution of hydrocarbons (nC_5-nC_{40}) was analysed using a Gas Chromatograph coupled with a Flame Ionisation Detector (GC/FID). The Gas Chromatograph used was an Agilent 6890N with a 30m DB1 column.
- The analysis and quantification of PAHs, phenols and alkylated phenols (C_0-C_4) were completed using an Agilent 6890 Gas Chromatograph coupled with a 5973 MSD detector (GC/MS) operating in SIM mode (Selected Ion Monitoring)
- The volatile components were in the range of nC_5-nC_{10} and were quantified by use of PT-GC-MS (Purge and Trap Gas chromatograph Mass Spectrometer operating in full-scan mode, and using a modified version of the EPA 8260 analysis method)

B.2.3 Emulsification properties

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

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

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

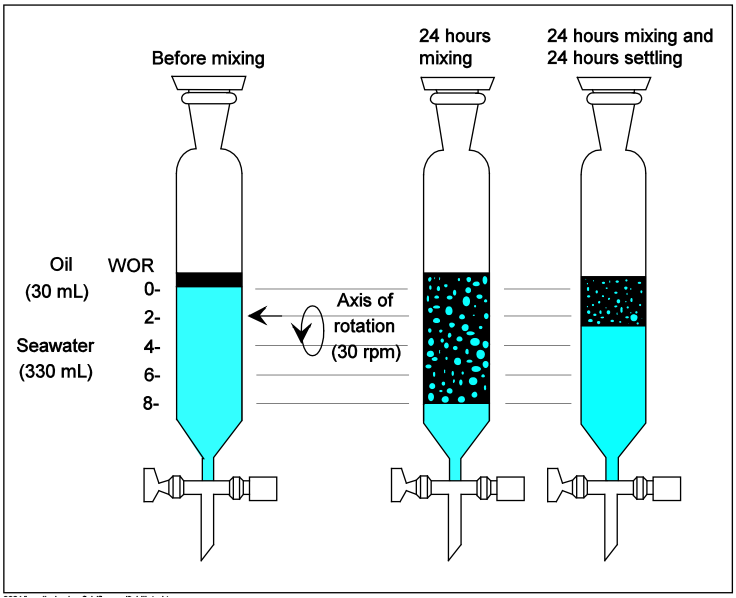


Figure B 3: Principle of the rotating cylinder method

B.2.3.1 Calculation of emulsion stability

The stabilities of the created emulsions and the effect of demulsifier were calculated using the following formulas.

Formation and properties of water-in-oil emulsions

$t_{1/2}$	Express relative rate of water-in-oil emulsification ability of an oil, i.e. the time needed for picking up half the maximum water content (in vol. %)
WOR	Volumetric water to oil ratio in the emulsion
WOR_{max}	Maximum volumetric relation of water to oil in the emulsion after a rotating time of 24 hours.

Stability of water-in-oil emulsions:

An emulsion is defined to be totally stable if no water is separated during a 24 hours settling period (no dehydration). The stability is thus expressed through the volumetric dehydration (D_{24h}, definition below) of the emulsion.

Breaking of water-in-oil emulsions by the use of demulsifiers:

WOR	Volumetric water to oil ratio in the emulsion
WOR_{ref}	Volumetric water to oil ratio in the emulsion after 24 hours rotation
WOR_{im}	Water to oil ratio in the emulsion "immediately" (i.e. 5 min. soaking + 5 min. mixing + 2 min settling) after treatment with emulsion breaker
WOR_{24}	Water to oil ratio in the emulsion after 24 hours of rotation + 24 hours of settling + 10 revolutions
D:	fractional dehydration of emulsion: $D = \frac{WOR_{ref} - WOR_x}{WOR_{ref}}$ where $_x$ means either $_{im}$ or $_{24h}$ D = 1 means a totally unstable, or broken, emulsion D = 0 means a totally stable emulsion
D_{im}	Dehydration obtained immediately (after 5 min. soaking + 5 min. mixing + 2 min. settling) after treatment with emulsion breaker
D_{24h}	Dehydration obtained after treatment with emulsion breaker and a 24 hour settling period.

B.2.4 Chemical dispersibility testing

As a screening test, the oils dispersibility properties were tested using five different dispersants at a dosage of 1:25 (4 wt%). The dispersants tested were; Dasic NS, Corexit 9500, Gamlen OD 4000, Finasol-OSR-62 and Superdispersant 25. For the dispersant showing greatest dispersibility, the optimal dosage and the time window for use of dispersants were surveyed. The screening and dosage tests were performed using the IFP method (discussed below) on a 200°C+ / 50% oil emulsion. In the systematic testing of all residues and emulsions, to establish the "time window" for effective dispersant use, both the IFP and the MNS tests were used. The viscosity of all the weathered samples was determined.

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

IFP (Institute Francais du Petrole test, Bocard *et al.*, 1984) is a low energy test estimated to represent low wave energies (2-5 m/s wind speed). A ring 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. The test apparatus is shown in **Error! Reference source not found.**.

MNS (Mackay and Szeto, 1980) is estimated to correspond to a medium to high sea-state condition. The energy input in this system, applied by streaming air across the oil/water surface, produces a circular wave motion. The sample of the oily water is taken under dynamic conditions after a mixing period of 5 min. The test apparatus is shown in **Error! Reference source not found.**.

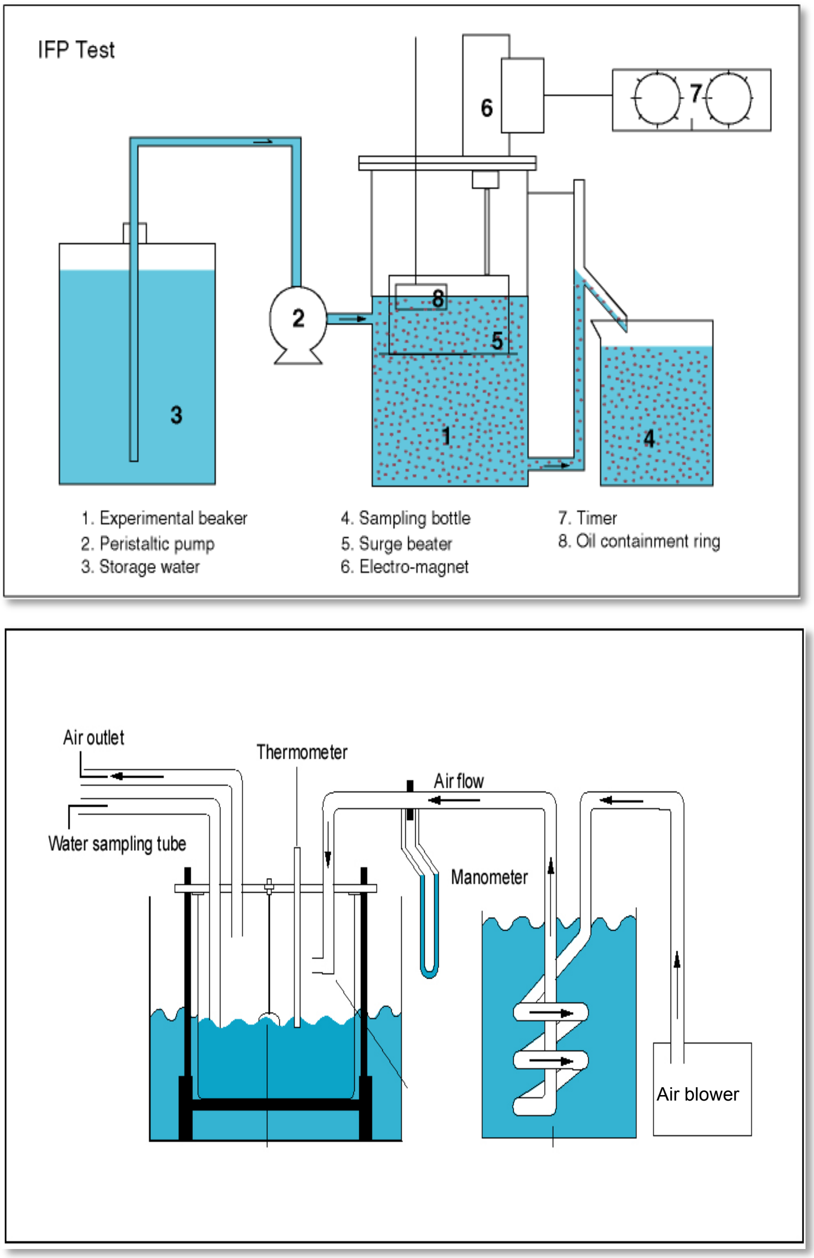


Figure B 4: IFP and MNS test apparatus

C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Vale is given in Table C 1 - Table C 3. The predictions were based on the 13°C study as predictions performed with the 5°C laboratory data harmonized will with predictions performed with 13°C.

Table C 1: Physical and chemical properties for Vale at 13°C and 5°C, used as input in the oil weathering model.

Properties of fresh oil	Value
Specific Gravity (60 F/15.5°C)	0.8156
Pour point (°C)	-9
Reference temperature (°C)	13
Viscosity at ref. temp. (mPas = cP) *	37
Asphaltenes (wt.%)	0.03
Flash Point (°C)	-
Wax Content (wt.%)	3.26
Dispersable for visc. <**	3000
Not dispersable for visc. > **	9000
Maximum water uptake (%)	75

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

*** Estimated*

- *No data available*

Table C 2: Lab weathering data for Vale at 13°C

Property	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	177	239	304
Vol. Topped (%)	0	27	40	53
Weight Residue (wt.%)	100	77	64	51
Specific Gravity (g/l)	0.8156	0.85115	0.86610	0.87943
Pour point (°C)	-9	6	18	27
Flash Point (°C)	-	33	69	107.5
*Viscosity of water-free residue (mPas =cP),	37	189	1169	5098
*Viscosity of 50% emulsion (mPas = cP)	-	342	643	2100
*Viscosity of 75% emulsion (mPas = cP)	-	244	331	1210
*Viscosity of max water (mPas = cP)	-	351	969	1680
Max. water cont. (vol.%)	-	32	62	81
(T1/2) Halftime for water uptake (hrs)	-	0.04	0.05	0.07
Stability ratio**	-	1	0.04	0.01

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

***Based on stability ratio of 24 hr settling + 10 rotations*

- *No data*

Table C 3: Lab weathering data for Vale at 5°C, used as input in the oil weathering model for simulation of winter conditions (viscosity measurements, water uptake and stability ratio are changed from the summer simulations).

Property	Fresh	150°C+	200°C+	250°C+

Boiling Point Temp. (°C)	-	177	239	304
Vol. Topped (%)	0	27	40	53
Weight Residue (wt.%)	100	77	64	51
Specific Gravity (g/l)	0.8156	0.85115	0.86610	0.87943
Pour point (°C)	-9	6	18	27
Flash Point (°C)	-	33	69	107.5
*Viscosity of water-free residue (mPas =cP),	169	1183	4105	15172
*Viscosity of 50% emulsion (mPas = cP)	-	510	1205	4436
*Viscosity of 75% emulsion (mPas = cP)	-	265	623	-
*Viscosity of max water (mPas = cP)	-	144	527	3190
Max. water cont. (vol.%)	-	88	79	68
(T1/2) Halftime for water uptake (hrs)	-	0.16	0.07	1.10
Stability ratio**	-	0.06	0.03	0.07

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

***Based on stability ratio of 24 hr settling + 10 rotations*

- *No data*

Table C 4: True boiling point (TBP) curve for Vale

Temperature (°C)	Volume (%)
5	0
63	4
84	9
97	14
113	18
126	22
142	27
154	31
175	35
197	40
217	46
236	50
255	54
272	58
291	62
310	66
331	70
355	73
379	77
403	81
430	84
458	88
493	91
542	95
632	98

Table C 5: Stressweep Vale 2013-0582 v/5°C

Fraksjon/emulsjon	Tau_0	Gamma_0
Fersk	0.42	0.21
150°C+/vannfri	2.87	0.71
150°C+/50%	0.61	0.3
150°C+/75%	0.83	0.37
150°C+/mw%	0.28	0.3
200°C+/vannfri	6.59	0.73
200°C+/50%	1.65	0.71
200°C+/75%	0.54	0.38
200°C+/mw%		
250°C+/vannfri	40.3	0.38
250°C+/50%	2.76	0.94
250°C+/63.1%	-	-
250°C+/63.1%/voksklump	-	-
250°C+/mw%	4.03	0.6
250°C+/mw%/voksklump	86.11	0.08

Table C 6: Stressweep Vale 2013-0582 v/13°C

Fraksjon/emulsjon	Tau_0	Gamma_0
Fersk	1.22	0.3
150°C+/vannfri	0.47	0.22
150°C+/50%	0.79	0.42
150°C+/75%	1.22	0.69
150°C+/mw%	1.23	0.67
200°C+/vannfri	3.12	0.55
200°C+/50%	1.03	0.63
200°C+/75%	1.23	1
200°C+/mw%	1.09	0.55
200°C+/mw%/voksklump	89.66	0.15
250°C+/vannfri	21.49	2.58
250°C+/50%	1.45	0.68
250°C+/75%	2.54	1.29
250°C+/mw%	2.57	2.53
250°C+/mw%/voksklump	113.5	0.49

D Chemical characterisation of the fresh oil on GC/MS

Group no.	Composition	Vale wt%
1	C1-C4 gasses (dissolved in oil)	3.000
2	C5-saturates (n-/iso-/cyclo)	2.500
3	C6-saturates (n-/iso-/cyclo)	2.947
4	Benzene	0.553
5	C7-saturates (n-/iso-/cyclo)	6.000
6	C1-Benzene (Toluene) et. B	1.008
7	C8-saturates (n-/iso-/cyclo)	9.992
8	C2-Benzene (xylenes; using O-xylene)	1.098
9	C9-saturates (n-/iso-/cyclo)	5.289
10	C3-Benzene	0.613
11	C10-saturates (n-/iso-/cyclo)	4.000
12	C4 and C5 Benzenes	0.042
13	C11-C12 (total sat + aro)	5.958
14	Phenols (C0-C4 alkylated)	0.000
15	Naphthalenes 1 (C0-C1-alkylated)	0.438
16	C13-C14 (total sat + aro)	8.062
17	Unresolved Chromatographic Materials (UCM: C10 to C36)	0.000
37	metabolite 1	0.000
38	metabolite 2	0.000
18	Naphthalenes 2 (C2-C3-alkylated)	0.481
19	C15-C16 (total sat + aro)	6.019
20	PAH 1 (Medium soluble polyaromatic hydrocrbns (3 rings-non-alkyltd;<4 rings)	0.370
21	C17-C18 (total sat + aro)	5.630
22	C19-C20 (total sat + aro)	5.000
23	C21-C25 (total sat + aro)	7.634
24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)	0.366
25	C25+ (total)	23.000

NA: Not analysed